Implementation of Emerging Technologies:

Treatment Capability of Peracetic Acid and Ultraviolet Irradiation

by

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A Thesis Presented in Partial Fulfillment
of the Requirements for the Degree
Master of Science

Approved March 2017 by the
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ARIZONA STATE UNIVERSITY

May 2017

ABSTRACT

Advanced oxidation processes (AOP's) are water/wastewater treatment processes simultaneously providing disinfection and potential oxidation of contaminants that may cause long-term adverse health effects in humans. One AOP involves injecting peracetic acid (PAA) upstream of an ultraviolet (UV) irradiation reactor.

Two studies were conducted, one in pilot-scale field conditions and another under laboratory conditions. A pilot-scale NeoTech UV reactor (rated for 375 GPM) was used in the pilot study, where a smaller version of this unit was used in the laboratory study (20 to 35 GPM). The pilot study analyzed coliform disinfection and also monitored water quality parameters including UV transmittance (UVT), pH and chlorine residual. Pilot study UV experiments indicate the unit is effectively treating flow streams (>6 logs total coliforms) twice the 95% UVT unit capacity (750 GPM or 17 mJ/cm^2 UV Dose). The results were inconclusive on PAA/UV inactivation due to high data variability and field operation conditions creating low inlet concentrations.

Escherichia coli (*E. coli*) bacteria and the enterobacteria phage P22—a surrogate for enteric viruses—were analyzed. UV inactivated >7.9 and 4 logs of *E. coli* and P22 respectively at a 16.8 mJ/cm^2 UV dose in test water containing a significant organics concentration. When PAA doses of 0.25 and 0.5 mg/L were injected upstream of UV at approximately the same UV Dose, the average *E.coli* log inactivation increased to >8.9 and >9 logs respectively, but P22 inactivation decreased to 2.9 and 3.0 logs, respectively. A bench-scale study with PAA was also conducted for 5, 10 and 30 minutes of contact time, where 0.25 and 0.5 mg/L had <1 log inactivation of *E. coli* and P22 after 30

minutes of contact time. In addition, degradation of the chemical N-Nitrosodimethylamine (NDMA) in tap water was analyzed, where UV degraded NDMA by 48 to 97% for 4 and 0.5 GPM flowrates, respectively. Adding 0.5 mg/L PAA upstream of UV did not significantly improve NDMA degradation.

The results under laboratory conditions indicate that PAA/UV have synergy in the inactivation of bacteria, but decrease virus inactivation. In addition, the pilot study demonstrates the applicability of the technology for full scale operation.

DEDICATION

In loving memory of my grandfather, Stephen Moulton.

ACKNOWLEDGMENTS

This thesis would not have been possible without the help of my committee members, who provided expert advice on performing these experiments. Dr. Morteza Abbaszadegan and Dr. Absar Alum gave their time to assist me with experimental set-up, procedure and to discuss next steps.

I want to especially thank my fellow graduate student, Majid Nikougoftar Zarif, for performing the P22 bacteriophage experiments, assisting with experimental set-up/clean-up and helping with a variety of other tasks around the lab.

Thank you to Ivo Hrabovsky and Laura McCasland at the City of Scottsdale for assisting with the NDMA analysis.

I would like to thank NeoTech Aqua Solutions, Inc. for providing the NeoTech UV units used in both the pilot and laboratory studies. Thank you to Solvay for sending a research sample of peracetic acid.

Thank you also to Dr. Teresa Valentine and Wesley Boerm for the opportunity to work on the pilot study as well as assisting on required supplies for performing experiments.

Finally, I must express my very profound gratitude to my family and my fiancé for providing continuous encouragement throughout my years of study and for lending an ear to listen to me discuss this research with them.

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PREFACE

The research discussed in the following pages was conducted in two different locations. The pilot study was conducted at the Global Water Palo Verde Water Reclamation Plant located in Maricopa, Arizona. The study was a joint contribution that lasted from July 2015 to October 2015 and included Valentine Environmental Engineers, LLC, Hennesy Mechanical Sales, Inc., NeoTech Aqua Solutions, Inc. and Global Water. The results of this study are included in the thesis with the permission of NeoTech Aqua Solutions, Inc.

Separately, additional Master's thesis laboratory research was conducted at Arizona State University beginning in April 2016 and ending in March 2017. The research was conducted in Dr. Morteza Abbaszadegan's laboratory on the 3rd floor of Interdisciplinary Science & Technology Building IV.

CHAPTER 1

INTRODUCTION

Clean water is a basic necessity of living organisms; however, the availability of clean water is decreasing over time as more water sources become polluted from human-related activity. For this reason, there is an increasing need to develop cost-effective methods to treat water sources in order to remove pollutants responsible for adverse health effects in organisms. These pollutants include both microbiological and chemical contaminants, where each type of contaminant presents treatment challenges. Traditionally, the methods reported for effective removal/inactivation of microbial and chemical contaminants have been separated into different treatment technologies, and in many cases this causes a comprehensive treatment process to be less cost effective. Some research has indicated a type of process that may be able to provide adequate disinfection of microorganisms, while also degrading chemical contaminants. This series of processes, known as advanced oxidation processes (AOP's), are currently being studied for their treatment capability.

Disinfection is a vital process in water and wastewater treatment. Disinfection reduces the risk of waterborne diseases by inactivating pathogenic microorganisms. There are various types of disinfection methods used in the field including chlorine injection and ultraviolet irradiation. The United States Environmental Protection Agency (U.S EPA) has provided literature to discuss the advantages and disadvantages of chlorine disinfection (U.S EPA, 1999a) and ultraviolet irradiation (U.S EPA, 1999b), which are briefly discussed in the following paragraphs.

Chlorine is commonly used in the field due to cost-effectiveness of the chemical and familiarity with the implementation of the safe use of it for disinfection. In general, chlorine is reliable and effective for a wide spectrum of microorganisms, though some microorganisms may require a higher dose and/or contact time. However, there are negative aspects pertaining to chlorine disinfection. One negative aspect is that chlorine can combine with organic compounds in the water and form disinfection by-products (DBPs), such as trihalomethanes (THMs), which have been associated with adverse health effects in organisms. In addition, maintaining an adequate level of chlorine residual to prevent biofilm formation in pipes is a concern, which creates an added cost in water/wastewater treatment. Dechlorination of excess chlorine or rechlorination may also be required in order to maintain the proper chlorine residual prior to discharge. The use of chlorine can also create a safety risk for plant operations personnel, so additional precaution is required in transporting, storing and handling the chemical.

Ultraviolet (UV) is an electromagnetic radiation where disinfection is accomplished by shortwave UV that is ultraviolet-C (UV-C) with a wavelength from 10 to 289 nm. UV disinfection works by applying specific electromagnetic energy at a 253.7 nm wavelength to water, which attacks the genetic core of the microbial cell and leaves the microbial cell unable to reproduce. UV irradiation eliminates the need for chemical transport and storage, and is effective at inactivating robust microorganisms such as viruses, spores and cysts. Unlike chlorine disinfection, ultraviolet irradiation is not known to have a harmful residual effect on aquatic life and humans. The technology generally has a lower footprint than other disinfection methods and requires shorter contact times, often on the order of seconds versus minutes for other methods. While there are many

advantages to UV irradiation, UV treatment capability is highly dependent on water quality and photoreactivation/dark repair can reverse the destructive effects of the UV on the microorganism. The UV disinfection also cannot maintain a residual to help prevent biofilm formation in discharge piping. In addition, power consumption and maintenance costs (cleaning the unit, replacing parts) are an additional expense for the treatment facility.

While UV irradiation is a method that helps to reduce toxic compounds discharged to the environment when implemented over chlorine disinfection, there has been additional research on methods to effectively destroy toxic compounds that can be detected in wastewater. Many studies have reported degradation of these compounds by advanced oxidation processes (AOP's). One purpose of advanced oxidation is to provide advanced treatment and transform toxic pollutants into compounds that are not harmful. Chemical oxidation can transform these pollutants into harmless products such as carbon dioxide and water (Andreozzi et al., 1999). Although different methods have been described for AOP systems, these processes rely on the production of hydroxyl (OH) radicals (Andreozzi et al., 1999).

The research discussed in the following section summarizes the studies reporting treatment capability of an AOP based on the chemical peracetic acid (PAA) combined with UV, where PAA is injected upstream of the UV reactor. PAA is a strong oxidant and, unlike chlorine, is not known to form DBP's associated with adverse health effects. Literature published on the process suggests that low doses of PAA combined with UV are effective in providing significant enhanced disinfection. The low PAA doses indicate

that applying the treatment process to wastewater or other types of treatment such as stormwater may allow for the method to be cost-effective in terms of operations and maintenance (O&M) costs. In general, there appear to be significant advantages to implementing the PAA/UV AOP over traditional disinfection methods. The benefits indicate that research on this subject should be continued.

Limited literature is available on this process, leaving plenty of research questions to be addressed. AOP's are not widely applied yet and may be considered an emerging technology due to the fact that the processes are not yet fully understood. In particular, reactant doses and operating conditions still need to be studied in order to understand optimal treatment conditions for different pollutants and water quality.

Currently, published literature on PAA/UV is generally focused on disinfection, not chemical degradation. Therefore, this thesis focuses on both the inactivation of *E. coli* and P22 bacteriophage (as a surrogate for enteric virus), as well as the degradation of N-Nitrosodimethylamine (NDMA), where NDMA is an extremely potent carcinogen that can be formed from industrial processes and as a byproduct of wastewater chlorination. The objective of the study is to determine whether relatively low doses of PAA combined with UV can achieve adequate disinfection, while also providing additional degradation of NDMA. A portion of the research discussed in the following pages is a pilot study conducted on tertiary-treated wastewater (filter effluent) in field conditions, while the remainder of the study is conducted using tap water as well as tap water containing organics under laboratory conditions. The pilot study research is focused on disinfection of coliform bacteria. The laboratory study analyzes the disinfection of *E. coli* and P22

bacteriophage as a surrogate for enteric viruses. The laboratory study also includes an experiment on the degradation of NDMA with UV and PAA/UV. In both types of studies, water quality parameters are monitored.

This thesis is organized to include background literature on AOP's including the PAA/UV AOP, provide a detailed methodology of the experimentation conducted, present the results of the study, discuss these results, and finally conclude and suggest future research related to the study.

CHAPTER 2

BACKGROUND LITERATURE

This section describes the background literature for the advanced oxidation processes (AOP's) and the components of the AOP selected for the study, peracetic acid (PAA) injected upstream of an ultraviolet (UV) reactor.

2.1 Advanced Oxidation Processes (AOP's)

AOP's have been utilized in treating wastewater as well as in groundwater remediation and manufacturing facilities (Bergendahl and O'Shaughnessy, 2005). In wastewater treatment, AOP's have been used to reduce organic concentrations, destroy specific pollutants, treat sludge, and reduce color and odor (Bergendahl and O'Shaughnessy, 2005).

Advanced oxidation relies on the highly reactive hydroxyl (OH) radicals to drive the process. In comparison with ozone (O_3), hydroxyl radicals attack organics with rate constants usually on the order of 10^6 to 10^9 M/s, over seven orders of magnitude higher than the rate constant of ozone (Andreozzi et al., 1999; Huang et al., 1993). Hydroxyl radicals are also not selective, which makes them useful for degrading a wide variety of pollutants. The hydroxyl radical is stably generated by UV irradiation over a wide range of pH, as high as pH 10 (Huang et al., 1993).

Using these hydroxyl radicals, chemical oxidation may be achieved to degrade chemical pollutants found in water. In particular, advanced oxidation may be effective in degrading chemicals that are not degraded by wastewater biological processes, which

may be due to high chemical stability or difficulty to become mineralized (Andreozzi et al., 1999). One example is the degradation of endocrine disrupting compounds (EDCs), which are chemicals that interfere with the endocrine system in organisms. In one study (Bergendahl and O'Shaughnessy, 2005) on advanced oxidation, ozone (O_3) was able to degrade estradiol, bisphenol A and nonylphenol by over 40%, with removal above 90% for doses of 3 mg/L or higher.

There are a variety of different ways to create advanced oxidation processes. Table 1 (Andreozzi et al., 1999) below lists a few methods that have been studied.

Table 1. Types of Typical Advanced Oxidation Processes

Type of Reactants for AOP	
Hydrogen Peroxide and UV	H_2O_2/UV
Titanium Dioxide and UV (Photocatalysis)	TiO_2/UV
Hydrogen Peroxide and Fenton	H_2O_2/Fe^{2+}
Hydrogen Peroxide and Fenton-Like	H_2O_2/Fe^{3+}
Ozone and UV	O_3/UV
Ozone and Hydrogen Peroxide	H_2O_2/ O_3

One setback/potential concern regarding the use of AOP's is the baseline quality of water required for achieving the optimal treatment efficacy, particularly for wastewater. In order to achieve adequate treatment, chemical oxygen demand (COD), must be at relatively low concentrations (≤5 g/L) (Andreozzi, 1999). At higher COD

concentrations, more reactants may be necessary which would increase the operating cost of performing the advanced oxidation.

2.1.1 Hydrogen Peroxide (H_2O_2)/UV Advanced Oxidation

The PAA/UV advanced oxidation process performed in this thesis is closely related to the H_2O_2 /UV AOP. In this process, the water is dosed with H_2O_2 upstream of the UV reactor. UV at wavelengths less than 280 nm causes the H_2O_2 to break apart (also referred to as hemolytic cleavage) into the hydroxyl radicals (Andreozzi, 1999). These hydroxyl radicals then can combine again with the H_2O_2 to produce water and hydroperoxyl (HO_2). The hydroperoxyl can then degrade to produce more H_2O_2 and oxygen (Andreozzi, 1999).

The decomposition rate of H_2O_2 by ultraviolet irradiation has proven to be inefficient in comparison to ozone, where the extinction coefficient of H_2O_2 is 19.6 ($M^{-1}cm^{-1}$), while the ozone extinction coefficient is 3,000 ($M^{-1}cm^{-1}$) (Huang et al., 1993). To support this concept, Kishimoto and Nakamura (2012) discovered that ozone combined with UV was more effective in decomposing 4-chlorobenzoic acid and inhibiting bromate formation than H_2O_2 combined with UV. Another study focusing on the removal of estrogenic compounds in wastewater reported that H_2O_2 at doses of 10 mg/L and higher injected upstream of UV generally helped to increase the removal of these compounds (Hansen and Andersen, 2012). It was also noted that the removal rate is also highly dependent on the UV dose, where significantly higher UV doses (1.2 kwh/m^3 and higher) were more effective. The higher H_2O_2 doses and UV doses required for optimal efficacy

indicate that this treatment combination makes it likely infeasible for treatment facilities from a cost perspective.

The removal efficiency of N-Nitrosodimethylamine (NDMA), which is studied as part of this research, is not significantly increased by H_2O_2/UV treatment as reported in some studies (Jobb et al., 1994; Liang, 2002).

2.2 Peracetic Acid (PAA)

PAA, also known as peroxyacetic acid, is a chemical that breaks down into H_2O_2 and an organic acid, which is typically acetic acid. The chemical structure is shown in the figure below (Zheng et al., n.d.).

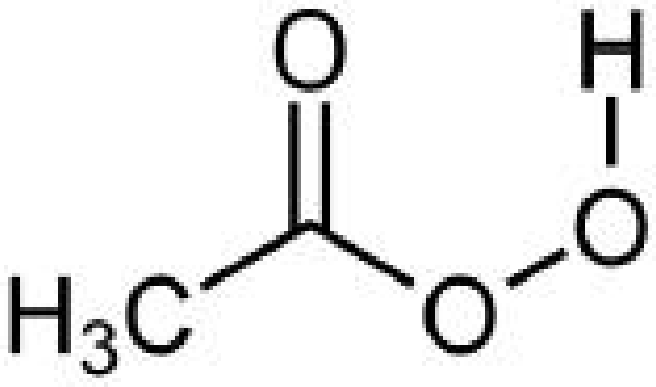

Figure 1. Peracetic Acid (PAA) Chemical Structure

PAA has been used in a variety of applications, including disinfection in the food and medical industries (Graham et al., 2010; Kitis, 2004; Wilson, 2014) as well as to provide disinfection of irrigation systems (Zheng et al., n.d.). The chemical has also been studied for the treatment of stormwater (U.S EPA, 1999c).

PAA is viewed as a “green chemical” that “poses no danger to the environment” (EPA, 2002). In treated wastewater effluents and surface waters, it has been demonstrated that PAA produces “none to little toxic or mutagenic by-products after reaction with organic material” (Kitis, 2004). In a study by Dell’Erba et al. (2007), “no brominated or chlorinated phenols are formed” (Luukonen et al., 2014). In fact, a study demonstrated that using PAA actually reduced the estrogenicity (endocrine activity) of wastewater, whereas chlorination increased the endocrine activity by over 100% (Block et al., 2015). In addition, PAA meets the aquatic toxicity test criteria (Graham et al., 2010).

Kitis (2004) identifies the consumption of PAA, which is discussed in this paragraph. In an aqueous solution, the three reactions involved with consumption of the PAA are hydrolysis, decomposition, and transition-metal-catalyzed decomposition. Within the pH range of 5.5 to 8.2 the consumption processes mainly involves spontaneous decomposition to acetic acid and oxygen. Above the pH of 9, the efficiency of PAA starts to decrease.

The decomposition of the PAA occurs relatively quickly, where the initial rate of decomposition depends on various factors depending on water quality, such as particulate concentration and microorganisms in the water (Luukkonen et al., 2014). The quick degradation of the PAA was observed in one study, where 5 ppm was dosed through a reactor, but concentrations less than 1 ppm were observed in various sampling points within the reactor and at the outfall (U.S EPA, 2012). In aquatic systems, the consumption processes are not complete as small residuals of PAA and H_2O_2 have been detected after some time when dosed in wastewater; however, this residual is not

considered harmful to aquatic environments and it can actually aid in reducing biofilm formation in discharge piping (Luukkonen et al., 2014) though this may be dependent on the length of pipe.

While there are a number of advantages involved with the use of PAA, including its efficacy and "green" nature, there are also disadvantages to using this chemical. One disadvantage is that the use of PAA produces increased organic loading in the effluent due to acetic acid (Kitis, 2004), which may also contribute to microbial regrowth if PAA residuals are low. According to Kitis (2004), PAA is also not nearly as effective against some viruses and parasites in comparison to other disinfection methods such as chlorine. Another drawback of this chemical is a relatively high cost, at approximately $3 per gallon for 12% PAA solution (Kitis, 2004). Another source states that the cost per gallon of 12% PAA solution is nearly double at approximately $5.50 per gallon (Dancey, 2009). The high cost may be due to a limited market, particularly since PAA is not yet commonly used in water/wastewater treatment in the United States. While the cost is higher, the added cost benefit of using PAA over traditional chlorine treatment is that dechlorination is not required.

PAA has been approved by the U.S EPA for use as a primary disinfectant for wastewater disinfection since 2007; however, PAA has been used to treat wastewater in Europe for over a decade (Dancey, 2009). Some wastewater treatment plants in the United States have adopted PAA as a primary disinfectant, including a wastewater treatment plant in St. Augustine, Florida (Graham et al., 2010) that discharges treated flow to environmentally-sensitive wetlands. Case studies have also been conducted at a

number of treatment plants including a wastewater treatment plant in Frankfort, Kentucky (U.S EPA, 2012).

PAA solutions are typically manufactured in solutions between 10 and 15%, as concentrations higher than 15% can begin to exhibit issues with instability, reactivity and explosiveness (Kitis, 2004). The Solvay Proxitane WW-12 chemical solution used in the experiments contains a stabilizer that has a relatively long shelf life of approximately six months (Wodalski, 2012). Quenching of the chemical is not required (Dancey, 2009) prior to discharge.

Since PAA is an oxidizing agent, disinfection occurs from the PAA and H_2O_2 (that PAA degrades into) “oxidizing the cell membranes and inner cell structures of pathogens” (Zheng et al., n.d.). The oxidation occurs through the fast transfer of electrons to the microorganism. The faster the electron-transfer, the more quickly the microorganisms are inactivated or killed (Wilson, 2014). Though H_2O_2 is another disinfectant, PAA is more stable and known to degrade at a slower rate than H_2O_2, allowing the chemical to perform further disinfection (Zheng et al., n.d.). The U.S EPA has stated that the PAA is a stronger oxidant than chloride dioxide and hypochlorite, though not as strong as ozone (Martin, 2014).

PAA was selected for the study due to the ease of implementation, treatment efficacy discussed further in Section 2.2.1 and 2.4 and other advantages associated with the chemical. The brand of PAA used in both the pilot study and laboratory study was Proxitane WW-12 manufactured by Solvay Chemical. This solution is a 12% PAA solution. The Material Safety Data Sheet (MSDS) for Proxitane WW-12 is provided as an

appendix to this thesis (Appendix A). In both the pilot study and laboratory settings, the PAA was used within approximately six months of receipt.

2.2.1 Effectiveness of PAA as a Primary Disinfectant

Research has been conducted to study the disinfection efficacy of PAA as a primary disinfectant. In one study, PAA doses of 1.5 mg/L to 2 mg/L with a contact time of 10 to 15 minutes were sufficient to inactivate 2 logs or more of *E. coli* (Luukkonen et al., 2014). In a pilot scale study, PAA doses and contact times were varied to determine the disinfection of total coliforms and enterococci (Koivunen and Heinonen-Tanski, 2005). For PAA doses that ranged from 2 to 7 mg/L with contact times ranging from 4 to 27 minutes, approximately 3-log inactivation of total coliforms and enterococci was achieved. In Koivunen and Heinonen-Tanski (2005), higher doses of 10 to 15 mg/L PAA achieved 3 to 4 logs inactivation. This study noted that minor changes in wastewater quality parameters such as chemical oxygen demand (COD), suspended solids (SS), turbidity, temperature and UV transmittance (UVT) did not affect PAA disinfection; however, large increases in concentrations of microorganisms, organic matter and suspended solids significantly decreased the log inactivation.

In addition to disinfection capability, use of PAA as a primary disinfectant may also be able to decrease the activity of endocrine disrupting compounds (EDCs). In one bench test study (Block et al., 2015), PAA was dosed at 1, 5 and 10 mg/L. After 10 minutes of stirring, the E2 (17-beta-estradiol) and EE2 (17-alpha-ethinyl estradiol, chemical derivative of estradiol) activity had decreased by over 75%. After 20 minutes, the percent decrease in EDC activity was over 80%.

The literature therefore suggests both disinfection and added benefit of decreased endocrine activity with the use of PAA.

2.3 Ultraviolet (UV) Disinfection System

In combination with the PAA, the AOP is made possible with the utilization of a UV unit. NeoTech Aqua Solutions Inc. produces UV systems that are in-line, enclosed units that contain low pressure mercury vapor lamp(s). The set-up for the unit includes power connection and the UV intensity monitor(s) connected to control box(es) to provide UV intensity readings.

The UV unit utilized in the pilot-scale study included eight lamps and four UV intensity monitors, while the UV unit used in the laboratory study only contained one lamp and one UV intensity monitor. Each lamp is enclosed within a quartz sleeve where the outside of this sleeve is in direct contact with the water. The pilot scale UV unit was rated for 375 GPM for 95% UVT, while the laboratory bench-scale UV unit was only rated for 20-35 GPM.

A unique feature associated with the NeoTech UV units is a reflective coating within the chamber that helps to distribute UV light through the water passing through the vessel. The concept behind this design is to provide efficient treatment of the water with less power consumption. While typical low pressure lamps have lower power consumption (typically less than 1 kW) in comparison to medium pressure lamps (typically around 15 kW), the footprint is typically larger (Water Research Foundation et al., 2011). The NeoTech UV unit, however, does not require a large footprint in comparison to other similar UV technologies.

The UV dose can be calculated based on the UV intensity (mW/cm^2) and contact time in seconds. The UV intensity is a value that is read by the UV intensity probe and displayed on the monitor. The contact time is adjusted based on flowrate, where the contact time is calculated based on this flowrate and volume of water in contact with the UV light. The UV Dose is calculated with the following equation:

UV Dose (mJ/cm^2) = UV Intensity (mW/cm^2) * Contact Time (seconds)

In many cases, the effectiveness of ultraviolet irradiation is often judged based on a UV Transmittance (UVT) measurement. UVT measures the amount of ultraviolet light that passes through a water sample as compared to the amount of light passing through a pure water sample (USAPHC, 2011). The UVT varies depending on organics, solids content and other material in the water that absorb and scatter the UV light. The measurement is typically expressed as a percentage. A low percentage indicates that the water quality cannot be treated as effectively by UV irradiation. Typically UVT for UV wastewater application ranges from 50% to 80%, where the specified UV Dose for this UVT range is 30 mJ/cm^2 (ATG Technology). The UVT of secondary effluent typically ranges from 60% to 70%, and ranges from 85% to 95% for tap water (Briley, 2015). Water temperature and pH do not generally have a major impact on UV disinfection (USAPHC, 2011).

2.4 Effectiveness of PAA Upstream of UV Reactor

While PAA and UV are both effective primary disinfectants, the implementation of PAA upstream of a UV reactor may contribute to much higher disinfection efficacy. The reason why the combination may contribute to better disinfection efficacy is that UV

helps produce the hydroxyl radicals more quickly by breaking the O-O bonds within the PAA molecule (Caretti and Lubello, 2003). The hydroxyl radicals are highly important in degrading the polluting molecules, but do not last for a significant length of time. According to Caretti and Lubello (2003), the H_2O_2 present in the commercial product of PAA, and which the PAA degrades into, helps extend the AOP by forming more hydroxyl radicals. In addition, the H_2O_2 also forms new PAA through chemical reactions as the PAA is consumed.

A few studies have been published that document the effectiveness of PAA and UV treatment. One study is titled "Wastewater disinfection with PAA and UV combined treatment" (Caretti and Lubello, 2003). The paper investigates the treatment efficiency of PAA and UV alone as well as PAA combined with UV. Injection of PAA downstream of the UV reactor was also tested. For this study, PAA was selected over H_2O_2 due to literature claiming that PAA was more effective and because spectroscopic analysis demonstrated that the PAA solutions produce more free hydroxyl radicals than H_2O_2. PAA doses ranged from 1 ppm to 8 ppm with UV doses ranging from 100 mJ/cm^2 to 300 mJ/cm^2. The different indicator bacteria analyzed in the study include total coliform, *E. coli* and *Pseudomonas aeruginosa*. The results overall indicated that both PAA and UV treatment as primary disinfectants were incapable of attaining the strict disinfection requirements for wastewater irrigation reuse (in Italy). Combining the two disinfectants provided significantly better disinfection efficacy when the PAA was upstream of the UV reactor. This combination provided sufficient treatment to meet the disinfection requirements for reuse (≤2 MPN/100 mL total coliforms) with 2 mg/L (ppm) or higher of PAA combined with the UV irradiation. The figure from the source shows the log

inactivation achieved at varying UV and PAA doses as well as the approximate cost per cubic meter of water to treat the water, which is depicted through isocost curves (€/m^3). This figure is depicted below in Figure 2.

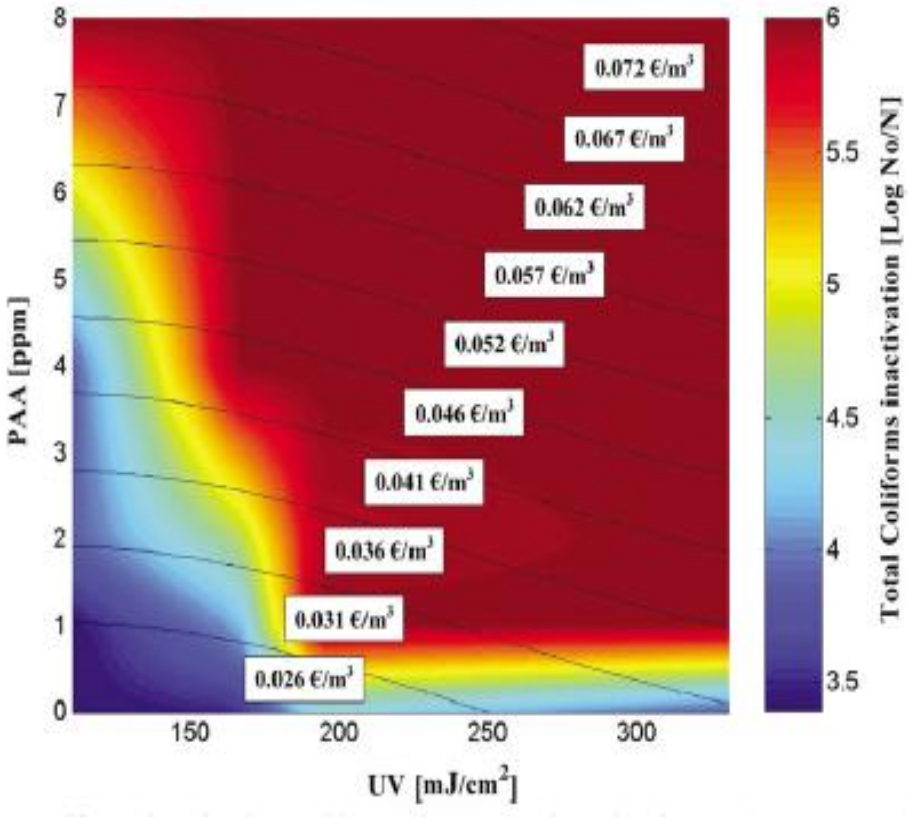

Figure 2. PAA Dose and UV Dose Total Coliform Log Inactivation with Isocost Curves (Caretti and Lubello, 2003)

The recorded data indicates a great synergy with injecting PAA upstream of the UV. Adding the PAA downstream of the UV reactor did not result in significant additional log inactivation of the microorganisms in comparison with the disinfectants on their own.

2.5 Microorganisms Used in the Study

The pilot study experiments were conducted by sampling for total coliform and *E. coli*. The present study laboratory experiments were performed using *E. coli* and P22 bacteriophage.

2.5.1 *Escherichia coli* (*E. coli*)

The type of bacteria used in the pilot and laboratory studies is *Escherichia coli* (*E. coli*). The "versatility, broad palate and ease of handling have made it the most intensively studied and best understood organism on the planet" (Blount, 2015). *E. coli* is naturally found in the gut of mammals, and is sometimes found in other animals as well as in soil, plants, water and food (Blount, 2015). High concentrations of *E. coli* are found in wastewater from human excretion. While excreted from the human body, consumption of pathogenic strains of the bacteria may cause adverse health effects in humans including diarrheal diseases, peritonitis, colitis, and urinary tract infections (Blount, 2015). For this reason, pathogenic strains of *E. coli* and other pathogenic bacteria are targeted for inactivation (through disinfection), particularly for treated wastewater discharges where humans may come in contact.

E. coli is commonly used as an indicator of fecal contamination in aquatic environments. If detected it may indicate the presence of other pathogenic microorganisms. The fecal coliform group is classified by characteristics including rod-shaped, non-spore forming, *Gram-Negative*, and lactose-fermenting in 24 hours at 44.5°C. The bacteria can also grow with or without oxygen.

The assay for the detection of bacteria can be performed using a variety of methods including membrane filtration and spread plate techniques. Membrane filtration is performed using a membrane filter with a particular pore size, which is generally 0.45 micron. Typically, 100 mL of water sample is filtered and any bacterial cells present in the water sample are captured on the surface of the membrane filter. The filter is then placed on sterilized media in a petri dish. Spread plate technique is performed by transferring 0.1, 0.25 or 0.5 mL of sample on media and then spreading the small volume with a sterilized spreader. The colonies are then counted on the plates and appropriate dilution factors are applied to provide the total colony forming units per volume (typically mL). Both techniques are appropriate assays for *E. coli* analysis; however, the membrane filtration method is best used for lower anticipated *E. coli* concentrations.

2.5.2 P22 Bacteriophage

A bacteriophage is a virus that infects bacterial cells. Bacteriophages can be classified by the degree to which the bacterial cell is damaged, where some bacteriophages cause lysis of the cell. “Bacteriophages ‘enter’ bacterial cells through absorption via appropriate receptors on their cellular wall” (Tokarz-Deptula et al., 2011). Bacteriophages are used for various studies including environmental protection studies, where bacteriophages have been used as specific bio-indicators for identifying sources of microbial pollution (Tokarz-Deptula et al., 2011). The bacteriophages, which are some of the most structurally-complex viruses, can also be used as a surrogate to estimate removal or inactivation of human viruses during treatment processes.

The bacteriophage known as P22 was the first phage shown to be able to perform generalized transduction (Casjens, 2000). P22 bacteriophage is a phage that infects *Salmonella*, where it is able to establish lysogeny and perform generalized transduction in *Salmonella typhimurium* (Rhoades et al., 1968). The DNA molecules of P22 are linear and double stranded. The genetic structure of P22 is similar to that of the coliphage, Λ (Susskind and Botstein, 1978). The P22 virion is an icosahedral particle approximately ca. 60 nm in diameters, with a baseplate approximately 20 nm wide and thin spike or fiber (ca. 20 nm long) (Susskind and Botstein, 1978).

Assay of the P22 bacteriophage is conducted through the double agar layer method, which is described further in Section 3.0, Methodology.

2.6 N-Nitrosodimethylamine (NDMA)

N-Nitrosodimethylamine (NDMA) is an organic, semi-volatile chemical formed in both industrial and natural processes (U.S EPA, 2014). The chemical has been used in the production process of industrial chemicals such as rocket fuel and antioxidants; however, it can also be produced during food processing. In addition, NDMA is also the unintended byproduct from chlorination of wastewater using chloramines for disinfection (U.S EPA, 2014).

Once produced, whether intentionally or unintentionally, NDMA's release into the environment through waste streams can contaminate water sources, including drinking water sources. If not degraded prior to coming into contact with humans or animals, it may cause adverse health effects in these organisms. The chemical is part of the N-nitrosamines family, a family known for potent carcinogens, where some studies

have observed tumors in various species, including rats and mice as a result of exposure to NDMA (U.S EPA, 2014). In fact, NDMA "cancer potencies are much higher than those of the trihalomethanes" (Mitch et al., 2003).

Based on studies conducted, the U.S EPA has listed NDMA on Contaminant Candidate Lists (CCL's), including CCL 4 published in November 2016. The CCL contains contaminants that are currently not nationally regulated in primary drinking water, but are known to be in drinking water sources and may be proposed for regulation in the future. In fact, results of sampling conducted in 2001 showed 3 of 20 chloraminated drinking water supplies contained 10 ng/L or higher NDMA concentrations (Tomkins et al., 1995; Tomkins and Griest, 1996). Though there is no EPA maximum contaminant level (MCL) specified for this chemical, many agencies have established NDMA guidelines (Mitch et al., 2003) due to research suggesting significant health impacts.

In literature, the observed concentrations of NDMA in water are discussed (Mitch et al., 2003). Influent wastewater may contain NDMA concentration as high as 105,000 ng/L. Effluents from circuit board manufacturing may contain raw sewage NDMA concentrations as high as 1,500 ng/L. Secondary treatment removes a considerable percentage of NDMA, with observed concentrations often less than 20 ng/L in unchlorinated secondary effluent.

Some removal of NDMA can occur with ultraviolet (UV) treatment. The UV photolysis may help to remove NDMA, but may not destroy NDMA precursors (Mitch et

al., 2003). Therefore, chlorine injection that occurs after the UV disinfection can still contribute to NDMA formation in the distribution system.

NDMA is analyzed through liquid-liquid extraction and gas chromatography/mass spectrometry (GC/MS) or through gas chromatography with a thermionic detector (Mitch et al., 2003). Through these methods or a combination of the methods, detection limits can be as low as 1 ng/L.

CHAPTER 3

METHODOLOGY

3.1 Materials

3.1.1 Description of NeoTech UV Unit

Two different UV units were used in the pilot scale and laboratory studies. The NeoTech Inline Magnum UV unit was used in the pilot scale study and the NeoTech D222 UV unit was used in the laboratory study. These units are described in further detail in the following sections.

3.1.1.1 NeoTech UV Unit Used in Pilot Scale Study

The NeoTech Inline Magnum UV unit contains eight 60-inch long low pressure mercury vapor UV lamps. In the pilot study, the flow entered via two 6-inch pipes connected at 45 degree angles to the main vessel. The flow exited the vessel in a similar manner. The unit was equipped with four UV intensity sensors, two located on the top of the vessel and two located on the bottom of the vessel. These intensity sensors were linked to two control boxes that provide dosimetry, UV intensity and lamp status information on the display screen. A close-up of the display screen is shown in Figure 5. The schematic of the NeoTech Inline Magnum UV unit is depicted on the next page in Figure 3.

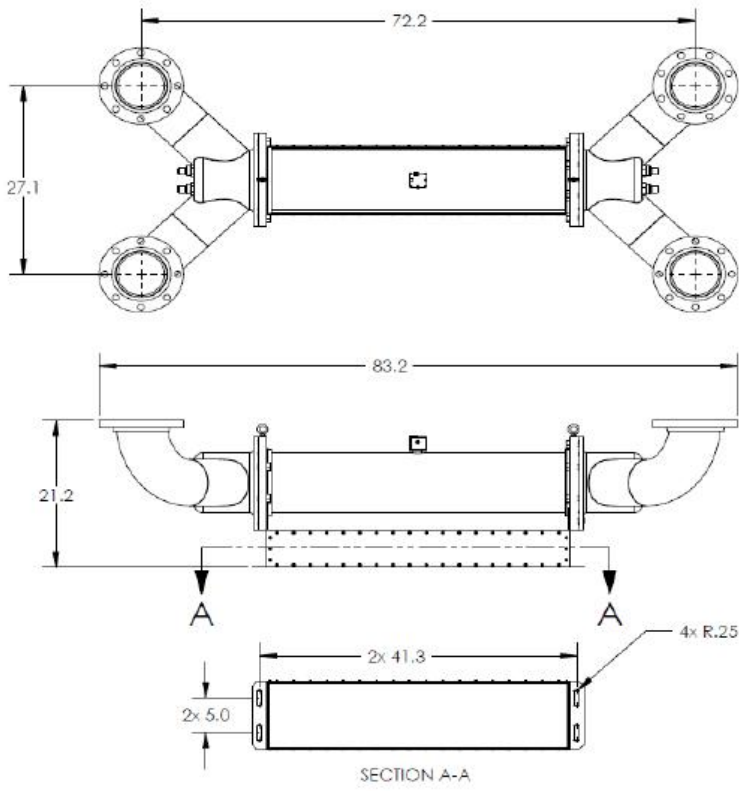

Figure 3. Pilot Study NeoTech Inline Magnum UV Unit Schematic

3.1.1.2 NeoTech UV Unit Used in Laboratory Study

The bench-scale NeoTech UV system (Model D222) is pictured in Figure 4. The unit consists of a vessel with one low pressure mercury vapor UV lamp.

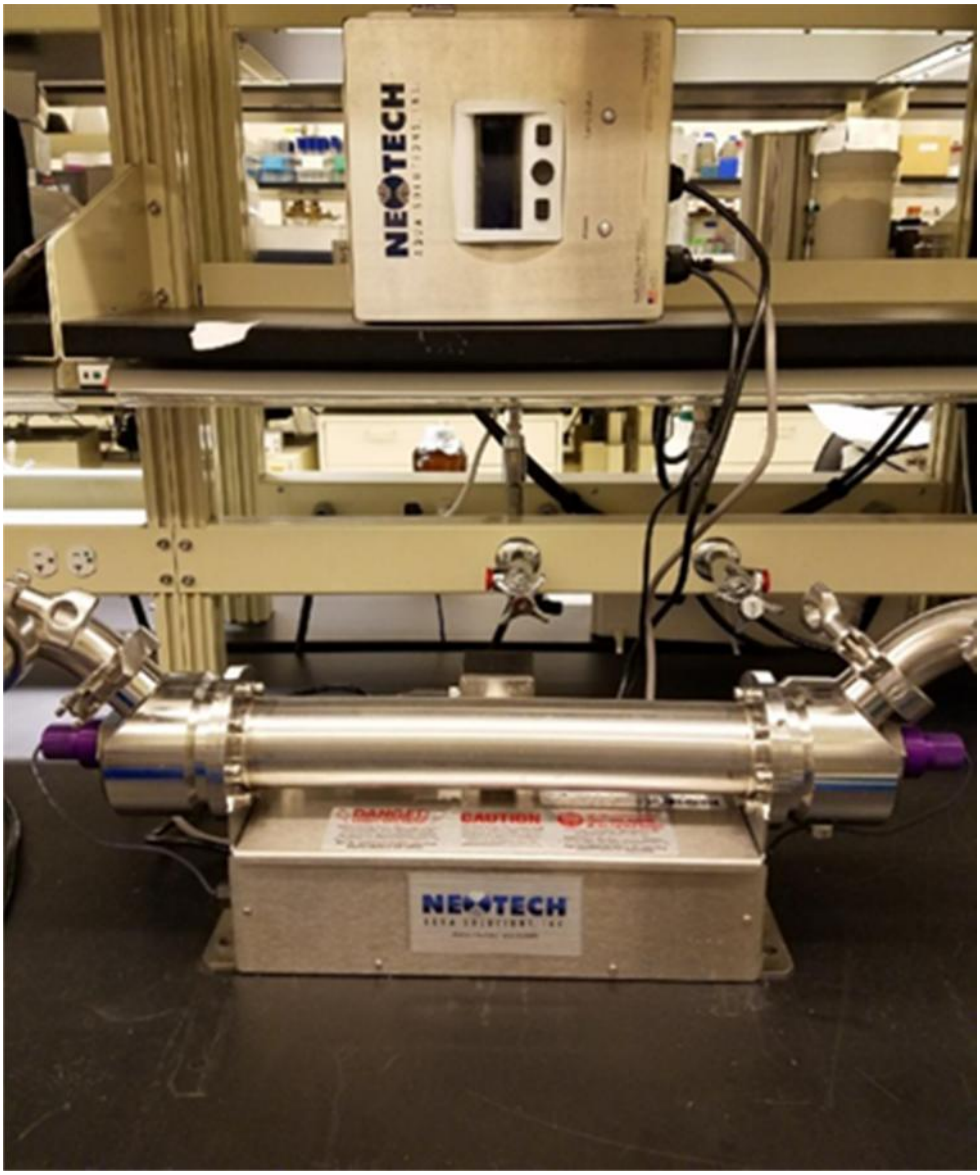

Figure 4. Close-Up View of Laboratory Scale NeoTech UV Unit (D222)

The UV unit is rated for 20 to 35 gallons-per-minute (GPM) of flow. The flow entered and exited the unit via 1-1/2 inch 90 degree elbows. These 90 degree elbows acted as a UV light trap to keep UV light from degrading the attached PVC. The UV unit is equipped with one UV intensity sensor which is hooked to one control box. The control

box is programmed to provide UV intensity readings. A close-up view of the control box is presented in Figure 5.

Figure 5. Close-Up View of Laboratory Scale UV Unit Control Box

3.1.2 Peracetic Acid (PAA)

The 12% PAA (Proxitane WW-12) stocks were obtained from Solvay Chemicals (Houston, TX) and kept in the chemical hood. The concentrated stock of PAA was diluted to the desired working concentration using deionized (DI) water.

3.1.3 Microbial Culture and Media

Pure culture of *E. coli* (ATCC 25922), bacteriophage P22 (ATCC 19585-B1) and P22 host bacterium *Salmonella typhimurium* (ATCC 19585) were obtained from American

Type Culture Collection (ATCC, Rockville, MD) and propagated according to the vendor's instructions.

Nutrients media used for propagation of bacterial cultures were Tryptic Soy Agar (TSA) and Tryptic Soy Broth (TSB). These media were obtained from Hardy Diagnostics (Santa Maria, CA) and prepared according to manufacturer's instruction. Briefly, 30 g of TSA powder or 7.5 g of TSB powder was dissolved in one liter of nanopure water under continuous mixing at medium heat, followed by autoclaving for 15 minutes at 121°C. Autoclaved media was aseptically dispensed in petri-dishes or test tubes and stored at 4°C until used.

For sample analyses Brilliance media (Brilliance Green Bile *E. coli*/Coliform Media Catalog #B1802, Sigma Aldrich) was used and prepared according to the manufacturer instructions. This media was used for the assay of *E. coli* because it is selective for *E. coli* and additional bacterial contamination from other types of bacteria in the tap water would not affect bacterial counts. Prior to assay, media plates were dried under the hood for 2 hours. During drying, UV light was turned on for at least 15 minutes to reduce the likelihood of plate contamination. The inlet samples were analyzed using the spread plate technique, after performing appropriate dilutions. The outlet samples were analyzed using both the spread plate technique (0.1 and 0.5 mL) and the membrane filtration (100 mL) method. The membrane filtration was performed due to the probability of very low concentrations of *E. coli* discovered in outlet samples. The plates are incubated upside down for 18 to 24 hours. The colonies were counted the following day, where the *E. coli* colonies were a bright purple color as shown in Figure 6.

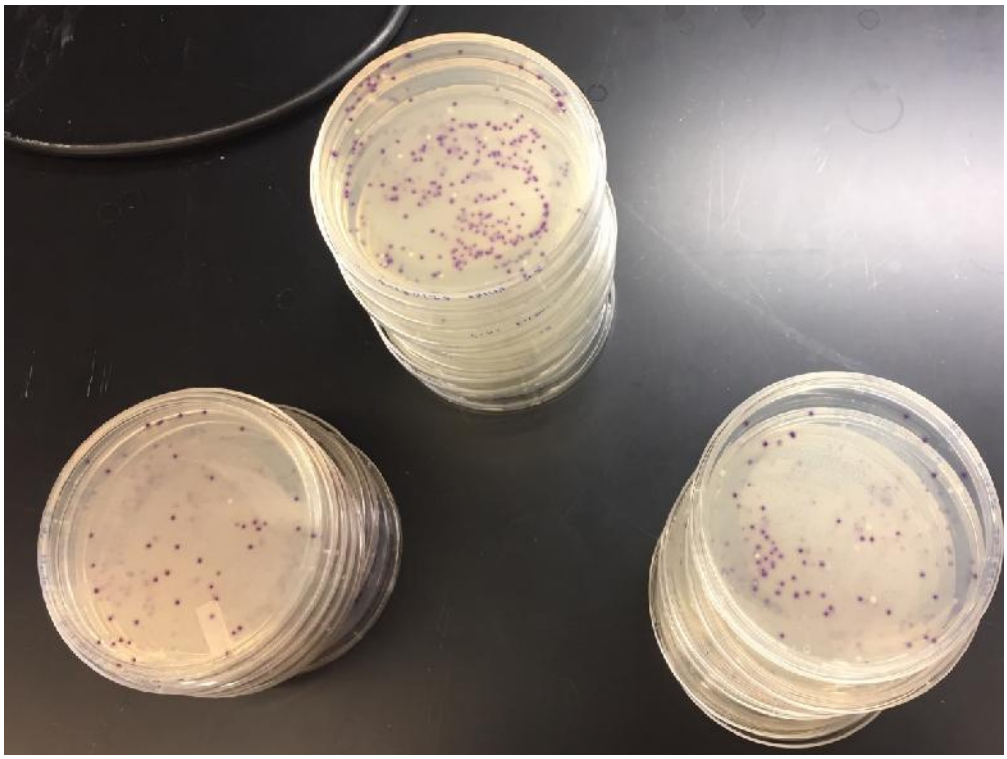

Figure 6. *E. coli* Colonies on Brilliance Media

The bacteriophages and bacterial hosts used in this study were obtained from the American Type Culture Collection (ATCC, Rockville, MD). The bacteriophages were propagated and assayed in duplicate using the double agar layer method (Adams, 1959). The propagation and purification of the bacteriophage stocks were performed as described in Abbaszadegan et al. (2007).

Briefly, 1 mL of bacteriophage sample, 1 mL of log phase host *Salmonella*, and 5 mL of 0.7% molten TSA (top agar kept in water bath at 48°C) were mixed and poured onto 1.5% TSA bottom agar plates. After solidifying, the plates were incubated inverted at 37ºC overnight and plaques (Figure 7) were counted after 12 hours. All the assays were performed in duplicate, and positive and negative controls were included in each set of

assays and for each experiment. A picture of these plaques is displayed in Figure 7 below. The unit of measurement for this technique is Plaque Forming Units (PFU) per milliliter and is reported as PFU/mL based on the dilution factors.

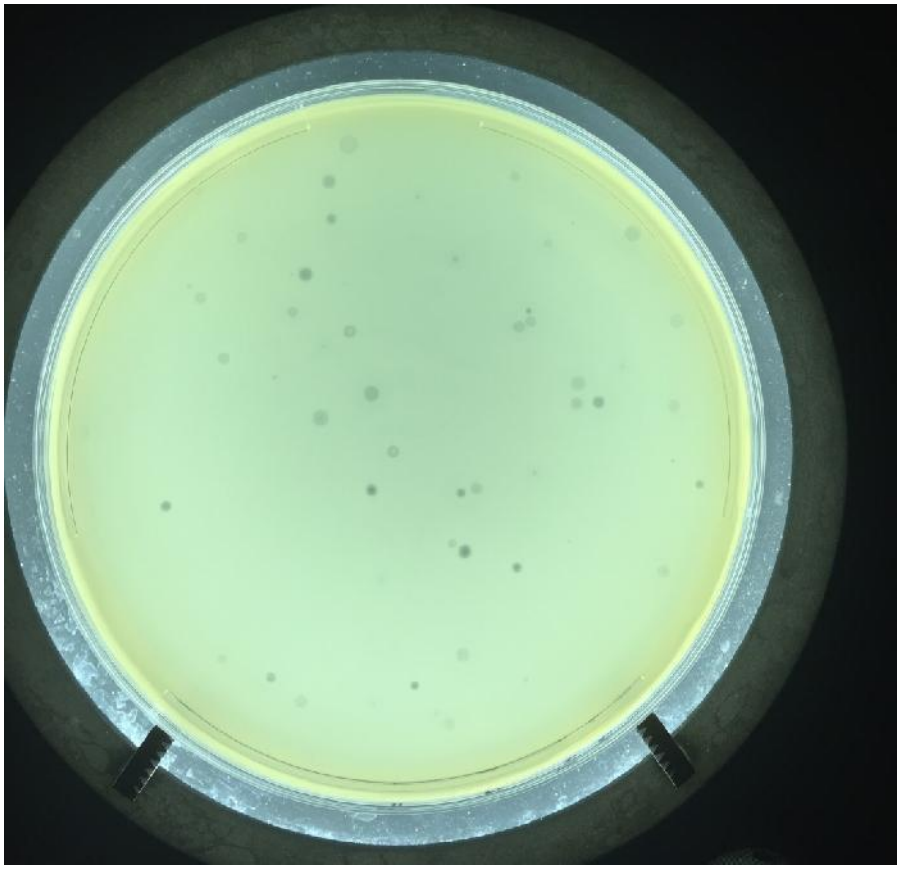

Figure 7. Plaques Created by P22 Bacteriophage

3.2 Pilot Scale Study

The pilot scale study set-up, methodology and test matrix are discussed within this section.

3.2.1 Set-Up

The pilot study was conducted at the Palo Verde Water Reclamation Plant (WRP), which is owned by Global Water located in Maricopa, Arizona. The pilot study took place from July to October 2015.

The NeoTech Inline Magnum UV unit rated for 375 GPM for 95% UVT was installed after cloth-media filtration and treated a slip-stream of filtered effluent. Global Water decided to evaluate the NeoTech UV unit for the pilot study because it appears to require less power consumption and has a smaller footprint than other similar technologies.

The set-up included a pump and a valve for adjusting flow rate to the desired level. As part of the set-up, a dimmer was installed to reduce/adjust power output to the UV unit. The set-up allowed for decreasing the UV intensity for simulating lamp aging and/or worsening water quality (lower UV transmittance, UVT). A small chemical feed pump was used to inject the PAA into the system through an injection port located just prior to the UV unit. The PAA feed pump was connected to the PAA storage container that was placed on a spill containment pallet.

The experimental set-up included two sampling ports: one located upstream and the other located downstream of the UV unit. These sampling ports were used to collect water samples. The sampling port located upstream of the UV unit served as the inlet sampling port and a sampling port located downstream of the UV unit served as the outlet sampling port. A flowmeter installed further down the piping, after the outlet sampling

port was used to record flowrate readings. The experimental set-up and site layout is depicted in Figure 8.

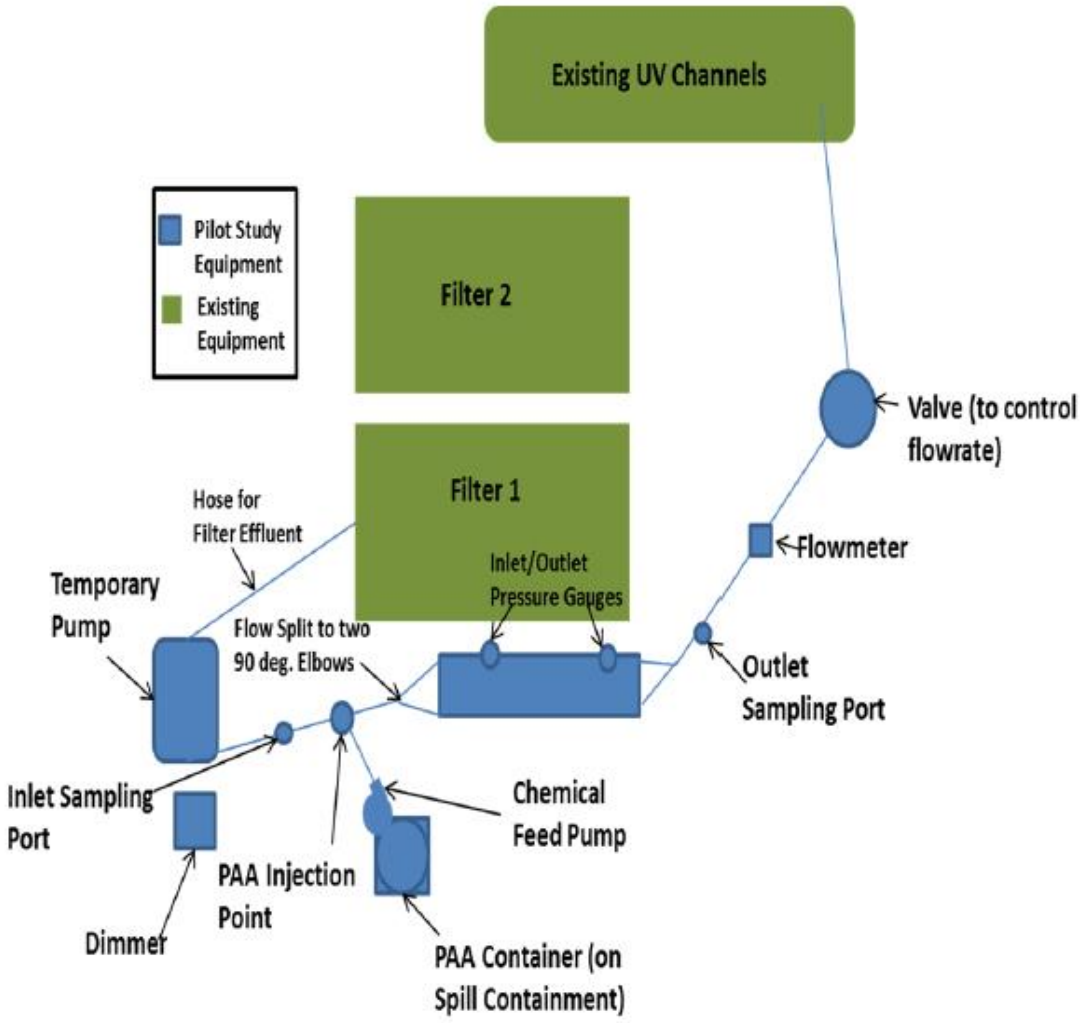

Figure 8. Pilot Study Site Layout

3.2.2 Testing Matrix

The testing matrix is presented in Table 2, which summarizes the tests performed in the pilot study.

Four flowrates (250, 375, 750 and 1,000 GPM) were selected for the pilot study. The design flowrate for the unit is 375 GPM (though for 95% UVT); however, higher flowrates were investigated to understand the treatment capability at lower UV doses.

Four PAA doses evaluated were: 0.5, 1.0, 1.5 and 2.0 mg/L. These are typical PAA concentrations used in combination with UV for synergistic disinfection (Caretti and Lubello, 2003).

Two UV intensities: 75 and 50% UV were selected for the pilot study. These intensities were percentages of the baseline intensity and selected to simulate slow failure of the system, which could be due to aging lamps, fouled quartz sleeves or other degradation of the system over time.

Table 2. Matrix of Pilot Study for Inactivation of Total Coliforms and *E. coli* (Triplicate Samples)

UV Only Testing	
Flow (GPM)	**Lamp Intensity, %**
Varying Flow Tests	
250	100%
375	100%
750	100%
1,000	100%
75% Intensity Test	
250	75%

Flow (GPM)	Lamp Intensity, %
375	75%
750	75%
1,000	75%
50% Intensity Test	
250	<50%(1)
375	<50%(1)
750	<50%(1)
1,000	<50%(1)
Peracetic Acid (PAA)/UV Test	
PAA Dose (mg/L)	**Lamp Intensity, %**
750 GPM(2), 100% UV Intensity PAA Test	
0.5	100%
1	100%
1.5	100%
Additional PAA/UV Tests (2 mg/L PAA Dose)	
Flow (GPM)	**Lamp Intensity(3) ,%**
750	50%
1,000	50%

Notes: (1) Actual percent UV intensity was initially around 28% (based on the 50% non potable water baseline intensity and 100% baseline intensity from the previous testing day).
(2) 750 GPM selected as flowrate for test because complete kill observed at 250 GPM and 375 GPM in 100% UV Intensity Test.
(3) Additional tests completed to understand treatment capability of the unit at true 50% UV intensity and a PAA dose of 2 mg/L

The total coliform and *E. coli* analyses were performed by Transwest Analytical Laboratories, located in Tempe, Arizona.

3.2.3 Pilot Study Experimental Procedure

The pilot study experiments discussed within this thesis were performed on different dates ranging from 7/8/2015 to 7/29/2015. The initial start-up of the pilot study involved thorough cleaning of the UV unit and quartz sleeves to provide an accurate baseline field intensity reading while operating the unit using non-potable water. The baseline field intensity reading for each test was selected based on the highest UV intensity reading out of the four intensity readings. If the baseline field intensity reading dropped by more than 10% between tests, the unit was cleaned.

At the start of each day of the pilot study, the baseline field intensity was determined using the non-potable water. Then the water was switched to filter effluent and flowrate was adjusted based on the test matrix using the pump and the post-unit valve shown in Figure 8. The dimmer and PAA pump were also set up based on the requirements for the test performed on that day.

3.3 Laboratory Experimental Set-Up

The main components of the laboratory scale experimental set-up are the NeoTech D222 UV unit, pump, and inlet and outlet barrels, which are all connected through PVC piping and fittings. The experimental set-up also includes the chemical feed pump and chemical injection port. Figures of the laboratory scale set-up and process flow schematic are shown below in Figures 9 and 10.

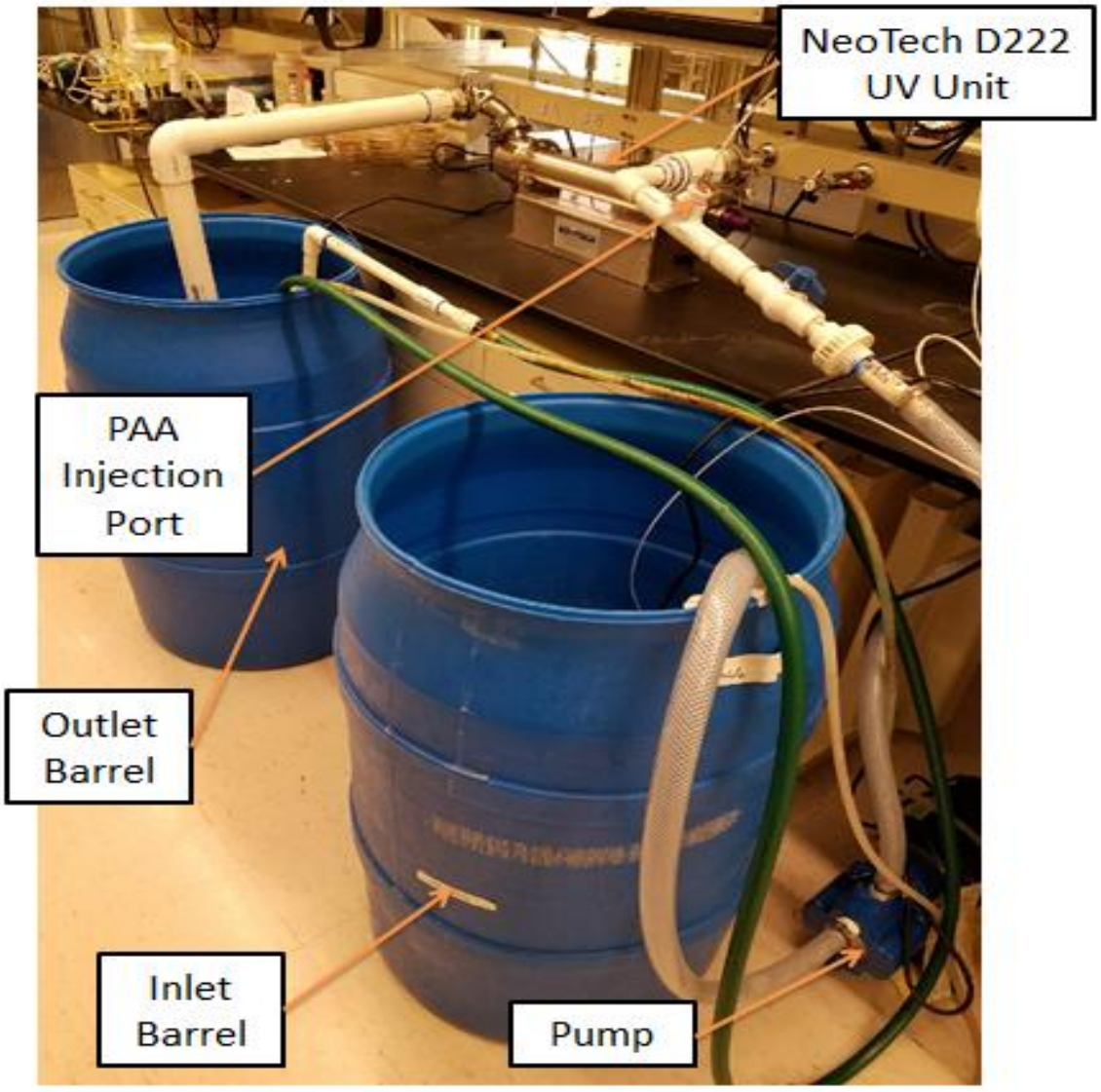

Figure 9. Laboratory Set-Up of Laboratory NeoTech UV Unit, Inlet/Outlet Barrels, Pump, Piping and Fittings

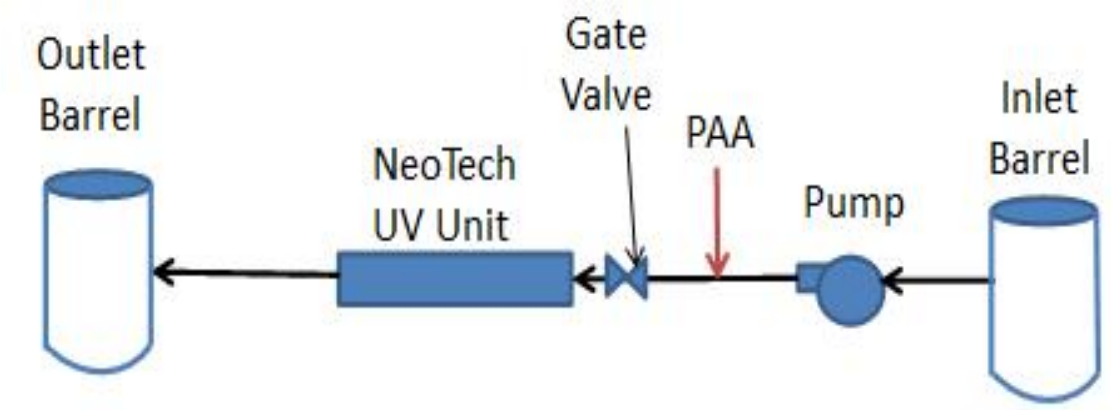

Figure 10. Process Flow Schematic of Laboratory Studies

3.3.1 Laboratory Scale UV Unit

The laboratory scale NeoTech UV Unit (Model D222) is depicted in Figure 4 and is discussed in Section 3.1.2.

3.3.2 Pumps

The laboratory scale experiments were performed using different pumps capable of yielding different flow rates. The low flow pump (2 GPM) was a submersible pump (ECO-185). The medium flow pump (10 GPM) was a centrifugal pump connected to the system using PVC suction piping extended from the suction side of the pump to the bottom of the inlet barrel. The high flow pump (20 GPM) was an AMT centrifugal 2851-6 (Model C63JXGWU-1114) pump connected to the system with a hose as described for the medium flow pump.

3.3.3 Inlet and Outlet Barrels

The laboratory scale experimental set-up included inlet and outlet barrels (208 liters or approximately 50 gallons). Inlet samples are collected directly from the inlet barrel. Outlet samples are collected from the short segment of PVC pipe extended from the 90 degree elbow attached to the outlet end of the UV unit and not directly from the outlet barrel. This location was selected in an effort to prevent potential contamination. Prior to each experiment, both the inlet and outlet barrels were thoroughly cleaned and disinfected with bleach.

3.3.4 Chemical Feed Pump and Injection Port

The chemical feed pump was used to inject PAA into the PVC piping using small diameter chemical-rated tubing. The suction tubing was placed directly into the working stock of PAA contained in conical flask solution. The discharge tubing entered the PVC piping via a chemical injection port. This chemical injection port prevented backflow into the PAA chemical feed line. In order to achieve the desired chemical feed rates, the chemical feed pump was tested before each experiment with water to set the correct pump feed rate.

3.3.5 Testing Matrix

The testing matrix for the laboratory scale experiments is provided in Table 3.

Table 3. Testing Matrix for Laboratory Experiments

Microbial Testing							
Test	**Control**	**UV Only (NeoTech D222 Unit)**				**PAA+UV**	
Microbe/ Chemical	No UV or PAA, 20 GPM	Low Flowrate (2 GPM)	Medium Flowrate (10 GPM)	High Flowrate (20 GPM)	High Flowrate, 20 GPM (*E. coli* and P22)[(1)]	20 GPM, 0.25 mg/L PAA[(1)]	20 GPM, 0.5 mg/L PAA[(1)]
E. coli	2	3	3	--	3	3	3
P22	2	--	--	3	3	3	3

Chemical Testing				
	UV, 4 GPM, No PAA	UV, 4 GPM, 0.5 mg/L PAA	UV, 0.5 GPM, No PAA	UV, 0.5 GPM, 0.5 mg/L PAA
NDMA	2	2	2	2

Notes: (1) In these experiments, both P22 bacteriophage and *E. coli* were added. The experiment included adding over 400 mL of TSB organics.

3.4 Laboratory Scale Experimental Procedure

The laboratory scale studies included four types of experiments: 1) UV only for microorganism inactivation, 2) PAA plus UV for microorganism inactivation, 3) PAA only for microorganism inactivation, and 4) UV and PAA/UV for NDMA degradation. The experimental procedures for these experiments are described below.

Prior to the experiments conducted with the NeoTech D222 UV unit, the experimental system was flushed with tap water. After filling and emptying the inlet barrel at least twice to flush the system, the barrel was filled with tap water. A mixer at the bottom of the barrel was turned on to provide thorough mixing within the barrel. The inlet pump was then turned on as well as the NeoTech UV unit (technician mode turned off). At the barrel fill point (approximately 80 L), the inlet pump was turned off and one mL of sodium thiosulfate was added to the inlet barrel. The sodium thiosulfate was allowed to mix for at least one minute to completely neutralize all residual chlorine.

3.4.1 Microbial Inactivation by UV

These experiments were conducted using overnight bacterial cultures. Approximately 18 to 24 hours before conducting each experiment, 400 mL of TSB was inoculated with the overnight culture from the prior day and incubated at 37°C. The overnight bacterial culture was added to the inlet barrel and mixed thoroughly to ensure homogenous distribution of test bacteria in tap water (with chlorine neutralized by 1 mL of sodium thiosulfate) to prepare spiked test water. The UV lamp in the NeoTech D222 unit was turned on and allowed to warm up until the UV intensity was stable. Then, spiked test water was allowed to run through the system for 45 seconds using the inlet pump. At this point, an inlet sample (from the inlet barrel) and outlet sample (from the PVC outlet pipe) were collected. The UV intensity was recorded during this time period. The barrels were immediately bleached after sample collection and disinfected properly using bleach before waste disposal. Throughout this experiment no PAA was injected in the system. In each experiment, control treatments (no UV) were also included and samples were

analyzed. The samples from control treatment plates demonstrated that *E. coli* and P22 concentrations were the same at inlet and outlet after 45 seconds, indicating that proper mixing and enough time prior to collecting the outlet sample was provided to maintain accurate outlet sampling.

The experiments for P22 inactivation were performed in conjunction with *E. coli* following the procedures described above. For these experiments, the inlet water was spiked with approximately 4 to 5 mL of P22 bacteriophage.

3.4.2 Microbial Inactivation by PAA/UV

The addition of PAA followed a similar methodology to the experimental procedure discussed in Section 3.2.1; however, a few differences are addressed. In preparation, the PAA/UV experiments had the additional component of chemical feed rate testing prior to experiments. The chemical feed rates were set based on achieving the intended PAA dose with the diluted PAA solution (working stock of PAA). The calculations for the proper dilution to prepare working stock of PAA and feed rate in order to reach the desired concentrations are provided as an appendix to this thesis (Appendix B). The working stock of PAA was prepared with DI water and the provided Solvay 12% Proxitane WW-12 PAA sample.

Outlet samples were quenched with approximately 40 µL of 50 mg/mL sodium thiosulfate solution immediately after collection.

3.4.3 Microbial Inactivation by PAA

The PAA experiments were performed with a bench scale set-up conducted in beakers and petri dishes for *E. coli* and P22 respectively. The *E. coli* and P22 testing were performed in different types and volumes of liquid, which is discussed further below. Each test was performed on a stir plate to promote ample mixing. Prior to each test, the PAA concentration was measured using a parallel control.

For the *E. coli* experiments, approximately 125 mL of tap water was dosed with approximately 20 µL of 50 mg/mL sodium thiosulfate to quench chlorine residual. Then, approximately 4 logs of *E. coli* were added to the beakers. After mixing for at least one minute, the inlet (or influent) sample was collected from the beaker. Then PAA was added to achieve the desired dose for each experiment (0.25 and 0.5 mg/L). After adding the PAA, samples were collected for each selected point in time (5, 10 and 30 minutes). Just after collecting the sample, 20 µL of 50 mg/mL sodium thiosulfate was added to the sample to quench the PAA. The samples were then assayed using the spread plate method.

The P22 bacteriophage inactivation experiments using PAA only were performed using phosphate-buffered saline (PBS) in 25 mL petri dishes. The P22 was added to 25 mL of PBS and mixed prior to adding the PAA. Samples were also collected after 5, 10, and 30 minutes. 20 µL of 50 mg/mL sodium thiosulfate was immediately added to the samples after collection.

3.4.4 NDMA Removal by UV and PAA/UV

These experiments were performed using the procedures described in Sections 3.4.1 and 3.4.2 with exception that the desired concentration of NDMA was added to the inlet tap water and no microorganisms were added. Approximately 400 µL of 200 µg/mL of NDMA in methanol solution was added to 108 Liters of tap water in the inlet barrel to create a 700 ng/L NDMA concentration. Inlet and outlet samples were collected in amber bottles (1 L volume).

The experimental flowrates were 0.5 and 4 GPM. A high 700 ng/L NDMA inlet concentration was selected in order to accurately determine % removal in the case that the UV treatment degraded a high percentage of the NDMA. Outlet samples were collected for UV and 0.5 mg/L PAA upstream of UV for each flowrate. The sample bottles contained a small amount of sodium thiosulfate powder preservative (approximately 250 mg). Experiments were conducted in the dark due to the light sensitivity of NDMA. The samples were analyzed at the City of Scottsdale Water Campus laboratory, Scottsdale, Arizona using EPA Method 521. The MRL for this method is 2 ng/L.

3.5 Data Analysis

The *E. coli* and P22 bacteriophage data was analyzed in terms of log inactivation, UV Dose and PAA Dose. The calculations were performed using Microsoft Excel.

The log inactivation measures the percent of microorganisms inactivated. For example, 99.9% of microorganisms inactivated corresponds with three logs inactivation

and 99.99% corresponds with four logs inactivation. The log inactivation is calculated using the following equation:

$$\text{Log Inactivation} = \text{Log}(N_0/N_f),$$

Where N_0 is the inlet concentration of P22 bacteriophage or *E. coli* and N_f is the outlet concentration of P22 bacteriophage or *E. coli*.

The UV Dose was calculated using the equation in Section 2.3, based on UV intensity and contact time. The contact time is based on the volume within the UV chamber in contact with water and flowrate. The volume within the UV chamber was determined based on the dimensions of the UV unit accounting for the UV bulb/outer quartz sleeve.

The NDMA results were expressed in terms of percent removal, UV Dose and PAA Dose. Percent removal is calculated using the following equation:

$$\% \text{ Removal} = (C_0-C_f)/C_0 * (100\%)$$

Where C_0 is the inlet concentration of NDMA and C_f is the outlet concentration of NDMA.

Experimental data analysis also includes the analysis of water quality parameters including PAA concentration (inlet and outlet), UVT (discussed in Section 2.3), pH and Dissolved Organic Carbon (DOC). These parameters were evaluated against typical water quality parameters stated in literature.

The PAA concentration was analyzed using a Hach DR 4000 Spectrophotometer instrument. Total chlorine reagent powder pillows (25 mL) were used with this instrument to provide a total chlorine concentration. Per the Hach protocol included in Appendix C, the total chlorine concentration is multiplied by 1.07 to get the PAA concentration in the sample

Since UVT could not be measured directly in the laboratory study using the available laboratory equipment, UV254 absorbance (UVA) was measured with a Hach DR5000 instrument. This UV254, also known as the spectral absorption coefficient (SAC), measures the amount of light absorbed by organic compounds at a specified wavelength of 254 nm. The UV254 and UVT measurements are related by the following equation:

$$UVT = 100 \times 10^{-UVA}$$

where UVA is the UV254 absorbance. The data was expressed in terms of UVT using the above equation.

CHAPTER 4

RESULTS

4.1 UV Only Inactivation of *E. coli*, Total Coliform and P22 Bacteriophage

In this section, the results of the UV experiments for both the pilot and the laboratory studies are discussed.

4.1.1 Pilot Study Results

Total coliform and *E. coli* log inactivation results using UV for flowrates at 250, 375, 750 and 1,000 GPM are summarized in Table 4. These experiments were conducted at the maximum or 100% UV intensity.

Table 4. Bacterial Log Inactivation at Varying Flowrates at 100% UV Intensity

Flow (GPM)	**Highest UV Dose (mJ/cm^2)**	**Inlet (MPN/100 mL)**						**Outlet (MPN/100 mL)**						**Calculated Average Log Inactivation**	
		Total Coliform			***E. coli***			**Total Coliform**			***E. coli***				
		1	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**	**Total Col.**	***E. coli***
250	52.9	>24,200[(1)]			>24,200[(1)]			<1	<1	<1	<1	<1	<1	≥4.4	≥4.4
375	35.3	>24,200[(1)]			>24,200[(1)]			<1	<1	<1	<1	<1	<1	≥4.4	≥4.4
750	17.6	>24,200[(1)]			>24,200[(1)]			<1	3	3.1	<1	1	1	≥3.9	≥4.4
1,000	13.2	>24,200[(1)]			>24,200[(1)]			15	13	12	10	6	8	≥3.3	≥3.5
Notes: (1) Same result in three different samples analyzed															

The results depict high degree of coliform inactivation for the 250 and 375 GPM flowrates. The higher flowrates (750 and 1,000 GPM) also resulted in >3 logs inactivation of *E. coli*, even though the NeoTech UV unit is only designed for the 375 GPM flowrate.

The water quality parameters for this testing were measured, where 3 samples were collected. Table 5 provides the maximum, minimum and average values for each water quality parameter.

Table 5. Influent Water Quality Parameters at Varying Flowrates at 100% UV Intensity

Parameter	**Minimum**	**Maximum**	**Average**
Turbidity, NTU	1.34	1.83	1.58
Temperature, °C	32.2	32.8	32.5
UVT, %	70.3	71.5	70.7
pH	7.08	7.23	7.14
UV Intensity (Filter Effluent), mW/cm^2	5.3	7.5	--
Chlorine Residual	0	0	0

In general, the 75% UV intensity testing resulted in less inactivation as shown in Table 6. The lower UV dose associated with the lower UV intensity is also displayed in this Table.

Table 6. Bacterial Log Inactivation at Varying Flowrates at 75% UV Intensity

Flow (GPM)	**Highest UV Dose (mJ/cm^2)**	**Inlet (MPN/100 mL)**						**Outlet (MPN/100 mL)**						**Average Log Inactivation**	
		Total Coliform			***E. coli***			**Total Coliform**			***E. coli***				
		1	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**	**Total Col.**	***E. coli***
250	38.1	>120,980[(1)]			49,000[(1)]			<1	<1	<1	<1	<1	<1	≥5.1	4.7
375	25.4	>120,980[(1)]			59,000[(1)]			10	<1	7.4	1	<1	2	≥4.5	4.7
750	12.7	>120,980[(1)]			64,100[(1)]			261	345	248	30	55	35	≥2.6	3.3
1,000	9.5	>120,980[(1)]			44,500[(1)]			>2,420	1,120	921	155	289	158	≥2.0	2.4
Notes: (1) Same result in three different samples analyzed															

The influent water quality parameters for the 75% UV intensity tests are listed in Table 7.

Table 7. Influent Water Quality Parameters at Varying Flowrates at 75% UV Intensity

Parameter	**Minimum**	**Maximum**	**Average**
Turbidity, NTU	1.19	1.61	1.43
Temperature, °C	32	32.7	32.4
UVT, %	69.9	71.2	70.6
pH	7.03	7.23	7.09
UV Intensity (Filter Effluent), mW/cm^2	0.7	5.4	--
Chlorine Residual	0	0	0

The dimmer malfunctioned when switching from the 75% to the 50% UV intensity test, which was likely due to overheating of the dimmer from the high Arizona summer temperature. Despite efforts to fix the broken resistors in the dimmer, the dimmer could not be brought back to its original performance. The effect was that the electrical ballast on the UV system began to expire and power to the lamps was lost over the course of the test, resulting in even lower UV intensities and therefore doses. It is possible that many lamps lost power completely resulting in low UV treatment of the filtered effluent. Therefore, the test did not reflect the true treatment capability at 50% and was instead closer to 28% UV intensity.

Table 8. Bacterial Log Inactivation at Varying Flowrates at <50% UV Intensity

Flow (GPM)	**Highest UV Dose (mJ/cm^2)**	**Inlet (MPN/100 mL)**						**Outlet (MPN/100 mL)**						**Calculated Average Log Inactivation**	
		Total Coliform			***E. coli***			**Total Coliform[1]**			***E. coli*[2]**				
		1	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**	**Total Col.**	***E. coli***
250	30.3	>242,000[1]			44,100[1]			>2,420[3]			>2,420[3]			2	≤1.3
375	20.2	>242,000[1]			29,100[1]			10	<1	7.4	>2,420			2	3.8
750	10.1	>242,000[1]			33,100[1]			261	345	248	>2,420			2	2.1
1,000	7.6	>242,000[1]			13,900[1]			>2420	1,120	921	>2,420			2	1

Notes: (1) Same result in three different samples analyzed
(2) The laboratory reported results indicate *E. coli* counts higher than total coliform counts, which should not occur. The results are shown in the Table as reported based on formal laboratory reports.
(3) These results are not consistent with the rest of the data, which could be due to error (sampling or lab)

Table 9. Influent Water Quality Parameters at Varying Flowrates at <50% UV Intensity

Parameter	**Minimum**	**Maximum**	**Average**
Turbidity, NTU	1.49	2.43	1.85
Temperature, °C	31.7	36.6	33.4
UVT, %	68.1	70.5	69.5
pH	7.01	7.28	7.10
UV Intensity (Filter Effluent), mW/cm^2	0	4.3	--
Chlorine Residual	0	0	0

The series of plots displaying the log inactivation of *E. coli* for the experiments discussed in this section are in Figure 11. Error bars are included on these plots to display standard deviation in the data.

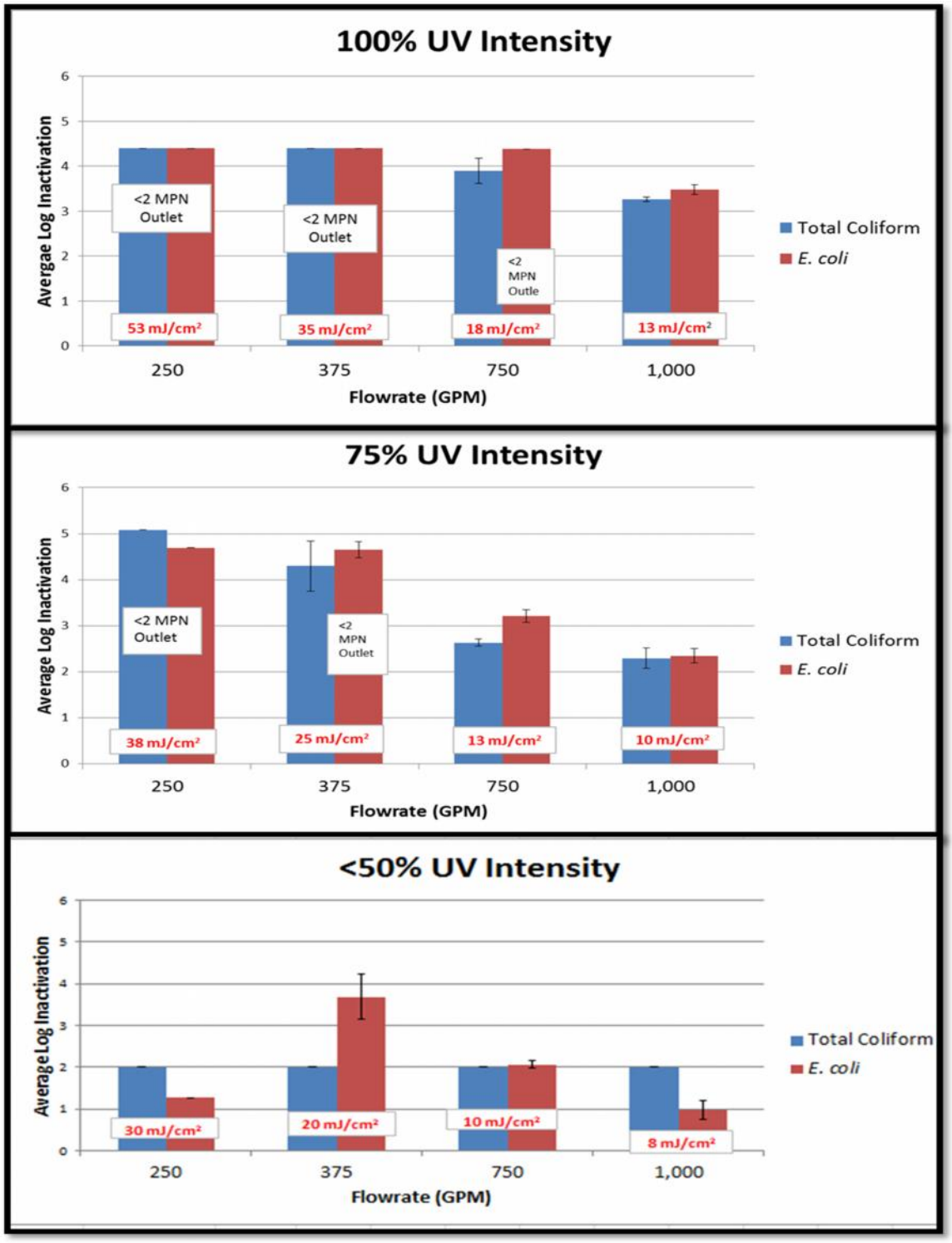

Figure 11. Log Inactivation of Total Coliform and *E. coli* for UV Pilot Study Experiments (100%, 75%, <50% UV Intensity)

4.1.2 Laboratory Study Results

The UV experiments performed under laboratory conditions were performed at low, medium and high flowrates: 2, 10 and 20 GPM. In these experiments, the UV dose was changed by the flowrate only as the UV intensity could not be adjusted. Only *E. coli* was analyzed for the 2 and 10 GPM flowrates. The 20 GPM flowrate included analysis of both *E. coli* and P22 bacteriophage, and both microorganisms were added together into the inlet barrel. Additionally, inactivation tests were performed on P22 without adding 400 mL of TSB to the inlet barrel, where TSB media is part of *E. coli* stock preparation. The results for *E. coli* at the three flowrates and P22 bacteriophage at the high flowrate (20 GPM, together with *E.coli* and separately) are shown in Tables 10 and 11.

Table 10. Log Inactivation of *E. coli* by UV under the Laboratory Conditions

Trial Number	**UV Intensity (mW/cm^2)**	**UV Dose (mJ/cm^2)**	**Average UV Dose (mJ/cm^2)**	***E. coli* Concentration (CFU/mL)**		**Log Inactivation**
				Inlet	**Outlet**	
<u>Low Flowrate, 2 GPM</u>						
1	22.1	164.8	166.1	3,362,500	0	>8.5
2	22.3	166.3		7,120,000	0.045	8.2
3	22.4	167.1		9,100,000	0.01	9.0
					Average	**≥8.2**
<u>Medium Flowrate, 10 GPM</u>						
1	24	35.8	39.3	14,750,000	0.035	8.6
2	28	41.8		12,100,000	0.01	9.1
3	27	40.3		13,250,000	0.095	8.1
					Average	**8.61**
<u>High Flowrate, 20 GPM</u>						
1	22.2	16.6	16.8	6,300,000	0.08	7.9
2	22.3	16.6		7,775,000	0.12	7.8
3	22.9	17.1		3,200,000	0	8.5
					Average	**≥7.8**

Table 11. Log Inactivation of P22 Bacteriophage by UV under the Laboratory Conditions

Trial Number	**UV Intensity (mW/cm^2)**	**UV Dose (mJ/cm^2)**	**Average UV Dose (mJ/cm^2)**	**P22 Concentration (PFU/mL)**		**Log Inactivation**
				Inlet	**Outlet**	
<u>High Flowrate, 20 GPM, *E. coli* and P22 Bacteriophage Added</u>						
1	22.2	16.6	16.8	371,535	42.7	3.94
2	22.3	16.6		1,380,384	114.8	4.08
3	22.9	17.1		1,479,108	154.9	3.98
					Average	**4**
<u>High Flowrate, 20 GPM, Only P22 Bacteriophage</u>						
1	31.5	23.5	23.1	1,122,018	0	>6.05
2	30.6	22.8		1,659,587	0	>6.22
3	31	23.1		1,548,817	0	>6.19
					Average	**>6.1**

The plot displaying the comparison of *E. coli* and P22 log inactivation for UV experiments is shown in Figure 12.

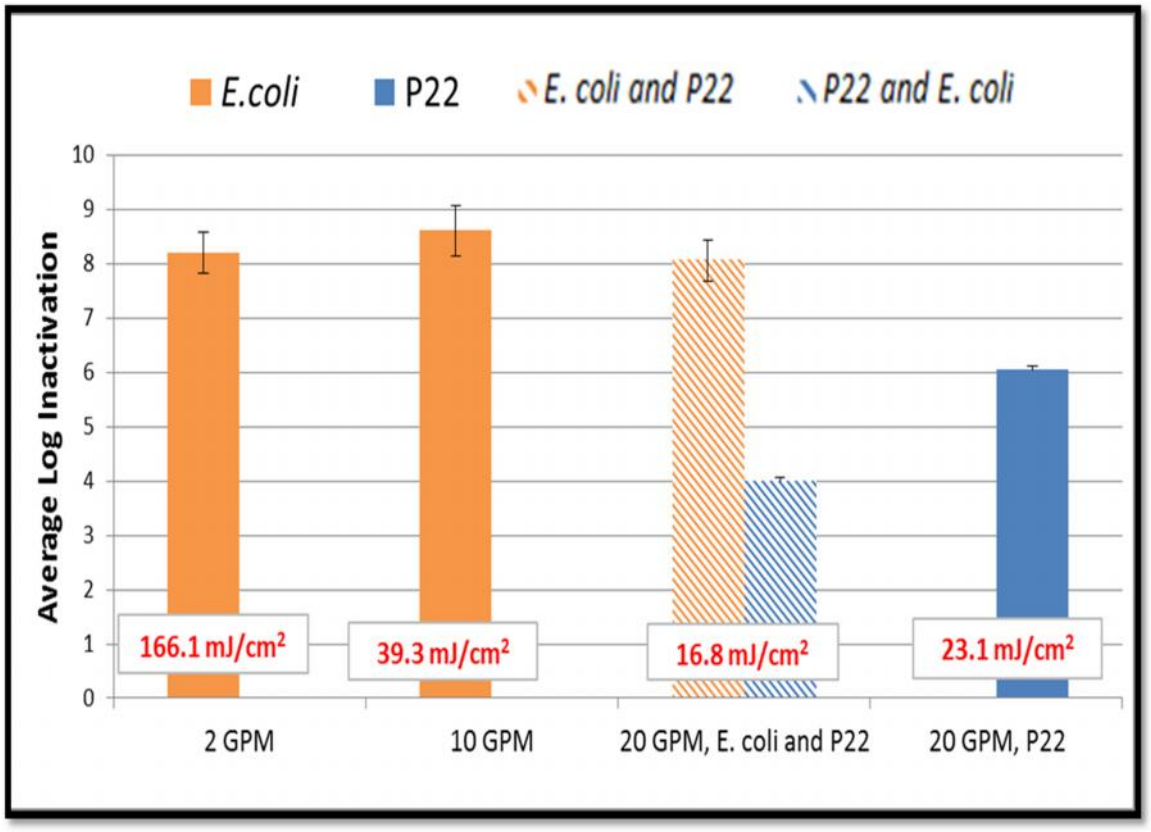

Figure 12. Log Inactivation of *E. coli* and P22 Bacteriophage by UV under the Laboratory Conditions

4.2 PAA/UV Inactivation of *E. coli*, Total Coliform and P22 Bacteriophage

4.2.1 Pilot Study Results

The results of the testing of PAA/UV at PAA doses of 0.5, 1.0 and 1.5 mg/L is displayed in Table 12. The testing was conducted at the 750 GPM flowrate with the required chemical feed rate for maintaining the doses. The 100% UV Intensity was utilized. The results of the test varied (Table 12), where some of the inlet samples were low concentrations for both total coliform and *E. coli*, and some outlet sample concentrations were significantly higher than inlet, which was not observed in the 100% UV intensity test conducted without PAA.

The bolded concentrations in Table 12 are the results that are believed to be inaccurate, whether due to sampling error (including incorrect labelling of inlet and outlet samples) or the type of analytical method used. The analytical method used by the commercial lab was the Most Probable Number method, which is based on dilutions and may not be as accurate compared to other analytical methods, such as membrane filtrations technique.

Table 12. Bacterial Log Inactivation at Varying PAA Dose at 750 GPM Flowrate and 100% UV Intensity

PAA Dose (mg/L)	**Highest UV Dose (mJ/cm^2)**	**Inlet (MPN/100 mL)**						**Outlet (MPN/100 mL)**						**Log Inactivation**	
		Total Coliform			***E. coli***			**Total Coliform**			***E. coli***				
		1	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**	**Total Col.**	***E. coli***
0.5	16.5	>242,000[(1)], **<100**[(2)]			51,200[(1)], **<100**[(2)]			**>2,420**[(2)]	19	21	**>2,420**[(2)]	2	1	2.3	2.6
1.0	16.5	>242,000[(1)], **<100**[(2)]			48,300[(1)], **100**[(2)]			31	119	19	<1	86	1	2.6	3.1
1.5	16.5	>242,000[(1)], **2490**[(2)]			53,300[(1)], **310**[(2)]			11	26	<1	<1	<1	<1	3.9	4

Notes: (1) This number indicates the same results for two samples
(2) Bolded results indicate results that appear to be affected by sampling or lab error.

The additional influent water quality parameters for the varying PAA doses at 100% UV intensity and 750 GPM flowrate test are listed in Table 13. The water quality testing particular to this pilot study experiment included testing the PAA concentration at the outlet for the highest inlet PAA dose of 1.5 mg/L. The results demonstrate significant

decrease in PAA concentration across the UV reactor, where the average outlet concentration indicates one-third of the inlet concentration.

Table 13. Influent Water Quality Parameters at Varying PAA Dose at 750 GPM Flowrate and 100% UV Intensity

Parameter	**Minimum**	**Maximum**	**Average**
Turbidity, NTU	1.29	1.88	1.62
Temperature, °C	31.5	31.8	31.6
UVT, %	68.2	71.7	69.8
pH	7.08	7.31	7.18
UV Intensity (Filter Effluent), mW/cm^2	5.9	7	--
Chlorine Residual	0	0	0
PAA Concentration (Outlet), mg/L	0.1	1.1	0.5

Due to the ambiguous results, another set of experiments were performed. The additional two tests were at the higher flowrates of 750 and 1,000 GPM at 50% UV intensity. A 2 mg/L PAA dose was selected due to the results of the previous PAA/UV testing displayed in Table 12; though, as previously mentioned, the results may have been affected by other factors. All *E. coli* results with this PAA dose were non-detect, despite a lower UV intensity and dose. However, it was observed that the inlet coliform concentrations were lower than concentrations in the previous tests including the 100%, 75% and 50% UV intensity tests (Tables 4, 6 and 8).

Table 14. Bacterial Log Inactivation at 2 ppm PAA Dose at 750 and 1,000 GPM Flowrates and 50% UV Intensity

Flow (GPM)	**Highest UV Dose (mJ/cm^2)**	**Inlet (MPN/100 mL)**						**Outlet (MPN/100 mL)**						**Average Log Inactivation**	
		Total			***E. coli***			**Total**			***E. coli***				
		1	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**	**Total**	***E. coli***
750	13.4	1,890, 630, <100			<100,100, 200			<1	5.2	<1	<1	<1	<1	2.5	2.1
1,000	10.1	9,800			657			<1	<1	<1	<1	<1	<1	4	2.8

The inlet coliform concentrations may have been low due to disinfection occurring from small concentrations of chlorine residual that were detected in this test. The detected chlorine residual is listed in the influent water quality parameters in Table 15. This chlorine residual was created by the chlorination of the upstream cloth media disk filters for maintenance purposes. Chlorination of the filers was typically coordinated with operations staff prior to pilot study sampling; however, this was a case where poor communication occurred.

Table 15. Influent Water Quality Parameters at 2 ppm PAA Dose at 750 and 1,000 GPM Flowrates and 50% UV Intensity

Parameter	**Minimum**	**Maximum**	**Average**
Turbidity, NTU	1.66	2.26	1.96
Temperature, °C	31.7	31.9	31.8
UVT, %	70	70.5	70.3
pH	6.87	6.87	6.87
UV Intensity (Filter Effluent), mW/cm^2	0.4	5.7	--
Chlorine Residual	0.2	0.2	0.2

The results of the PAA/UV testing discussed above are shown in Figure 13. The sizeable error bars in the plot displaying 100% UV intensity at the 750 GPM demonstrate the high variability in the data collected.

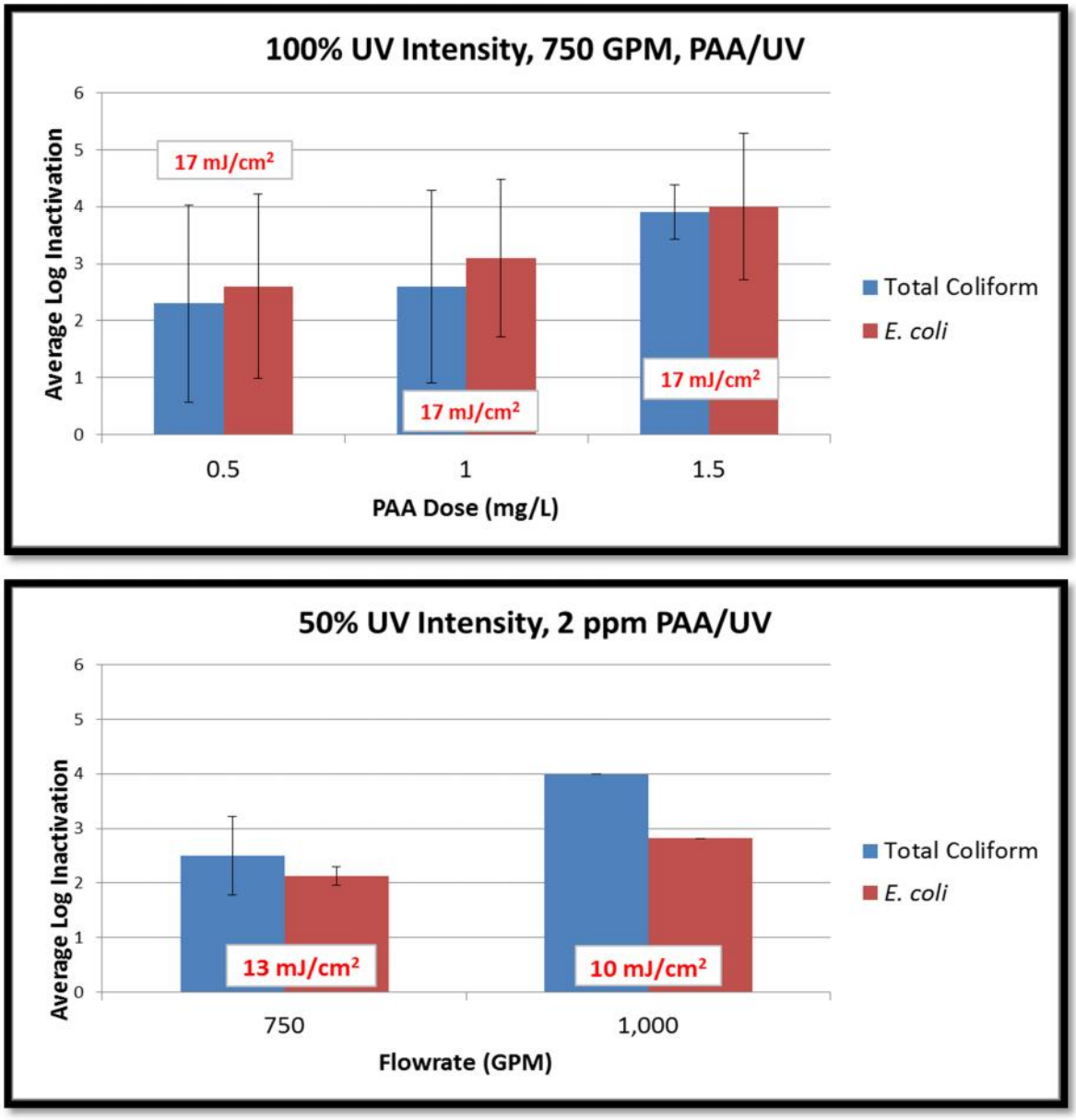

Figure 13. Log Inactivation of Total Coliform and *E. coli* for PAA/UV Pilot Study Experiments

4.2.2 Laboratory Study Results

The research results of the laboratory testing involving the PAA dosing upstream of the UV reactor are presented in this subsection. The 0.5 mg/L PAA Dose testing was

completed first. Following the results of the 0.5 mg/L, a 0.25 mg/L PAA dose was selected for the second round of experiments.

Table 16. Log Inactivation of *E. coli* by PAA/UV under the Laboratory Conditions at High Flow (20 GPM) and PAA Doses of 0.5 and 0.25 mg/L

Trial Number	**UV Intensity (mW/cm^2)**	**UV Dose (mJ/cm^2)**	**Average UV Dose (mJ/cm^2)**	***E. coli* Concentration (CFU/mL)**		**Log Inactivation**
				Inlet	**Outlet**	
<u>20 GPM Flowrate, 0.5 mg/L PAA Dose</u>						
1	21.3	15.89	16.0	55,666,667	0	≥9.75
2	21.3	15.89		3,800,000	0	≥8.6
3	21.9	16.33		4,733,333	0.01	≥8.6
					Average	**≥9**
<u>20 GPM Flowrate, 0.25 mg/L PAA Dose</u>						
1	22.1	16.48	16.1	25,166,667	0	≥9.4
2	21.5	16.04		4,766,667	0	≥8.7
3	21.3	15.89		4,300,000	0	**≥8.6**
					Average	**≥8.9**

The P22 results for this flowrate and selected PAA doses are listed in Table 17.

Table 17. Log Inactivation of P22 Bacteriophage by PAA/UV under the Laboratory Conditions at High Flow (20 GPM) and PAA Doses of 0.5 and 0.25 mg/L

Trial Number	**UV Intensity (mW/cm^2)**	**UV Dose (mJ/cm^2)**	**Average UV Dose (mJ/cm^2)**	**P22 Concentration (PFU/mL)**		**Log Inactivation**
				Inlet	**Outlet**	
<u>20 GPM Flowrate, 0.5 mg/L PAA Dose</u>						
1	21.3	15.89	16.0	4,786,301	2,512	3.3
2	21.3	15.89		1,047,129	2,818	2.6
3	21.9	16.33		1,778,279	891	3.3
					Average	**3.1**
<u>20 GPM Flowrate, 0.25 mg/L PAA Dose</u>						
1	22.1	16.48	16.1	6,165,950	8,710	2.9
2	21.5	16.04		3,801,894	6,607	2.8
3	21.3	15.89		5,248,075	5,495	3.0
					Average	**2.9**

The 0.5 mg/L PAA dose achieved higher *E. coli* inactivation than UV experiments; however, less inactivation of P22 occurred. Since no *E. coli* colonies were detected in the outlet samples, a 0.25 mg/L PAA dose was selected for the second round of PAA/UV experiments.

The plot displaying the average log inactivation for all PAA/UV experiments described in Section 4.2.2 is shown in Figure 14.

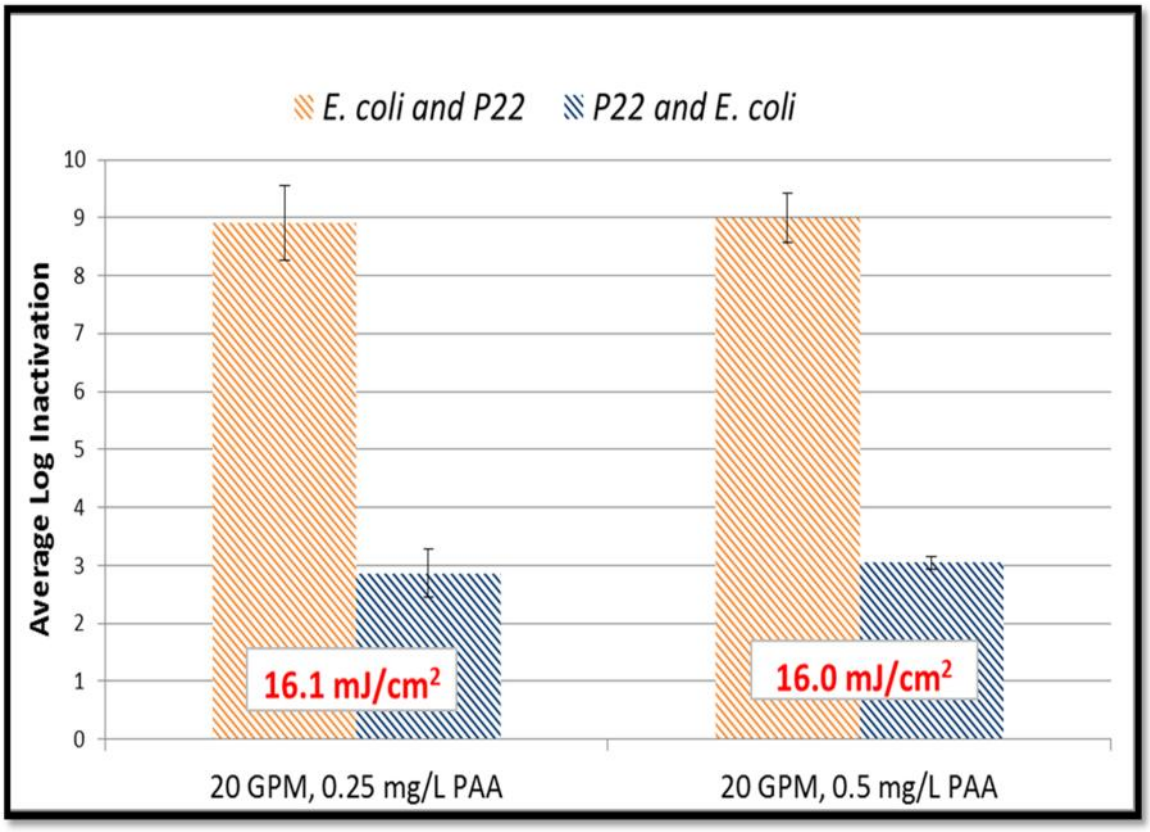

Figure 14. Log Inactivation of *E. coli* and P22 Bacteriophage by PAA/UV under the Laboratory Conditions

4.2.2.1 Water Quality and PAA Inlet/Residual Testing

The concentration of PAA at the inlet was measured to confirm that the dose entering the UV reactor was the intended concentration. The PAA residual was also measured when the UV was on in the reactor. The PAA concentration at the inlet and the residual testing results for 0.25 and 0.5 mg/L doses are shown in Table 18. The values are an average of 3 measurements.

Table 18. PAA Inlet and Residual Measured Concentrations for PAA/UV Tests under the Laboratory Conditions

Intended Inlet PAA Dose (mg/L)	**Inlet PAA Concentration (mg/L)**	**Residual PAA Concentration (mg/L)**
0.25	0.20	0.02
0.50	0.44	0.016

The results from Table 18 show that the measured PAA concentration at the inlet was close to the intended dose. In fact, the actual dose in the experiments may have been closer to this intended dose; however, some PAA may have degraded during the short time that elapsed before measurement of each sample.

The residual PAA dose measured after the UV reactor was low, suggesting that the PAA was quickly degraded within the UV reactor. The calculated contact time in the UV reactor is less than one second.

The water quality for the UV and PAA/UV experiments with addition of the 400 mL of TSB was analyzed in order to determine the organic loading concentration in the inlet water. Table 19 displays the calculated percent of UV Transmittance (UVT), which is the light energy that reaches the detector and is calculated from the UV Absorption (UVA) at 254 nm wavelength according to the equation in Section 3.4. The dissolved organic carbon (DOC) was also measured (Table 19). The instrument used for measuring DOC was not calibrated to provide accurate readings for concentrations above 20 mg/L. The DOC measurement was approximately 98 mg/L for all sample types. Due to the fact

this reading was significantly than the 20 mg/L calibration limit, the 98 mg/L DOC concentration may not be an accurate representation of DOC within the sample. Therefore, the DOC measurements listed in Table 19 are displayed as >20 mg/L.

Table 19. Measured UVT and DOC for the PAA/UV Tests under the Laboratory Conditions

Type of Sample	**% UVT**				**DOC, mg/L**			
	1	**2**	**3**	**Average**	**1**	**2**	**3**	**Average**
Inlet	72.3	77.8	77.6	75.9	>20	>20	>20	>20
Outlet (UV Only)	76.9	77.9	77.3	77.4	>20	>20	>20	>20
Outlet, 0.25 mg/L PAA	76.4	77.4	77.4	77.1	>20	>20	>20	>20
Outlet, 0.5 mg/L PAA	76.9	77.4	77.4	77.3	>20	>20	>20	>20

The UVA at 254 nm wavelength for tap water was also measured and converted into UVT. The UVT for the tap water sample was 84%. The DOC for the tap water sample was ~2 mg/L.

The pH of the inlet and outlet samples was also monitored (Table 20).

Table 20. Measured Inlet and Outlet pH for the PAA/UV Tests under the Laboratory Conditions

Type of Sample	pH			
	Sample 1	**Sample 2**	**Sample 3**	**Average**
Inlet	7.68	7.67	7.67	7.67
Outlet (UV Only)	7.64	7.67	7.67	7.66
Outlet, 0.25 mg/L PAA, No Sodium Thiosulfate	7.63	7.64	7.64	7.64
Outlet, 0.25 mg/L PAA, Sodium Thiosulfate Added	7.70	7.71	7.72	7.71
Outlet, 0.5 mg/L PAA, Sodium Thiosulfate Added	7.66	7.59	7.62	7.62

The results in Table 20 demonstrate that there is a minimal pH change associated with the PAA/UV exposure. The results are concurrent with the low PAA residual observed in the outlet.

4.3 PAA Inactivation of *E. coli* and P22 Bacteriophage

The PAA experimental results are discussed in the following sections.

4.3.1 Pilot Study Results

For the pilot study, no PAA inactivation testing was performed without UV.

4.3.2 Laboratory Study Results

The PAA experiments were conducted separately for *E. coli* and P22. The experiments were conducted using tap water and PBS buffer for *E.coli* and P22, respectively. The average *E. coli* inactivation at 5, 10 and 30 minutes of contact time is displayed in Table 21. A zero is incorporated into the calculated average for tests where no inactivation was observed.

A control experiment was performed without PAA to measure the natural inactivation of *E. coli* in water over time, which could potentially be due to external factors. Out of the three experiments, the maximum average inactivation after 30 minutes was 0.12 log. There was no inactivation after 5 and 10 minutes exposure time.

Table 21. Log Inactivation of *E. coli* by PAA under the Laboratory Conditions

Trial Number	**PAA Dose (mg/L)**	**Average PAA Dose (mg/L)**	***E. coli* Concentration (CFU/mL)**		**Log Inactivation**
			Inlet	**Outlet**	
<u>0.25 mg/L PAA Dose</u>					
5 Minutes of Contact Time					
1	0.26	0.25	40,000	69,000	None
2	0.24		33,500	26,500	0.10
3	0.26		29,500	44,000	None
				Average	**0.03**
10 Minutes of Contact Time					
1	0.26	0.25	40,000	52,500	None
2	0.24		33,500	22,000	0.18
3	0.26		29,500	39,500	None
				Average	**0.06**
30 Minutes of Contact Time					
1	0.26	0.25	N/A	N/A	N/A
2	0.24		33,500	3,050	1.04
3	0.26		29,500	32,000	None
				Average	**0.52**
<u>0.50 mg/L PAA Dose</u>					
5 Minutes of Contact Time					

1	0.25	0.25	50,000	52,500	None
2	0.24		46,000	36,500	0.10
3	0.26		32,000	27,000	0.07
				Average	**0.06**
10 Minutes of Contact Time					
1	0.25	0.25	50,000	39,500	0.10
2	0.24		46,000	20,500	0.35
3	0.26		32,000	25,000	0.11
				Average	**0.19**
30 Minutes of Contact Time					
1	0.25	0.25	50,000	20,500	0.21
2	0.24		46,000	24,500	0.27
3	0.27		32,000	12,000	0.43
				Average	**0.30**

The PAA P22 results are displayed in Table 22. The inactivation of P22 was measured in PBS buffer (instead of tap water) at contact times of 5, 10 and 15 minutes. One experiment for PAA at 0.25 mg/L was performed at a contact time of 30 minutes.

Table 22. Log Inactivation of P22 Bacteriophage by PAA under the Laboratory Conditions

Trial Number	**PAA Dose (mg/L)**	**Average PAA Dose (mg/L)**	**P22 Concentration (PFU/mL)**		**Log Inactivation**
			Inlet	**Outlet**	
<u>0.25 mg/L PAA Dose</u>					
5 Minutes of Contact Time					
1	0.26	0.25	4,295,000	-	-
2	0.24		2,650,000	1,900,000	0.14
3	0.26		3,200,000	2,200,0000	0.16
				Average	**0.15**
10 Minutes of Contact Time					
1	0.26	0.25	4,295,000	3,205,000	0.13
2	0.24		2,650,000	2,050,000	0.18
3	0.26		3,200,000	2,200,000	0.16
				Average	**0.16**
15 Minutes of Contact Time					
1	0.26	0.25	4,295,000	-	-
2	0.24		2,650,000	1,900,000	0.14
3	0.26		3,200,000	2,250,000	0.15
				Average	**0.15**
30 Minutes of Contact Time					

1	0.26	-	4,295,000	2,200,000	0.29
<u>0.50 mg/L PAA Dose</u>					
5 Minutes of Contact Time					
1	0.25	0.25	5,000,000	4,200,000	0.08
2	0.24		5,350,000	3,500,000	0.18
3	0.26		4,700,000	3,850,000	0.09
				Average	**0.12**
10 Minutes of Contact Time					
1	0.25	0.25	5,000,000	4,050,000	0.09
2	0.24		5,350,000	3,200,000	0.22
3	0.26		4,700,000	3,300,000	0.15
				Average	**0.15**
15 Minutes of Contact Time					
1	0.25	0.25	5,000,000	3,050,000	0.21
2	0.24		5,350,000	2,600,000	0.31
3	0.27		4,700,000	2,400,000	0.29
				Average	**0.27**

Figure 15 depicts the results of the *E. coli* and P22 bacteriophage inactivation for the 0.25 and 0.5 mg/L PAA doses at the different contact times.

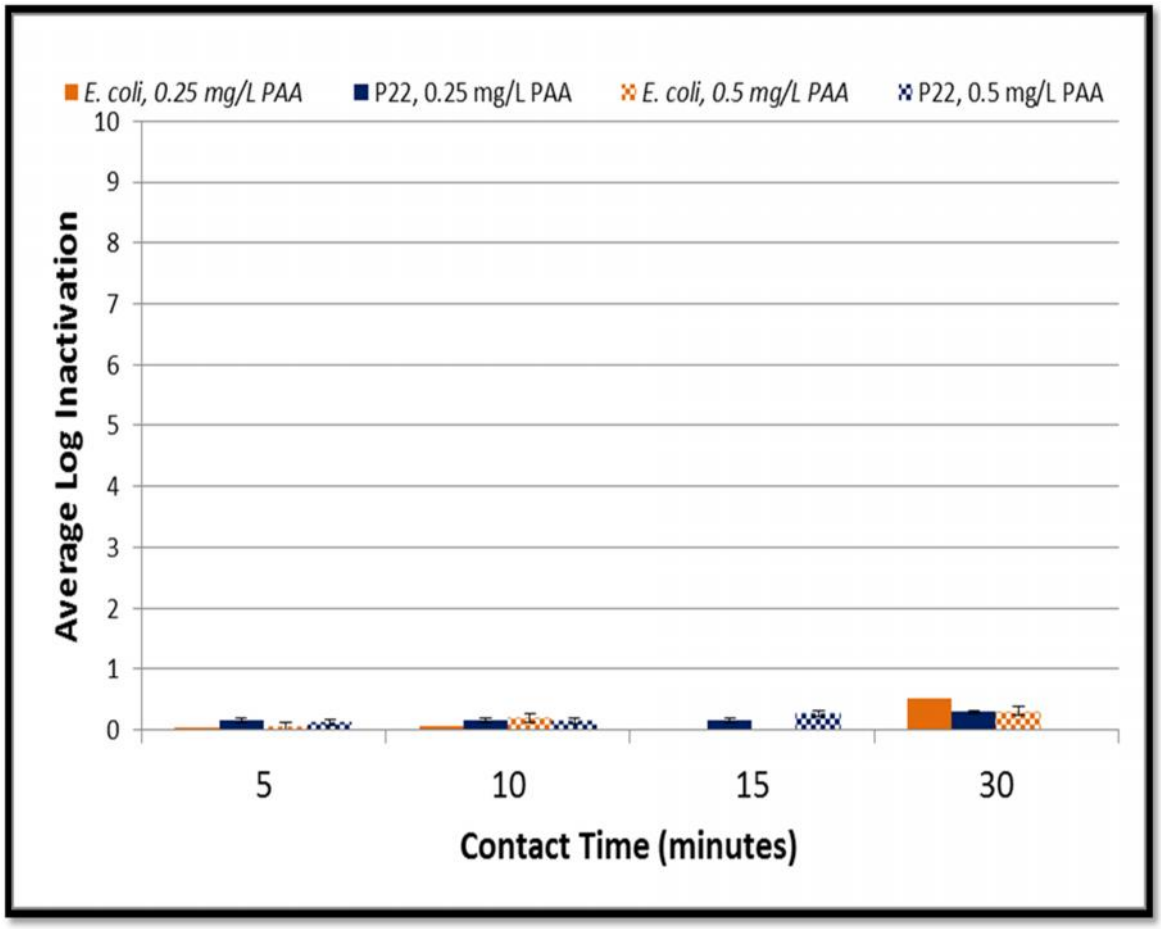

Figure 15. Log Inactivation of *E. coli* and P22 Bacteriophage by PAA under the Laboratory Conditions

4.4 NDMA Removal by UV and PAA/UV

The NDMA removal experiments were conducted with UV as well as PAA/UV. The average UV doses for these experiments were 700 and 100 mJ/cm^2 for 0.5 and 4 GPM flowrates, respectively (Table 23).

Table 23. NDMA Removal by UV and PAA/UV at 0.5 and 4 GPM Flowrates

Experiments	**Average NDMA Concentration (ng/L)**		**% NDMA Removal**
	Inlet	**Outlet**	
0.5 GPM, UV	655	19	97.1
0.5 GPM, 0.5 mg/L PAA/UV	655	37	94.4
4 GPM, UV	655	343	47.6
4 GPM, 0.5 mg/L PAA/UV	655	330	49.6

There is a slight increase in the percent NDMA removal for the 4 GPM flowrate when 0.5 mg/L PAA was added upstream of the UV reactor; however, there is no significant change in percent removal for both flowrates (Figure 16).

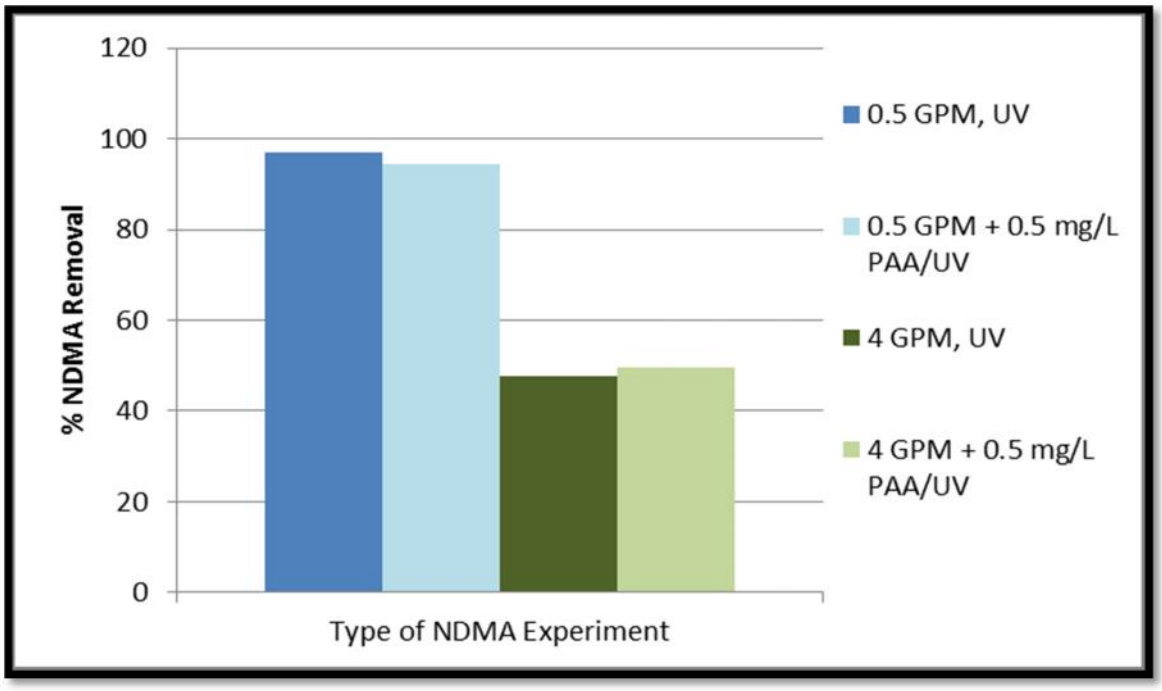

Figure 16. Percent NDMA Removal for UV and 0.5 mg/L PAA/UV for 0.5 and 4 GPM Flowrates

CHAPTER 5

DISCUSSION

Results from the pilot and the laboratory studies provided useful information pertaining to advanced oxidation processes (AOP's), as well as ultraviolet irradiation (UV) and peracetic acid (PAA) disinfection capability as primary disinfectants. The treatment capability was analyzed in terms of disinfection and chemical degradation. Microorganisms studied for disinfection were total coliforms, *E. coli* and P22 bacteriophage as a surrogate for enteric viruses. The chemical studied in terms of degradation was NDMA.

The pilot study performed on tertiary-treated (filter effluent) wastewater at the Palo Verde Water Reclamation Plant focused on total coliform and *E. coli* inactivation and monitoring of several physico-chemical water quality parameters. As shown in Table 4, the experimental data from the pilot study conducted at 100% UV intensity showed that the NeoTech Inline Magnum UV unit was capable of disinfecting >4 logs of *E. coli* at flowrates above its 95% UVT rated capacity of 375 GPM, with <2 MPN/100 mL *E. coli* at the outlet of the reactor at 750 GPM flowrate (equivalent to a UV dose of approximately 18 mJ/cm^2). Even under the high flowrate condition of 1,000 GPM (13 mJ/cm^2), 10 MPN/100 mL or less *E. coli* cells were detected in the outlet, which translates into >3 logs of *E. coli* inactivation.

The experiments conducted at 75% UV intensity, in general, had a higher initial *E. coli* concentration at the inlet than the experiments conducted at 100% UV intensity. Even with these higher initial concentrations of *E. coli*, the log inactivation was slightly

less at 3 logs for a 12.7 mJ/cm^2 UV dose as shown in Table 6. Generally, lower *E.coli* inactivation levels were achieved at higher flowrates, with 3.2 and 2.3 logs at 750 and 1,000 GPM flowrates, respectively.

The experiments conducted at the <50% UV intensity produced anomalous results as the *E. coli* concentrations (>2,420 MPN/100 mL) were greater than the total coliform concentrations (261, 345 and 248 MPN/100 mL) in outlet samples for all flowrates (Table 8). These reported results appear inaccurate since the total coliform concentrations are expected to be greater than the *E. coli* concentrations as *E. coli* are a subpopulation of total coliforms. If the *E. coli* and total coliform concentrations in this Table are switched, the results are consistent with the other UV data previously discussed showing approximately 3.7 logs of *E. coli* inactivation at the UV dose of 20 mJ/cm^2.

According to ATG UV technology, UV systems at wastewater treatment plants are specified for 30 mJ/cm^2 for UVT ranging from 50% to 80%. Hassen et al. (2000) recommends that UV doses do not fall below 30 mJ/cm^2. In the pilot scale experiments conducted using UV, the UVT ranged from 68 to 72%. The results highlight the potential application of the NeoTech Inline Magnum UV unit for improving the bacteriological quality of the filter effluent at the Palo Verde Water Reclamation Plant. The technology requires a UV dose that is approximately half of the typically specified 30 mJ/cm^2 UV dose. The capability of adequate disinfection at lower UV doses may be due to the unique design attributes of the NeoTech UV unit that includes the reflective interior to effectively spread the UV light throughout the UV reactor. Additional experiments should be performed to measure the unique capability of the NeoTech UV technology

against a broad range of microorganisms such as viruses, parasites and bacteria listed in the U.S EPA Candidate Contaminant List.

The UV experiments performed under the laboratory conditions for *E. coli* indicates that the log inactivation is proportional to UV dose. The water used in the experiments performed under laboratory conditions was tap water. Experiments conducted with the *E. coli* utilized tap water spiked with the cells suspended in TSB resulting in the test water containing a significant DOC concentration, which was measured to be >20 mg/L in all samples (Table 19). The average UVT for the test water ranged from 75.9 to 77.4%, whereas the measured UVT of tap water was approximately 85% indicating that the addition of the organics decreased the UVT resulting in less UV light transmitted through test water than regular tap water.

The UVT measured for test water used in the laboratory studies is within the typical wastewater range of 50% to 80% (ATG Technology). Despite a lower UVT, approximately 8 logs of *E. coli* was inactivated with an average UVT ranging from 75.9 to 77.4%. According to literature DOC concentrations in raw wastewater can be approximately 70 mg/L (Katsoyiannis and Samara, 2007; Amiel et al., 1990). Though a precise measurement was not provided due to calibration limits of the instrument, the measured DOC in the test water (>20 mg/L) was still significantly higher than the DOC concentration of tap water (~2 mg/L), further indicating a high organics content in the test water.

The UV experiments conducted under the laboratory conditions resulted in approximately 4 logs inactivation of P22 (a surrogate for enteric viruses) at the UVT (~

76%) and at a UV dose of ~17 mJ/cm^2. Without the addition of the 400 mL of Tryptic Soy Broth (TSB) in the influent water, P22 inactivation was ≥ 6 logs for a UV dose of ~23 mJ/cm^2. Since both experiments were performed at the same flowrate, the observed difference between the inactivation of P22 with *E. coli* in test water at the DOC of >20 mg/L was correlated with an increased UV intensity, which is directly linked to the water quality. As reported in literature, ~2 logs of P22 are inactivated at a 30 mJ/cm^2 UV Dose using a low pressure UV system in PBS (Linden and Sobsey, 2005).

Comparing the inactivation results of *E. coli* and P22 from this study with published data indicate that the selected NeoTech UV unit provides higher microbial inactivation compared with other UV based microbial inactivation devices. Once again, the higher observed inactivation may be due to the reflective coating within the reactor.

PAA/UV experiments were performed both in the pilot scale and the laboratory scale studies. The pilot study total coliform and *E. coli* concentrations in the influent samples for PAA/UV were significantly lower than observed in the UV pilot study experiments. The possible reason for variation in influent concentrations may be ascribed to the fact that the inlet sampling port was located in close proximity upstream of the PAA injection port, which may have caused minor reverse flow of the PAA back through the sampling port. Pulling some PAA into the sample bottle may have provided additional disinfection in the sample (no sample quenching was used). In addition, the influent water quality in the PAA/UV pilot study indicates low levels of chlorine residual in the 2 ppm PAA dose/UV experiment. The low level of chlorine residual observed is attributed to the chlorination of the cloth-media disk filters located upstream of the pilot

scale UV unit. Though chlorination of the filters was typically coordinated with plant operations staff to ensure no chlorine residuals during pilot study testing, chlorination of the filters during the 2 ppm PAA dose/UV experiment was necessary to maintain operation of the plant, and it was unknown that chlorine residual was present in the influent samples until after samples had been collected. The low inlet chlorine residual may correspond with low inlet coliform concentrations (Table 14).

The inlet concentrations in the varying PAA dose (0.5, 1 and 1.5 mg/L)/UV experiment showed wide variation. The inconclusive results indicate that no concrete conclusion can be derived from the data. One noteworthy observation in the PAA/UV pilot study is that the water quality parameters did not significantly change, particularly pH, from inlet to outlet. A few water quality measurements performed on inlet and outlet sampling ports determined that the outlet PAA residual was a fraction of the injected PAA concentration. The lower outlet PAA residual indicates that the PAA may have been degraded quickly within the UV reactor.

The laboratory PAA/UV study was conducted using the *E. coli* and P22. Injection of PAA upstream of the UV reactor resulted in increased *E. coli* inactivation in comparison to UV inactivation. However, P22 inactivation was decreased when PAA was injected upstream of the UV reactor. The organics content of water could decrease the effectiveness of the UV by absorbing UV light. In addition, *E. coli* cells are much larger in size than P22 and they could shield P22 as the microorganisms flow through the chamber. Addition of the PAA could result in breaking up the organics contents in the water to further prevent inactivation of P22. This possibility is merely conjecture based

on the observation of decrease in the P22 inactivation when PAA was added. Additional studies need to be performed to further investigate this phenomenon. The outlet samples collected in the PAA/UV experiments indicate a significant decrease in the PAA residual concentration (approximately one-tenth of the inlet PAA concentration was detected in the outlet sample). Based on these results, it is presumed that PAA is effectively broken down within the UV reactor indicating that the PAA is efficiently used when in combination with the UV.

In the PAA experiments performed under the laboratory conditions, minimal inactivation (<1 log) of *E. coli* and P22 was observed even after significant contact time of 30 minutes. The results are consistent with literature discussed in Section 2.2.1. For example, significantly higher PAA doses (2-7 mg/L) are required to achieve 3 logs inactivation of total coliform with 4-27 minutes of contact time (Koivunen and Heinonen-Tanski, 2005). The results of this study is supported by the literature and indicate that PAA is not effective as a primary disinfectant of *E. coli* and P22, particularly at the lower PAA doses of 0.25 and 0.50 mg/L.

The experiments conducted for the removal of NDMA under the laboratory conditions demonstrated high NDMA removal with UV treatment, obtaining approximately 48% removal at 4 GPM and 97% removal at 0.5 GPM. Though the UV degraded a high percent of NDMA, the flowrates selected are much lower than the rated capacity and the experiments were conducted using tap water (UVT ~85%). Therefore, this high degradation was obtained at much higher UV doses, but it is unknown whether lower UV doses would result in a similar removal. Adding 0.5 mg/L PAA upstream of

the UV reactor did not significantly increase NDMA removal. The NDMA removal increased to 50% for the 4 GPM flowrate when 0.5 mg/L PAA was dosed, but did not increase for the 0.5 GPM flowrate. Therefore, adding the PAA at 0.5 mg/L upstream of the UV reactor did not provide significant additional chemical oxidation of NDMA.

The results of the pilot and the laboratory studies may help in understanding treatment capability of AOP's. However, there are copious tangential research experiments that should be conducted to better understand the PAA/UV AOP process. In particular, the experiments need to be repeated with varying water quality parameters (DOC, turbidity, UVT, pH, etc.) to examine the effects of each water quality parameter on PAA/UV treatment. The components within wastewater may provide a disadvantage for system treatment, which was suggested by the lower inactivation of P22 observed when PAA was injected upstream. In addition, other microorganisms and chemical compounds should be studied in terms of disinfection and degradation.

Further investigation may aid in implementing this technology for large scope applications. The benefits of the process—including the "green" nature of the PAA—warrant further analysis. Though only an emerging technology, the preliminary results have revealed potential for its effective use through the combination of PAA and UV. With relatively small PAA doses required, there is opportunity for the process to be cost-effective, while providing additional treatment. Future regulation shifts should also be considered. As the U.S EPA studies more contaminants in terms of health, regulations may be adopted that include more contaminants or lower limits on regulated contaminants. The Contaminant Candidate List (CCL) indicates contaminants that are

considered for future regulation. If studies suggest that a contaminant from the CCL is to be regulated, scope of treatment may need to be modified in order to provide effective treatment of the regulated contaminant if conventional treatment (such as UV) does not adequately remove/inactivate the contaminant. The PAA/UV AOP may be a solution for various issues in the future, where the goal is to provide the safe water sources for global use applications.

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APPENDIX A

SOLVAY PERACETIC ACID MATERIAL SAFETY DATA SHEET PROXITANE WW-12

Product Safety Summary
Peracetic Acid
CAS No. 79-21-0

This Product Safety Summary is intended to provide a general overview of the chemical substance. The information on the summary is basic information and is not intended to provide emergency response information, medical information or treatment information. The summary should not be used to provide in-depth safety and health information. In-depth safety and health information can be found on the Safety Data Sheet (SDS) for the chemical substance.

Names

- Peracetic acid (PAA)
- Peroxyacetic acid
- Ethaneperoxy acid
- Peroxyethanoic acid
- Equilibrium peracetic acid
- Proxitane®

Product Overview

Solvay Chemicals, Inc. does not sell peracetic acid (PAA) directly to consumers. Solvay Chemicals, Inc.'s PAA is a mixture of peracetic acid, hydrogen peroxide, acetic acid and water. PAA can be used as an oxidant in chemical processes or as a bleaching agent. However, most of the PAA sold in North America is used as an antimicrobial, disinfectant or biocide. In the United States, these applications are typically regulated by the Food and Drug Administration (FDA) or the Environmental Protection Agency (EPA).

Exposure to PAA can cause severe irritation, burns and other health effects to the skin, eyes and respiratory tract. Ingestion should be avoided at all concentrations. Most PAA is consumed in applications where it is used; however, it is not persistent in the environment and decomposes to acetic acid, water and oxygen when exposed to soils, sediments and surface or ground waters.

Manufacture of Product

PAA is manufactured by adding hydrogen peroxide (H2O2) to acetic acid.

$$CH_3COOH \text{ (acetic acid)} + H_2O_2 \leftrightarrow CH_3COOOH \text{ (PAA)} + H_2O$$

Product Description

PAA solutions are clear, colorless liquids that have strong, vinegar like odors. Solvay Chemicals, Inc. commonly manufactures PAA in concentrations of 5 to 15%. Typical physical properties for some of these solutions are provided in Table I.

Table I: Typical physical properties for some 5%, 12% and 15% PAA solutions.

PAA Content	5%	12%	15%
H2O2 Content	20%	20%	15%
Acetic Acid Content	10%	20%	30%
Boiling Point	Product decomposes before boiling		
Freezing Point	<-4°F (<-20°C)	<-4°F (<-20°C)	<-4°F (<-20°C)
Flash Point	N/A	N/A	241°F (116ºC)
Density (lbs/gal @ 68ºF (20ºC)	9.18	9.26	9.35
SADT*	≥131°F (55ºC)	≥131°F (55ºC)	≥131°F (55ºC)

Product Uses

PAA is an effective bleaching agent and oxidizer, but it is most commonly used as an antimicrobial, disinfectant or biocide in a variety of applications, including some healthcare, food and water treatment applications. In the United States, these applications are regulated by the Food and Drug Administration (FDA) or the Environmental Protection Agency (EPA).

Exposure Potential

Workplace Exposure - Exposure can occur at a PAA manufacturing facility, a manufacturing, packaging or treatment facility that stores, packages or uses PAA, or during transport. Most of the production and manufacturing processes where PAA is used are “closed” (not exposed to the environment). Treatment facilities that use PAA either employ closed systems or take measures to reduce or eliminate the evolution of PAA vapor. Persons involved in maintenance, sampling and testing activities, or in the loading and unloading of hydrogen peroxide PAA vessels are at greater risk of exposure. Following good industrial hygiene practices will minimize the likelihood of exposure; however, persons involved in higher risk activities should always wear proper personal

protective equipment such as rubber gloves and boots, an acid or slicker suit, goggles and a hard hat. In instances where the potential for splashes is high, a face shield should also be worn.

Consumer Exposure to Products Containing PAA - Solvay Chemicals, Inc. does not sell PAA directly to consumers. PAA is used as a sterilant, disinfectant or biocide in some food and drinking water applications; however, residual PAA usually decomposes to acetic acid, oxygen and water. Consequently, the probability of consumer exposures to PAA is low.

Environmental Releases - Spills of PAA should be contained and isolated from waterways, sewer drains and any flammable or combustible materials. Small spills should be diluted with large amounts of water and disposed of in accordance with applicable local, state or federal regulations. Do not use absorbents or adsorbents to soak up PAA spills. Absorbents and adsorbents may contain organics that can react with the residual PAA and hydrogen peroxide in PAA solutions. Rinse PAA contaminated cloth or paper towels with water until they are free of any residuals. Failure to do so may result in a fire once they dry. Persons attempting to clean up PAA spills should wear proper personal protective equipment, including respiratory protection (see guidelines in Workplace Exposure section of this document or Safety Data Sheet).

Large Spills - Large spills of PAA should be contained and isolated from waterways, sewer drains and any flammable or combustible materials by constructing dikes of earth, sand or some other inert material. Diluting large spills with water will reduce the evolution of steam, oxygen, acetic acid, PAA and/or hydrogen peroxide vapors. Emergency responders should wear proper personal protective equipment, including respiratory protection, and should only approach spills from up wind. Once the spill is contained, the PAA and hydrogen peroxide should be allowed to decompose before being collected and disposed of in accordance with applicable local, state and federal regulations. If required, report spills to the appropriate state or federal authorities.

Fires - Fires involving PAA should be extinguished with water. Containers of PAA involved in a fire should be cooled with water sprays. If the container begins to discolor or vent violently, emergency responders should evacuate the area. If heated or decomposed, higher concentration PAA solutions may give off toxic and/or flammable vapor.

For additional information concerning PAA emergency response procedures, please consult the Safety Data Sheet.

Health Information

Exposures to PAA can produce the following adverse health affects:

Contact - Skin exposures can cause symptoms ranging from minor skin irritation to painful redness and swelling. Eye exposure to PAA solutions may result in severe eye irritation, burns, irreversible eye damage or even blindness.

Inhalation - The inhalation of PAA can irritate mucous membranes of the nose and throat causing symptoms ranging from nose and throat irritation to coughing and difficulty breathing. Repeated or prolonged exposures may cause sore throat, nosebleeds, chronic bronchitis, chemical pneumonitis (inflammation of the lungs) and edema (fluid in the lungs).

Ingestion - Ingestion of PAA may cause bloating, belching, irritation of the upper digestive and respiratory tracts, nausea, vomiting, difficulty breathing, excessive fluid in the mouth and nose, and risk of suffocation. Ingestion may also cause severe burns to the mouth and throat, perforations to the esophagus and stomach, chemical pneumonitis and edema. The ingestion of concentrated solutions of PAA can be fatal.

•

Other Effects - Animal testing with PAA has shown no evidence that it is a carcinogen. Some testing has indicated that PAA may have mutagenic effects.

For more information on health effects and routes of exposure, or for information concerning proper first aid measures, please consult the Safety Data Sheet.

Environmental Information

Small amounts of PAA may be released to the aquatic environment from sites that manufacture it or use it. PAA may also be released to the environment through spills and other unintentional releases. PAA can be toxic to fish and microorganisms, but it is not known to bioaccumulate or persist in the environment. PAA degrades into oxygen, water and acetic acid, which is relatively non-toxic at low concentrations. For more ecological and environmental information concerning this product, please consult the Safety Data Sheet.

Physical Hazard Information

PAA is an oxidizer and will support combustion. PAA solutions can cause fires when left in contact with combustible materials such as paper, wood or cloth. Mixing PAA solutions with certain organics should be done with care, as they may form explosive mixtures. Oxygen enrichment from the decomposition of PAA solutions in vessels containing certain volatile organics can also form explosive mixtures in the headspace of the vessel. If heated or decomposed, higher concentration PAA solutions may give off toxic and/or flammable vapor.

Exposure of PAA solutions to impurities such as strong acids, bases and transition metals (copper, manganese, chrome, etc.) can cause decomposition. PAA decomposition will result in the liberation of heat and gases which can result in a rapid pressure buildup. Systems used to store or transport PAA solutions must be properly vented and must have enough emergency venting

capacity to allow the contents of the system to withstand a catastrophic decomposition event.

For more information concerning the physical hazards of this product, please consult the Safety Data Sheet. For information concerning the proper design of hydrogen peroxide and PAA systems, please contact Solvay Chemicals, Inc.

Regulatory Information

Regulations may exist that govern the manufacture, sale, transportation, use and/or disposal of this chemical. These regulations can vary by city, state, country or geographic region. Information may be found by consulting the relevant Safety Data Sheet specific to your country or region.

Additional Information

- Solvay America, Inc. www.solvaynorthamerica.com
- Solvay Chemicals, Inc. www.solvaychemicals.us
- Solvay Chemicals Inc. Safety Data Sheets www.solvaychemicals.us/EN/Literature/LiteratureDocuments.aspx
- Contact Solvay Chemicals, Inc. solvaychemicals.us@solvay.com
- NJ Department of Health & Senior Services Hazardous Substance Fact Sheets http://web.doh.state.nj.us/rtkhsfs/factsheets.aspx

This summary was prepared in January, 2012

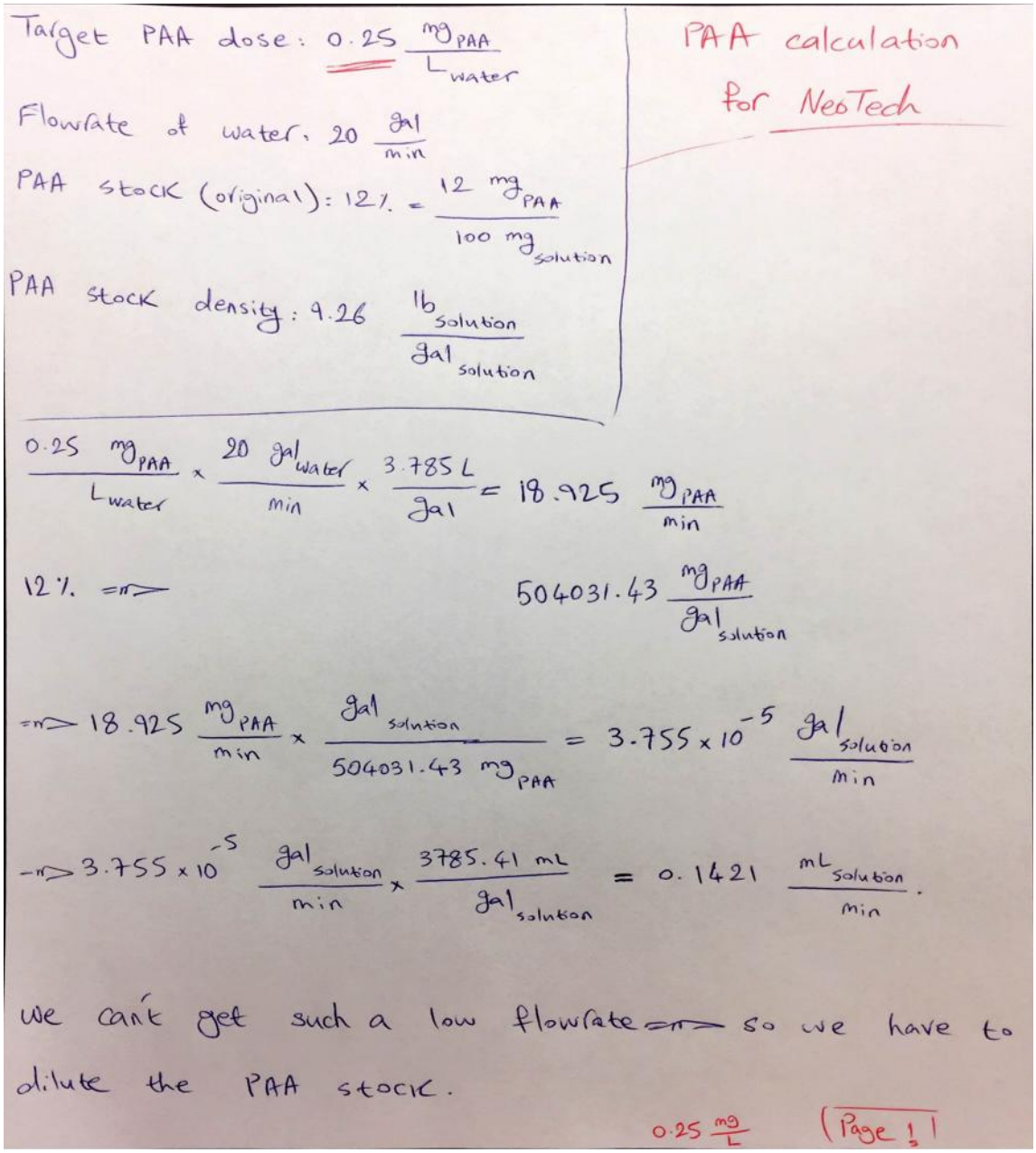
This summary was revised in September, 2013

NOTICE

APPENDIX B

CALCULATIONS OF FEED RATE AND DILUTION FOR INTENDED PAA DOSES

0.25 mg/L:



PAA calculation for NeoTech

Target PAA dose: 0.25 $\frac{mg_{PAA}}{L_{water}}$

Flowrate of water: 20 $\frac{gal}{min}$

PAA stock (original): 12% = $\frac{12\ mg_{PAA}}{100\ mg_{solution}}$

PAA stock density: 9.26 $\frac{lb_{solution}}{gal_{solution}}$

$\frac{0.25\ mg_{PAA}}{L_{water}} \times \frac{20\ gal_{water}}{min} \times \frac{3.785\ L}{gal} = 18.925\ \frac{mg_{PAA}}{min}$

12% ⇒ $504031.43\ \frac{mg_{PAA}}{gal_{solution}}$

$\Rightarrow 18.925\ \frac{mg_{PAA}}{min} \times \frac{gal_{solution}}{504031.43\ mg_{PAA}} = 3.755 \times 10^{-5}\ \frac{gal_{solution}}{min}$

$\Rightarrow 3.755 \times 10^{-5}\ \frac{gal_{solution}}{min} \times \frac{3785.41\ mL}{gal_{solution}} = 0.1421\ \frac{mL_{solution}}{min}$.

We can't get such a low flowrate ⇒ so we have to dilute the PAA stock.

$0.25\ \frac{mg}{L}$ (Page 1)

$C_1V_1 = C_2V_2 \Rightarrow 0.0025 \times 100 = 0.12 \times V_2 \Rightarrow V_2 = 2.083\ mL$

So we add 2.083 mL of original stock (12%) to 97.917 mL of DI water. (100 − 2.083 = 97.917).

We didn't take densities into account. So ⇒

$$\left(2.083\ mL_{\text{old stock}} \times 9.26 \frac{lb}{gal} \times \frac{gal}{3785.41\ mL}\right) + \left(97.917\ mL_{\text{water}} \times 8.345 \frac{lb_{\text{water}}}{gal} \times \frac{gal}{3785.4\ mL}\right)$$

$$100\ mL \times \frac{gal}{3785.41\ mL}$$

$= 8.364 \frac{lb}{gal}$ = Density of the new stock.

- Density of 12% stock = $9.26 \frac{lb}{gal}$
- Density of water = $8.34 \frac{lb}{gal}$

$0.25 \frac{mg}{L}$ | Page 2/5 |

So now we have to check the PAA content in the new stock: $C_1V_1 = C_2V_2$

$$C_1 \times 8.364 \frac{lb}{gal} \times \frac{gal}{3785.41\ mL} \times 453592 \frac{mg}{lb} \times 100\ mL = 0.12 \frac{mg_{PAA}}{mg_{solution}} \times 9.26 \frac{lb}{gal} \times \frac{gal}{3785.41\ mL} \times \frac{453592\ mg}{lb} \times 2.083\ mL$$

$$\Rightarrow C_1 = 0.00276 = \frac{0.27\ mg_{PAA}}{100\ mg_{solution}} = \boxed{0.27\ \%} \Rightarrow \text{PAA content in new solution.}$$

---

* Now that we have PAA content in new solution, we can calculate the desired flowrate for chemical injection to get the target PAA dose in our reactor. (Basically repeating the first step using $\left(\frac{0.27\ mg_{PAA}}{100\ mg_{solution}}\right)$ instead of $\left(\frac{12\ mg_{PAA}}{100\ mg_{solution}}\right)$

$\Rightarrow$ Target PAA dose: $\frac{0.25\ mg_{PAA}}{L_{water}}$

$$\Rightarrow \frac{0.25\ mg_{PAA}}{L_{water}} \times \frac{20\ gal_{water}}{min} \times \frac{3.785L}{gal} = 18.925 \frac{mg_{PAA}}{min}$$

$0.25 \frac{mg}{L}$

$$\frac{0.27\ mg_{PAA}}{100\ mg_{solution}} \times \frac{8.364\ lb_{solution}}{gal_{solution}} \times \frac{453592\ mg}{lb} = 10{,}243.377\ \frac{mg_{PAA}}{gal_{solution}}$$

$$\Rightarrow 18.925\ \frac{mg_{PAA}}{min} \times \frac{gal_{solution}}{10243.377\ mg_{PAA}} \times \frac{3785.41\ mL}{gal} = \boxed{6.99\ \frac{mL}{min}}$$

chem injection rate.

$0.25\ \frac{mg}{L}$

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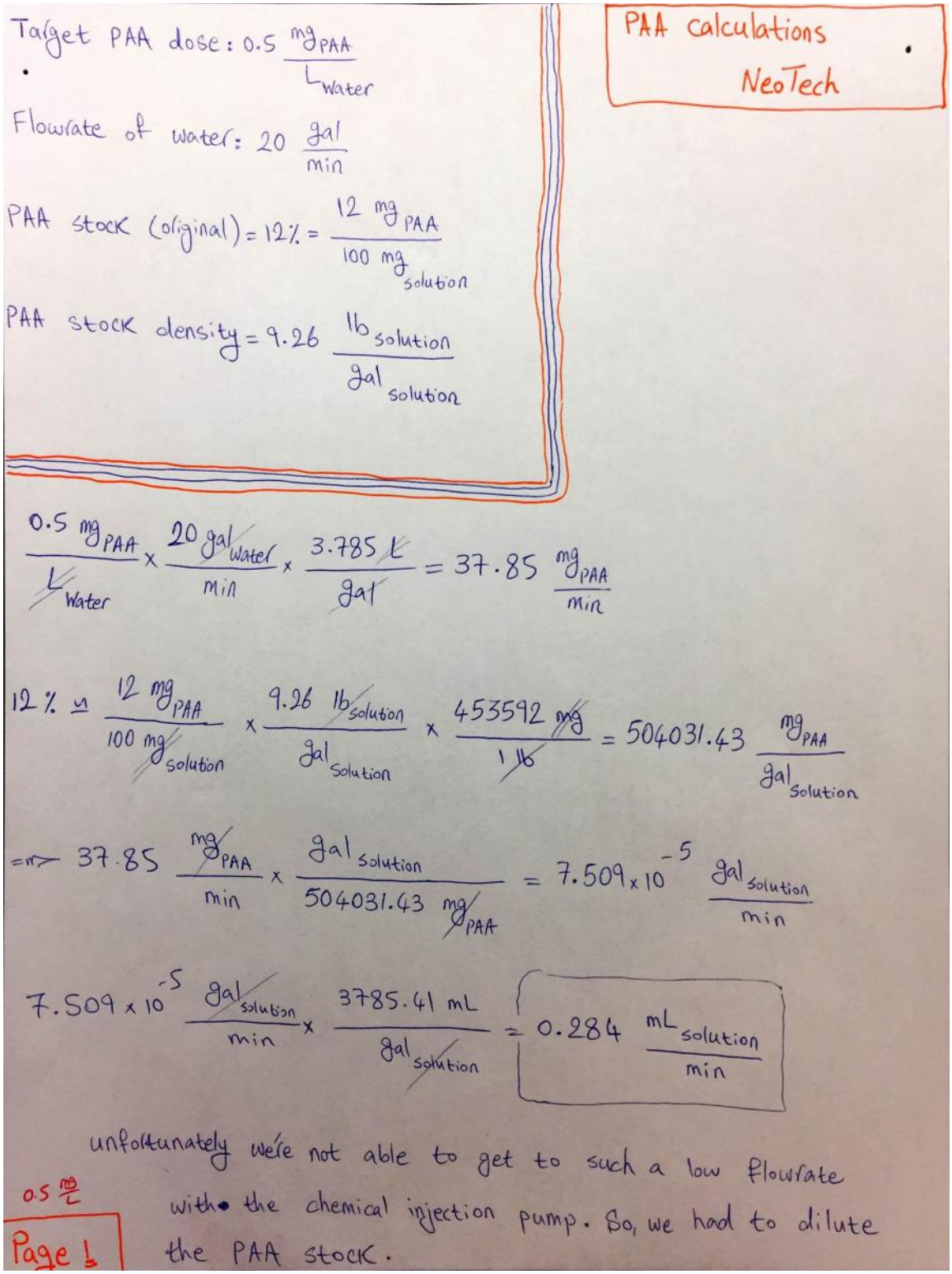
0.50 mg/L:


PAA calculations
NeoTech
Target PAA dose: 0.5 mg PAA / L water
Flowrate of water: 20 gal / min
PAA stock (original) = 12% = 12 mg PAA / 100 mg solution
PAA stock density = 9.26 lb solution / gal solution
0.5 mg PAA / L water x 20 gal water / min x 3.785 L / gal = 37.85 mg PAA / min
12% ≈ 12 mg PAA / 100 mg solution x 9.26 lb solution / gal solution x 453592 mg / 1 lb = 504031.43 mg PAA / gal solution
=> 37.85 mg PAA / min x gal solution / 504031.43 mg PAA = 7.509 x 10^-5 gal solution / min
7.509 x 10^-5 gal solution / min x 3785.41 mL / gal solution = 0.284 mL solution / min
unfortunately were not able to get to such a low flowrate with the chemical injection pump. So, we had to dilute the PAA stock.
0.5 mg/L
Page 1

So we did this for dilution of 12% PAA stock to 0.5% PAA stock

$C_1V_1 = C_2V_2 \rightarrow 0.005\,(100\text{ mL}) = (0.12)V_2 \rightarrow V_2 = 4.1667\text{ mL}$

So we added 4.17 mL of original stock (12% PAA solution) to 95.83 mL of DI water. (100 − 4.17 = 95.83). But when doing $C_1V_1 = C_2V_2$, we didn't take the densities into account.

But we can calculate what density we're actually making for the new stock.

$$\frac{\left(4.17\text{ mL}_{\text{old stock}} \times 4.26\ \frac{\text{lb}_{\text{old stock}}}{\text{gal}_{\text{old stock}}} \times \frac{\text{gal}}{3785.41\text{ mL}}\right) + \left(95.83\text{ mL}_{\text{water}} \times 8.345\ \frac{\text{lb}_{\text{water}}}{\text{gal}_{\text{water}}} \times \frac{\text{gal}}{3785.41\text{ mL}}\right)}{(4.17\text{ mL} + 95.83\text{ mL}) \times \frac{\text{gal}}{3785.41\text{ mL}}}$$

$$= 8.386\ \frac{\text{lb}_{\text{new stock}}}{\text{gal}_{\text{new stock}}} = \text{Density of new stock.}$$

* Density of water: 8.345 $\frac{\text{lb}}{\text{gal}}$

* Density of old stock: 9.26 $\frac{\text{lb}}{\text{gal}}$

0.5 $\frac{\text{mg}}{\text{L}}$

Page 2

So now we have to check the PAA content in the new solution:

$C_1V_1 = C_2V_2$

$$C_1 \times 8.386 \frac{lb}{gal} \times \frac{1}{3785.41} \times 453592 \times 100mL = 0.12 \frac{mg_{PAA}}{mg_{solution}} \times \frac{9.26\ lb}{gal} \times \frac{gal}{3785.41mL} \times \frac{453592mg}{lb} \times 4.17\ mL$$

$$\Rightarrow C_1 = 0.0055 = \frac{0.55\ mg_{PAA}}{100\ mg_{solution}} = \boxed{0.55\%} \rightarrow \text{PAA content in new solution.}$$

$\Rightarrow$ Now that we have PAA content in the new solution, we can calculate the desired flowrate for chemical injection to get the target PAA dose in our reactor. (Basically repeating the first step using $\left(0.55 \frac{mg_{PAA}}{100\ mg_{solution}}\right)$ instead of $\left(\frac{12\ mg_{PAA}}{100\ mg_{solution}}\right)$.

$\Rightarrow$ Target PAA dose: $\frac{0.5\ mg_{PAA}}{L_{water}}$

$$\frac{0.5\ mg_{PAA}}{L_{water}} \times \frac{20\ gal_{water}}{min} \times \frac{3.785\ L}{gal} = 37.85 \frac{mg_{PAA}}{min}$$

$$0.55\% = \frac{0.55\ mg_{PAA}}{100\ mg_{solution}} \times \frac{8.386\ lb_{solution}}{gal_{solution}} \times \frac{453592\ mg}{1\ lb} = 20921.024 \frac{mg_{PAA}}{gal_{solution}}$$

$$\Rightarrow 37.85 \frac{mg_{PAA}}{min} \times \frac{gal_{solution}}{20921.024\ mg_{PAA}} \times \frac{3785.41\ mL}{gal} = 6.848 \approx \boxed{6.85 \frac{mL}{min}}$$

$0.5 \frac{mg}{L}$

Page 3

chem injection flowrate.

Now let's check what PAA dose we (actually) have in the reactor if were doing another flowrate for chemical injection.

For example for the 3rd experiment (UV + 0.5 $\frac{mg}{L}$ PAA) we measured chemical injection flowrate to be 7.2 $\frac{mL}{min}$.

$$7.2 \frac{mL_{solution}}{min} \times \frac{gal}{3785.41\ mL} \times \frac{20921.024\ mg_{PAA}}{gal_{solution}} = 39.7926 \frac{mg_{PAA}}{min}$$

$$39.7926 \frac{mg_{PAA}}{min} \times \frac{min}{20\ gal_{water}} \times \frac{gal}{3.785\ L_{water}} = 0.5256 \approx 0.53 \frac{mg_{PAA}}{L_{water}}$$

(*) All of the calculations above are done with the assumption of all of the content being monodispersed in the original stock and new stock.

0.5 $\frac{mg}{L}$

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APPENDIX C

HACH TEST PROCEDURE TO MEASURE PERACETIC ACID (PAA)

Determination of Peracetic Acid (PAA) in Water

Concentration Range of 0.1 to 10 mg/L

Equipment and Reagents:

MR and HR Chlorine Pocket Colorimeter (PCII) – Hach PN 5870062 (Use HR program)

DR800 (Program 12)

DR900, DR1900, DR2800, DR3800, DR3900, DR5000, DR6000 (Program 88)

10-mL/1-cm Sample Cell – Hach PN 4864302

DPD Total Chlorine Reagent Powder Pillow, 25-mL, 100/pkg – Hach PN 1406499; Do Not use Free DPD Reagents

Test Procedure for PAA:

When using the PCII, make sure that the program is in the HR mode, use program 12 for the DR800 series colorimeters,and for all other Hach colorimeters and spectrophotometers use program 88 for HR Total Chlorine, Hach Method 10070.

(1) Fill both 10 mL sample cells with the water sample. One of these cells will be the blank and the other will be the prepared sample.

(2) Place the blank into the instrument and press the ‘zero’ key.

(3) Add the contents of one DPD TOTAL 25-mL Chlorine powder pillow to the prepared sample cell.

(4) Cap the prepared sample cell and shake gently to mix the DPD powder. A pink color will develop indicating the presence of PAA.

(5) After 15 to 20 seconds after adding the DPD powder to the prepared sample cell, ensure that the DPD powder has dissolved and there are no air bubbles present (invert lightly to dislodge the air bubbles), use a lab wipe to clean off the 10-mL/1-cm cell. Between 45 and 60 seconds of reaction time, place the sample cell into the cell compartment and then press ‘read’. Do not wait more than 60 seconds to read the sample.

(6) The results are in mg/L as total Cl2. Convert the mg/L Cl2 value to mg/L of PAA by multiplying the value by 1.07. If you instrument has the built in dilution factor function, you can input the 1.07 with this option. mg/L PAA = 1.07 x mg/L Total Cl2 PAA.

BIOGRAPHICAL SKETCH

Samantha Cooper attended Arizona State University for her undergraduate career and received her Bachelor of Science in Engineering (B.S.E) in May 2015. She decided to continue her education because she was interested in gaining a better understanding of water treatment processes to apply this knowledge to her professional life. In addition to her work as a student, she has also been employed at an environmental engineering consulting firm, Valentine Environmental Engineers, for over three years. Projects through her firm have included the pilot study for the PAA/ UV technology discussed in this thesis, though on a larger scale for a water reclamation plant in Maricopa, Arizona (July-September 2015). This pilot study inspired the Master's research idea. After Samantha graduates with a M.S Degree, she plans to continue to conduct studies, in the form of pilot studies, to further understand the PAA/UV emerging technology.