



**DESTRUCTION OF AQUEOUS PHASE ORGANIC POLLUTANTS USING
ULTRAVIOLET LIGHT EMITTING DIODES AND PHOTOCATALYSIS**

THESIS

Morgan M. Russell, Civ, USAF

AFIT-ENV-MS-17-M-220

**DEPARTMENT OF THE AIR FORCE
AIR UNIVERSITY**

AIR FORCE INSTITUTE OF TECHNOLOGY

Wright-Patterson Air Force Base, Ohio

DISTRIBUTION STATEMENT A.

APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED.

The views expressed in this thesis are those of the author and do not reflect the official policy or position of the United States Air Force, Department of Defense, or the United States Government. This material is declared a work of the U.S. Government and is not subject to copyright protection in the United States.

AFIT-ENV-MS-17-M-220

DESTRUCTION OF AQUEOUS PHASE ORGANIC POLLUTANTS USING
ULTRAVIOLET LIGHT EMITTING DIODES AND PHOTOCATALYSIS
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

Morgan M. Russell, B.S.

Civ, USAF

March 2017

DISTRIBUTION STATEMENT A.
APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED.

AFIT-ENV-MS-17-M-220

DESTRUCTION OF AQUEOUS PHASE ORGANIC POLLUTANTS USING
ULTRAVIOLET LIGHT EMITTING DIODES AND PHOTOCATALYSIS

Morgan M. Russell, B.S.

Civ, USAF

Committee Membership:

Dr. David M. Kempisty
Chair

Dr. Sushil Kanel
Member

Dr. Sudarshan Kurwadkar
Member

Abstract

The photocatalytic degradation of dyes (Allura Red AC and Brilliant Blue FCF) in water using ultraviolet light emitting diodes (UV-LED) and an immobilized titanium dioxide (TiO_2) as a photocatalyst; was investigated using a novel bench-top Teflon[®] reactor. This reactor has been uniquely designed to contain low-powered UV-LEDs combined with TiO_2 immobilized substrates. A sol-gel method was used to anneal TiO_2 to three different substrates: standard microscope quartz slides, quartz cylinders and borosilicate beads. TiO_2 characterization was performed using Scanning Electron Microscope (SEM), Raman spectroscopy, and mass comparisons. High resolution SEM images confirmed the presence and morphology of TiO_2 on the substrates. SEM and Raman analyses demonstrated the TiO_2 coating was uniform and predominantly has the anatase crystalline phase structure. The slide had the largest individual TiO_2 surface area of 0.187 mg cm^{-2} . Size, shape, packing and stirring properties were factors that determine overall photocatalytic properties and degradation. For an ideal completely mixed batch reactor (CMBR), the largest adjusted rate constants were 1.69×10^{-3} , 5.39×10^{-3} and $4.46 \times 10^{-3} \text{ min}^{-1}$ for the slide, beads and cylinders respectively. Borosilicate beads were the best performing substrate as determined by the greatest degradation rate for Allura Red AC. The beads and cylinders showed 58% and 51% degradation of a model organic compound, Allura Red AC. Actinometry experiments revealed quartz cylinders had the largest fluence value of $0.0461 \text{ J L}^{-1} \cdot \text{s}^{-1}$. Optimization of the sol-gel application method and reactor operating parameters was performed to maximize the degradation rate and

overall degradation of Allura Red AC. Electric energy per order (E_{EO}) was calculated and optimized at 9.20, 10.5 and 12.7 kWh m⁻³·order⁻¹ for the glass beads, cylinders and slides, respectively.

Acknowledgments

Every so often we come across leaders who are committed to help you achieve personal success and bring out the best of who you are and what you can do. I am fortunate and grateful to have met so many of these people throughout my academic endeavors including this research and Thesis. The people mentioned here represent only some of the phenomenal people that have had a positive impact on my life. My success and support system is anchored by my parents, loving family, girlfriend and close friends who all gave me the hope and strength to persevere and continue until I met my goals.

Lt Col Racz afforded me the opportunity to further my education and experiences. Lt. Col. Kempisty provided me with the guidance, knowledge and wisdom necessary to bring out the best of my abilities. His patience and perseverance is unmatched. Dr. Sushil Kanel gave me the hope and inspiration of how my work will ultimately contribute to the Department of Defense and benefit the scientific community. Dr. Kurwadkar consistently maintained a positive outlook, listened and offered advice in an instant. My supervisor, Mr. Clay Roberts consistently supported me during this time and ensured that I maintained a healthy work life balance. I am truly blessed by God to have had these leaders present in my life throughout this time. Success is shared among these great people with many more to come.

Morgan Russell

Table of Contents

	Page
Abstract	v
Acknowledgments.....	vii
Table of Contents	viii
List of Figures	x
List of Tables	xii
List of Equations	xii
I. INTRODUCTION.....	1
1.1 GENERAL PERSPECTIVE	1
1.2 PROBLEM STATEMENT	5
1.3 RESEARCH QUESTIONS	7
1.4 SCOPE AND APPROACH.....	8
1.5 SIGNIFICANCE	9
II. SCHOLARLY ARTICLE	10
DESTRUCTION OF AQUEOUS PHASE ORGANIC POLLUTANTS USING ULTRAVIOLET LIGHT EMITTING DIODES AND PHOTOCATALYSIS	10
2.1 ABSTRACT	10
2.2 INTRODUCTION.....	11
2.3 MATERIALS AND METHODS	15
2.3.1 <i>Preparation of TiO₂ thin films</i>	15
2.3.2 <i>UV LED Configuration</i>	16
2.3.3 <i>Reagents and Analysis</i>	18
2.4 RESULTS AND DISCUSSION.....	21

2.5 CONCLUSIONS	38
III CONCLUSIONS	41
3.1 CHAPTER OVERVIEW.....	41
3.2 REVIEW OF FINDINGS.....	41
3.3 LIMITATIONS	43
3.4 SIGNIFICANCE OF FINDINGS.....	45
3.5 FUTURE RESEARCH.....	46
APPENDIX A. EXPANDED LITERATURE REVIEW	47
A.1 Background.....	47
A.2 Photocatalyst Substrates	48
APPENDIX B. EXPANDED RESULTS AND DISCUSSIONS.....	49
B.1 Photocatalysis Optimization	49
B.2 Photocatalytic Degradation of 2, 4-Dinitrotoluene.....	52
B.3 Photocatalytic Degradation of Tartrazine	53
B.4 Photocatalytic Degradation of Brilliant Blue FCF	58
B.5 Photocatalytic Degradation of Allura Red AC	66
APPENDIX C. SUPPLEMENTAL MATERIAL	68
C.1 Allura Red AC UV-Vis Method Parameters	68
C.2 Brilliant Blue FCF AC UV-Vis Method Parameters	69
C.3 Paired t-test results.....	70
C.4 Standard Operating Procedure for 2,4-Dinitrotoluene (2,4 – DNT) Solution Prep.....	71
C.5 Modified Sol-Gel Procedure Worksheet.....	72
C.6 Lab Sphere Results	73

C.7 SETI LED Certificate of Analysis	74
C.8 Reactor Design.....	76
REFERENCES	78

List of Figures

	Page
Figure 1. Molecular structures of Allura Red AC (left), Brilliant Blue FCF (center) and Tartrazine (right).	14
Figure 2. Schematic for photocatalytic reactor setup.....	17
Figure 3. Averaged 5 Dip Raman Intensity for beads, cylinders and slide.	22
Figure 4. Raman TiO ₂ intensity scanned at three different cylinder positions.	23
Figure 5. High resolution SEM image of (a) borosilicate bead control and (b) TiO ₂ thin film (b).	24
Figure 6. (a) EDS analysis of cross sectional cut of a sample borosilicate bead and (b) an SEM image of the same sample.	25
Figure 7. Mass of TiO ₂ per slide dip-coat using the sol-gel method. Slides were pre-cleaned with a 50:50 Ethanol/H ₂ O mixture and allowed to air dry.	26
Figure 8. (a) UV-LED Photocatalytic Degradation of Allura Red AC comparing a standard microscope quartz slide, beads, and cylinders with TiO ₂ thin film. (b) Shows the degradation based on exposure time.....	29
Figure 9. Brilliant Blue with Borosilicate Bead repeatability experiment. The horizontal lines are Controls 1 and 2.....	30
Figure 10. Extended Brilliant Blue FCF experiment using TiO ₂ coated beads.	31

Figure 11. Analysis of 10 mg L ⁻¹ 2, 4-DNT without photocatalyst and LED off.....	44
Figure 12. CSTR Reactor model using beads with Allura Red AC.....	51
Figure 13. CMFR Reactor model using beads with Allura Red AC.	52
Figure 14. Normalized absorbance plot of 2, 4-DNT versus time using a 5-Dip slide. ...	53
Figure 15. Slide and H ₂ O ₂ comparison: Normalized Tartrazine absorbance units (a.u.) vs. Time (min).....	54
Figure 16. Slide and H ₂ O ₂ comparison: Normalized Tartrazine absorbance units (a.u.) vs. Time (min).....	56
Figure 17. Tartrazine with TiO ₂ slurry experiment: Normalized Tartrazine absorbance units (a.u.) vs. Time (min).....	57
Figure 18. Brilliant Blue/TiO ₂ Anatase Slurry Comparison.	59
Figure 19. Brilliant Blue FCF with 5-Dip slide/TiO ₂ slurry comparison.	60
Figure 20 Normalized absorbance comparison of 5 dip beads versus 5-dip slide.....	62
Figure 21. Immobilized TiO ₂ slide vs. beads comparison: (a) Normalized absorbance versus exposure time treated. (b) Normalized absorbance versus time.	64
Figure 22. Brilliant Blue FCF calibration curve for the Cary 60 UV-Vis.	65
Figure 23. Allura Red AC Calibration curve	67

List of Tables

	Page
Table 1 TiO ₂ Substrate versus experimental degradation results.....	32
Table 2 Fluence value comparison from Actinometry results.	35
Table 3 Photocatalysis of organic dye findings.	37

List of Equations

	Page
Equation 1: Exposure time (ET) calculation.....	32
Equation 2: Overall photochemical reaction of triiodide formation under UV light.....	33
Equation 3: Moles of I ₃ ⁻¹ as determined from Beer's Law.....	33
Equation 4: Einstein's unit calculation.	34
Equation 5: Temperature dependence on quantum yield.....	35
Equation 6: E _{EO} calculation for an ideal batch reactor.	36
Equation 7: CMBR Model equation.	38

DESTRUCTION OF AQUEOUS PHASE ORGANIC POLLUTANTS USING ULTRAVIOLET LIGHT EMITTING DIODES AND PHOTOCATALYSIS

I. INTRODUCTION

1.1 GENERAL PERSPECTIVE

The primary mission of Department of Defense (DoD) is to provide military forces needed to deter war and to protect the country (Department of Defense, 2015). Military forces require exceptional and unique training to ensure American freedom and to protect the Constitution of the United States. Training and operations are solely executed and understood by the DoD and few supporting agencies. These training exercises are performed within the U.S. airspace, land and seas. This may include live fire exercises, weapons testing, deployment of naval arsenals and supporting activities. The pollutant stream developed during these exercises requires that the nation's natural resources are monitored and protected. Past environmental management practices are unable to protect the nation's limited natural resources. As such, it is imperative that new and innovative engineering practices must be considered and promulgated across the DoD so that the physical, chemical and biological characteristics of nation's water can be maintained. The nation's aquifers and groundwater are among many limited natural resources impacted from training exercises. Groundwater contamination has been reported from rocket fuel, range operations and the use of specific chemicals to facilitate firefighting activities aboard naval vessels. This may adversely impact military and civilian population living on or near the DoD installations.

Priorities include protecting the environment for military readiness and protecting the health of military and civilian personnel who live and work on DoD installations. According to the Office of the Under Secretary of Defense for Acquisition, in 2016, under the Installation Restoration Program (IRP), there are 7,500 sites addressing contamination from hazardous substances (Office of the Under Secretary of Defense for Acquisition, 2016). According to one estimate, large swathe of range land (nearly seven million acres) in the continental United States has been impacted with groundwater organic contamination (USAF, 2016). These sites include “complex groundwater sites where progress is limited by the need for more advanced technology” (Office of the Under Secretary of Defense for Acquisition, 2016).

DoD groundwater contamination is grouped into chlorinated solvents, explosives, fuels, metals, oxygenates or propellants (United States Government Accountability Office, 2005). Common and emerging contaminants include perchlorate and nitroaromatic compounds from rocket fuel and munitions. Range residues, target byproducts, and many other components associated with the munition sites which have the potential to leach into groundwater. Ultimately, the contaminants migrate from the application sites and impact the groundwater resources that may be used as a source of drinking water by communities. Some of these contaminants include hexahydro-1,3,5-trinitro-s-triazine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7 tetrazocine (HMX), and nitroaromatic compounds such as trinitrotoluene (TNT) and dinitrotoluene and others are under consideration for drinking water regulation (U.S. EPA, 2016).

Perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) compounds used in aqueous film forming foams are another source of groundwater

contamination on DoD and USAF installations. Recently, the US Environmental Protection Agency (EPA) has declared both the PFOA and PFOS as emerging contaminants of concern. It also lowered the lifetime exposure health advisories limits for PFOA and PFOS to a sum concentration of 70 parts-per-trillion (ppt). This action on the part of the EPA has raised awareness and provided impetus to conduct more site investigations and monitor potential impact to drinking water sources. Past literature review regarding the fate and transport of these compounds shows that they are known to move through groundwater and can potentially contaminate drinking water sources (Sharma, Mayes, & Tang, 2013). Currently, at least 30 USAF bases and 202 homes show levels of PFOS and PFOA above the EPA health advisory levels (Affairs, 2016).

All of the contaminants discussed earlier are known to cause adverse health effects in humans and wildlife (Grandjean, Andersen, Budtz-Jørgensen, & al, 2012; Tchounwou et al., 2003; Wang, Fuller, Schaefer, Caplan, & Jin, 2012; Zheng, Lichwa, D'Alessio, & Ray, 2009). TNT, RDX and HMX have been linked with serious liver effects (U.S. EPA, 2014; CDC, 2015). In 2008, TNT was added as a chemical known to cause cancer under the Toxic Enforcement Act of 1986 (U.S. EPA, 2014). The EPA has determined that RDX is a possible human carcinogen and targets the nervous system in humans and animals (United States Environmental Protection Agency, 2014). DNT is a suspected carcinogen and may damage the liver, kidneys and cause anemia under chronic exposure (Tchounwou et al., 2003). According to a study by Grandjean et al. (2012), PFOA and PFOS have shown immunotoxic effects by inducing a reduced immune response to childhood vaccinations. Toxicological studies involving animals shows that

exposure to PFOA and PFOS could potentially lead to endocrine disruption, liver and pancreas damage as well as developmental problems (NIEH, 2016).

Groundwater contamination due to PFOA and PFOS at known sites has initiated a variety of cleanup efforts. Past techniques such as pump and treat technologies which are costly, ineffective and take years or possibly decades to remediate yielded limited success (United States Government Accountability Office, 2005). To overcome the shortcomings of the earlier technologies for remediation of groundwater contamination, an innovative technology using low-cost Ultraviolet Light Emitting Diodes (UV-LED) with a newly designed reactor was investigated. New and improved LEDs can now extend into the UV portion of the Electromagnetic Spectrum (EM) and are small, robust and can endure harsh conditions as required in water remediation. This research explores the capabilities of the reactor using LEDs with organic contaminant simulants. Photocatalytic degradation of organic contaminants are among these water research initiatives that have long proven to be a reliable and sustainable method for removing contaminants from water (Umar & Aziz, 2013). In a reactor design, LED configurations are almost limitless allowing for a wide variety of reactor configurations to optimize contaminant destruction. This also serves as an innovative and cost savings effort to remediate groundwater contamination known to cause adverse health effects. A study by Hölz et al. (2017) shows nearly an 87-fold decrease in electricity used per year, an 8-fold decrease in initial startup cost and a 48-fold decrease in consumables needed per year; all can be achieved by selecting UV-LED over mercury based light sources (Hölz, 2017). This research shows promising effort that UV-LED could serve as an economically feasible technology for groundwater remediation.

Although recent advancements in UV-LED shows promise for water treatment at significantly reduced operational costs, their limited power output is a cause of concern. This is particularly important since lower power output may cause insufficient hydroxyl radical production which is responsible for the organic contaminant destruction. Lower power output also means that the power may not be sufficient to overcome the minimal energy threshold for band gap excitation, thereby leading to partial or no degradation of the contaminants (Umar & Aziz, 2013).

This was evidenced in this research during initial experiments involving degradation of 2, 4-DNT as the choice contaminant. Initial experimental design we anticipated LED output would sufficiently degrade this compound. The molecular stability of 2, 4-DNT and the lack of adequate LED power output proved that degradation might not occur under these conditions. Organic contaminants in water can still be degraded despite the lower power outputs from UV-LED over traditional mercury-vapor lamps. It may take longer time than expected. Efforts were made to increase power output including maximizing the power input to the maximum permitted by the manufacturer and extending LED contact time. The present research evolved from degradation of 2, 4-DNT to organic dyes as a contaminant simulant. The larger molecular size and less stability proved suitable for degradation with current LED technology.

1.2 PROBLEM STATEMENT

Although photocatalytic degradation and other Advanced Oxidation Processes (AOPs) have been studied extensively, a majority of past research has been dedicated to using low and medium pressure mercury-vapor lamps with various reactor configurations

and power outputs. It's widely known that mercury-vapor lamps are more energy intensive and contain toxic materials. As UV-LEDs continue to become more energy efficient and cost effective, mercury-vapor lamps will be phased out. The LED industry now has the technology to produce more powerful diodes in the UV-C (200 to 280 nm) range (Hecht, 2016). Additionally, LEDs are rapidly evolving to produce more powerful and longer lasting economical lights with little to no warmup times (Crystal IS, Inc., 2014). This warmup delay for mercury-vapor lamps to achieve maximum output potential gives LEDs more advantage through cost savings and efficiency. Additionally, lamp life of traditional mercury-vapor lamps are significantly reduced if it is re-powered during the cool down period. This is critical, because ex-situ remediation applications are completed in a field environment, where sites may be located in places with limited or intermittent power may be available. This is one of the major limitations of the mercury-vapor lamps. Such is not the case with lower power LEDs. The instant on/off feature provides distinct advantage for LEDs because they use low voltage direct current which enables them to be used with solar power. These factors are an important consideration, if water treatment is to occur in remote locations where power supply may not be readily available. Furthermore, there has been little to no standardization in quantifying the amount of energy or quantum yield inside the reactors. It's currently uncertain how reactor design configuration can affect overall contaminant degradation.

To further enhanced rate of contaminant degradation, a widely used photocatalyst Titanium Dioxide (TiO_2) nanoparticles can be used as an immobilized photocatalyst or thin film annealed on borosilicate or quartz. The advantages of a photocatalytic reaction on an immobilized surface allowed for a fast and sustainable treatment method using UV-

LED light under standard environmental conditions. Since TiO_2 has a band-gap energy between 3.1 and 3.2 eV, it can be activated in the near UVC range (<400 nm). Therefore, UVC -LED light can be used for photocatalysis (Chong et al., 2010; Swarnakar et al., 2013). Few characterization studies have been completed to further the understanding of degradation of organic contaminants using LEDs and photocatalysts.

To quantify the actual energy imparted by LEDs, chemical actinometers were used. These actinometers are a reliable and low cost method to determine energy (as photons) from LEDs into the reactor. More recently, this has been standardized as photon fluence or fluence rate. It was previously demonstrated that the method and terminology utilized for determining this power were inconsistent in bench scale reactors (Bolton et al., 2015). Bolton and Linden helped standardize this process so that various research in LEDs and gas lamps could be compared (Bolton & Linden, 2003). Specifically, potassium iodide actinometers are widely employed since they may be used at standard temperatures and lighting (Rahn, 2013). The potassium iodide preparation and procedure has been optimized by R.O. Rahn, and meets the quality control criteria from the International Union of Pure and Applied Chemistry (Rahn, 1997). This procedure is a useful methodology to evaluate photon distribution and quantum yield using different photocatalyst surfaces.

1.3 RESEARCH QUESTIONS

This research was designed to explore new capabilities of UV-LED combined with nano-sized TiO_2 immobilized on quartz slides, cylinders and glass beads for photocatalytic degradation. A new and novel Teflon[®] reactor containing two LEDs was

designed. The reactor is unique, since it contains a large reflection coefficient and allows for continuous treatment. Questions to be answered through this research include:

Thesis Question 1: Will this reactor design with LEDs sufficiently degrade organic dyes using various TiO₂ immobilized substrates?

Thesis Question 2: What are the reaction rate constants of the three different substrates using these dyes?

Thesis Question 3: How does the TiO₂ mass deposition affect degradation?

1.4 SCOPE AND APPROACH

Photocatalytic degradation of organic dyes in water using TiO₂ as a photocatalyst in a reactor was experimented. The sol-gel method was used to anneal the TiO₂ nanoparticles on quartz slides, cylinders and borosilicate beads. Each annealed substrate was characterized using a microbalance (as a mass basis), Raman Spectroscopy and a Scanning Electron Microscope (SEM). A second TiO₂ catalyst loading methodology was also investigated using a 15% anatase TiO₂ nanoparticle suspension. The reactor configuration included a small cylindrical Teflon[®] reactor connected via high performance tubing with two entries and two exits on adjacent sides. Solutions of known concentrations of Tartrazine, Brilliant Blue FCF, and Allura Red AC were prepared and recirculated for UV-LED treatment. The recirculation was facilitated through a peristaltic pump with real time detection using a UV-Vis spectrometer. The corresponding absorbance values were recorded after treatment over time. A potassium iodide/iodate chemical actinometer was used to determine the different fluence rates of the reactor

containing the beads, cylinders and slides. Lastly, electric energy per order (E_{EO}) and apparent rate constants were determined.

1.5 SIGNIFICANCE

Given the recent advancements in UV-LEDs; reactor material and design may be re-engineered. It is anticipated that the new reactor design will provide a more sustainable and economical approach to water treatment. Two notable advancements of this research include an effective photocatalyst design and loading. Various photocatalyst substrate material allows for a unique advantage for contaminant degradation. Beads and cylinders allowed for stirring inside the reactor during treatment. Effectiveness of TiO_2 coating was evaluated between the TiO_2 substrates. Data generated from this research could be utilized in future modeling approaches for degrading organic contaminants. Variables including contaminant concentration, molecular descriptors, reactor design and photocatalyst material could be utilized in modelling software. Ultimately, this could be utilized to predict degradation of current and emerging water contaminants.

II. SCHOLARLY ARTICLE

Written for submission to the *Journal of Water Research*

DESTRUCTION OF AQUEOUS PHASE ORGANIC POLLUTANTS USING ULTRAVIOLET LIGHT EMITTING DIODES AND PHOTOCATALYSIS

2.1 ABSTRACT

The photocatalytic degradation of dyes (Allura Red AC and Brilliant Blue FCF) in water using ultraviolet light emitting diodes (UV-LED) and an immobilized titanium dioxide (TiO₂) as a photocatalyst; was investigated using a novel bench-top Teflon[®] reactor. This reactor has been uniquely designed to contain low-powered UV-LEDs combined with TiO₂ immobilized substrates. A sol-gel method was used to anneal TiO₂ to three different substrates: standard microscope quartz slides, quartz cylinders and borosilicate beads. TiO₂ characterization was performed using Scanning Electron Microscope (SEM), Raman spectroscopy, and mass comparisons. High resolution SEM images confirmed the presence and morphology of TiO₂ on the substrates. SEM and Raman analyses demonstrated the TiO₂ coating was uniform and predominantly has the anatase crystalline phase structure. The slide had the largest individual TiO₂ surface area of 0.187 mg cm⁻². Size, shape, packing and stirring properties were factors that determine overall photocatalytic properties and degradation. For an ideal completely mixed batch reactor (CMBR), the largest adjusted rate constants were 1.69 x10⁻³, 5.39 x10⁻³ and 4.46 x10⁻³ min⁻¹ for the slide, beads and cylinders respectively. Borosilicate beads were the best performing substrate as determined by the greatest degradation rate for Allura Red AC. The beads and cylinders showed 58% and 51% degradation of a model organic

compound, Allura Red AC. Actinometry experiments revealed quartz cylinders had the largest fluence value of $0.0461 \text{ J L}^{-1}\cdot\text{s}^{-1}$. Optimization of the sol-gel application method and reactor operating parameters was performed to maximize the degradation rate and overall degradation of Allura Red AC. Electric energy per order (E_{EO}) was calculated and optimized at 9.20, 10.5 and $12.7 \text{ kWh m}^{-3}\cdot\text{order}^{-1}$ for the glass beads, cylinders and slides, respectively.

2.2 INTRODUCTION

Advancements in science and technology have allowed quantification at much lower detection limits of emerging contaminants in groundwater. Combined with evolving and increasingly stringent regulations and health advisories, there is new emphasis for low cost and efficient water treatment technologies. Photocatalytic degradation has shown potential as a viable method for degrading organic contaminants (Cho et al., 2004; Kim et al., 2016; Natarajan et al., 2011). Disadvantages to current photocatalytic technologies are high energy consumption and the use of toxic mercury-vapor lamps with limited lifetimes. Solar light photocatalysis is optimal, however only 4-5% of naturally light constitutes sufficient UV radiation for the needed reactions to occur (Han et al., 2014). Recent technological development led to the advent of UV-LEDs that have emerged as a viable alternative to traditional photocatalysis and are now proving to be useful and practical in industrial scale water treatment processes. In a recent study, an 85-fold overall efficiency increase was observed when using a 365 nm UV-LED source compared to an ultrahigh pressure mercury arc-source (Hölz, 2017). LEDs are portable, robust, small, with most of the electrical energy being transformed into light (Natarajan et

al., 2011). A precise improvement in quantum efficiency of deep UV-LED performance is expected to continue (Pernot et al., 2010). Combining photocatalytic degradation with UV-LEDs is a promising technique for water treatment targeting organic contaminants (Swarnakar et al., 2013). The robustness and ease of use of this technology has facilitated the success of many innovative reactors.

In addition to LED advancement, reactor design and material are continuously upgraded for a more pragmatic water treatment approach. Many parameters have been investigated to include number of LEDs, flow rate, power, reactor type, pH and temperature (Eskandarloo et al., 2015; Ghosh et al., 2009; Rasoulifard et al., 2014). These reactor designs could be applicable for industrial scale water treatment processes.

TiO₂ thin films have been used extensively as a photocatalyst due to its low toxicity, cost effectiveness, and small band gap (Choi et al., 2006; Hales et al., 2014; Han et al., 2011, 2014; Naumenko et al., 2012; Swarnakar et al., 2013; Wu et al. 2013). A simple, cost-effective sol-gel procedure has been used to create TiO₂ thin films with enhanced catalytic activity and structural properties (Choi et al., 2006). TiO₂ has been previously immobilized with glass slides, beads, fibers, quartz and fiberglass cloth (Natarajan et al., 2011). In each instance, the TiO₂ may be retained for repeated use since it is not consumed during the formation of hydroxyl radicals, making it a preferred catalyst. (Kent et al., 2011). Most recently, these results have been compiled and summarized for cross comparison (Varshney et al., 2016). Reactor design is based on substrate variations including different surface areas, light dispersion or absorbance properties, and the volume available inside the reactor for treatment. Substrate TiO₂ annealing properties include surface type (i.e. borosilicate or quartz), shape and thickness

as well as smoothness or roughness of surface finish. There are several advantages and disadvantages of using different substrates.

Since the sol-gel process may be used on different substrate types, it serves as an important method for photocatalyst development. Each photocatalyst type provides differences in TiO₂ morphology (e.g. anatase versus rutile crystalline structure, coating efficiency and aggregates on the surface). Raman spectroscopy and SEM are important methods capable of thin film characterization. These procedures have proven useful when qualitatively determining coating efficiency and phase transformation as well as identifying types of crystalline structure. Intrinsic properties of TiO₂ are important for the transport of reactants or products to and from the active sites. They are also important for the production of electron-hole pairs which ultimately determine overall degradation (Choi et al., 2006).

Actinometers are often used as an easy and cost effective method for determining the number of UV light photons entering the solution aka quantum yield and fluence. The amount of light collected and directed into the reactor has been considered one of the most relevant metrics in photochemistry applications (Hölz, 2017). Advantages of using actinometry includes its low cost, ease of use, and published standardized conditions. It may also be used in ambient light since it is unaffected at wavelengths greater than 320 nm. Recently, there have been some discrepancies reported in many publications on quantitative analysis of photochemical processes (Bolton et al., 2015). These discrepancies result from the lack of correct terminology, correct use of power units, reactor design and configuration. As the shift from mercury-vapor lamps to UV-LEDs continues, this will potentially impact the research data.

Experimental dyes included in this research are Allura Red AC, Brilliant Blue FCF, and Tartrazine. These were utilized as a surrogate to study the degradation of various organic contaminants. Each dye is complex and has different chemical and structural property relationships (Fig. 1). Different functional groups on these molecules are susceptible to oxidation from $\cdot\text{OH}$. The reaction typically involves the removal of hydrogen which destabilizes the compound and facilitate its mineralization. These may provide unique molecular descriptors.

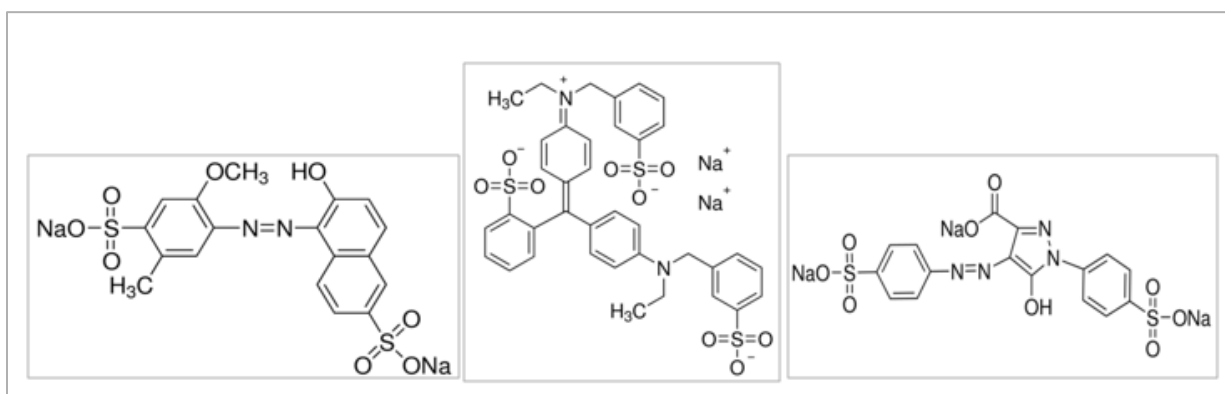


Figure 1. Molecular structures of Allura Red AC (left), Brilliant Blue FCF (center) and Tartrazine (right).

Rate constants determined from this research may be used with Quantitative structure-property relationships (QSPR) modeling. Experimental dyes may serve as predictors for determining rate constants for other pollutants for this reactor design.

The Department of Defense (DoD) is continuously seeking more affordable and cost effective technologies for ground water treatment (Government Accountability Office, 2005). Using a newly design reactor, this research was conducted to address the limited knowledge of reactor performance. This include quantification of LED performance through actinometry and contaminant degradation kinetics. Information

gained from this research will assist in the decision making of treatment technologies for large scale environmental restoration efforts on or near DoD installations. Ultimately, this will simultaneously mitigate adverse human health effects, ecological damage and provide economic savings.

2.3 MATERIALS AND METHODS

2.3.1 Preparation of TiO₂ thin films

TiO₂ thin films were prepared using borosilicate beads, quartz cylinders and standard microscope slides as substrates. Standard solid borosilicate glass beads (Sigma-Aldrich, St. Louis, MO) measured 6 mm in diameter with $\pm 10\%$ variation in bead size. Quartz cylinders were custom cut and obtained locally from Quality Quartz Engineering (Dayton, OH). Each solid quartz cylinder precisely measured 0.635 x 0.47625 cm. Standard microscope slides (Ted Pella Redding, CA) were made of quartz and borosilicate and measuring 7.62 x 2.54x 0.15875 cm.

A modified version of the sol-gel procedure was used to immobilize TiO₂ to the substrate of interest (Han and Swarnakar et. al (2011)). Before the coating procedure began, the substrate was thoroughly rinsed with a 50:50 ethanol and water solution then vigorously shaken followed by a rinse of pure deionized water. Each were then heat treated at 500 °C for twenty minutes to remove any organic contaminants and particulates. Each were weighed before and after to determine the amount of TiO₂ immobilized on each substrate. Sol-gel was prepared in duplicate by combining five grams of Tween 80 (Sigma-Aldrich) and 40.15 mL of 2-Propanol (Fisher Scientific) in a 50-mL centrifuge tube. After adding small stir bars, solutions were capped tightly and slowly

inverted two times to ensure a homogenous mixture without bubbles. Each was stirred for 10 minutes at 350 rpm. While continuously stirring, 0.67 mL of acetic acid (Sigma-Aldrich) and 3.4 mL of 99.999% titanium (IV) isopropoxide (Sigma-Aldrich) were added. Solutions were again inverted two times then set to stir for 20 minutes. The solution appeared viscous and clear with a pale yellow to brownish color. A small hole was punctured in the bottom of three other centrifuge tubes containing the beads, slides and cylinders. The sol-gel solution was poured into the tube which dip coated the substrate at a rate of 1 mL s^{-1} while collecting and retaining the original solution. The substrate was placed into a crucible and allowed to air dry for 10 minutes. A furnace (Paragon Sentry 2.0; Mesquite, TX) was programmed with temperature control to anneal the substrates starting at 100°C and ramping to 500°C and holding this temperature for 20 minutes. Slides were cooled at room temperature; this cycle represents a one-dip cycle. The process was repeated until the desired dip count was reached. Due to the extended period of heat cycling and cooling, the solution turned into a pale milky color by the end of the procedure. Each dip coated substrate was wrapped in foil and placed in a 50-mL centrifuge tube, then stored at room temperature to mitigate potential surface organic contamination or photooxidation reaction.

2.3.2 UV LED Configuration

The experimental setup included a small 37-mL cylindrical reactor (I.D. =2.2 cm, O.D. =3.3 cm) using tubing connected to ports on adjacent sides. The reactor was specially designed to hold a standard microscope slide with removable end caps containing the UV-LEDs (Fig. 2). The water spiked with the contaminant of concern was recirculated for treatment using a peristaltic pump (upward direction) and detection with

a UV-Vis spectrometer. The beads and cylinders were inserted for each experiment through the removable end cap using a packed bed column design. The top end cap contained two entry ports and the bottle, contained two exit points, for the influent and effluent solutions, respectively.

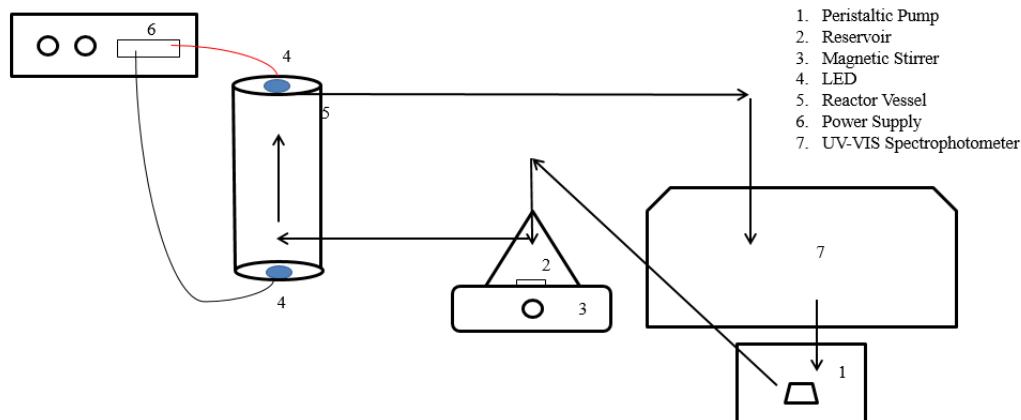


Figure 2. Schematic for photocatalytic reactor setup.

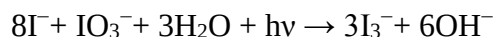
A single 255 nm LED from Sensor Electronic Technology, Inc. (SETi; Columbia, South Carolina) was silicon sealed into each end of the reactor, followed by a heat sink tightly screwed in with a layer of thermal grease to ensure adequate heat dissipation. The power output of each LED was tested and verified which closely matched the manufacturer specification using an integrating lab sphere (illumia[®] Pro System; North Sutton, NH). Results were averaged and determined to be 2.72×10^{-3} W at a peak wavelength of 255 nm. LED leads were soldered and wired in series to a circuit board containing resistors and connected to the power supply, then tested and validated for a total system power of 23.5 V at 200 mA. The voltage drop across a single LED was measured with a multi-meter then averaged, yielding a net output of ~6.2 V. The system

was leak tested prior to each analysis to ensure that no losses could be attributed to the reactor or tubing.

2.3.3 Reagents and Analysis

All purchased reagents were analytical grade and in the highest purity available (>97%). A typical 1000 mg L⁻¹ stock solution was prepared by adding a known mass of organic dye; typically Allura Red AC (Tokyo Chemical Industry; Tokyo, Japan) into a 100-mL volumetric flask and brought to volume with deionized water (DI-H₂O) followed by 5 minutes of sonication. The 5 mg L⁻¹ working solution was prepared by adding 5 mL of this stock solution pipetted into a 1 L volumetric flask and brought to volume with DI-H₂O. A calibration curve was prepared using the stock standard at 0.5, 1, 5, 10 and 20 mg L⁻¹ concentrations at 509.9 nm. Each absorbance value was recorded three times and averaged to obtain a calibration curve with linear correlations of 0.995 or greater.

Chemicals used for actinometry were all procured in neat form at >99.5% purity (Sigma- Aldrich; St. Louis, MO). Chemicals were dried at 105° C for 48 to 72 hours to remove moisture. After drying, 0.6 M potassium iodide (KI) and 0.1 M potassium iodate (KIO₃) were combined with a 0.01 M borate buffer in an aqueous solution at room temperature. The solution was vigorously shaken and sonicated for 10 minutes, then diluted to 100 mLs. The mixture was clear and colorless and wrapped in foil prior to use. Potassium iodide-iodate actinometers measure photons as energy using use a well-known photochemical reaction:



By measuring triiodide production at 352 nm using a UV-VIS spectrophotometer, reactor fluence was determined based on a known quantum yield. Actinometry experiments were performed in the same manner as degradation experiments. Blank beads, slides and cylinders were used to exclude the photocatalyst reaction and achieve a more accurate fluence measurement.

For experimental analyses, the solution containing the desired concentration of organic contaminant was injected into the system through the inlet using chemical resistant and opaque PharMed tubing (Cole-Parmer; Vernon Hills, IL). The experiment continued until the flow at the outlet was continuous. Depending on the experiment, either the TiO₂ coated beads, cylinders or a slide was inserted into the reactor. Controls were analyzed in two different methods under the same operating parameters as the experiments. The first method used non-TiO₂ coated materials with the LED off. The second non-TiO₂ coated materials with the LED on. This proved that degradation could not be attributed to mixing or LEDs alone. Solutions were then recirculated through the system using a peristaltic pump (Cole-Parmer; Vernon Hills, IL). The pump was calibrated and verified prior to each experiment for accurate flow. A UV-Vis spectrometer (Agilent Cary 60; Santa Clara, CA) was used for detecting the contaminant by recording absorbance values every minute. Background subtraction was performed using deionized water (DIH₂O). A 3-mL beaker was used to connect the influent with the effluent and sustained continuous stirring. After the system was leak tested and no air pockets were observed, absorbance readings were recorded at the instant the LED was turned on. During experiments the solution was wrapped in foil to minimize potential light contamination (Fig. 2).

2.3.4 Thin film characterization

Microbalance

A microbalance (Mettler Toledo; Columbus, OH) was used to weigh the slides, beads and cylinders before, during, and after the sol-gel analysis. The beads and cylinders were rinsed in a 50:50 ethanol-water mixture twice to remove any impurities. Each were placed in a furnace at 500 °C for 20 minutes then allowed to cool. During early experiments, standard borosilicate slides (Sigma-Aldrich, St. Louis, MO) were used to dip-coat and TiO₂ mass on each slide was recorded. The slides plus a non-coated control were weighed five times each using the average values to calculate the difference after each dip coat. The control slide was included during the entire sol-gel procedure and showed no mass added which could have been attributed to contamination in the furnace. Comparisons were made between the masses of the one dip coat versus five dip coat. Environmental conditions in the laboratory were ~68 °F with a relative humidity of ~83%.

Raman Spectroscopy

A Raman spectrometer model LabRam HR 800 (Horiba Scientific; Kyoto, Japan) provided by Wright-State University was used to analyze TiO₂ coated substrates. TiO₂ presence or absence and phase structure was closely examined. Raman experiments were performed with a daily calibration and using a silicon wafer for quality control verification. Laboratory temperature was <72° F and with relative humidity <73%. The sample was examined in the region of interest using the piezostage and the 10X and 100x objectives. After ensuring the Raman spectrometer was focused, a 532.134-nm laser was used to acquire sample results as point spectra. The slides were scanned on the left, center

and right side. The beads and cylinders were scanned on the top, bottom and sides. All scans were reported as averaged Raman shift.

SEM-EDS Analysis

A scanning electron microscope (SEM) was used for imaging and Energy Dispersive Spectroscopy (EDS) was used for chemical analysis using FEI® models (Sirion and Quanta 650) (FEI; Hillsboro, OR). Samples were cut using a diamond saw for cross sectional images and EDS analysis. Silver paint was applied to each sample to facilitate conductivity and grounding. Medium and high resolution samples were collected using a 30 μm aperture. Sample images were collected for the top, side and center of the beads, cylinders and slides.

2.4 RESULTS AND DISCUSSION

Thin film characterization

Raman spectrometer results for the borosilicate beads are shown in Fig. 2 and 3. The presence of the strongest band at the energy shift of $\sim 143\text{ cm}^{-1}$ of the E_g mode indicates the characteristic presence of TiO_2 for both anatase and rutile phase structures (Balachandran & Eror, 1982). The remaining three bands at ~ 405 (B1g), ~ 525 doublet (A1g and B1g) and $\sim 645\text{ cm}^{-1}$ (E_g) indicate anatase phase. Previous research reports that the conversion from anatase to rutile begins around 750°C (Balachandran & Eror, 1982). The programmable furnace used during the sol-gel procedure ensured that the temperature was held constant at 500°C . Secondly, rutile phase may be excluded due to the absence of the strong broad band around 235 cm^{-1} typical of rutile (Balachandran &

Error, 1982). This is significant, since the anatase phase is considered to have greater photocatalytic properties than rutile (Choi et al., 2006).

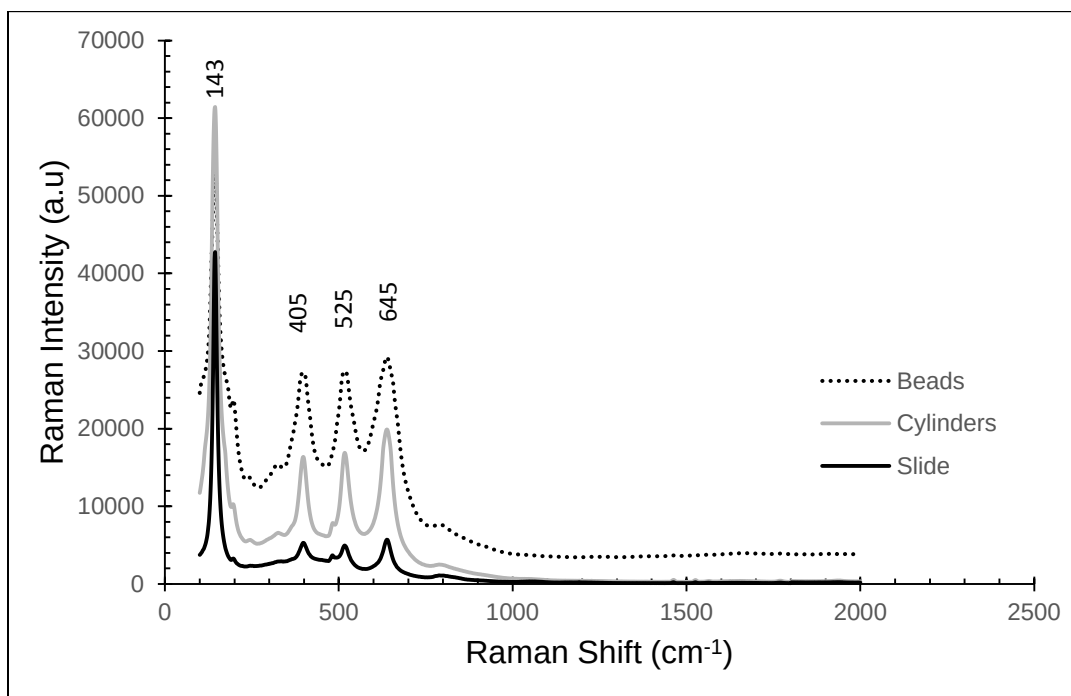


Figure 3. Averaged 5 Dip Raman Intensity for beads, cylinders and slide.

Raman spectra consistently indicated that the 5-Dip samples had the largest intensity for all substrates. Results from the cylinders and slides indicated the TiO_2 deposition was more uniform with increasing in Raman intensity with each TiO_2 application. Fig. 3 shows that the beads has the largest intensity. This observation was due to a greater thin film thickness on the surface of the beads. However, this may be highly variable since the Raman laser is focused only on a small ($<10\ \mu\text{m}$) portion of the sample. Scans were therefore averaged to obtain the most representative sample.

In Fig. 4, the average intensity for different portions of the quartz cylinders are compared. The average intensity for the sides of the cylinders was more than 5 times

greater than the top and bottom portions. This may be a result of additional Rayleigh scattering due to a porous and unfinished surface.

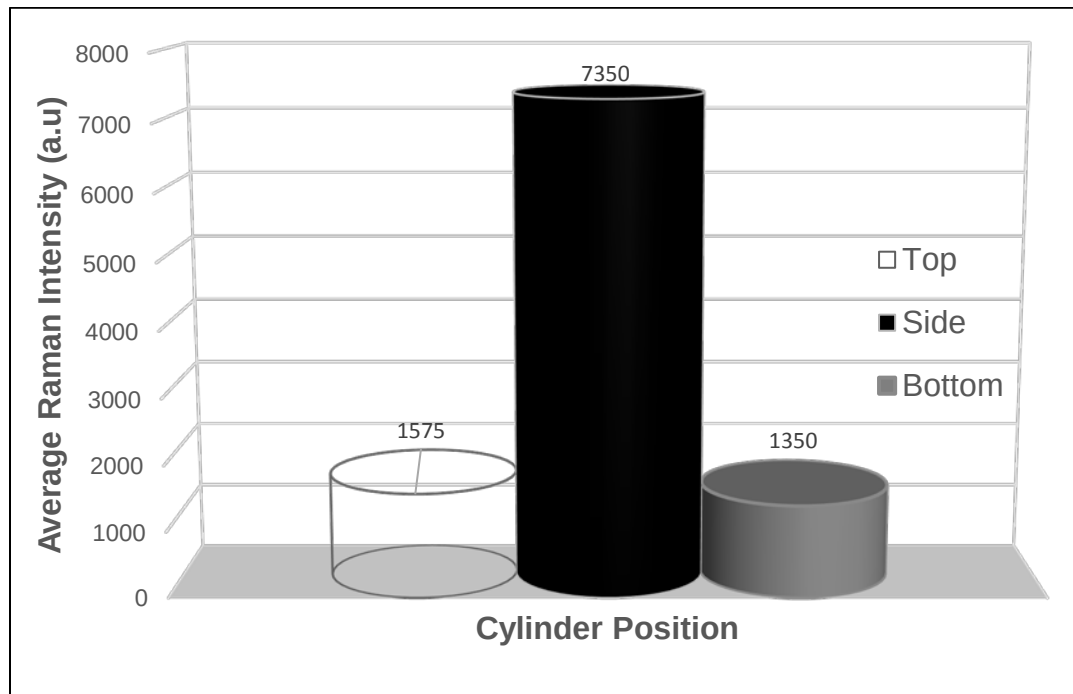


Figure 4. Raman TiO₂ intensity scanned at three different cylinder positions.

SEM analyses demonstrated the effectiveness of the TiO₂ immobilized on various substrates. Fig. 5 (b) depicts the surface after TiO₂ application indicating a homogenous crystalline structure with a spherical shape. This image is consistent with previous TiO₂ thin film results (Prusakova et al., 2015; Swarnakar et al., 2013; Vasuki et al., 2015).

(a)



(b)

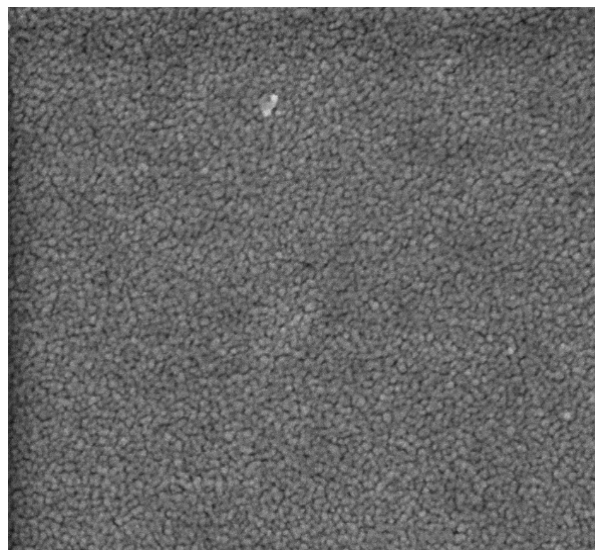


Figure 5. High resolution SEM image of (a) borosilicate bead control and (b) TiO₂ thin film

Fig. 6 (a) depicts the SEM-EDS line spectra of the borosilicate bead scanning from the inside to the outside of the cross-sectional area. As the scan reaches the TiO₂ coating, the silicon dioxide is reduced and simultaneously the Titanium increases from the K shell spectra. The thin film thickness was variable around the bead, as observed in Fig. 6 (b) and confirmed by the Raman spectra (Fig. 3). One location was approximated at 25 nm thickness. Despite a porous bead surface the TiO₂ was uniformly annealed over the outside layer while filling the apparent voids.

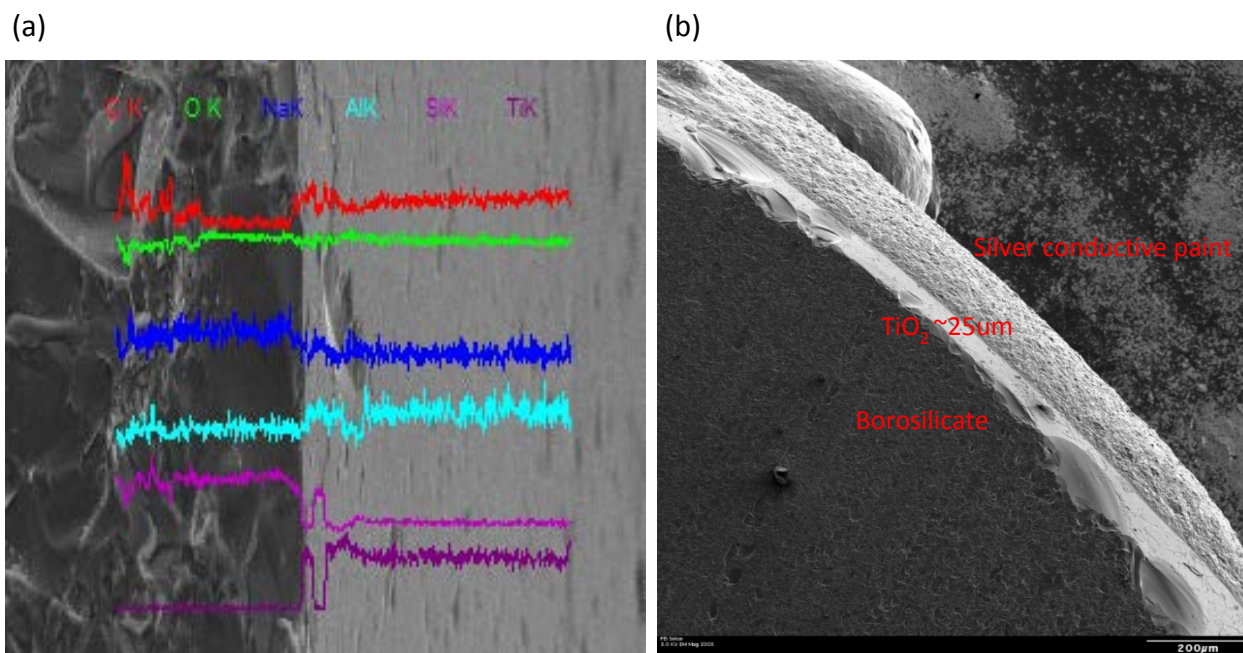


Figure 6. (a) EDS analysis of cross sectional cut of a sample borosilicate bead and (b) an SEM image of the same sample.

Initial mass characterization experiments used standard borosilicate microscope slides. A microbalance confirmed the presence of TiO₂ by weight. Fig. 7 depicts the application of TiO₂ annealed at approximately 1.3 mg per treatment. A line of best fit was forced through zero for an accurate TiO₂ coat rate. The mass per dip for the beads and cylinders was not determined due to the nature of the sol-gel method. A large sample population would be required for accurate results for both beads and cylinders. It would require to each substrate accurately weighed between each coating processes. This would be too time consuming, since there is a limited shelf life of the sol-gel solution. The largest standard deviation (S.D.) noted for the beads (12σ). The S.D. for the cylinders was 1.7 and 0.012 for the slide. Each bead would require to be tracked and weighed after each dip-coat process. Although there was a relatively smaller S.D., cylinders were much more costly and thus the experimental quantity was limited.

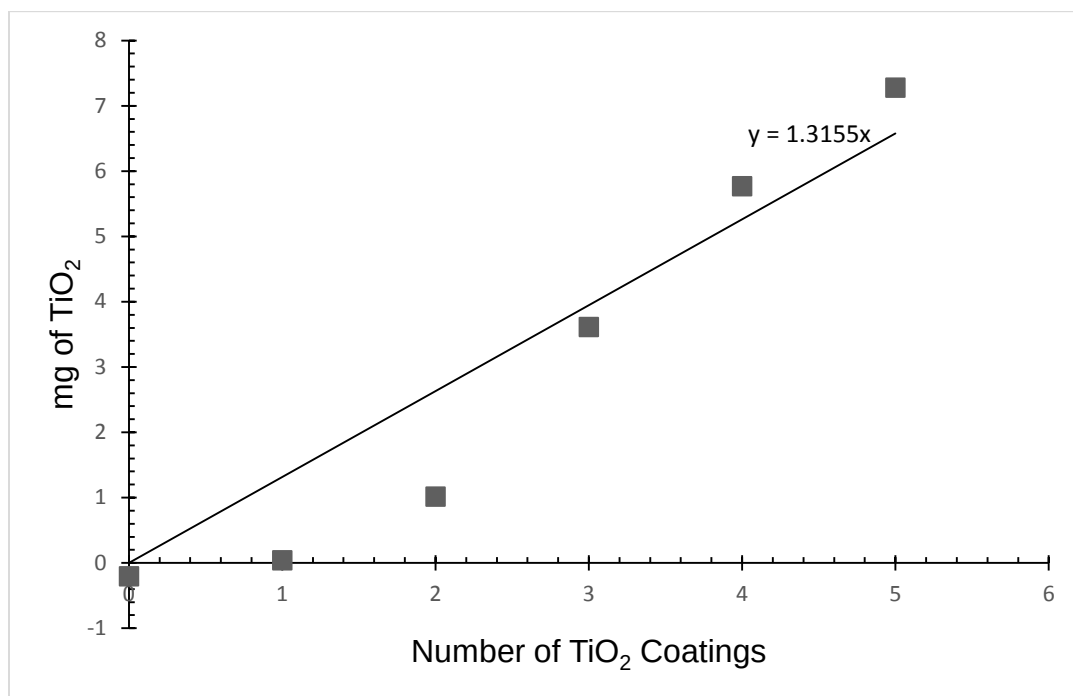


Figure 7. Mass of TiO₂ per slide dip-coat using the sol-gel method. Slides were pre-cleaned with a 50:50 Ethanol/H₂O mixture and allowed to air dry.

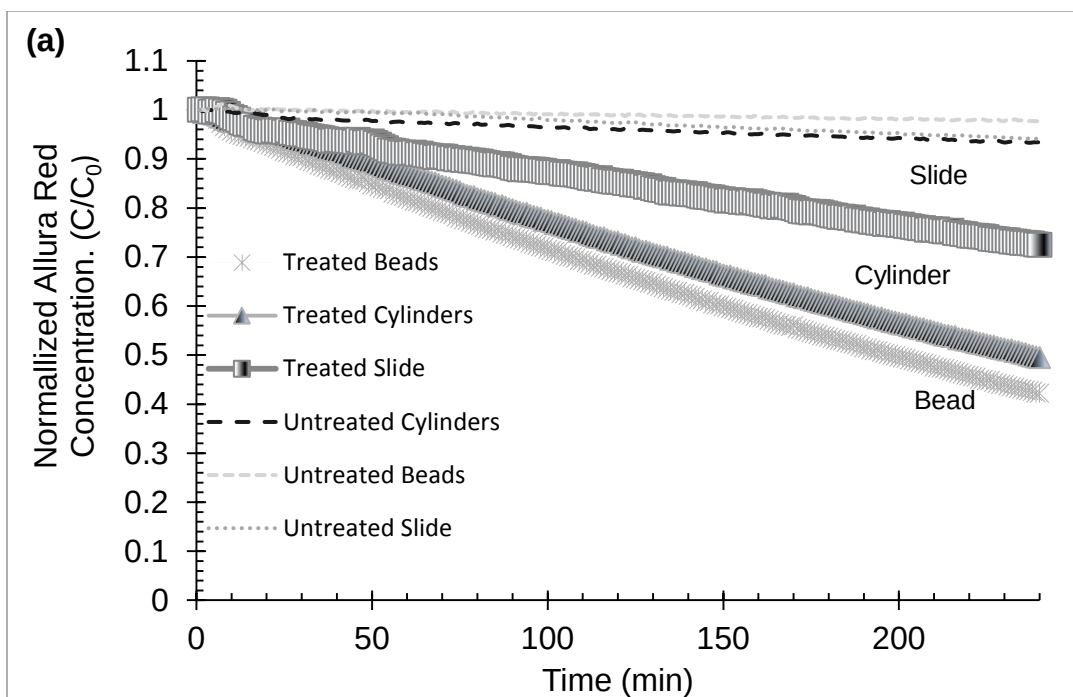
Photocatalytic activity increases with increasing surface area (Dariani et al. 2016). The total area available for TiO₂ loading for all beads contained in the reactor was ~630 cm², 175 cm² for the cylinders and 37.5 cm² for the slide (accounting for both sides). The total mass for 5-treatments of the slide was determined to be 7.3 mg which corresponded to 0.194 mg cm⁻² TiO₂ mass per area treated. The glass beads contained the second largest mean TiO₂ loading per surface area at 0.187 mg cm⁻² per bead, however the standard deviation (S.D.=12) was also the largest (n=140). This was due to the inconsistent mass of each uncoated bead and may be a result of the ±10% variation (which is reported by Sigma-Aldrich). The quartz cylinders had the smallest standard

deviation (S.D.=1.7) but also the smallest loading determined to be 0.022 mg cm^{-2} per cylinder. It was noted that the cylinders have unfinished sides while the ends were smooth and finished. The average mass of TiO_2 for the 5-dip cylinder was 0.035 mg (n=111) and 0.85 mg for the 5 dip bead (n=140). The TiO_2 did not anneal to the quartz as efficiently as the borosilicate.

According to Choi et al. (2006) there is a TiO_2 loading amount where photocatalytic activity no longer increases. TiO_2 thickness effects on photocatalysis have also been previously reported to follow Langmuir type kinetics (Wu et al., 2013). Additionally, it was reported by Wu et al. that the maximum photocatalytic activity is observed at 5 coatings. Due to the differences in geometric shape and material, it's uncertain if 5 coatings would be optimum for these substrates.

UV-LED Degradation

The overall degradation results for Allura Red AC is shown in Fig. 8. Results are normalized as C/C_0 with an influent concentration of 5 mg L^{-1} plotted over a four-hour period. Results indicated that the TiO_2 treated borosilicate beads achieved the highest overall degradation at 58% followed by the treated cylinders at 50% and the treated slide at 27%. Allura Red AC controls were analyzed with the LED on using untreated beads, cylinders and slides and indicated 2, 7 and 6% degradation, respectively. These were not factored into reported results.



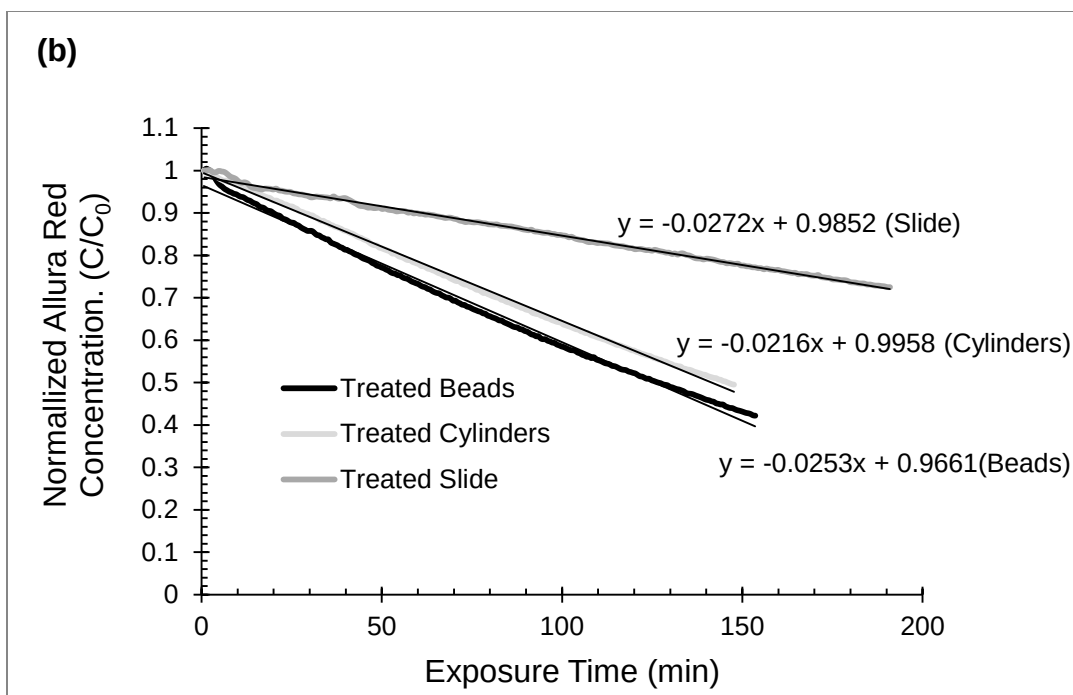


Figure 8. (a) UV-LED Photocatalytic Degradation of Allura Red AC comparing a standard microscope quartz slide, beads, and cylinders with TiO₂ thin film. (b) Shows the degradation based on exposure time.

Furthermore, repeatability studies were performed using Brilliant Blue FCF (10 mg L⁻¹) with treated beads validated these results with 34, 33 and 32% degradation over an 11-day period (Fig. 9).

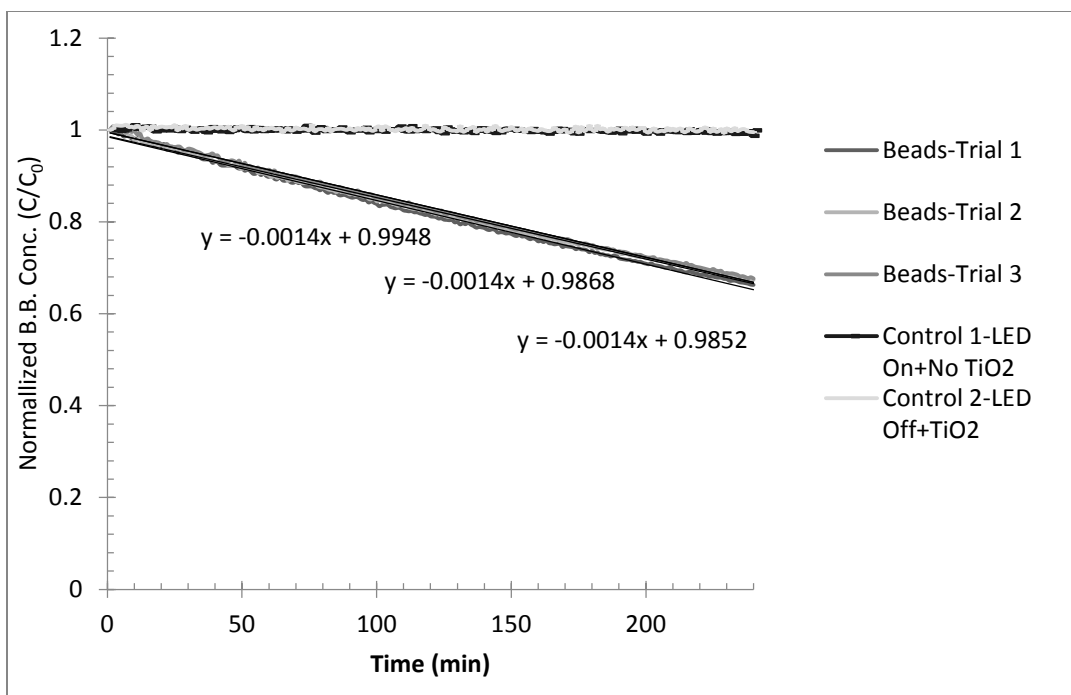


Figure 9. Brilliant Blue with Borosilicate Bead repeatability experiment. The horizontal lines are Controls 1 and 2.

Fig. 9 shows the Brilliant Blue degradation with consistent slopes indicating the performance and reliability of the experimental procedure. A modest decrease in performance may be attributed to organic matter adhering to the TiO₂ surface, which could potentially reduce surface area needed for photoactive sites (Konstantinou et al. (2004)). A paired t-test was conducted between trials 1 and 2, 2 and 3 and 1 and 3. A null hypothesis was conducted stating that there was no statistical difference between means with an alternative hypothesis stating there is a difference between means. Results showed that the null could not be rejected and there was not statically difference between means with a 95% confidence level. A 16-hour experiment was performed to determine the extent of the reaction.

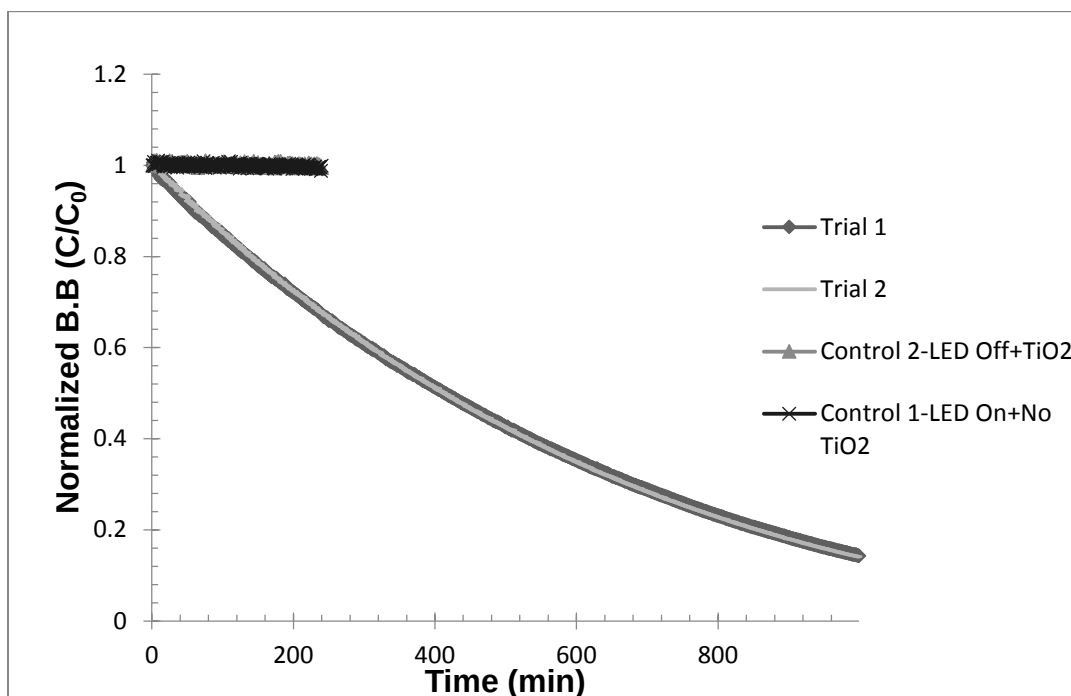


Figure 10. Extended Brilliant Blue FCF experiment using TiO₂ coated beads.

Fig. 10 shows that degradation continued after 16 hours. An 86% degradation is observed with Brilliant Blue FCF after ~1000 minutes of continuous analysis. Controls were not analyzed for this extended period of time, however 4 hour controls were plotted as a comparison. These controls showed little to no degradation.

Controls showed negligible degradation with an observed 0.08% degradation after four hours with the LED on, using untreated TiO₂ beads. Another Brilliant Blue FCF control exhibited little to know degradation (<0.5%) using non-coated beads with the LED off.

Exposure time was investigated between each substrate by plotting normalized concentration versus fractional time in the reactor (Fig. 7b). Exposure time for treatment was calculated using the flow as seen in Equation.

Equation 1: Exposure time (ET) calculation.

$$ET = t * \frac{RV}{SV}$$

Where:

RV= Reactor Volume (mL) with TiO₂ treated substrate

t= time at absorbance reading (min)

SV=System Volume (mL)

Fig. 8 (b) highlights a four-hour experiment where the cylinders and beads had comparable degradation rates per exposure time. Accounting for a 37-mL reactor volume and the total beads/cylinder count, the TiO₂ loading was calculated to be 0.707, 0.0662, 0.00524 mg cm⁻² mL⁻¹ for the beads, cylinders and slides.

Table 1 TiO₂ Substrate versus experimental degradation results.

Allura Red AC							
Substrate	Sample Size (n)	S.A.(cm ²)	TiO ₂ per area (mg cm ⁻²)	S.D. (σ)	TiO ₂ mg cm ⁻² mL ⁻¹	Exp. Time (min)	% Degradation
Beads	140	4.52	0.187	12	0.70762	154	58
Cylinders	111	1.58	0.022	1.7	0.06618	148	50
Slide	5	37.5	0.194	0.012	0.00524	191	28

This was later approximated to 140 beads and 111 cylinders. Overall degradation and TiO₂ mass deposition results are tabulated in Table 1. Accounting for the quantity of beads and cylinders, the beads had the most TiO₂ surface area which contributed to the most degradation. This was expected, since there are more photoactive sites available for increased hydroxyl radical and superoxide anion production. Interestingly, the slide had less degradation with more LED exposure time. This be a result of a larger volume in the

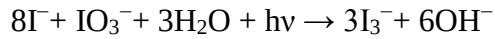
reactor in the slide experiments. The beads and cylinders provided more mixing in a smaller reactor volume. This may have contributed to a larger degradation.

Actinometry

Actinometry experiments were performed under the same conditions as the degradation experiments to estimate fluence rate in the reactor. Uncoated TiO₂ substrates were inserted into the reactor, to accurately represent the experimental setup. This ensured that mixing and stirring were accounted for.

The overall reaction is given by Equation 2:

Equation 2: Overall photochemical reaction of triiodide formation under UV light.



Absorbance values at 352 nm were recorded with the LED on and off at 30 second intervals, using the difference in these absorbance values, reactor volume, and molar extinction coefficient provided by R.O. Rahn (1997). The moles of triiodide produced were calculated using Beer's Law (Equation 3).

Equation 3: Moles of I₃⁻ as determined from Beer's Law.

$$\text{mole } \text{I}_3^{-1} = RV * \frac{\Delta OD_{352}}{\epsilon b}$$

Where:

ΔOD_{352}

= Absorbance at 352 nm (LED on) minus absorbance at 352 nm (LED off).

RV = Reactor volume (L)

ϵ = molar extinction coefficient 26,400 M⁻¹cm⁻¹

b = cuvette path length (cm)

Results were plotted by calculating the known quantum yield of 0.75 using the procedure developed by Rahn (1997) for a KI/KIO₃ actinometer using Equation 4. Einsteins were used to convert the number of photons in one mole of UV light to energy reported as Joules (Equations 4).

Equation 4: Einstein's unit calculation.

$$Einstein = \frac{moles I_3^{-1}}{\Phi}$$

Where:

$$\Phi = \text{Quantum yield (0.75)}$$

$$moles I_3^{-1} = \text{moles of triiodide (from eqn. 3)}$$

Using the energy of a single photon at 255 nm, the energy reported in Joules is calculated by determining the number of photons absorbed in the solution. This was calculated using Planck's Equation and determined to be 4.72x10⁵ Joules per Einstein. The energy reported as Joules was then determined by multiplying by Einsteins. UV intensity was calculated by dividing the reactor volume. Volume was chosen over surface area, since photon distribution varied depending on the substrate in the reactor. Secondly, the reaction is thought to occur at the surface closest to the LED but is mixed as it flows through the reactor. Final fluence values were determined by using the slope of the regression line from a plot of intensity over the duration of the experiment. Additional research is needed to better understand reactor photon distribution in the reactor. As seen in Table 2 below, results are summarized for both the system and reactor.

Table 2 Fluence value comparison from Actinometry results.

Substrate	Temp.	20.7° C	20.7° C	23.7 -17.7° C	23.7 -17.7° C
	System Volume (mL)	Reactor Fluence (J L ⁻¹ *s ⁻¹)	System Fluence (J L ⁻¹ *s ⁻¹)	Reactor Fluence (J L ⁻¹ *s ⁻¹)	System Fluence (J L ⁻¹ *s ⁻¹)
None	48	0.0545	0.0420	0.0515 - 0.0580	0.0397 - 0.0447
Beads	25	0.0961	0.0615	0.0906 - 0.102	0.0580 - 0.0654
Cylinders	26	0.120	0.0782	0.113 - 0.127	0.0738 - 0.0832

Rahn (1997) reported that quantum yield increases with increasing solution temperature. In these experiments, temperature fluctuations were not accounted for; since there was very minor changes in quantum yield as can be seen in the 5th and 6th columns of Table 2. Rahn (1997) developed an equation to correct quantum yield for temperature dependence using Equation 5 below.

Equation 5: Temperature dependence on quantum yield.

$$\Phi = 0.75(1 + 0.02 (T - 20.7))$$

Where:

Φ = Adjusted quantum yield

T = KI solution temperature

Based on this equation, the fluence value range corrects for a $\pm 3^\circ\text{C}$ temperature adjustment that may have occurred from variable water and laboratory temperatures. These adjusted quantum yields did not provide an overlap in fluence values. Exposure times (not shown) were compared between each experiment. In each experiment,

uncoated beads and cylinders were used. This was to eliminate potential interaction between the $\cdot\text{OH}$ radical and triiodide. The slide had the most exposure time, followed by the beads and then cylinders. Cylinders still contained the largest values, possibly due to shape and quartz composition. These were unexpected results, considering that the cylinders yielded less degradation than the beads. However, it has been reported that quartz is the most appropriate material for optimum quantum efficiency (Habibi et al., 2012). Another possibility is more thorough mixing in the reactor, which would allow more triiodide production.

E_{EO} Determination

Electrical Energy per order (E_{EO}) is defined as the electric energy in kilowatt hours required to degrade a contaminant by one order of magnitude (IUPAC Technical Report, Bolton et al. 2001). E_{EO} is typically used with first-order reactions and generally used when there is low contaminant concentrations. It provides a unique method for standardizing electrical energy required for different reactor conditions. For an idealized batch reactor, E_{EO} is determined using Equation 6 (Bolton et al., 2001).

Equation 6: E_{EO} calculation for an ideal batch reactor.

$$E_{EO} = \frac{38.4P}{Vk'}$$

Where:

P = Rated Power (kW)

V = Batch reactor volume (L)

k' = Pseudo – first order rate constant (min^{-1})

38.4 = Log conversion factor of $1000 * \ln(10)/60$

An ideal batch reactor assumes the solution is in a closed system and flow is constant. Additionally, assumptions include complete mixing and a uniform concentration throughout the reactor.

Table 3 Photocatalysis of organic dye findings.

Substrate	Dye	Conc. mg L ⁻¹	Exposure Time (min)	Adj. k (min ⁻¹)	Reactor Volume (L)	E _{EO} kWh m ⁻³ order ⁻¹
Beads	A.R.	5	154	5.39E-03	0.016	9.20
Beads	B.B.	10	154	2.57E-03	0.016	19.31
Beads	B.B.	10	154	1.37E-03	0.016	36.22
Cylinders	A.R.	5	148	4.46E-03	0.017	10.45
Slide	A.R.	5	191	1.69E-03	0.037	12.66
Slide	B.B.	10	191	1.21E-03	0.037	17.78

A summary of experimental E_{EO} values are observed in Table 3. Results closely match previously reported valued by Behnajady et al. (2009) and Domiguez et al. (2015) for a recirculated batch reactor. Although, values may depend on initial starting concentration, reactor type and the molecular structure of the compound (Behnajady et al., 2009; Muruganandham et al., 2007). Smaller values are preferable because they indicate less energy requirement to degrade the organic contaminant. Experimental input power was held at 200 milliamps (mA) and the voltage drop was measured at ~6.2 Volts (V). Using these power requirements, LED power outputs were measured using a Lab Sphere (illumia[®] Pro System; North Sutton, NH) and closely matched the manufacturer's specifications. This power input was used in Equation 6. It was observed that beads had the optimal E_{EO} value under experimental conditions.

Reaction rate constants were experimentally determined again using a pseudo-first order reaction kinetic model, as shown in Table 2. Apparent rate constants were calculated using an ideal CMBR model. Equation 7 was used to calculate values for k.

Equation 7: CMBR Model equation.

$$C_t = C_0 * e^{-kt}$$

Where:

C_0 = Initial concentration ($mg * L^{-1}$)

C_t = Model concentration ($mg * L^{-1}$)

k = Pseudo – first order rate constant (min^{-1})

t = Fractional time (min)

Previous research suggests that Allura Red AC follows pseudo-first order kinetics when it reacts with a hydroxyl radical (Thiam et al., 2015). Rate constants closely match values previously reported by (Dominguez et al., 2015). The difference between the experimental and modeled results were squared and summed. Microsoft Excel® Solver feature was used to minimize the differences and solve for k. Beads showed the largest rate constant, indicating that they are the preferred choice substrate for the fastest degradation.

2.5 CONCLUSIONS

Photocatalytic degradation of organic dyes using LEDs and a novel reactor design was found to be highly effective. The sol-gel method proved to be a successful approach to anneal TiO₂ to different types of glass substrates, as indicated by mass comparison, SEM, and Raman. A smooth and flat surface provided adequate area for TiO₂ loading. SEM results verified TiO₂ presence and morphology matching results previously reported by Vasuki et al., (2015) and Prusakova et al. (2015). Raman results further demonstrated that the crystalline structure was anatase phase. This was indicated by the peaks observed

at 405, 525 and 645 cm^{-1} which closely matches results from Prusakova et al. (2015). TiO_2 coating was the most effective for the borosilicate beads, yielding 207% more degradation than the slide and 116% more than the cylinders. However, there was a 43% decrease in exposure time from the beads compared to the slide.

If full scale water treatment operations use this reactor type, beads would allow for more cost savings due to less energy consumption. Glass beads demonstrated the largest final degradation and rate constant. Different physical properties contributed to the variable degradation results observed. Repeatability experiments conducted over a 12-day period using Brilliant Blue FCF and beads further demonstrated ~ 34% degradation in 3 four-hour experiments. Quality control objectives were met using controls and repeatability tests. A paired t-test proved there was no statistical difference between means for repeatability experiments with a 95% confidence level. This demonstrated that the TiO_2 is effective at degrading the organic contaminant over time. Most notably, degradation of Allura Red AC was observed at 58%.

Using a KI/ KIO_3 actinometer, experiments showed that cylinders had the largest fluence values over the beads. This is most likely due increased photon efficiency from the quartz composition. It also may be a result of efficient reactor mixing with an increased triiodide concentration in the cuvette. Another possibility includes more incident light reflection or scattering throughout the reactor. Both are due to an increasing the number of photons absorbed.

Results between the beads and cylinders are similar, indicating the beads may still be the optimal choice as a packed bed reactor. These all provided the maximum surface area for the photocatalytic reaction. When designing, future reactors containing LEDs,

experimentally determined fluence values could be used in research efforts as a means of comparison. Beads provided mixing and consequently larger fluence values, due to more UV-LED exposure. The beads had the lowest E_{EO} value using an ideal batch reactor model. Additionally, the beads yielded the largest apparent rate constant. It was shown that quartz proved optimal for photon efficiency. Unfortunately, the unfinished sides of the quartz cylinders prevented TiO_2 from annealing which yielded smaller degradation results. These were significant findings, since mixing could occur simultaneously with photocatalysis.

This research demonstrates that UV-LEDs can be successfully used in photocatalytic degradation of organic dyes that employ a new reactor design. Results indicate that low power LEDs may be used with various substrates for groundwater treatment. The uniquely designed Teflon[®] reactor proved reliable and robust, using low powered UV-LEDs with various substrates. Borosilicate beads proved to be the optimal photocatalyst in the reactor, providing efficient mixing and contact time for the most degradation. Beads were determined to have the largest rate constant and smallest E_{EO} in less exposure time. Further research could benefit from characterizing reactor fluid dynamics. Future studies should consider equating exposure time in experiments between different photocatalysts. Groundwater contaminants should be used with various TiO_2 immobilized media to determine the success of the photocatalysis.

III CONCLUSIONS

3.1 CHAPTER OVERVIEW

This chapter summarizes and expands on experimental findings and other scientific discoveries not addressed in the scholarly article. Findings are also supplemented by material provided in the expanded Literature Review in Appendix A. This review provides the history and related information for the entire thesis. Thesis research questions are answered individually and discussed in detail.

3.2 REVIEW OF FINDINGS

Thesis Question 1: Will this reactor design with LEDs sufficiently degrade organic dyes using various TiO₂ immobilized substrates?

Thesis research concluded that organic dyes could be degraded using TiO₂ immobilized on a standard glass microscope slide, borosilicate beads and quartz cylinders. The largest degradation (58%) and an adjusted rate constant ($5.4 \times 10^{-3} \text{ min}^{-1}$) was observed using TiO₂ immobilized on beads. Brilliant Blue was analyzed at a 10 mg L⁻¹ concentration and demonstrated similar results. A 33% degradation was observed with a $2.6 \times 10^{-3} \text{ min}^{-1}$ adjusted rate constant. Tartrazine was the most difficult compound to degrade, however an 18% degradation was observed using the TiO₂ coated slide. Dyes did not undergo complete mineralization. HPLC analysis has been used to identify proposed structures of Brilliant Blue FCF as reported by Gosetti et al. (2004). Additionally, Thiam et al. (2014 and 2015) used GC-MS to propose structures of Allured A.C. and Tartrazine intermediates

Thesis Question 2: What are the reaction rate constants?

Reaction rate constants were determined for the beads, cylinders and slide using Allura Red AC and Brilliant Blue FCF. Multiple reactor designs were considered when evaluating kinetics; pseudo-first order kinetics for a batch reactor system had the best fit to the experimental data. Previous literature also found pseudo-first order reactions to be the best fit for with similar organic dyes. The reaction rate constants were determined to be 5.4×10^{-3} , 4.5×10^{-3} , and $2.6 \times 10^{-3} \text{ min}^{-1}$. Allura Red AC combined with the beads the largest rate constant.

Thesis Question 3: How do the different photocatalyst substrates affect degradation?

Results conclude that dyes could be effectively removed from water using UV-LED with TiO_2 immobilized on beads. The beads contained the largest mass of TiO_2 per unit surface area. They degraded Allura Red AC the most at nearly (60%) and had the smallest E_{EO} value of 9.2. When the reactor was filled with beads, it contained the smallest volume (compared to cylinders and the slide). The beads provided mixing and stirring during treatment time.

Results for the cylinders had the second largest Allura Red AC degradation. Cylinders were not used during Brilliant Blue FCF experiments since they were acquired after these experiments. It was unclear if this shape had any effect on degradation since there was less TiO_2 coating per surface area. More experiments need to be conducted using the cylinders to determine what type of effects they have on degrading contaminants.

The slide had the smallest surface area available for coating but showed more TiO_2 by mass than the cylinders. One disadvantage using the slide included a lack of

solution mixing during treatment. Increased degradation may have been possible if there was stirring or mixing.

3.3 LIMITATIONS

Thesis research initially began by investigating photocatalytic degradation of 2, 4-dinitrotoluene (2,4-DNT) using UV-LED with TiO₂ immobilized on a standard glass microscope slide. The initial experimental setup proved inconclusive at degrading 2,4-DNT. However, it was later observed that the UV-LEDs didn't have a sufficient power output. More powerful UV-LEDs would allow for more fluence and consequently more production of hydroxyl radical ($\cdot\text{OH}$) species. This technology has yet to meet the same power output or fluence values as mercury vapor lamps. To study degradation, experiments were continued with the use of organic dyes with different immobilized photocatalyst substrate and more power.

Limitations were initially discovered with 2, 4-DNT solubility in water. Although this contaminant is persistent and common in groundwater at or near munition ranges, the fate and transport into groundwater varies with different environmental matrices (i.e. soil, water, climate) (Sharma et al., 2013; Wang et al., 2012). The amount of time for 2, 4-DNT to dissolve in water is variable when comparing laboratory to environmental conditions. Experiments conducted with the LEDs on demonstrated increased absorbance at 255 nm. It was thought that, LEDs on would result in increasing solution temperature which could raise the solubility of 2, 4-DNT (O'Sullivan, 2006). This could affect absorbance values during the experiment. If there were any remaining 2, 4- DNT particulates in the solution then then may have formed agglomerates and adhered to the

cuvette. The initial flow-cell cuvette contained only a narrow opening (1 mm) for scanning. This may have resulted in fluctuating absorbance values.

Several additional problems were also noted during experiments. Control experiments without photocatalyst and with the LED off absorbance values for 2, 4-DNT decreased with time. Fig. 11 shows 1 scan per minute of 10 mg L⁻¹ recirculated for 500 minutes at a flow of 2 mL min⁻¹.

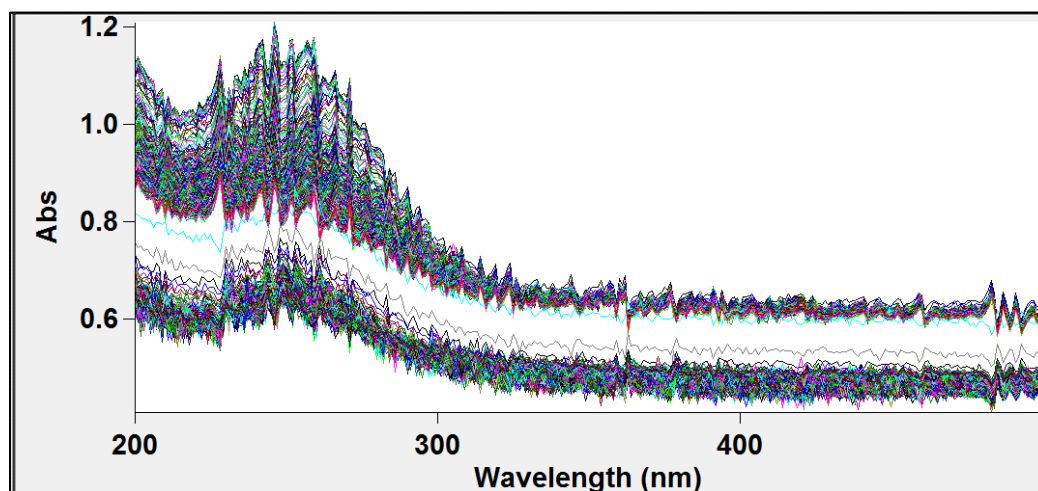


Figure 11. Analysis of 10 mg L⁻¹ 2, 4-DNT without photocatalyst and LED off.

Full scans also indicated “noisy” spectra around 255 nm, the peak region of interest. The absorbance values fluctuated between 0.8 and 1.2 absorbance units. The flow-cell cuvette could have contributed to the noisy spectra if the beam was improperly aligned, since there is a narrow sampling window. DIH₂O was used as a background subtraction. Experiments analyzing only water showed degrading values over a 12-hour period. After contacting Agilent, it was discovered that 2, 4 -DNT absorbed in the same region as H₂O and it was possible the UV lamp on the instrument needed replacement. Instrument maintenance was performed by conducting a beam alignment. Furthermore, the flow-cell

cuvette was also susceptible to trapping small air bubbles which can alter instrument readings and can give faulty absorbance values thereby generating noisy spectrums. Agilent recommended using a different UV instrument or technology for analysis (Agilent Cary 100 UV-Vis or higher) and to stop the flow during readings.

Due to these discrepancies and lack of faster degradation, experimental design shifted to using organic dyes and explored the use of TiO₂ slurries. Slurries were investigated using nano-sized anatase TiO₂ concentration ranges from 500 to 2500 mg L⁻¹. Limitations were also observed during these analyses. It was noted that the TiO₂ slurry showed strong absorbance from 200 to 360 nm which is in the same region as H₂O absorption. Slurry data proved inconclusive for degrading the dye. (Fig. 17).

3.4 SIGNIFICANCE OF FINDINGS

Results demonstrated an enormous impact of water treatment using UV-LED photocatalytic degradation. Low-power UV LEDs with the Teflon[®] reactor design proved to be robust and effective throughout this research. Research demonstrated that the sol-gel procedure may be used to coat nano-size TiO₂ onto substrates with various physical properties. Furthermore, it was shown that these substrates may be used in various configurations with the unique reactor design. Experimental data suggested that the reactor is characterized as CMBR, which will facilitate future research using this design. The largest degradation results were shown using TiO₂ annealed beads. Secondly, beads simultaneously provided mixing in the reactor during treatment. This configuration may be used with QSPR modelling techniques to predict the degradation of emerging contaminants. Combining these findings, significant advancements were made in the field

of water research. The DoD should consider this approach as a low-cost option for groundwater treatment.

3.5 FUTURE RESEARCH

Additional research should be completed using different organic contaminants at the same concentrations and under identical experimental conditions (flow, pH, temp etc.). UV-LED exposure time should also be equal during treatments. This would allow for a more straightforward comparison of overall degradation and apparent rate constants unique to this reactor design.

Enhanced technologies such as Gas Chromatograph Mass Spectrometry (GCMS) or Liquid Chromatography (LC) are preferable for more detection capabilities. GCMS and LC analysis could also be used to identify intermediates and degradation pathways. Additionally, different contaminants will provide further understanding of degradation pathways through oxidation by non-selective hydroxyl radicals. Experimental data provided here will benefit future modelling requirements to predict degradation.

Other miscellaneous future research noteworthy includes substrate geometry, $\cdot\text{OH}$ concentration, potential loss of TiO_2 into the system and flow-rate. It's uncertain how geometry would affect photocatalytic degradation in terms of mixing. Methods have been previously used to determine $\cdot\text{OH}$ concentration and rate constants (Dominguez et al., 2015). These should be further evaluated using this reactor configuration. When flow rates were adjusted to compensate for a reduced reactor volume, the beads outperformed the slide. This evidence suggests that a longer reactor residence time was not as significant as the number of cycles through the reactor. It should be further investigated

how the slide would compare with a faster flow rate. It's uncertain if previous research has shown TiO_2 to become immobilized and lost into the system. However, Swarnakar et al. (2013) demonstrated only weak evidence to suggest degradation efficiency decreases after multiple uses.

APPENDIX A. EXPANDED LITERATURE REVIEW

The expanded literature review provides additional background and historical aspects that is significant to this research. Vast improvements have been made in the science of photocatalysis and the substrates used. Appendix A intends to further illustrate significant advances in this research as it relates to water remediation.

A.1 Background

Since the discovery of the “Honda-Fujishima effect” there has been a vast amount of information dedicated to photocatalysis in water using Titanium dioxide (TiO_2) as a photocatalyst (Fujishima & Honda, 1972). TiO_2 has a band-gap energy between 3.1 and 3.2 eV and can be activated in the near UV range ($<400\text{ nm}$), this makes UV-LED light a promising technology for photocatalysis. Through these reactions, the formation of a hydroxyl radical ($\cdot\text{OH}$) produced from an irradiated metal- TiO_2 is considered to be the dominant species (Swarnakar et al., 2013). The radical then proceeds to degrade organic pollutants to CO_2 and H_2O . Recently, TiO_2 as a photocatalyst is being studied for remediating water contaminated with a variety of organic pollutants including nitroaromatic compounds (NACs) (Dillert et al., 1995; Nahen et al., 1997; Schmelling & Gray, 1995; Schmelling et al., 1997; Son et al., 2004).

A.2 Photocatalyst Substrates

Titanium dioxide has been used extensively as a photocatalyst. It is also widely known for its ability to break down organic pollutants and achieve complete mineralization (Umar & Aziz, 2013). There have been many recent developments of titanium dioxide annealed to various surfaces and being used as a slurry. Various studies have reported that TiO₂ has been immobilized onto glass slides, beads, fibers, nanofibers, quartz and fiberglass cloth; among others (Natarajan et al., 2011) (Ghosh et al., 2009). Optimal TiO₂ slurry loading rates have also been researched depending on the organic contaminant of concern.

Two emerging water remediation techniques involve using a TiO₂ slurry and immobilization on glass. These technologies are known to destroy organic contaminants in water. TiO₂ slurries have been prepared in various concentrations ranging from 500 to 2500 mg L⁻¹ and investigated with photocatalytic degradation (Chen et al.,2007; Fabiyi & Skelton, 2000; Malkhasian et al., 2014; Natarajan et al., 2011; Schmelling & Gray, 1995). A TiO₂ slurry is often considered more effective at oxidizing and degrading organic contaminants, however, removing TiO₂ from water can be tedious and time consuming.

The advantages of a photocatalytic reaction on an immobilized glass slide or other substrate has allowed for a fast and sustainable treatment method without the need to recover TiO₂. The research presented here explores the advantages of higher surface-to-volume ratios and greater specific surface areas of TiO₂ nanoparticles. Future commercial UV-LED applications using TiO₂ semiconductors as thin film reactor substrates may prove highly effective at removing organic contaminants in an environmentally sustainable manner.

Past research has shown Hydrogen Peroxide (H_2O_2) reacts with UV light and generates $\cdot\text{OH}$ radicals in the presence of UV light (Daneshvar et al., 2005; Daneshvar et al., 2005; Duckworth et al., 2015; Malkhasian et al., 2014). Using H_2O_2 as a photocatalyst, additional experiments were performed to determine if there was an increased production of $\cdot\text{OH}$ radicals.

APPENDIX B. EXPANDED RESULTS AND DISCUSSIONS

Appendix B expands on important experimental procedures not presented in the Scholarly Article.

B.1 Photocatalysis Optimization

Degradation experiments were optimized by different methods including the use of different photocatalysts and increased LED power supply. Traditional UV photocatalysis typically uses more powerful mercury vapor lamps to achieve reasonable degradation (>30%). The power supply and circuitry was therefore reconfigured to increase experimental input power from 150 mA to 220 mA. This was done for 2, 4-DNT experiments prior to analyzing dyes.

Another method is to apply different immobilized photocatalyst substrates and at different loading rates. This was evaluated with the use of TiO_2 immobilized on beads, cylinders and slides. Table 1 of Chapter 2 provides a summary of these results.

Additionally, TiO_2 was analyzed in suspension as a slurry and found to be predominantly in anatase phase. Impacts of TiO_2 loading may be observed by comparing fluence values.

Final fluence results are presented in Table 2 of Chapter 2. Cylinders had the largest fluence values for the experimental setup with the least TiO_2 per surface area.

Since the borosilicate beads showed the largest degradation, it was anticipated that they would also have the largest fluence values. It is possible that the difference was due to material composition. The cylinders were made up of quartz, whereas the beads were made up of borosilicate. There were potentially more photon interactions with the cylinders. A small difference in the reactor volumes between the beads and cylinders may have affected these results. It should be noted that the fluence depends on reactor design and configuration.

When developing a model for the reactor, a rate constant was needed. When plotting experimental data using first and second-order kinetics, the correlation was virtually identical for corresponding rate constants. This reactor was modelled using continuous stirred tank reactor (CSTR), plug flow reactor (PFR) and as a completely mixed batch reactor (CMBR). Adjusted rate constants were determined based on the volume of water treated per exposure time in the reactor. Thiam et al. (2015) have previously shown that photocatalytic degradation of Allura Red AC follows pseudo-first order kinetics. This is apparent for Brilliant Blue FCF as well, since it is assumed that the concentration of the dyes are much larger than the concentration of $\cdot\text{OH}$ species.

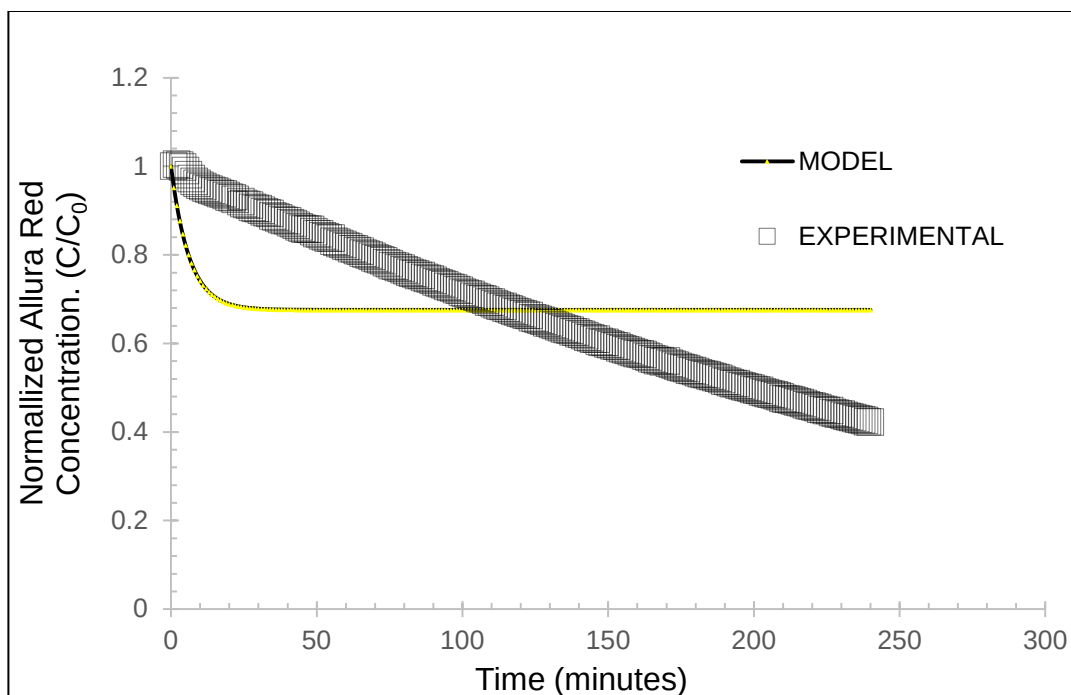


Figure 12. CSTR Reactor model using beads with Allura Red AC.

CSTR was modeled under non-steady state assumptions. Fig.12 clearly shows experimental data did not match CSTR model parameters.

A PFR was then considered to better understand how the reactor was performing. It was thought that this would be an ideal choice, when the glass slide was in use. However, with beads and cylinders, plug flow would not be the best choice. When modelled, the line of best fit didn't match the predicted rate constants. Since the experimental setup included recirculating the flow and no new reactants or products were added, it was determined the system was closed. This allowed for the consideration of a CMBR.

An ideal CMBR model was chosen to further analyze the data. Assumptions include a uniform contents of the reactor (no density gradient), temperature and chemicals are uniformly distributed (Crittenden, 2005). Accounting for exposure time of

the volume treated, the reactor was again modeled as explained in Chapter 2. The slope of the experimental data matched the CMBR model accordingly.

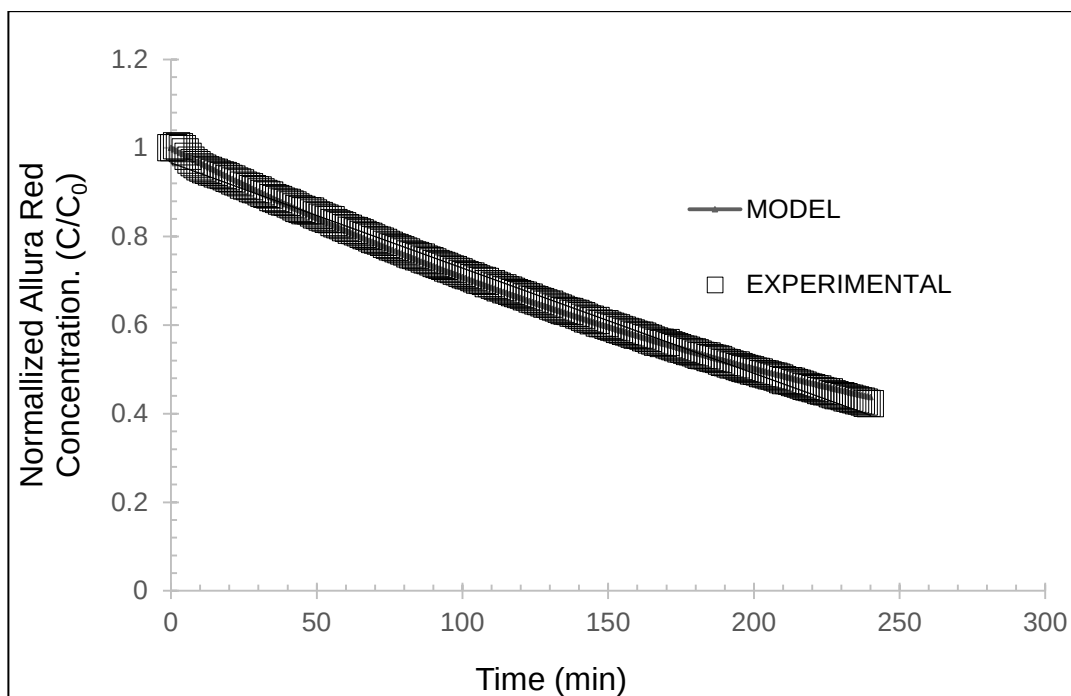


Figure 13. CMFR Reactor model using beads with Allura Red AC.

The reaction rate constant as seen in Figure 13 closely matched first-order kinetics. These results were compiled into Table 3 of Chapter 2.

B.2 Photocatalytic Degradation of 2, 4-Dinitrotoluene

A 50 mg L⁻¹ stock solution of 2,4-DNT was prepared as per the Standard Operating Procedure for 2, 4 – DNT Solution Prep. (Appendix C). A 10 mg L⁻¹ working solutions was prepared by pipetting 10 mL of the stock solution into a 50-mL volumetric flask. The solution was brought to volume with DIH₂O. The UV-Vis spectrometer was configured to scan every minute between 200-800 nm for a total of 500 minutes. Maximum absorbance values between the stated scan ranges were used for all plots. A

peristaltic pump was calibrated and set to 2 mL min^{-1} recirculating the solution. For this and all remaining experiments, the LED was turned on at the instant the UV-Vis began acquiring data. As discussed in the Limitations section there were discrepancies during the 2, 4-DNT analyses. These are clearly seen in Fig. 14.

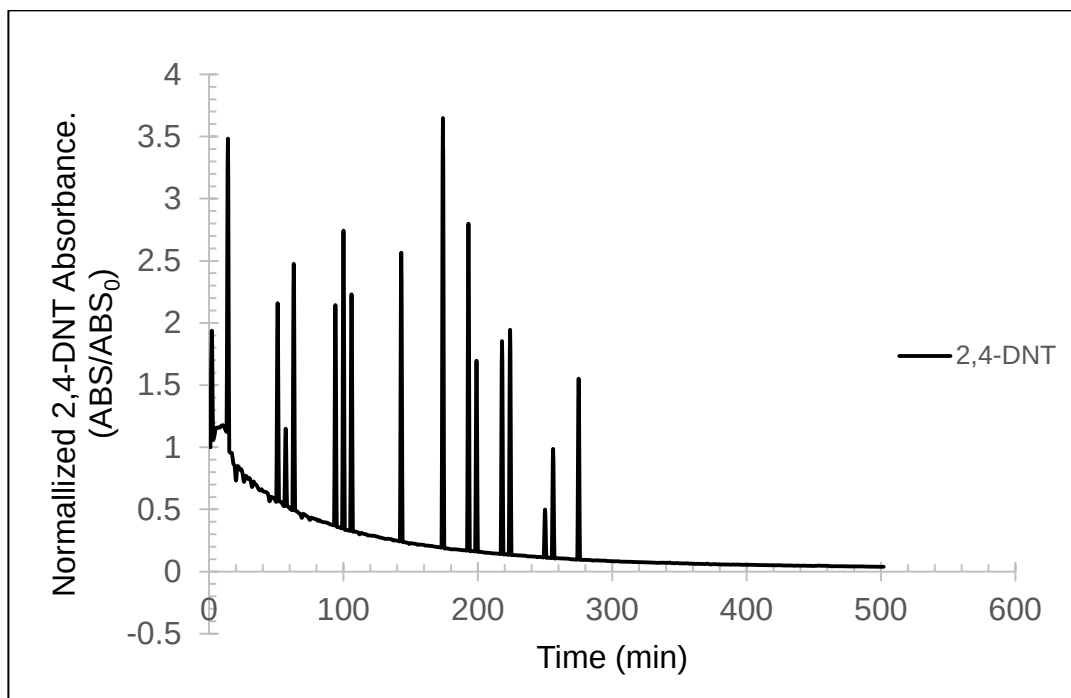


Figure 14. Normalized absorbance plot of 2, 4-DNT versus time using a 5-Dip slide.

Since erroneous data points were observed in these experiments, dyes were used for further experiments.

B.3 Photocatalytic Degradation of Tartrazine

A 5 millimolar (mM) solution of Tartrazine and Hydrogen Peroxide was prepared by mixing 0.02660 g Tartrazine (Sigma-Aldrich, St. Lois, MO; Purity $\geq 85\%$) and 2.87416 g (AFIT Bal. H9002) 30% H_2O_2 (Fisher-Scientific, Pittsburgh, PA) into a 1-L volumetric flask brought to volume with DI H_2O . The solution was well mixed and

stirred with a magnetic stir bar for 5 min. The same solution was used for all four experiments. The UV-Vis spectrometer was configured to scan every minute between 300-550 nm for a total of 180 minutes. The flow rate was calibrated and set to 4 mL min⁻¹ using the same peristaltic pump as described in earlier section. Three control samples were analyzed prior to the experiment as can be seen in Figure 15 below.

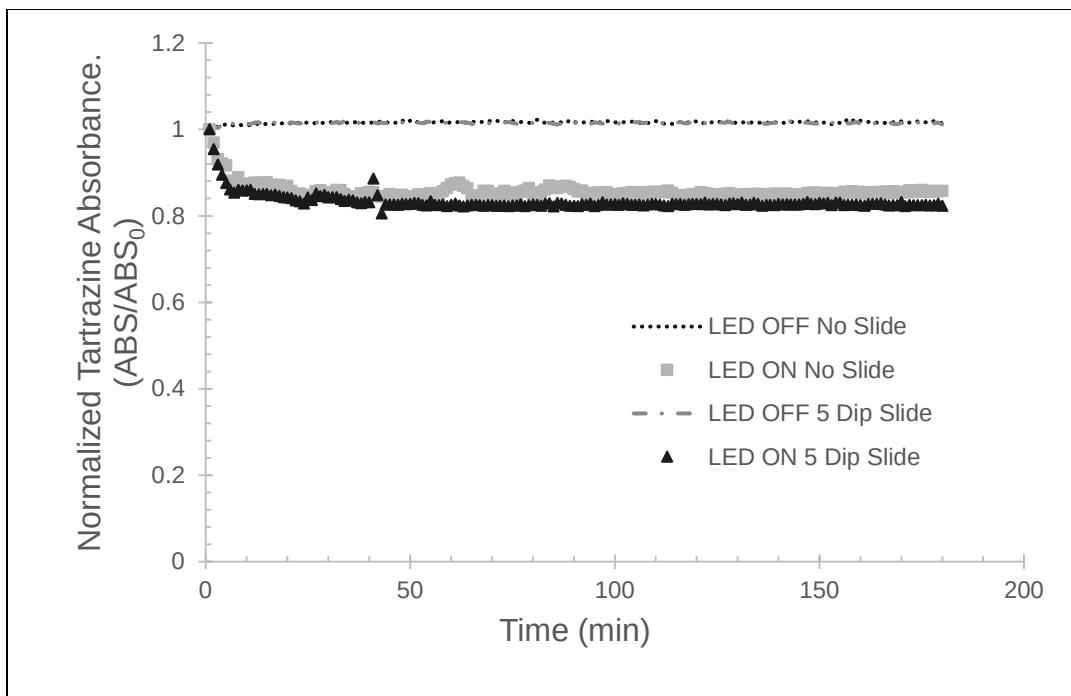


Figure 15. Slide and H₂O₂ comparison: Normalized Tartrazine absorbance units (a.u.) vs. Time (min).

It was observed that the percent degradation (18 and 15%, respectively) results were similar to the case when the LED was on, with and without a 5-dip slide (18 and 15%, respectively). Secondly, the reaction occurs fast initially, then progresses slowly. Almost all degradation occurred within the first 25 minutes. These results indicated that most of the degradation was a result of H₂O₂ instead of TiO₂.

The experiment was repeated with a few deviations to verify these results. A 5 mM solution of Tartrazine was used for all experiments, except H₂O₂ was added for only the last analysis. The last analysis was performed using a freshly prepared solution of H₂O₂ (2.55840 g of 30% H₂O₂ + 890 mL Tartrazine solution). The flow was recalibrated and decreased to 1.5 mL min⁻¹ and different 5-Dip slides were investigated. These results are presented in Figure 16. It was noted that the input power had reduced to 200 mA at the end of the experiment. This was later determined to be a result of a failed resistor in the circuit board. The remaining experiments were based on this amperage.

These results closely matched the previous experiment. UV-LED with H₂O₂ yielded approximately 30% degradation. This further proved that degradation could only be attributed to increased ·OH radical production from H₂O₂ and not necessarily due to the presence of the 5 Dip slide.

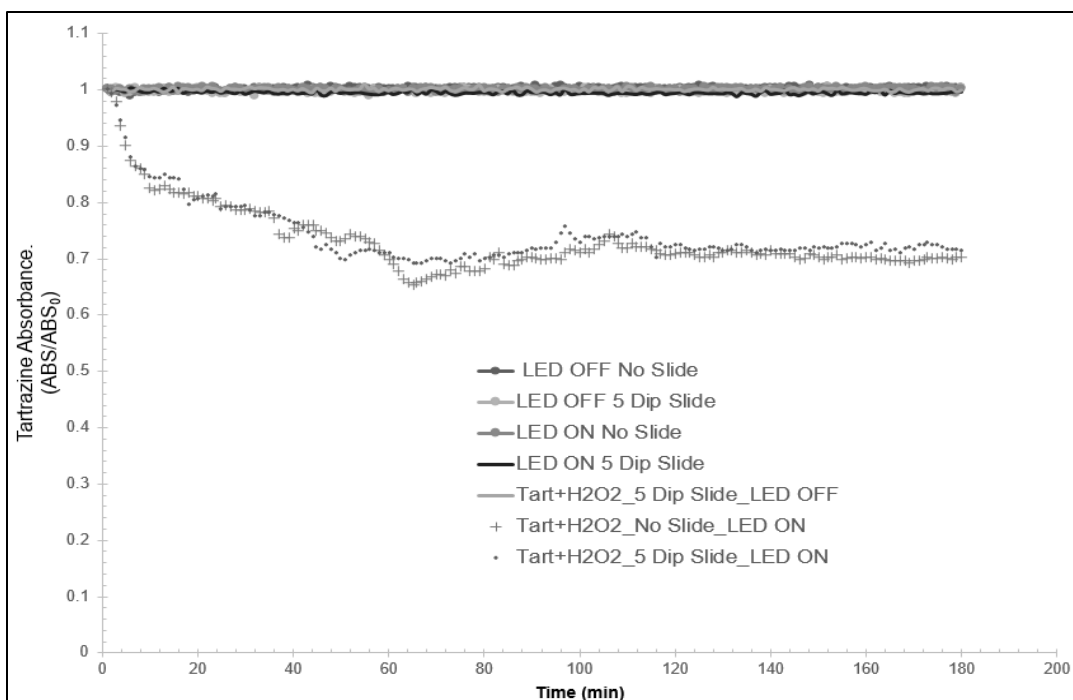


Figure 16. Slide and H2O2 comparison: Normalized Tartrazine absorbance units (a.u.) vs. Time (min).

Tartrazine degradation was also explored using TiO₂ slurry. A solution of 500 mg L⁻¹ TiO₂ was prepared by using the 1.67 mL of the 15% TiO₂ (US Research Nanomaterials, 5-30 nm) into a 500-mL volumetric flask and brought to volume with DI-H₂O. This was used as a background which was later subtracted. A 10 mg L⁻¹ solution of Tartrazine was prepared by adding 2.505 mg Tartrazine into a 250-mL volumetric flask and brought to volume with the previously made TiO₂ Solution. The scan range was set to 475-375 nm with 1 scan per minute for 360 minutes. The flow was calibrated and adjusted to 3 mL min⁻¹ and the solution was recirculated (Natarajan et al., 2011). Using the TiO₂ solution, two analysis were performed one as controls with the LED on and the other one with LED off. A third control was analyzed using the TiO₂ solution with Tartrazine and the LED off.

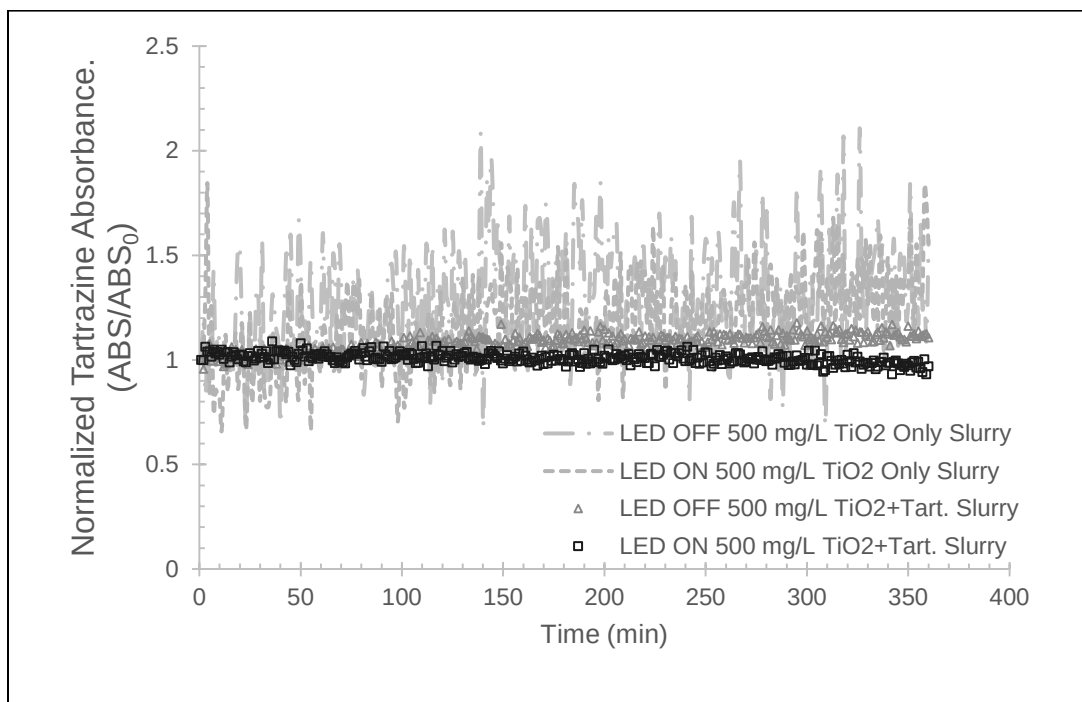


Figure 17. Tartrazine with TiO₂ slurry experiment: Normalized Tartrazine absorbance units (a.u.) vs. Time (min).

Figure 17 results show a noisy spectrum when only TiO₂ was analyzed. This may be attributed to TiO₂ agglomerates that formed and were retained in the flow-cell cuvette. This procedure showed minimal degradation and further experiments were analyzed.

A second experiment was performed using a TiO₂ slurry with Tartrazine. The slurry concentration was increased and the flow was decreased to 1.5 mL min⁻¹. A 100 mg L⁻¹ TiO₂ solution was prepared by adding 3.333 mL of 15% TiO₂ (US Research Nanomaterials, 5-30 nm) into a 500-volumetric flask and brought to volume with DI H₂O. A 10 mg L⁻¹ solution of Tartrazine was prepared by adding 2.521 mg Tartrazine into a 250-mL volumetric flask and brought to volume with the previously made TiO₂ solution. The scan range was set from 475-375 nm with 1 scan per minute for 360 minutes.

B.4 Photocatalytic Degradation of Brilliant Blue FCF

Further experiments were conducted using Brilliant Blue FCF as the organic contaminant. The effectiveness of photocatalytic degradation was evaluated using TiO_2 as a slurry and immobilized on a glass slide. Flow rates were adjusted to investigate the effects of contact time with the photocatalyst. The UV-Vis spectrophotometer was configured to scan every minute between 620-640 nm for a total of 240 minutes. Background subtraction was performed using the TiO_2 slurry solution (see narrative below). Flow rates were calibrated and set to 1.5 and 0.75 mL min^{-1} using the same peristaltic pump as described in earlier section. The solution was recirculated using a 250-mL volumetric flask and continuously stirred with a magnetic stir bar. The power was set to 200 mA and 23.5 volts.

A 1000 mg L^{-1} Brilliant Blue FCF Stock Solution was prepared by weighing 0.101933 g (AFIT Microbalance) Brilliant Blue FCF (Crescent Chemical E133, Islandia, NY; Purity=98%) into a 100-mL VF. The solution was diluted to volume with DIH_2O and well mixed using a wrist shaker for 5 minutes. A 250 mg L^{-1} TiO_2 anatase slurry was prepared by pipetting 1.667 mL of 15% TiO_2 anatase (US Research Nanomaterials, 5-30 nm; Houston, TX) into a 1-L volumetric flask. The solution was brought to volume using DIH_2O . A 10/250 mg L^{-1} Brilliant Blue/ TiO_2 working mixture solution was prepared by pipetting 2.5 mL of the Brilliant Blue FCF Stock solution into a 250-mL volumetric flask and brought to volume with the 250 mg L^{-1} TiO_2 slurry. A 500 mg L^{-1} TiO_2 slurry was prepared by pipetting 3.334 mL of 15% TiO_2 anatase into a 1-L volumetric flask and brought to volume using DIH_2O . A 2,500 mg L^{-1} TiO_2 slurry was prepared by pipetting 8.333 mL of 15% TiO_2 anatase into a 1-L volumetric flask and brought to volume using

DIH₂O. A 10/500 and a 10/2500 mg L⁻¹ Brilliant Blue/TiO₂ mixture was prepared in the same manner as the 10/250 mg L⁻¹ working solution.

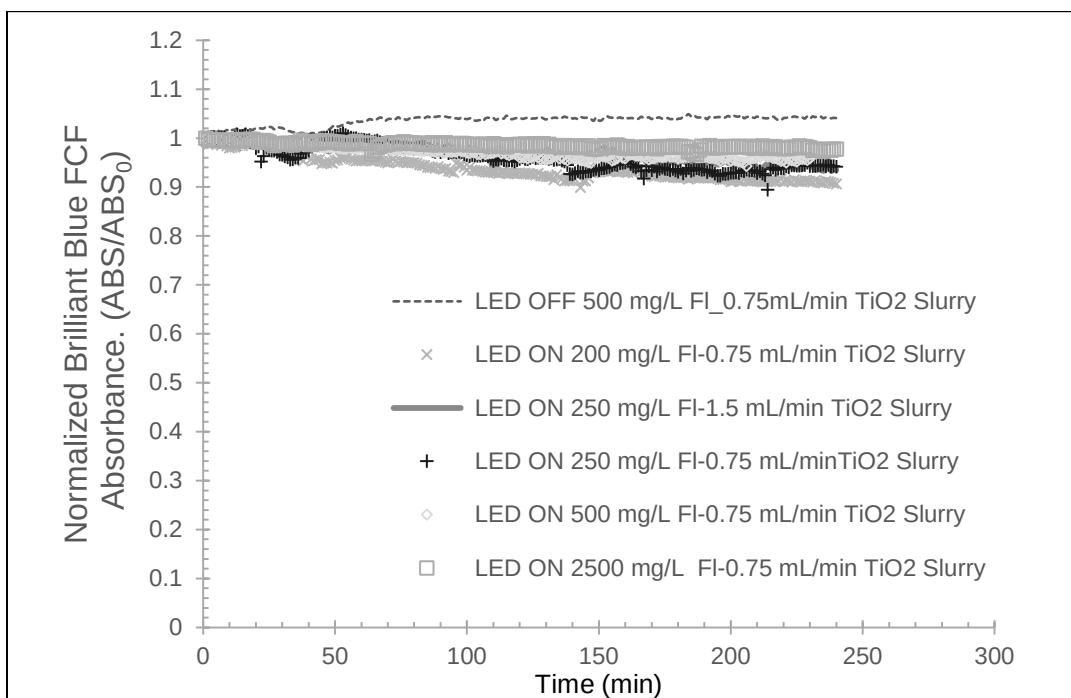


Figure 18. Brilliant Blue/TiO₂ Anatase Slurry Comparison.

As seen in Figure 18, the slurry analyses exhibited <10% overall degradation (all solutions contained 10 mg L⁻¹ of Brilliant Blue FCF). It was anticipated that the TiO₂ slurry would yield larger degradation given that there is more opportunity for UV light interaction with TiO₂ in suspension. It was observed that the solutions became white with increased turbidity when TiO₂ was added. This could have potentially interfered with the depth UV light could penetrate the reactor. Which may have caused reduced photoactivity leading to less degradation.

An additional experiment was completed using TiO₂ immobilized on a glass slide and compared to the TiO₂ slurry. This experiment was conducted to determine if the mass

of TiO_2 on the slide compared to the mass of TiO_2 as a slurry would effect degradation. Since photocatalytic degradation using H_2O_2 has been well established and was outside the scope of this research, it was excluded from further experiments. Experimental setup and solutions were prepared as per the previous experiments. A $200 \text{ mg L}^{-1}\text{TiO}_2$ slurry was prepared to closely match the TiO_2 mass (189 mg) calculated from the slide. Results are presented in Figure 19.

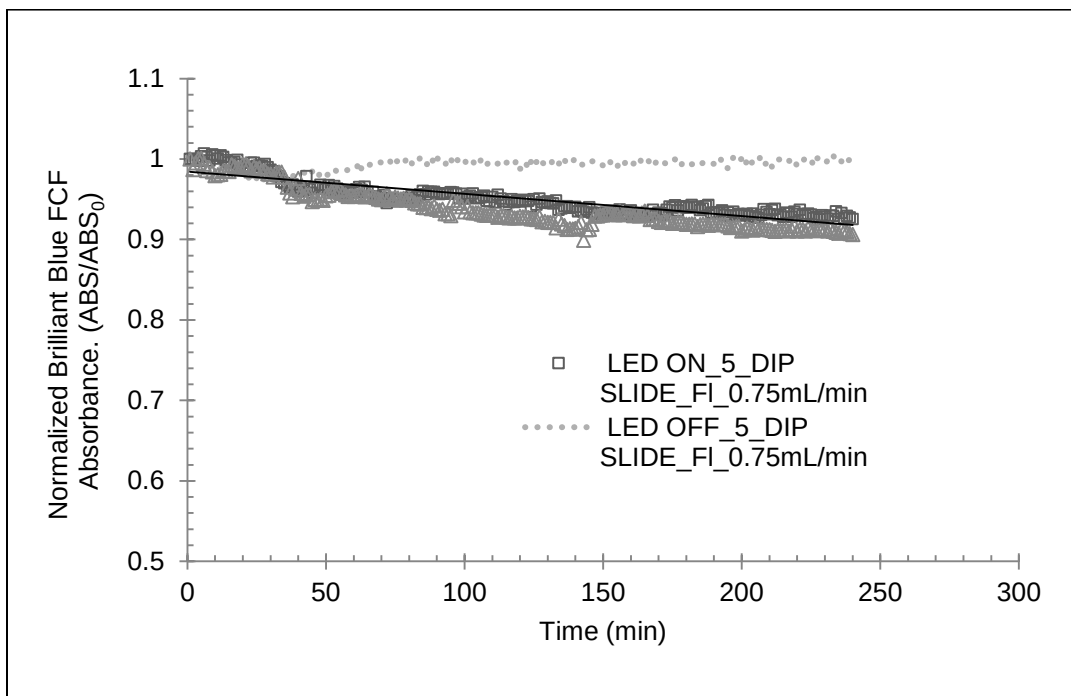


Figure 19. Brilliant Blue FCF with 5-Dip slide/ TiO_2 slurry comparison.

Results showed that the overall degradation using TiO_2 slurry has slightly higher degradation compared to TiO_2 immobilized on the slide. The control samples showed a steady baseline with little to no degradation of the contaminant throughout the experiment duration. However, with <10% degradation, it was decided that the experimental protocol should be redesigned.

Minimal degradation in the current experimental design may have been the result of several factors. First, there was a large volume of solution that recirculated (~250 mL) in the system. With large volume being treated, the energy imparted by UV-LEDs may have been insufficient to achieve maximum degradation. A magnetic stir bar was used to mix the solution in the 250-mL volumetric flask but the mixing was occurring only outside the reactor and not during the treatment process. Improper mixing could have diminished contact frequency with the photocatalyst (Fabiya & Skelton, 2000). Additionally, the concentration used was higher than other experimental set ups doing similar research using UV-LED with dyes (Natarajan et al., 2011; Tayade et al., 2009). It was decided to use beads coated with TiO₂ as a substrate. The same sol-gel procedure was used to coat the slide was used to coat the beads five times. This method simultaneously solved several problems with the current experimental setup. First bed volumes and contact frequency with the photocatalyst were increased. Second, mixing could now occur in the reactor during treatment. Experimental parameters were adjusted to compensate for the reduced volume in the reactor. The volume of solution measured in the reactor when it contained packed beads was determined to be 16 mLs. Since the reactor volume was previously measured at 37 mL, the volume was reduced by a factor of 2.3. The flow was increased by this factor, from 0.75 to 1.73 mL min⁻¹, which decreased reactor residence time but increased the exposure time.

An experiment was conducted to determine if the beads could further degrade Brilliant Blue FCF than the previously used 5-dip slides. A 10 mg L⁻¹ solution of Brilliant Blue FCF was prepared by adding 1 ml of the Brilliant Blue stock solution into a 100-ml volumetric flask and diluting it to volume with DIH₂O. A magnetic stir bar was placed

inside the flask and stirred during the experiment. Instrument parameters were the same as previous experiments. Results can be seen in Figure 20 below.

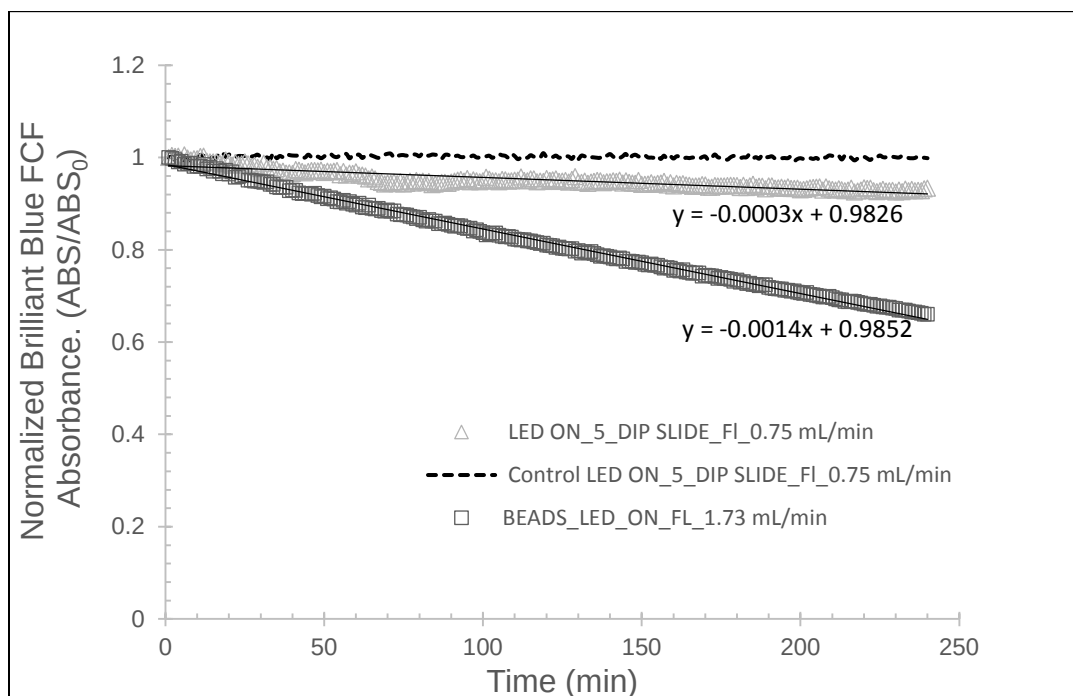
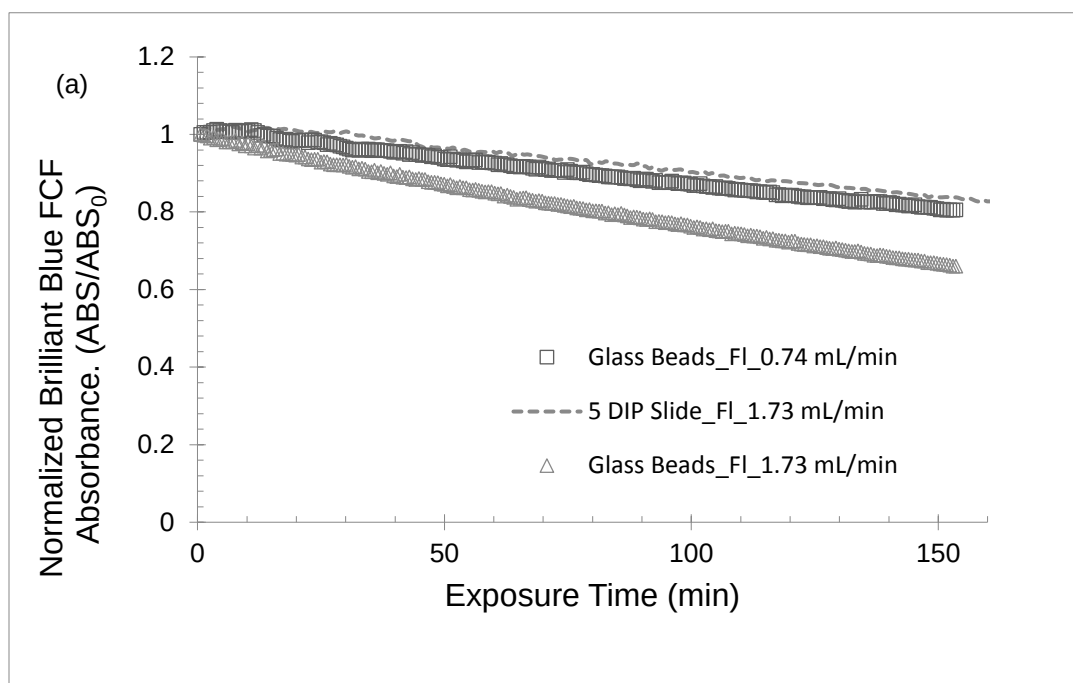


Figure 20 Normalized absorbance comparison of 5 dip beads versus 5-dip slide.

Beads showed an overall 34% degradation compared to the 5-dip slide. It should be noted that the total volume was ~250 mL for the slide and ~100 mL for the beads. Since there was a larger mixing vessel for the slide, the same Brilliant Blue FCF molecules may not have been treated as many times as the beads.

Additional experiments were analyzed to normalize the data between the TiO₂ immobilized slide and beads based on exposure time. Flow was adjusted to 0.74 for the beads and 1.73 mL min⁻¹ for the slide. A 154 minute exposure time was calculated for each treatment in a four-hour experiment. A small beaker was setup to maintain the influent and effluent volumes at ~3-mL for both the beads and the side. The volume was

measured in the tubing by filling it with DIH₂O and draining into a 10-mL graduated cylinder. The total system volume was calculated by summing the reactor volume containing the immobilized substrate, tubing volume, beaker volume and cuvette volume. Total system volume for the beads was calculated at ~25 mL for the beads and 46.5 mL for the slide. Results are presented in Figure 21: (a) exposure time treated during the four-hour experiment and (b) further confirms that the beads and the slide perform equally when flow is adjusted. In this experiment, beads performed slightly better when exposure time is normalized.



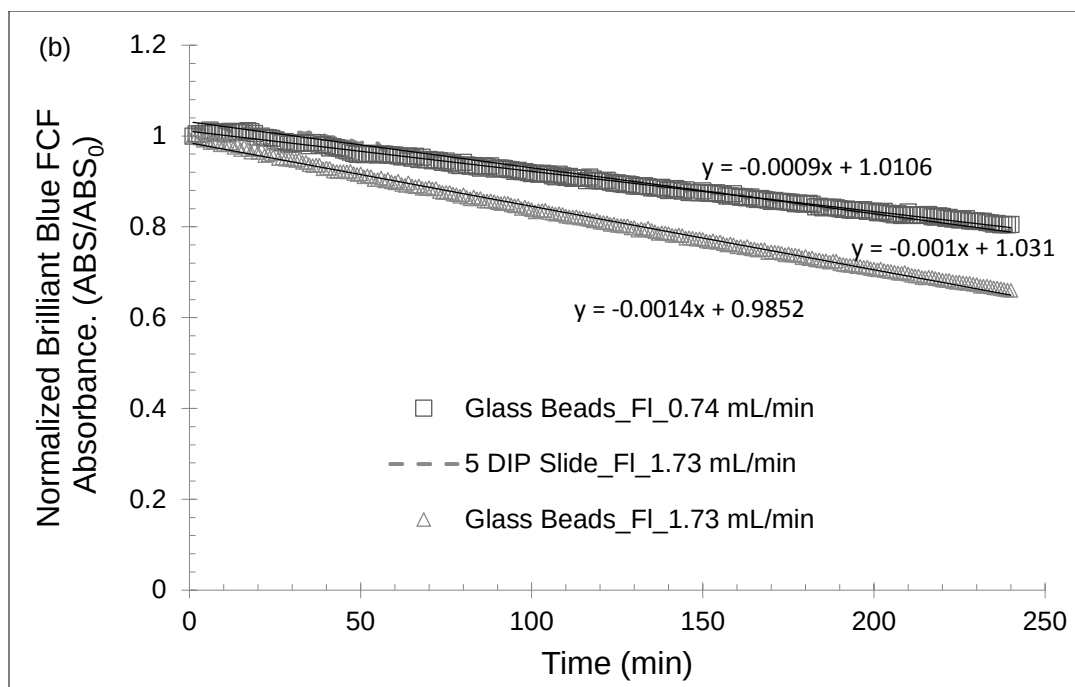


Figure 21. Immobilized TiO₂ slide vs. beads comparison: (a) Normalized absorbance versus exposure time treated. (b) Normalized absorbance versus time.

Although there was a larger system volume treated for the slide, it requires the flow to be increased to compensate for the exposure time. These are important factors to consider when engineering and evaluating treatment cost. A faster flow would require more power to continuously pump and treat an organic contaminant; albeit a larger volume is treated. The beads may provide better mixing and could prove more valuable for organic contaminants with different physical properties. For example, some contaminants may be less soluble and could have more effective treatment using beads over a slide positioned in the middle of the reactor. Beads may provide an increased frequency of surface TiO₂ interaction.

To confirm beads results, additional experiments were conducted to verify that the results are reproducible. These experiments were conducted with more controls. A magnetic stir bar was again placed inside a small beaker containing ~3 mL of the influent

and effluent concentration and the solution was well mixed during all experiments. Three experiments were analyzed in a two-week period. These results are presented in detail in Chapter 2.

A calibration curve was developed to convert absorbance values to concentration and determine the mass of Brilliant Blue degraded. Serial dilutions were prepared volumetrically at 0.1, 0.5, 1, 5, 10 and 20 mg L⁻¹ with each solution analyzed three times and averaged for plotting using the UV-Vis spectrophotometer. The calibration curve further demonstrated the accuracy and precision of the Carey 60 UV-Vis spectrometer. A 1 mg L⁻¹ check standard was quantified at 1.04 mg L⁻¹ against the curve. This can be seen in Figure 22 below.

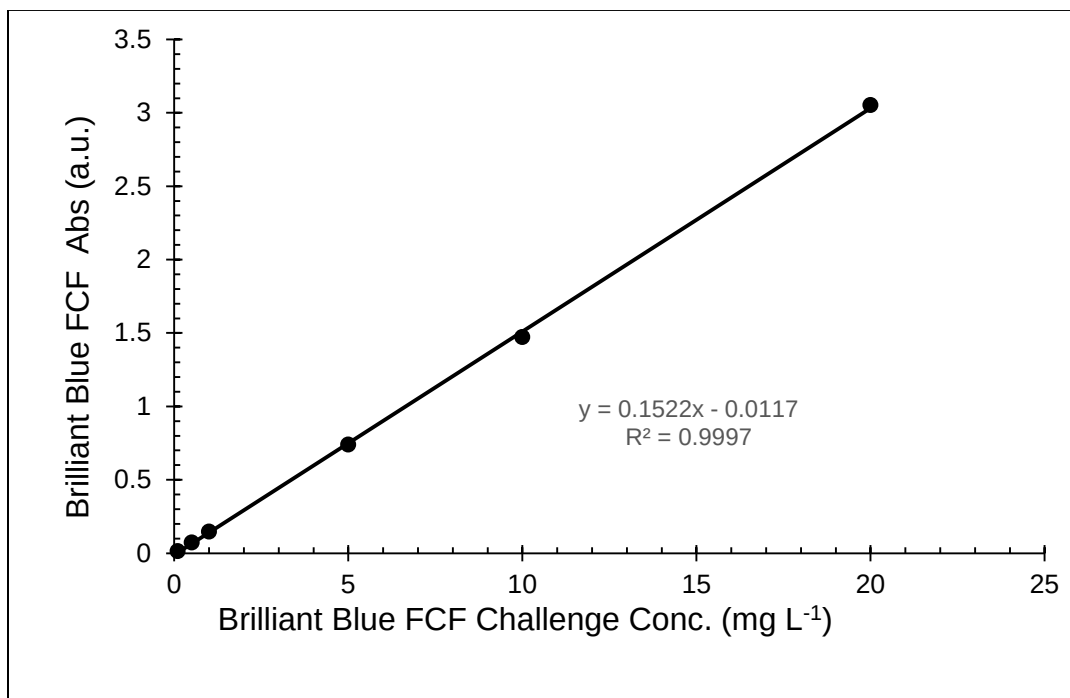


Figure 22. Brilliant Blue FCF calibration curve for the Cary 60 UV-Vis.

Two of the previous experiments were analyzed for a 16-hour period to determine reaction rate constants and final degradation values. Final values were determined to be 1.38 and 1.36 mg L⁻¹ after 16.65 hours. This is almost an order of magnitude degradation after a 16-hour period. Although these results appear promising, the extended treatment time may be costly and may not be suitable as a practical groundwater treatment technology.

B.5 Photocatalytic Degradation of Allura Red AC

Glass beads demonstrated to be an ideal photocatalyst in a packed bed reactor design. Quartz cylinders were acquired to further investigate the effects of physical shape and material had on degradation of Allura Red AC, an organic dye. This dye was chosen to compare optimal degradation using beads, cylinders and slides.

A 1000 mg L⁻¹ stock solution was prepared by adding 0.10558 g (AFIT Bal. H9002) of Allura Red AC (Tokyo Chemical Industry, Tokyo, Japan; Purity=95%) into a 100-mL volumetric flask. The solution was brought to volume with DIH₂O, well mixed using a wrist shaker and sonicated for 5 minutes. A 5 mg L⁻¹ working standard was prepared by pipetting 5 mL of the stock standard into a 1-L volumetric flask and brought to volume using DIH₂O. A calibration curve was established to convert absorbance values to concentration and determine the mass of Allura Red AC degraded. Serial dilutions were prepared volumetrically at 0.5, 1, 5, 10 and 20 mg L⁻¹ with each solution analyzed three times. The three absorbance values were then averaged and plotted using Microsoft Excel[®]. This can be seen in Fig. 23.

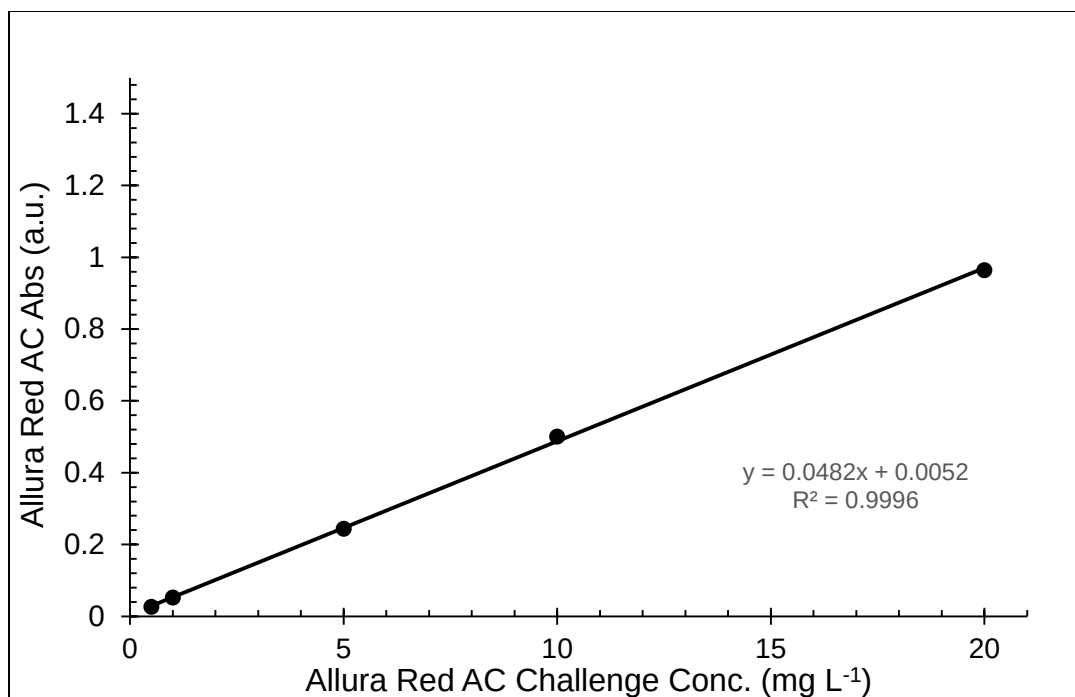


Figure 23. Allura Red AC Calibration curve

A 5 mg L⁻¹ check standard was quantified against the curve and calculated to be 5.04 mg L⁻¹. Detailed results for Allura Red AC are fully summarized in Chapter 2.

APPENDIX C. SUPPLEMENTAL MATERIAL

Appendix C covers supplemental material is provided to support overall quality assurance objectives of laboratory data.

C.1 Allura Red AC UV-Vis Method Parameters

The screenshot shows the 'Setup' dialog box for the Cary Instrument Control software. The 'Cary' tab is selected, and the 'Baseline' sub-tab is active. The 'Cary Instrument Control' section contains the following settings:

- X Mode:** Start is 510.0 nm, Stop is 500.0 nm.
- Y Mode:** Mode is 'Abs', Factor is 1.0000, Y min is -0.05, Y max is 1.00.
- Cycle:** Cycle mode is checked, Cycle count is 240, Cycle time is 1.00 min.
- Beam Mode:** Beam mode is 'Dual Beam'.
- Scan Controls:** 'Simple' is selected over 'Advanced'. The 'Fast' scan rate icon is highlighted.
- Temperature Monitor:** Monitor is 'Bath'.
- Display Options:** 'Overlay data' is selected over 'Individual data'.

At the bottom, there is a 'Show Status Display' checkbox (unchecked) and three buttons: 'OK', 'Cancel', and 'Help'.

C.2 Brilliant Blue FCF AC UV-Vis Method Parameters

Setup 25

Cary Baseline Accessories 1 Accessories 2 Samplers Reports Auto Store

Cary Instrument Control

X Mode

Start nm Stop nm

Y Mode

Mode Abs Factor

Y min Y max

Cycle

☒ Cycle mode

Cycle count

Cycle time min

Beam Mode

Beam mode Dual Beam

Scan Controls

☒ Simple ☐ Advanced

 Slowest  Slow  Medium  Fast  Fastest  Survey

Temperature Monitor

Monitor Bath

Display Options

☐ Individual data ☒ Overlay data

☐ Show Status Display

OK Cancel Help

C.3 Paired t-test results

Paired t-test for beads repeatability experiments using Brilliant Blue FCF				
$H_0: \mu=0$ $H_a: \mu \neq 0$				
t-Test: Paired Two Sample for Means		t-Test: Paired Two Sample for Means		
	<i>Trial 1</i>	<i>Trial 2</i>		<i>Trial 1</i> <i>Trial 3</i>
Mean	7.8599407	7.939246	Mean	7.859941 8.003923
Variance	0.8610563	0.803911	Variance	0.861056 0.829847
Observations	240	240	Observations	240 240
Pearson Correlation	0.9994153		Pearson Correlati	0.999471
Hypothesized Mean Difference	0		Hypothesized Me	0
df	239		df	239
t Stat	-27.79452		t Stat	-64.85626
P(T<=t) one-tail	3.913E-77		P(T<=t) one-tail	5.2E-154
t Critical one-tail	1.6512542		t Critical one-tail	1.651254
P(T<=t) two-tail	7.826E-77		P(T<=t) two-tail	1E-153
t Critical two-tail	1.9699394		t Critical two-tail	1.969939
t-Test: Paired Two Sample for Means				
	<i>Trial 2</i>	<i>Trial 3</i>		
Mean	7.9392457	8.003923		
Variance	0.8039113	0.829847		
Observations	240	240		
Pearson Correlation	0.9994003			
Hypothesized Mean Difference	0			
df	239			
t Stat	-29.10068			
P(T<=t) one-tail	8.106E-81			
t Critical one-tail	1.6512542			
P(T<=t) two-tail	1.621E-80			
t Critical two-tail	1.9699394			

C.4 Standard Operating Procedure for 2,4-Dinitrotoluene (2,4 – DNT) Solution

Prep.

Date: 07/07/2015

Objective: To prepare 1000 mL of 50 mg L⁻¹ 2,4 – DNT stock solution.

Materials:

2,4-DNT Sigma Aldrich brand

Analytical Balance

Spatula

1-L Volumetric Flask

DI H₂O

Sonicator

Stir bar

Stir Plate

Molecular weight: 182.13 g mol⁻¹

CAS# 121-14-2

Assay/Purity = 97%

Storage requirement: 4 °C

Procedure:

- Prepare 1000 mL of stock solution of 2, 4–DNT with a concentration 50 mg L⁻¹ using an amber or foil wrapped volumetric flask.
- Since the 2, 4 DNT is only 97% pure solution is adjusted for purity.

To prepare 1000 mL of 50 mg L⁻¹ stock solution of 2, 4 DNT we need:

$$= 50 \text{ mg} \cdot (100/97)$$

$$= 51.54639175 \text{ mg}$$

$$= 0.051546391 \text{ g}$$

- Add 0.051546391 g of 2,4 DNT to 1000 mL cylindrical flask to make a stock solution of 50 mg L⁻¹.
- Bring to volume with DI H₂O.
- Sonicate for 30 min and add stir bar. Stir for 24 hours at a minimum.
- Store the stock solution in an amber colored bottle in the refrigerator.

C.5 Modified Sol-Gel Procedure Worksheet

Revision: 0

6/2015

SOP: TiO₂ and Ag-TiO₂ coating on glass surface: Sol-Gel Procedure

Modified Sol-Gel Procedure Worksheet

Date: _____

Analyst: _____

Slides

Manufacturer	Lot No.

Reagents

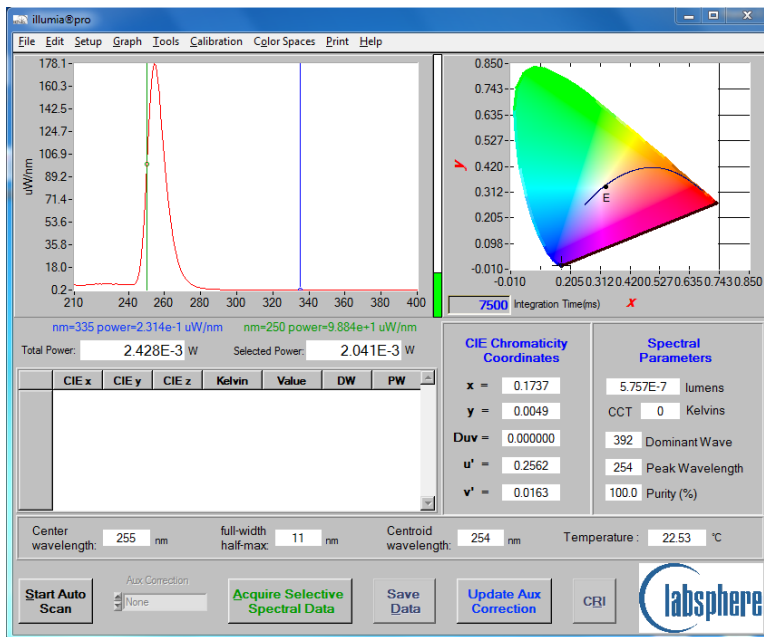
Reagent	Manufacturer	Lot No.	Quantity (circle)
Tween 80			(g)
2-Propanol			40.15 / 80.3 mL
Acetic Acid			0.67 / 1.34 mL
Titanium (IV) Isopropoxide			3.4 / 6.8 mL

Furnace

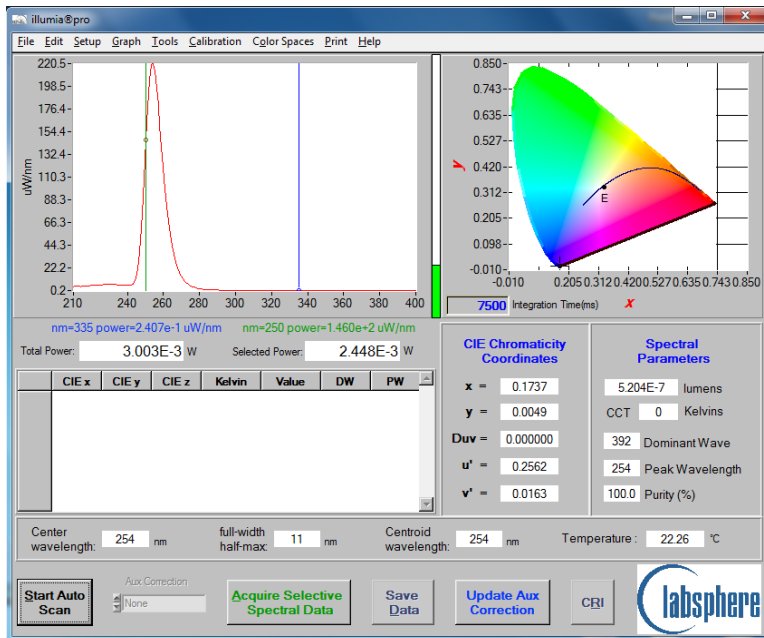
Temp (C)	Time	Time Out
100		
200		
300		
400		
500		

C.6 Lab Sphere Results

LED G7



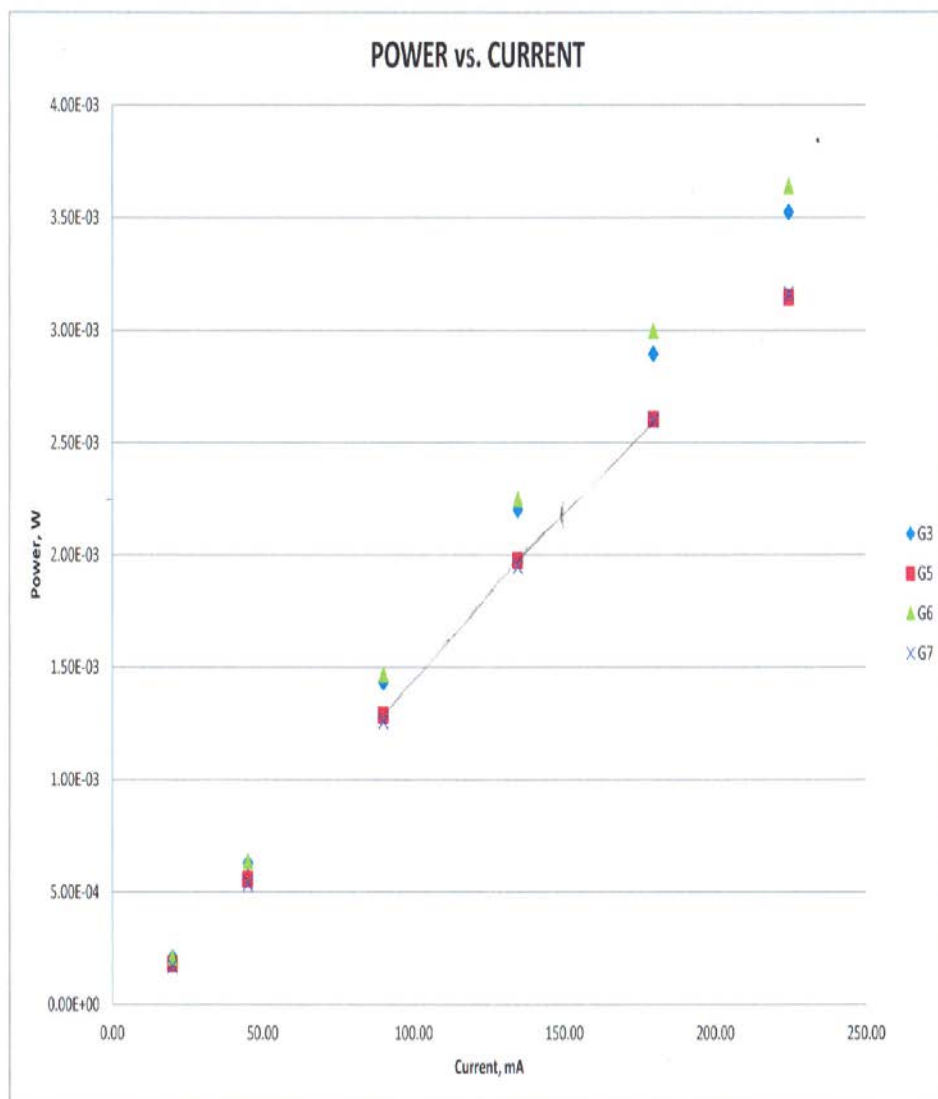
LED G5



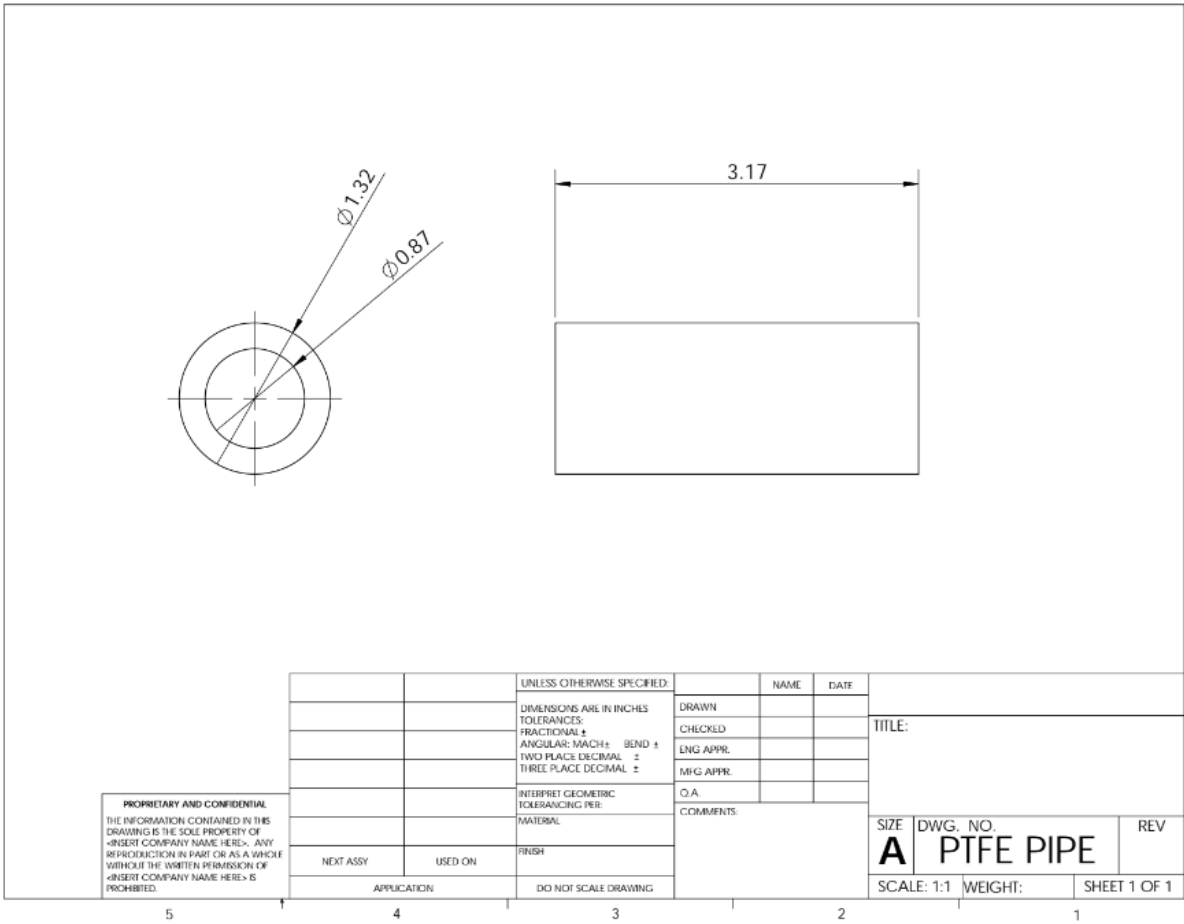
C.7 SETI LED Certificate of Analysis

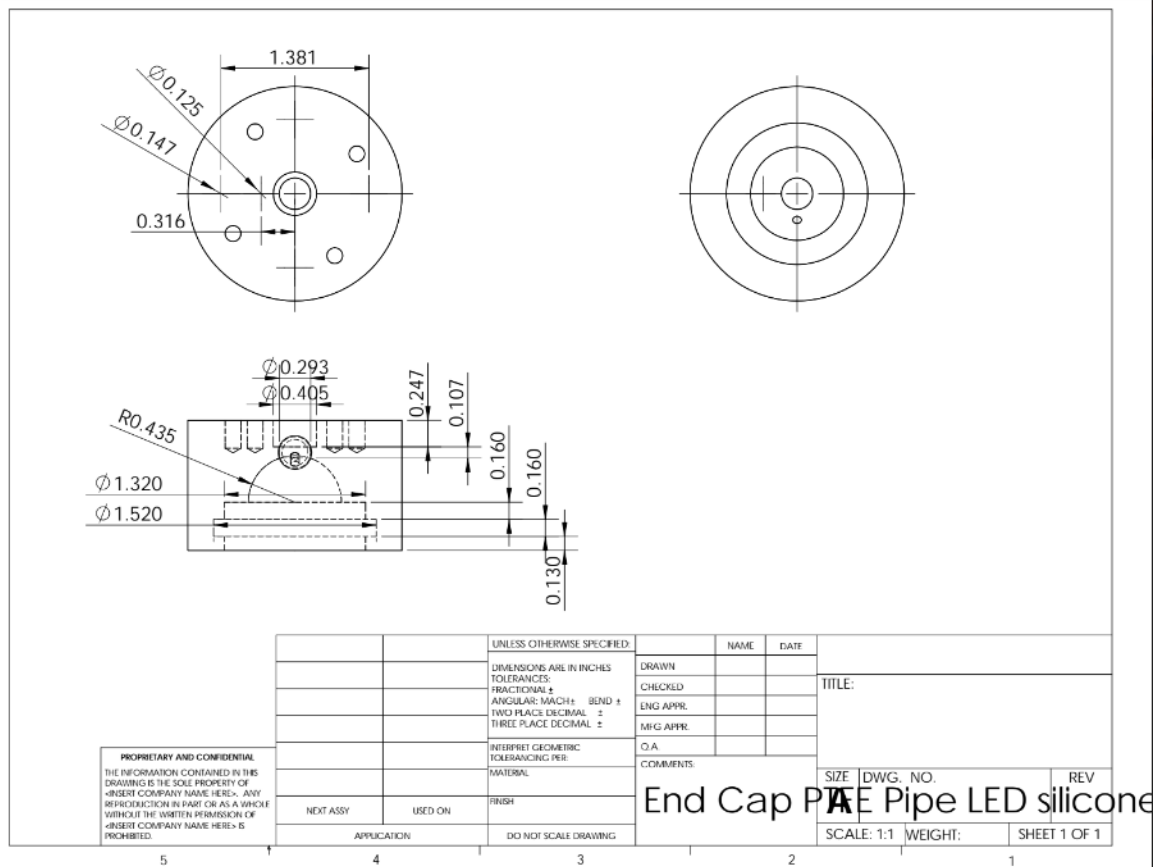
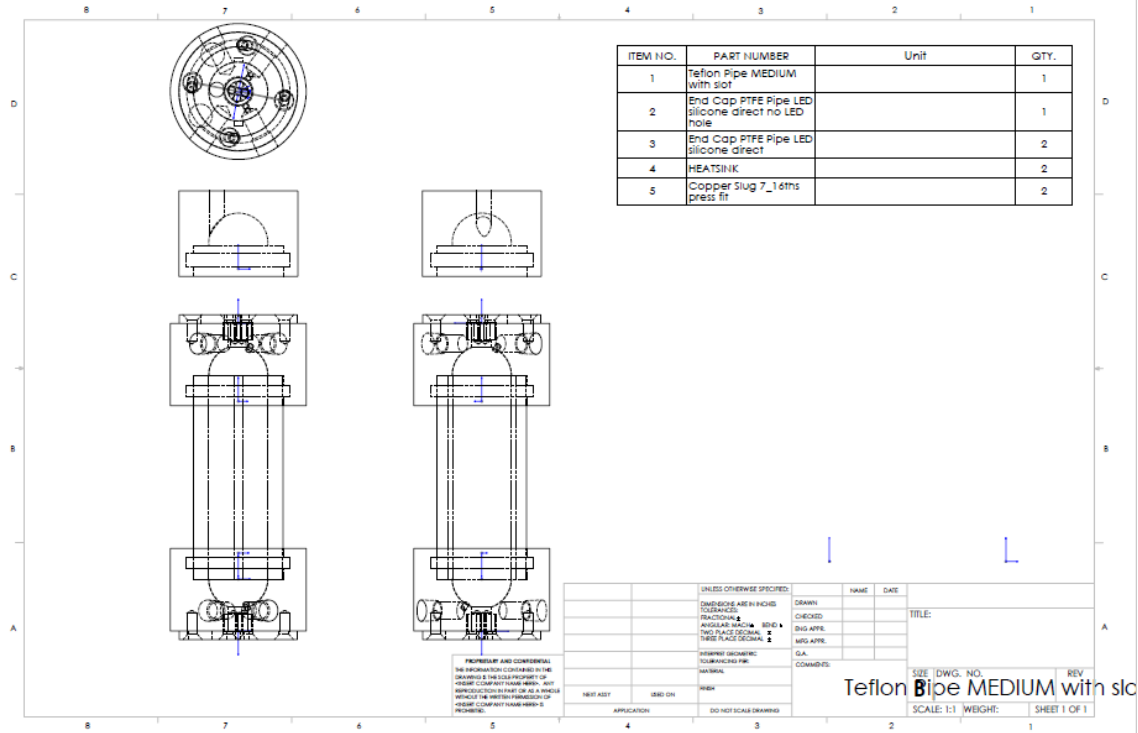
 SETI SENSOR ELECTRONIC TECHNOLOGY, INC.		QC Inspection Report						
	Customer	AFIT WP AFB		Date		6/3/2015	PO #	052815CR
	Part #	UVCLEAN 255 TO39 FW					Box #	0
	Tested	CWG					Item #	0
#	Voltage*, V	Current, mA	Power*, W	Peak Wave*, nm	HB, nm	PSV*, W / nm	Date / Time	
G3	5.143908	20.00	2.10E-04	256.0	11.1	1.51E-05	6/3/15 12:00	
	5.39005	45.00	6.29E-04	256.0	11.0	4.58E-05	6/3/15 12:01	
	5.684412	90.00	1.43E-03	256.0	11.1	1.04E-04	6/3/15 12:01	
	5.901371	134.63	2.20E-03	256.0	11.1	1.60E-04	6/3/15 12:02	
	6.078032	179.65	2.90E-03	256.0	11.1	2.10E-04	6/3/15 12:03	
	6.23917	224.63	3.53E-03	256.0	11.1	2.57E-04	6/3/15 12:03	
G5	5.224681	20.00	1.82E-04	255.4	11.1	1.32E-05	6/3/15 12:04	
	5.499359	45.00	5.58E-04	255.4	11.1	4.06E-05	6/3/15 12:04	
	5.808615	90.00	1.29E-03	255.4	11.0	9.42E-05	6/3/15 12:05	
	6.035964	134.63	1.98E-03	255.4	11.1	1.44E-04	6/3/15 12:06	
	6.218296	179.64	2.60E-03	255.4	11.1	1.90E-04	6/3/15 12:07	
	6.379959	224.64	3.15E-03	255.4	11.1	2.30E-04	6/3/15 12:08	
G6	5.146935	20.00	2.11E-04	256.0	11.1	1.52E-05	6/3/15 11:50	
	5.397049	45.00	6.38E-04	256.0	11.1	4.63E-05	6/3/15 11:50	
	5.689622	90.00	1.47E-03	256.0	11.1	1.07E-04	6/3/15 11:51	
	5.902812	134.63	2.25E-03	256.0	11.1	1.64E-04	6/3/15 11:51	
	6.081319	179.64	3.00E-03	256.0	11.1	2.18E-04	6/3/15 11:52	
	6.233696	224.64	3.64E-03	256.0	11.1	2.64E-04	6/3/15 11:52	
G7	5.160202	20.00	1.72E-04	255.4	11.1	1.24E-05	6/3/15 11:53	
	5.419005	45.00	5.38E-04	255.4	11.1	3.92E-05	6/3/15 11:53	
	5.716164	90.00	1.26E-03	255.4	11.1	9.18E-05	6/3/15 11:53	
	5.932406	134.63	1.95E-03	255.4	11.1	1.42E-04	6/3/15 11:54	
	6.112586	179.65	2.60E-03	255.4	11.1	1.89E-04	6/3/15 11:55	
	6.273168	224.63	3.16E-03	255.4	11.1	2.30E-04	6/3/15 11:56	
25								
26								
27								
28								
29								
30								
MIN	5.143908	20.00	1.72E-04	255.4	11.0	1.24E-05	*Peak wavelength measurement tolerance is +/- 2 nm *Optical power output measurement tolerance is +/- 10% *Forward voltage measurement tolerance is +/- 2%	
MAX	6.379959	224.64	3.64E-03	256.0	11.1	2.64E-04		
AVG	5.777865875	115.65	1.73E-03	255.7	11.1	1.26E-04		
TESTED BY			CWG					
QC INSPECTOR			FJ					

Rev 1
022113



C.8 Reactor Design





REFERENCES

- Affairs, A. F. (2016, May 19). *Air Force applies new EPA guidance*. Retrieved from U.S. Air Force: <http://www.af.mil/News/ArticleDisplay/tabid/223/Article/777074/air-force-applies-new-epa-guidance.aspx>
- Air Force Surgeon General Public Affairs. (2016, March 23). *Total Exposure Health: an innovation in precision health*. Retrieved from Air Force Medical Service: <http://www.airforcemedicine.af.mil/News/Article/702564/total-exposure-health-an-innovation-in-precision-health/>
- Balachandran, U., & Eror, N. G. (1982). Raman spectra of titanium dioxide. *Journal of Solid State Chemistry*, 42(3), 276–282. [http://doi.org/10.1016/0022-4596\(82\)90006-8](http://doi.org/10.1016/0022-4596(82)90006-8)
- Behnajady, M. a, Vahid, B., Modirshahla, N., & Shokri, M. (2009). Evaluation of electrical energy per order (E EO) with kinetic modeling on the removal of Malachite Green by US / UV / H 2 O 2 process. *Des*, 249(1), 99–103. <http://doi.org/10.1016/j.desal.2008.07.025>
- Bolton, J. R., & Linden, K. G. (2003). Standardization of Methods for Fluence (UV Dose) Determination in Bench-Scale UV Experiments. *Journal of Environmental Engineering*, 129(March), 209–215. [http://doi.org/10.1061/\(ASCE\)0733-9372\(2003\)129:3\(209\)](http://doi.org/10.1061/(ASCE)0733-9372(2003)129:3(209))
- Bolton, J. R., Mayor-Smith, I., & Linden, K. G. (2015). Rethinking the Concepts of Fluence (UV Dose) and Fluence Rate: The Importance of Photon-based Units - A Systemic Review. *Photochemistry and Photobiology*, 91(6), 1252–1262. <http://doi.org/10.1111/php.12512>
- Chen, H. W., Ku, Y., & Irawan, A. (2007). Photodecomposition of o-cresol by UV-LED/TiO₂ process with controlled periodic illumination. *Chemosphere*, 69(2), 184–190. <http://doi.org/10.1016/j.chemosphere.2007.04.051>
- Cho, M., Chung, H., Choi, W., & Yoon, J. (2004). Linear correlation between inactivation of E. coli and OH radical concentration in TiO₂ photocatalytic disinfection. *Water Research*, 38(4), 1069–1077. <http://doi.org/10.1016/j.watres.2003.10.029>
- Choi, H., Stathatos, E., & Dionysiou, D. D. (2006). Sol-gel preparation of mesoporous photocatalytic TiO₂ films and TiO₂/Al₂O₃ composite membranes for environmental applications. *Applied Catalysis B: Environmental*, 63(1–2), 60–67. <http://doi.org/10.1016/j.apcatb.2005.09.012>
- Chong, M. N., Jin, B., Chow, C. W. K., & Saint, C. (2010). Recent developments in photocatalytic water treatment technology: a review. *Water Research*, 44(10), 2997–3027. <http://doi.org/10.1016/j.watres.2010.02.039>

- Crittenden, J. C., & M. W. H. (Firm). (2005). *Water treatment principles and design* (2nd ed). Hoboken: Hoboken, N.J. : J. Wiley.
- Crystal IS, Inc. (2014). *Resources Documents*. Retrieved from Crystal IS High Performance UVC LEDs: www.cisuv.com/content/media-files/InstantOn-Off-MiniWP-022614.pdf
- Daneshvar, N., Aleboyeh, A., & Khataee, A. R. (2005). The evaluation of electrical energy per order (EEo) for photooxidative decolorization of four textile dye solutions by the kinetic model. *Chemosphere*, 59(6), 761–767. <http://doi.org/10.1016/j.chemosphere.2004.11.012>
- Daneshvar, N., Salari, D., Niaei, a, Rasoulifard, M. H., & Khataee, a R. (2005). Immobilization of TiO₂ nanopowder on glass beads for the photocatalytic decolorization of an azo dye C.I. Direct Red 23. *Journal of Environmental Science and Health. Part A, Toxic/hazardous Substances & Environmental Engineering*, 40(8), 1605–1617. <http://doi.org/10.1081/ESE-200060664>
- Dariani, R. S., Esmaeili, A., Mortezaali, A., & Dehghanpour, S. (2016). Photocatalytic reaction and degradation of methylene blue on TiO₂ nano-sized particles. *Optik*, 127(18), 7143–7154. <http://doi.org/10.1016/j.ijleo.2016.04.026>
- Dillert, R., Brandt, M., Fornefett, I., Siebers, U., & Bahnemann, D. (1995). Photocatalytic degradation of trinitrotoluene and other nitroaromatic compounds. *Chemosphere*, 30(12), 2333–2341. [http://doi.org/10.1016/0045-6535\(95\)00105-H](http://doi.org/10.1016/0045-6535(95)00105-H)
- Dominguez, S., Rivero, M. J., Gomez, P., Ibanez, R., & Ortiz, I. (2015). Kinetic modeling and energy evaluation of sodium dodecylbenzenesulfonate photocatalytic degradation in a new LED reactor. *Journal of Industrial and Engineering Chemistry*, 37, 237–242. <http://doi.org/10.1016/j.jiec.2016.03.031>
- Duckworth, K., Spencer, M., Bates, C., Miller, M. E., Almquist, C., Grimaila, M., ... Racz, L. (2015). Advanced oxidation degradation kinetics as a function of ultraviolet LED duty cycle. *Water Science and Technology*, 71(9), 1375–1381. <http://doi.org/10.2166/wst.2015.108>
- Eskandarloo, H., Badiei, A., Behnajady, M. A., & Ziarani, G. M. (2015). UV-LEDs assisted preparation of silver deposited TiO₂ catalyst bed inside microchannels as a high efficiency microphotoreactor for cleaning polluted water. *Chemical Engineering Journal*, 270, 158–167. <http://doi.org/10.1016/j.cej.2015.01.117>
- Fabiyi, M. ., & Skelton, R. . (2000). Photocatalytic mineralisation of methylene blue using buoyant TiO₂-coated polystyrene beads. *Journal of Photochemistry and Photobiology A: Chemistry*, 132(1–2), 121–128. [http://doi.org/10.1016/S1010-6030\(99\)00250-6](http://doi.org/10.1016/S1010-6030(99)00250-6)
- Fujishima, A., & Honda, K. (1972). Electrochemical Photolysis of Water at a Semiconductor Electrode. *Nature*, 238(5358), 37–38. Retrieved from <http://dx.doi.org/10.1038/238037a0>

- Ghosh, J. P., Sui, R., Langford, C. H., Achari, G., & Berlinguette, C. P. (2009). A comparison of several nanoscale photocatalysts in the degradation of a common pollutant using LEDs and conventional UV light. *Water Research*, 43(18), 4499–4506. <http://doi.org/10.1016/j.watres.2009.07.027>
- Government Accountability Office, U. S. (2005). *GROUNDWATER CONTAMINATION: DOD Uses and Develops a Range of Remediation Technologies to Clean Up Military Sites. Report to Congressional Committees.*
- Habibi, M. H., & Mikhak, M. (2012). Titania/zinc oxide nanocomposite coatings on glass or quartz substrate for photocatalytic degradation of direct blue 71. *Applied Surface Science*, 258(18), 6745–6752. <http://doi.org/10.1016/j.apsusc.2012.03.042>
- Hales, M. C., Steinberg, T. A., & Martens, W. N. (2014). Synthesis and characterization of titanium sol-gels in varied gravity. *Journal of Non-Crystalline Solids*, 396–397, 13–19. <http://doi.org/10.1016/j.jnoncrysol.2014.04.010>
- Han, C., Andersen, J., Likodimos, V., Falaras, P., Linkugel, J., & Dionysiou, D. D. (2014). The effect of solvent in the sol-gel synthesis of visible light-activated, sulfur-doped TiO₂ nanostructured porous films for water treatment. *Catalysis Today*, 224, 132–139. <http://doi.org/10.1016/j.cattod.2013.11.052>
- Han, C., Pelaez, M., Likodimos, V., Kontos, A. G., Falaras, P., O'Shea, K., & Dionysiou, D. D. (2011). Innovative visible light-activated sulfur doped TiO₂ films for water treatment. *Applied Catalysis B: Environmental*, 107(1–2), 77–87. <http://doi.org/10.1016/j.apcatb.2011.06.039>
- Kim, S. H., Lee, S. W., Lee, G. M., Lee, B. T., Yun, S. T., & Kim, S. O. (2016). Monitoring of TiO₂-catalytic UV-LED photo-oxidation of cyanide contained in mine wastewater and leachate. *Chemosphere*, 143, 106–114. <http://doi.org/10.1016/j.chemosphere.2015.07.006>
- Malkhasian, A. Y. S., Izadifard, M., Achari, G., & Langford, C. H. (2014). Photocatalytic degradation of agricultural antibiotics using a UV-LED light source. *Journal of Environmental Science and Health. Part. B, Pesticides, Food Contaminants, and Agricultural Wastes*, 49(1), 35–40. <http://doi.org/10.1080/03601234.2013.836871>
- Muruganandham, M., Selvam, K., & Swaminathan, M. (2007). A comparative study of quantum yield and electrical energy per order (EEo) for advanced oxidative decolourisation of reactive azo dyes by UV light. *Journal of Hazardous Materials*, 144(1–2), 316–322. <http://doi.org/10.1016/j.jhazmat.2006.10.035>
- Nahen, M., Bahnemann, D., Dillert, R., & Fels, G. (1997). Photocatalytic degradation of trinitrotoluene: reductive and oxidative pathways. *Journal of Photochemistry and Photobiology A: Chemistry*, 110(2), 191–199. [http://doi.org/10.1016/S1010-6030\(97\)00171-8](http://doi.org/10.1016/S1010-6030(97)00171-8)
- Natarajan, K., Natarajan, T. S., Bajaj, H. C., & Tayade, R. J. (2011). Photocatalytic reactor based on UV-LED/TiO₂ coated quartz tube for degradation of dyes.

- Chemical Engineering Journal*, 178, 40–49. <http://doi.org/10.1016/j.cej.2011.10.007>
- Natarajan, T. S., Thomas, M., Natarajan, K., Bajaj, H. C., & Tayade, R. J. (2011). Study on UV-LED/TiO₂ process for degradation of Rhodamine B dye. *Chemical Engineering Journal*, 169(1–3), 126–134. <http://doi.org/10.1016/j.cej.2011.02.066>
- Naumenko, A., Gnatiuk, I., Smirnova, N., & Eremenko, A. (2012). Characterization of sol-gel derived TiO₂/ZrO₂ films and powders by Raman spectroscopy. *Thin Solid Films*, 520(14), 4541–4546. <http://doi.org/10.1016/j.tsf.2011.10.189>
- (NIEH), N. I. of E. H. S. (2016). Perfluorinated Chemicals (PFCs). U.S. Department of Health and Human Services. Retrieved from https://www.niehs.nih.gov/health/materials/perflourinated_chemicals_508.pdf
- Pernot, C., Kim, M., Fukahori, S., Inazu, T., Fujita, T., Nagasawa, Y., ... Amano, H. (2010). Improved Efficiency of 255–280 nm AlGaIn-Based Light-Emitting Diodes. *Applied Physics Express*, 3(6), 61004. <http://doi.org/10.1143/APEX.3.061004>
- Prusakova, V., Armellini, C., Carpentiero, A., Chiappini, A., Collini, C., Dirè, S., ... Chiasera, A. (2015). Morphologic, structural, and optical characterization of sol-gel derived TiO₂ thin films for memristive devices. *Physica Status Solidi (c)*, 12(1–2), 192–196. <http://doi.org/10.1002/pssc.201400101>
- Rahn, R. O. (1997). Potassium Iodide as a Chemical Actinometer for 254 nm Radiation: Use of Iodate as an Electron Scavenger. *Photochemistry and Photobiology*, 66(4), 450–455. <http://doi.org/10.1111/j.1751-1097.1997.tb03172.x>
- Rahn, R. O. (2013). Fluence measurements employing iodide/iodate chemical actinometry as applied to upper-room germicidal radiation. *Photochemistry and Photobiology*, 89(4), 816–818. <http://doi.org/10.1111/php.12094>
- Rasoulifard, M., Fazli, M., & Eskandarian, M. (2014). Kinetic study for photocatalytic degradation of Direct Red 23 in UV–LED/nano-TiO₂/S₂O₈²⁻ process: Dependence of degradation kinetic on operational parameters. *Journal of Industrial and Engineering Chemistry*, 20(5), 3695–3702. <http://doi.org/10.1016/j.jiec.2013.12.068>
- Report, I. T., Bolton, J. R., Bircher, K. G., Tumas, W., & Tolman, C. A. (2001). FIGURES-OF-MERIT FOR THE TECHNICAL DEVELOPMENT AND APPLICATION OF ADVANCED ELECTRIC- AND SOLAR-DRIVEN SYSTEMS † Figures-of-merit for the technical development and application of advanced oxidation technologies for both electric- and solar-driven systems (, 73(4), 627–637.
- Schmelling, D. C., & Gray, K. A. (1995). Photocatalytic transformation and mineralization of 2,4,6-trinitrotoluene (TNT) in TiO₂ slurries. *Water Research*, 29(12), 2651–2662. [http://doi.org/10.1016/0043-1354\(95\)00136-9](http://doi.org/10.1016/0043-1354(95)00136-9)
- Schmelling, D. C., Gray, K. A., & Kamat, P. V. (1997). The influence of solution matrix on the photocatalytic degradation of TNT in TiO₂ slurries. *Water Research*, 31(6), 1439–1447. [http://doi.org/10.1016/S0043-1354\(96\)00358-2](http://doi.org/10.1016/S0043-1354(96)00358-2)

- Sharma, P., Mayes, M. A., & Tang, G. (2013). Role of soil organic carbon and colloids in sorption and transport of TNT, RDX and HMX in training range soils. *Chemosphere*, 92(8), 993–1000. <http://doi.org/10.1016/j.chemosphere.2013.03.028>
- Son, H.-S., Lee, S.-J., Cho, I.-H., & Zoh, K.-D. (2004). Kinetics and mechanism of TNT degradation in TiO₂ photocatalysis. *Chemosphere*, 57(4), 309–17. <http://doi.org/10.1016/j.chemosphere.2004.05.008>
- Swarnakar, P., Kanel, S. R., Nepal, D., Jiang, Y., Jia, H., Kerr, L., ... Rakovan, J. (2013). Silver deposited titanium dioxide thin film for photocatalysis of organic compounds using natural light. *Solar Energy*, 88, 242–249. <http://doi.org/10.1016/j.solener.2012.10.014>
- Tayade, R. J., Natarajan, T. S., & Bajaj, H. C. (2009). Photocatalytic Degradation of Methylene Blue Dye Using Ultraviolet Light Emitting Diodes, 10262–10267.
- Thiam, A., Sirés, I., Garrido, J. A., Rodríguez, R. M., & Brillas, E. (2015). Decolorization and mineralization of Allura Red AC aqueous solutions by electrochemical advanced oxidation processes. *Journal of Hazardous Materials*, 290, 34–42. <http://doi.org/10.1016/j.jhazmat.2015.02.050>
- Thiam, A., Zhou, M., Brillas, E., & Sirés, I. (2014). Two-step mineralization of Tartrazine solutions: Study of parameters and by-products during the coupling of electrocoagulation with electrochemical advanced oxidation processes. *Applied Catalysis B: Environmental*, 150–151, 116–125. <http://doi.org/10.1016/j.apcatb.2013.12.011>
- Umar, M., & Aziz, H. A. (2013). Photocatalytic Degradation of Organic Pollutants in Water. *Organic Pollutants - Monitoring, Risk and Treatment*, 195–208. <http://doi.org/10.5772/53699>
- United States Environmental Protection Agency. (2014). Technical Fact Sheet – 2,4,6-Trinitrotoluene (TNT), (January), 1–8. Retrieved from http://www2.epa.gov/sites/production/files/2014-03/documents/ffrrofactsheet_contaminant_tnt_january2014_final.pdf
- United States Environmental Protection Agency. (2014). Technical Fact Sheet – Hexahydro-1,3,5-trinitro- 1,3,5-triazine (RDX), (January), 1–7. Retrieved from https://www.epa.gov/Fsites/Fproduction/Ffiles/F2014-03/documents/ffrrofactsheet_contaminant_rdx_january2014_final.pdf
- United States Government Accountability Office. (2005). *GROUNDWATER CONTAMINATION: DOD Uses and Develops a Range of Remediation Technologies to Clean Up Military Sites*. Washington, D.C.: The Government Accountability Office.
- USAF. (2016, August 22). *Military Ranges*. Retrieved from U.S. Air Force Civil Engineering Center: <http://www.afcec.af.mil/resources/militaryranges/index.asp>

- Varshney, G., Kanel, S. R., Kempisty, D. M., Varshney, V., Agrawal, A., Sahle-Demessie, E., ... Nadagouda, M. N. (2016). Nanoscale TiO₂ films and their application in remediation of organic pollutants. *Coordination Chemistry Reviews*, 306(July), 43–64. <http://doi.org/10.1016/j.ccr.2015.06.011>
- Vasuki T., Saroja M., Venkatachalam, S. S. (2015). RESEARCH ARTICLE SYNTHESIS AND CHARACTERIZATION OF TiO₂ THIN FILM FOR PHOTOCATALYTIC DEGRADATION OF TEXTILE DYE EFFLUENT. *International Journal of Recent Scientific Research*, 6, 3511–3514.
- Wang, C., Fuller, M. E., Schaefer, C., Caplan, J. L., & Jin, Y. (2012). Dissolution of explosive compounds TNT, RDX, and HMX under continuous flow conditions. *Journal of Hazardous Materials*, 217–218, 187–193. <http://doi.org/10.1016/j.jhazmat.2012.03.012>
- Wu, C.-Y., Lee, Y.-L., Lo, Y.-S., Lin, C.-J., & Wu, C.-H. (2013). Thickness-dependent photocatalytic performance of nanocrystalline TiO₂ thin films prepared by sol–gel spin coating. *Applied Surface Science*, 280, 737–744. <http://doi.org/10.1016/j.apsusc.2013.05.053>
- Zheng, W., Lichwa, J., D'Alessio, M., & Ray, C. (2009). Fate and transport of TNT, RDX, and HMX in streambed sediments: Implications for riverbank filtration. *Chemosphere*, 76(9), 1167–1177. <http://doi.org/10.1016/j.chemosphere.2009.06.043>

REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.					
1. REPORT DATE (DD-MM-YYYY) 23-03-2017		2. REPORT TYPE Master's Thesis		3. DATES COVERED (From - To) January 2014 - March 2017	
4. TITLE AND SUBTITLE				5a. CONTRACT NUMBER	
DESTRUCTION OF AQUEOUS PHASE ORGANIC POLLUTANTS USING ULTRAVIOLET LIGHT EMITTING DIODES AND PHOTOCATALYSIS				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Russell, Morgan, M, Mr. GS-11 Occupational And Environmental Analytical Services Division United States Air Force School of Aerospace Medicine (USAFSAM) 711th Human Performance Wing				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Air Force Institute of Technology Graduate School of Engineering and Management (AFIT/EN) 2950 Hobson Way Wright-Patterson AFB OH 45433-7765				8. PERFORMING ORGANIZATION REPORT NUMBER AFIT-ENV-MS-17-M-220	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Matthew L. Magnuson, Ph.D. Environmental Protection Agency Office of Research and Development/National Homeland Security Research Center Water Infrastructure Protection Division MS NG-16 26 W. Martin Luther King Drive				10. SPONSOR/MONITOR'S ACRONYM(S) EPA	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION / AVAILABILITY STATEMENT Distribution Statement A. Approved for Public Release; Distribution Unlimited.					
13. SUPPLEMENTARY NOTES "This work is declared a work of the U.S. Government and is not subject to copyright protection in the United States."					
14. ABSTRACT The photocatalytic degradation of dyes (Allura Red AC and Brilliant Blue FCF) in water using ultraviolet light emitting diodes (UV-LED) and an immobilized titanium dioxide (TiO ₂) as a photocatalyst; was investigated using a novel bench-top Teflon® reactor. This reactor has been uniquely designed to contain low-powered UV-LEDs combined with TiO ₂ immobilized substrates. A sol-gel method was used to anneal TiO ₂ to three different substrates: standard microscope quartz slides, quartz cylinders and borosilicate beads. TiO ₂ characterization was performed using Scanning Electron Microscope (SEM), Raman spectroscopy, and mass comparisons. High resolution SEM images confirmed the presence and morphology of TiO ₂ on the substrates. SEM and Raman analyses demonstrated the TiO ₂ coating was uniform and predominantly has the anatase crystalline phase structure. The slide had the largest individual TiO ₂ surface area of 0.187 mg cm ⁻² . Size, shape, packing and stirring properties were factors that determine overall photocatalytic properties and degradation. For an ideal completely mixed batch					
15. SUBJECT TERMS UV-LED, photocatalytic degradation, organic dye, nano-TiO ₂ , thin film					
16. SECURITY CLASSIFICATION OF: 1.			17. LIMITATION OF ABSTRACT UU	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT U	b. ABSTRACT U	c. THIS PAGE U		83	Lt Col David M. Kempisty
				19b. TELEPHONE NUMBER (include area code) (937)255-3636 x4711 David.Kempisty@afit.edu	
					Standard Form 298 (Rev. 8-98) Prescribed by ANSI Std. Z39.18