Treatment of Emerging Chemical and Microbial Contaminants in Water Using Advanced Reflective UV Technology

by

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ABSTRACT

In the recent years, there have been massive technological advancements which have led to increased radical industrialization resulting in a significant impact on the environment. Effluents and by-products of the production processes from industries such as pharmaceutical and personal care products (PPCPs) have increased the concerns of "emerging contaminants" (ECs) in surface waters and drinking water systems. This study focuses on the treatment of emerging chemical contaminants including nitrosodimethylamine (NDMA) and 1,4-dioxane. In addition, the inactivation of microbial contaminants of concern in water including *E. coli*, *Legionella*, *Mycobacterium* and fungal spores were studied using the same treatment technologies. The ECs chosen are not susceptible to conventional treatment process and there still remains a need for alternate processes for their removing/remediating to ensure safe drinking water. The treatment technologies utilized were Advanced Oxidation Processes (AOP) involving UV 220 /254 nm employing an excimer lamp and a low-pressure mercury lamp with ReFLeX^{TM} technology and peracetic acid (PAA). The main objective of this study was to develop a new alternate technology for the enhanced remediation of chemical and microorganisms of concerns in water. The specific research objectives included: 1) To study the efficacy of the UV system to treat the selected contaminants. 2) To study the effect of PAA on the remediation of the contaminants. 3) To explore a new AOP technology under dynamic flow conditions with varying UV and PAA doses. 4) To determine optimized UV and PAA dosages to obtain enhanced remediation of the selected contaminant under dynamic flow conditions to better mimic the real-world applications.

In memory of my loving grandmother Balamba Murthy who was and will be my biggest cheerleader in life.

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TABLE OF CONTENTS

Page

CHAPTER Page

LIST OF TABLES

Table Page

LIST OF FIGURES

Figure Page

Figure Page

1 INTRODUCTION

Historically water supply and treatment of fresh water received more importance than water reuse. However, over the past decade the realization of the existing imminent threat of water scarcity in the future has directed some importance towards developing new treatment technologies to make water reuse a real and safe possibility for potable use. With the growing issue of urban water scarcity, water treatment technologies have also seen advancements which have led to increased quantity of wastewater (WW) to be recycled/reclaimed for industrial use throughout the world (Levine & Asano, 2004). The ever-growing dependence on fresh source waters is further intensified by the severity of pollution of our water sources and this is a direct result of increased urbanization, industrialization, and climate change. Thereby, generation of large volumes of toxic contaminants as either the finished product or by-products produced in the industrial production processes in wastewater effluents are the major sources to which freshwater pollution is attributed. We also need to recognize the growing demand of clean water especially in regions experiencing water stress due to industrialization and population growth (Xiao et al, 2015). Thus, there is a need to further advance technologies with economically viable treatment methodologies to ensure safe reuse and reclamation of WW.

Xenobiotics like pharmaceutical products, personal care products (PPCPs), endocrine disruptor compounds (EDCs), chemical additives used by industries, with increased and continuous release into the environment has non-arguably caused concerns about the impact these emerging contaminants (ECs) have in short and log terms on the environment and on public health. While acknowledging the detrimental effects of ECs

on the environment, it is important to recognize undesirable effects such as reduction in the diversity of macroinvertebrates in rivers (Kuzmanovic et al., 2016), impact on fish populations in affected areas (Yeh et al., 2017), and increased physiological stress on freshwater mussels (Oliveira et al., 2017). Currently, there is a limited knowledge on methods to control the ECs from entering the environment and no accurate information pertaining the sources of these contaminants. For example, the quantity of 1,4-dioxane that is used/bought/released annually. According to the U.S. Environmental Protection Agency (U.S. EPA), the regulated release of this compound summed up to 280,454 kg in 2017 for industrial solvents applications (U.S. EPA 2017a; U. S. EPA 2018a) and Chemical Data Reporting Database in 2015 report 450,000 kg of 1,4-dioxane either produced or imported. These numbers do not take the concentration/quantity of this chemical which are used as an additive, and which might be released as a by-product of their production processes. Most ECs compounds are extremely persistent in the environment and are resistant to biodegradation. Thus, there can be steps taken to protect fresh water by identifying the source of these ECs, assess the extent of their effects and treatment techniques to minimize the environmental and health impact of these compounds.

Most wastewater treatment plants (WWTPs) employ technologies which concentrate on the remediation of certain group of macro-organic and inorganic compounds with little focus on ECs. Thus, the eventual discharge of the ECs enters the environment and accumulate in freshwater bodies. To remedy this problem, WWTPs have made advancement in their wastewater sludge managing technologies which need to comply with the regulations pertaining to their discharge. Additionally, remediation

technologies like Advanced Oxidation Processes (AOPs), adsorption technologies such as Granular Activated Carbon (GAC), hydrolysis techniques, membrane bioreactors and constructed wetlands can be employed to achieve the end use quality requirements (Matamoros et al., 2017).

There are a few major issues related to these ECs due to the absence of regulations limiting the production and release, by-products, pharmaceuticals, PPCPs of these compounds in industrial effluents. The regulatory practices are outpaced and outmatched by scientific and industrial breakthroughs and thus, very few or no precautionary measures and/or monitoring systems are established for the micro-concentration range which are released into source waters. Some environmental agencies like European Commission have worked on developing strategies in dealing with endocrine disruptors. Their amendment of the European Community on the subject of Risk Assessment and Directive on classification of dangerous substances is one of the examples for their efforts to deal with ECs on a regulatory front (Europa, 2006). In the United States of America there are no such regulatory limitations or maximum limit of these compounds in potable water or natural source waters. However, the Food and Drug Administration (FDA) have regulations in place which require ecological testing and analysis of pharmaceuticals at regions where their concentrations exceed 1µg/L (Snyder et al., 2003). Food Quality Protection Act (FQPA) and 1996 amendments to the Safe Drinking Water Act (SWDA) have given authority to the U.S. EPA to screen for chemicals and formulations known with potential endocrine activities (Snyder et al., 2003; Filale-Meknassi et al., 2004).

AOPs are technologies which use highly reactive strong radical oxidants like ($OH.$, $SO_4.$) to accelerate and thus facilitate the remediation of numerous organic pollutants from water (Sun & Bolton, 1996). Hydroxyl radical or $OH^{\cdot}$ Is known to be most reactive oxidative species used in AOPs with a redox potential of 2.8v and is a non-selective radical species which allows it to be used to remediate multiple different contaminants (Brillas et al., 2009). There have been many different types of AOPs which have been explored in the past: catalytic ozonation (Bing et al., 2015; Bai et al., 2016), ozone derived AOPs like ozone/Fenton, ozone/UV, ozone/hydrogen-peroxide etc. (Cuerda-Correa et al., 2016), Fenton and electro-Fenton process, sono-electro-Fenton and photoelctro-Fenton (Babuponnusami & Muthukumar, 2012), catalytic peroxide oxidation (Ribeiro et al., 2016), UV/H_2O_2 and UV (Merel et al., 2015) that have been used to treat and remediate emerging contaminants.

This study focuses on the development of alternate enhanced remediation technologies for the treatment of two emerging chemical contaminants and four microbial organisms of concern in water under dynamic flowing conditions. N-Nitrosodimethylamine (NDMA) is a semi-volatile organic compound which belongs to the family of extremely potent carcinogens called N-Nitrosamines. The potency of this acute hepatotoxin compound to cause cancer surpasses that of trihalomethane (Mitch, Gerecke et al., 2003). The problems associated with NDMA in public drinking water especially near contamination sites are real-time existing threats to public health. For example: A rocket engine testing facility in Sacramento County, California used rocket fuel with unsymmetrical dimethylhydrazine (UDMH) base. Off-site ground water NDMA concentrations of 20,000 ng/L and on-site concentrations as high as 400,000 ng/L was

measured (Mitch, Gerecke et al., 2003, U.S. Department of Homeland Security, 2002). The U.S. EPA conducted risk assessment studies and calculated a cancer risk of 1*10-6 for NDMA concentrations as low as 0.7 ng/L (EPA IRIS, 1993). Based on the same risk level, a screening level of 0.42 ng/L of NDMA was calculated (U.S. EPA, 2013a). Even though NDMA is considered as a priority toxic pollutant in the Code of Federal Regulations (CFR) (40 CFR 131.36), there is no established maximum contaminant level (MCL) (U.S. EPA, 2011). 1,4-Dioxane (1,4-D) is an aliphatic compound with a six membered carbon ring with oxygen at C1 and C4. It is extensively used in industrial processes especially as stabilizers for chlorinated compounds like 1,1,1 – trichloroethane (TCA) and as a industrial solvent (Mohr, 2010). Even though there is scarce information about the effect of this compound on human health, the International Agency for Research on Cancer (IARC) classified 1,4-D as a Group 2B agent or as a potential carcinogen to humans based on carcinogenicity studies conducted on experimental animals which suggest strong carcinogenicity. 1,4-D remediation by conventional physical treatment techniques presents challenges due to certain physical characteristics associated with the contaminant. Properties such as low Henry's constant, boiling point of 101oC render physical treatment techniques like thermal destruction, air stripping, distillation and to an extent absorption inefficient in the remediation of 1,4-D in water. In the environment 1,4-D is known to be persistent and therefore strong chemical oxidant options were considered for the remediation. But the existing chemical remediation technologies lack practical achievability and were performed in lab scale under static conditions using batch reactors, leaving a huge knowledge gap in efficient remediation of

1,4-D in water. Although this compound was included in the third candidate contaminant list (CCL3), MCL for 1,4-D in drinking water is not established (U.S. EPA, 2009a).

Over 150 million people in the U.S. depend on groundwater supply as their primary water supply and yet water treatment facilities are not required to treat ground water before releasing it to the public water distribution system (Hynds et al., 2014). Opportunistic pathogens (OPs) can travel through soil and into the aquifers causing ground water contamination which could be a potential public health hazard (Lauren R. McBurnett et al., 2018; Mondal et al., 2020). They are not only known to be resistant to conventional treatment technologies but are persistent in water distribution systems even in the presence of residual disinfectants. Each of the four microorganisms selected in this study – Escherichia coli (*E. coli*), *Legionella pneumophila*, *Mycobacterium avium* and *Aspergillus niger* spores, have associated human health risks and pose unique challenges for their remediation in water.

E. coli can be found in the lower intestinal tract of humans, warm-blooded animals and is usually introduced through fecal contamination (Berth et al., 2013). It is known to cause gastrointestinal illnesses and is responsible for approximately 2 million deaths every year (Edberg et al., 2000; Kaper et al., 2004). The U.S. EPA guidelines state a Maximum Contaminant Level Goal (MCLG) and Maximum Contaminant Level (MCL) of <1 CFU/100 mL of water for *E. coli* (U.S. EPA, 2013a).

Legionella pneumophila is one of the most significant opportunistic pathogens responsible for large portion of waterborne diseases in the U.S. (Beer et al., 2015). Pontiac fever from mild exposure and Legionnaires' disease in the case of major exposure are some of the most commonly associated health risks of *Legionella* .

Additionally, they are known to survive in high temperatures and possess the ability to parasitize and multiply in protozoans even in the presence of residual disinfectants which present challenges for efficient disinfection. Although U.S. EPA has a MCLG of 0 CFU/mL for *Legionella* in drinking water, no MCL has been determined (MCL of 4 log for viruses and 3 log for Giardia lamblia are considered to be safe goals to ensure the prevention of *Legionella* presence in drinking water) (U.S. EPA, 2009b).

The annual cost of hospitalizations pertaining to health issues like pulmonary infection, soft tissue, skin and post-operative infections caused by Non-Tuberculosis *Mycobacterium* (NTM) is reported to be $194 million every year in the U.S. (Collier et al., 2013; Allen et al., 2017; Misch et al., 2018). NTM generally possess highly hydrophobic lipid-rich cell walls which not only allow to them survive in rough environments from desert soil to water distribution systems, but also pose a resilient challenge in their efficient treatment in water systems. They are called as biofilm pioneers due to their ability to survive in amoeba like *Legionella* and proliferate by consuming the nutrients as a part of the biofilm (Delafont et al., 2014). *Mycobacterium avium*, the third organism selected for this study, is a part of the NTM family. There is no set MCLG or MCL numbers for the selected microorganism. Fungal spores are considered a threat to drinking water safety and therefore attracted a lot of attention in the recent years (Novak Babič et al., 2017). Despite their low concentrations in aquatic environments, mycotoxins produced by fungal spores pose a variety of problems to aquatic life (Thandazile et al., 2019). Respiratory disorders like different types of Aspergillosis, allergies can be caused by Aspergillus and is responsible for approximately 13 million cases worldwide every year (Richardson et al., 2012). Generally fungal spores

are known to be highly resistant to existing UV disinfection technologies. Thus, to test the enhanced remediation capability of the new UV system with reflective technology, the fourth microorganism selected for the study is *Aspergillus niger* spores.

1.1 Research Objectives

The main objective of this study was to develop a new alternate technology for the enhanced remediation of chemical and microorganisms of concerns in water using a new AOP technology employing reflective UV system and PAA. The specific objectives are:

1. To study the efficacy of the UV system with reflective technology alone to treat the selected contaminants.
2. To study the effect of PAA on the remediation of the contaminants of interest.
3. To explore a new AOP technology under dynamic flow conditions with varying UV and PAA doses.
4. To report optimized doses of UV and PAA to obtain enhanced remediation of each individual selected contaminant under dynamic flow conditions to better mimic the real-world applications.

2 LITERATURE REVIEW

The comprehensive literature review of the important concepts pertaining to this study and the target chemical and microbial contaminants selected for this study are listed below:

2.1 Advance Oxidation Process (AOP): Different types of AOP and sub-types of UV-based AOPs

Advanced Oxidation Processes (AOPs) are being considered as viable alternatives to conventional treatment technologies to tackle the issue of ECs in our water systems. AOPs usually employ a combination of two or more physical treatment system/s and chemical agent/s with redox potential. These then undergo a series of reactions to produce highly reactive species of radicals which in turn destabilize and initialize the breakdown pathways of organic ECs and thereby resulting in their remediation. There are numerous different types of AOPs; few of which are discussed in the upcoming sections; and thus, choosing the appropriate AOP technique to result in the efficient remediation of targeted ECs is of prime importance. Few of the most commonly used AOPs at WWTP and at in-situ remediation systems at source sites are O_3/H_2O_2, O_3/UV, UV/H_2O_2, UV/O_3/H_2O_2, and UV/Cl_2/O_3. The continued production of ECs of concern in water due to radical industrialization and advancement of technology have posed resilient challenges while exposing research gaps and drawbacks of the existing commonly used AOP technologies. There is a necessity to study and develop alternative treatment technologies to achieve enhanced remediation of ECs in water.

Different AOP technologies employ varied methods of activation which leads to the production of specific highly reactive radical species. Depending on the type of

radicals produced, they either act on specific contaminants directly or non-specifically destabilize the contaminants in water. AOPs can broadly be classified into five different categories namely: ozone-based, UV-based, electrochemical (eAOP), catalytic (cAOP) and physical (pAOP). This characterization is strictly to give us a basic overview of the different types of AOPs. Conceptually all the different types of AOPs employ two distinct steps: first being the in-situ formation of highly reactive oxidizing species and the second step would be the reaction between the generated oxidative species and the target pollutants. Variables like system design, water treatment parameters and the composition of compounds involved in the remediation process determine the mechanism of radical formation. Once the radicals are formed, the efficacy of the remediation process is dependent on factors such as – UV absorption peaks of the target contaminants, susceptibility of the contaminants to UV irradiation, hydrodynamic design of the system, quantity of radical mass transfer in the case of surface based AOPs and most importantly the hydroxyl stability accompanied with the capability of the produced radical species to scavenge UV irradiation.

The remainder of this section will provide an overview on the different types of commonly used UV-based AOP systems used in the treatment emerging contaminants.

2.1.1 UV with Hydrogen peroxide (H_2O_2)

This is the most commonly used UV-based AOP technology. When H_2O_2 is irradiated with UV light, H_2O_2 is photolytically cleaved into two hydroxyl radicals. But since the molar absorption of H_2O_2 is low, when low pressure UV lamps are used in the process, high concentrations of H_2O_2 is required to achieve a turnover of less than 10% of the applied dosage of H_2O_2. In-turn this can lead to the remaining dose of H_2O_2 to

scavenge some UV radiation bringing down the efficiency of the entire remediation process (Buxton et al., 1988). Additionally, the economic factors govern the dosage of the H_2O_2 used in treatment systems. For TOrC removal from water systems, H_2O_2 has been widely studied for waters ranging from ultrapure to landfill leachate (Wols & Hofman-Caris, 2012; Wols et al., 2013; Keen et al., 2016). UV/ H_2O_2 is not an established method for advanced treatment of wastewater mainly because of low transmittance of UV and increased scavenging capacity of tertiary treated WW effluents but is used in potable water reuse trams which employ a high-grade filtration system (Drewes & Khan, 2015).

2.1.2 UV with Ozone

In this process, dissolved ozone is cleaved as a result of UV irradiation of wavelengths less than 300 nm which is then followed by a rapid reaction of the atomic oxygen present in water resulting in the formation of thermally excited H_2O_2. This mechanism then follows the H_2O_2 cleavage as discussed previously. Since the molar extinction of ozone is a lot higher than H_2O_2 at this wavelength only a small portion of the compound produces the hydroxyl radicals (Reisz et al., 2003). Moreover, ozone production when combined with the operational and maintenance cost of UV is at an economic disadvantage. The main advantage of this process is the fact that this covers a huge variety of TOrC reactivity.

2.1.3 UV with $SO_4^{\cdot-}$ radical

This can be considered as an alternative to the generation of hydroxyl radicals. This process relies on the production of highly oxidative sulfate radicals which act more selectively on specific target contaminants (Lutze et al., 2014; Lutze et al., 2015). PDS or

peroxydisulfate is usually used and cleaved by UVC irradiation. The positives of using PDS is its high quantum yield and higher molar absorption when compared to H_2O_2 which results in a higher production of radicals (Lutze et al., 2015; Legrini et al., 1993). PMS or peroxymonosulfate is another alternative to PDS but due to its lower quantum yield, PDS is considered as the preferred option. But the applications are limited since PDS is known to be a selective oxidant which can only effectively treat specific target contaminants. The biggest disadvantage of this AOP technology is its capacity of produce a high concentration of DBPs which renders this technology unfavorable in a lot of applications.

2.1.4 UV with Chlorine

This is another type of UV-based AOP technique where chlorine is irradiated with UV which leads to the formation of chlorine radical species and hydroxyl radicals which then act on the target contaminants (Watts & Linden, 2007). Chlorine radicals are more selective than the hydroxyl radicals and favorably react with contaminants which are electron rich (Fang et al., 2014). The two starting compounds which are commonly used in the process are hypochlorite and chlorine dioxide. Hypochlorite results in $HOCl/OCl^-$ which is highly pH dependent. UV/Cl_2 is favorable in low pH conditions and can be used in applications such as RO permeates (Watts et al., 2007). However, the biggest drawback of using chlorine is the formation of DBPs which directly contribute to the production of emerging contaminants such as NDMA.

2.1.5 UV with Peracetic acid (PAA)

This study focuses on development of a new alternative treatment technologies using AOPs involving UV/PAA to achieve enhanced remediation of emerging contaminants in water. Thus, this section contains a detailed review on the working mechanisms of UV/PAA.

History of PAA based water treatment technologies. PAA as a compound was synthesized and studied for the very first time in the year 1902 (Freer and Novy, 1902). In the year 1955, the bactericidal capabilities of PAA were established (Fraise et al., 2013) and PAA became accepted as an oxidant or disinfectant in various industries. During the early 1970s the discovery of chloroform in water became the source of major growing public health concerns with the presence of extremely toxic DBPs in the public drinking water supply (Bellar et al., 1974). Since chlorination was associated with a high DBP formation potential, focus shifted to identifying new chemical oxidant species as an alternative to use of chlorine or chlorinated compounds. Treatment processes employing PAA were first studied and implemented during the early 1970s and late 1980s (Meyer, 1976; Baldry, 1983). The U.S. EPA first registered PAA as an antimicrobial agent for surface disinfection applications at hospitals in the year 1985. More than a decade later, PAA application on sewer overflow disinfection was approved in the year 1999 and later for wastewater disinfection in the year 2012. Since then, the application of PAA has been extensively studied to a wide range of water matrices. Recent studies have highlighted some of the important advantages of using PAA in disinfection processes. Advantages include: low to zero DBPs formation potential; like chlorine, PAA can be effective

against a wide range of microorganisms in water and it is economically viable (Garg et al., 2016; McFadden et al., 2017; Xue et al., 2017; Hassaballah et al., 2020).

Physical and chemical properties of PAA. PAA (CH_3COOOH) belongs to the family of organic peroxides. It is known have a high reduction potential of 1.96 V which is close to that of H_2O_2 and more than chlorine/chlorine dioxide. Therefore, PAA is considered to be a strong oxidizing agent. It is synthetically made through reactions between acetic acid and H_2O_2 in the presence of a catalyst like sulfuric acid (Zhao et al., 2007; Fiege et al., 2012). Commercially, PAA is available at standard equilibrium concentrations ranging from 5 – 15% because beyond this threshold concentration PAA displays some explosive, reactive and instable tendencies (Fraise et al., 2013). The thermal stability of organic peroxide compounds in general are determined by the dissociation energy associated with the breakage of their peroxide bond. When compared to H_2O_2 (213 kJ/mol), PAA (159 kJ/mol) has a weaker peroxide bond (Bianchini et al., 2002). Industrially available PAA is a colorless clear liquid and is accompanied by a strong pungent acrid odor with no foaming capabilities (Wagner et al., 2002; Flores et al., 2014).

UV irradiation of PAA. Initially, UV irradiation of PAA results in homolytic cleavage of peroxide bond yielding $HO^{\cdot}$ and acetyloxy radicals. According to literature this is first step and the rate determining step in the formation of highly reactive radicals (Caretti and Lubello, 2003; Lubello et al., 2002). The radicals produced can further react with either PAA or acetic to yield secondary radicals. The hydroxyl radicals react with PAA through H-abstraction to yield acetylperoxyl radical (Rokhina et al., 2010). The acetyloxyl radical produced in the first step can also react with PAA through H-

abstraction to produce acetylperoxyl radical and acetic acid. The primary acetyloxyl radicals can undergo decay through decarboxylation to yield methyl radical and carbon dioxide. The primary hydroxyl radicals can also react with acetyloxyl radicals to produce PAA. Thereby the oxidation cycle is partly restarted. Although there is sufficient literature on the capabilities of hydroxyl radicals to achieve remediation of emerging contaminants in water, future studies to investigate the remediation properties of the multiple secondary radicals produced during the UV/PAA process are necessary.

2.2 Background, Sources and ECs selected for this study

Treatment plants usually focus on priority chemical and microbial pollutants, nutrients in the water and heavy metals. But recent studies have clearly indicated the presence of a multiple organic emerging chemical/microbial contaminants that have significant effects on the water quality. These compounds originate from various sources and can commonly found in concentrations of ng/L to µg/L in the water. These are what we consider as Emerging Contaminants (ECs) (Pal et al., 2014). These contaminants are not monitored by the treatment facilities but are known to have ill-effects on human health and environmental health. Thus, they are rightly included in the compound group known as EDCs or endocrine disrupting compounds. These compounds may be naturally occurring or synthetically produced and used in the production of personal care products (PPCPs), pharmaceutical, rocket fuels, herbicides, pesticides etc. Factors such as: these compounds going unmonitored, their capability to bio accumulate in macro invertebrates and other organisms in the food web and humans, the issue of conventional treatment systems and natural attenuation failing to remediate these micro-contaminants; make it necessary if not imperative to study new remediation techniques to treat these

contaminants from surface water, wastewater and drinking water systems (Ruhi et al., 2015; Huerta et al., 2015; Annamalai & Namasivayam, 2015). It is important to understand that successfully reusing water does not just depend on the availability of water but also on appropriate treatment. Even though in-depth investigations are carried out for nutrients, microbial population and select chemical contaminants, very few studies have reported with respect to ECs and even lesser number of studies report the treatment for these ECs in our water nexus. Thus, the treatment of ECs is an ongoing battle for appropriate and safe water reuse.

2.3 Importance of treatment in water and associated health risks

2.3.1 NDMA

NDMA is a semi volatile organic compound and belongs to a highly potent family of nitrosamines. In drinking water systems, NDMA has attracted a lot of interest primarily due to its potent carcinogenicity and detection rate. In China, to evaluate the human health risk caused by this compound in potable water and to devise solutions/recommendations to develop DWS (Drinking Water Standards), a two-stage disease model along with the method of disability adjusted life years were utilized to estimate the risk of getting liver cancer from drinking water contaminated with NDMA. A conducted surveys in 35 cities in China from 2009 to 2012 and detection was conducted from 23 cities from 2012 -14 at 146 different sites (Chen Chao et al., 2012). The incidence of cancer was 5.69×10^{-6} and thus it was 5.69 times higher than the risk specified by U.S. EPA i.e. 1×10^{-6}. According to the results of this study, the deaths caused by NDMA is 844.15 human-years, the incapacity loss was 25.84 person years. The death percentage in this case was more than incapacity. The ability of emerging

contaminants like NDMA in concentrations as low as ng/L to cause serious damage to human health is reason enough to take steps to further study this compounds and methods to achieve enhanced remediation from water systems.

2.3.2 1,4-Dioxane

This compound was primarily used as a stabilizer for solvents that were chlorinated in industrial processes. This is also used in a variety of industries in the production of antifreeze, deodorants, paints etc. (Agency for Toxic Substances and Disease Registry [ATSDR], 2012; U.S. EPA, 2006). In the U.S., 1,4-dioxane is regulated and considered hazardous waste only in the case of this chemical being used as a solvent used in the industries and when used for different applications like additives or as pesticides, its disposal goes completely unregulated (U.S. EPA, 2017b). The health risks which are primary concerns are damage to liver, kidneys and nasal & ocular effects have also been reported (DeRosa et al., 1996; Dourson et al., 2014).

In some studies when this compound was administered to rodents via their drinking water and it was shown that this compound can induce liver toxicity which was highly dose dependent which ultimately manifested in terms of hepatic cells showing degeneration (Fishbein, 1981; Goldsworthy et al., 1991). Other ill-effects of 1,4 – dioxane include increased liver compared to the body weight, enzymatic leakage, and damage to the chromosome in rodents (Kano et al., 2009, Roy et al., 2005). EPA in 2015 also reported chronic exposure through drinking water can have impacts on the kidneys by degenerating the cells belonging to the cortical tubule, necrosis of the same and glomerulonephritis (U.S. EPA, 2015).

2.4 Existing treatment options and requirement of alternate treatment options for Nitrosodimethylamine (NDMA)

NDMA is a semi-volatile organic compound which belongs to the family of extremely potent carcinogens known as N-Nitrosamines. Their potency to cause cancer at very low concentration of 0.7 ng/L makes it more potent than trihalomethane (Mitch, Gerecke et al., 2003). According to U.S DHHS reports, NDMA was found to be adept to form tumors in the kidneys, liver, blood vessels and trachea in experimental animals (International Agency for Research on Cancer [IARC], 1999). Unsymmetrical UDMH used in rocket engine fuel facilities such the ones in Sacramento County, California; have been known to produce NDMA as an undesirable by-product. Offsite concentrations up to 20,000 ng/L and onsite concentrations up to 400,000 led to the shutdown of downstream drinking water wells. On further investigations by the CDC, it was discovered that high concentrations of NDMA was reported when chlorine was used for wastewater disinfection and high concentration of NDMA was discovered in the nearby aquifer as well (Mitch, Gerecke et al., 2003). According to the EPA fact sheet on NDMA, it can be found in air, water and soil. In air, NDMA is expected to exist in vapor form in ambient temperature and is likely to be broken down by sunlight alone within a few minutes (Europa, 2006). However, when in soil, NDMA is known to have high mobility and might either volatilize or leach through the layers of the soil and get introduced in the groundwater. In water, NDMA is a completely miscible compound and is not known to adsorb on any solid surface/sediment. It might either be broken down by sunlight or by biological process.

UV irradiation is the most commonly used method in the remediation of NDMA. The UV absorption peak of this compound is at 222nm. A range of 220 nm to 254 nm is known to be used in its remediation. Many Advanced Oxidation Process involving UV and a chemical compound to increase the remediation efficiency have been investigated but each come with their drawbacks. Low transmittance and high scavenging capacity of secondary and tertiary wastewater effluents coupled up with low hydroxyl stability of H_2O_2 (hydrogen peroxide) and the low conversion of H_2O_2 to free radicals in normal plant conditions make AOP using UV/ H_2O_2 selectively efficient for only certain potable water reuse trains (Fujioka et al., 2012; Miklos et al., 2018). Studies were conducted using ozone with UV and realizing the low radical production capability and the high energy demand for ozone production, this technique is not desirable for the treatment of NDMA. Sulfate radicals along with UV yielded higher quantum yields when compared to H_2O_2 but their high sensitivity to water matrix makes it a viable option for any certain selective contaminants (ATSDR, 2012). Chlorine could not be considered as the choice of chemical for AOP process responsible for the remediation of NDMA since there is always the possibility of reoccurrence of the formation of NDMA. Thus, there is a requirement to study and obtain an efficient AOP in the treatment of NDMA to fill the knowledge gap.

2.5 Existing treatment options and requirement of alternate treatment options for 1,4-dioxane

A synthetic organic chemical which is a cyclic diether; 1,4-dioxane has a widespread impact on the drinking water sources. Despite the fact that the U.S. has been aware of this chemical as a known water contaminant since 1978, this compound is still

considered a contaminant with emerging concern (ATSDR, 2012). Major concerns include: its classification as a carcinogen to humans by all exposure routes (U.S. EPA, 2013b), missing presence of enforcing water standard laws for this compound and the fact that it cannot be treated effectively by the current standard water treatment process (Sun et al., 2016). The reason this compound is relevant to this study is that this compound is highly miscible in water which makes it non-volatile when in water, low affinity for adsorption by activated carbon, it does not readily oxidize while using commonly applied oxidants and it's not easily biodegraded. (Eckhardt, 2018; U.S. EPA, 2017b).

It is important to understand the possible effects of 1,4-dioxane to understand its relevance to human health and the ecosystem. Exposure to this compound through drinking water can occur by either ingestion, or dermal contact, or inhalation. The reference values for this compound have been calculated to 10^{-6}, 10^{-5} and 10^{-4} lifetime cancer risks for corresponding drinking water concentrations of 0.35, 3.5 and 35mg/L respectively (U.S. EPA, 2013b; U.S. EPA, 2018b). Even though 1,4-dioxane is known to be non-volatile in water at room temperature, its volatility increases with temperature rise which in turn increases inhalation exposure while using hot water for showers/baths (U.S. EPA, 2018c). In 2005, the WHO adopted a guideline concentration of 50mg/L which was the same level adopted by New Zealand, Japan and South Korea. Germany adopted a precautionary guideline of 0.1mg/L in their drinking water systems (World Health Organization [WHO], 2005; Karges, 2018; An et al., 2015).

Facilities that manufacture, process and/or use 1,4-dioxane in their process are associated with releasing 1,4-dioxane to surface water. In the U.S. alone, according to the

Chemical Data Reporting database 2015, approximately 450,000 kg of this compound was either produced or imported. Of that, around 320,000 kg was released into the environment according to the Toxics Release inventory (TRI) in the year 2015 (U.S. EPA, 2018c). These numbers are at best underestimated because this compound's production volume data is considered to be confidential business information (U.S. EPA, 2018c). One of the other major drawbacks for our inability to accurately quantify the volume metric of 1,4-dioxane in the environment is that Chemical Data Reporting and TRI do not consider the generation of 1,4-dioxane as a manufacturing by-product like in the production of ethylene oxide, surfactants used in detergents and soaps, polymers like polyester (Sun et al., 2016). Large concentrations of 1,4-dioxane which cannot be neglected are emitted from production facilities: 200 – 2000 mg/L in wastewater associated with polyester production units, close to 300mg/L in wastewater associated with chemical industries (Shen et al., 2017; Zenker et al., 2003).

From the treatment standpoint, 1,4-dioxane in water proves to be a challenging task. Based on the EPA models, < 5% of the compound can be treated at municipal WWTPs using conventional treatment systems which is not enough to ensure safe water (U.S. EPA, 2018c). Alternatively, in the drinking water treatment plants' perspective, there was no noticeable removal of 1,4-dioxane using conventional surface water treatment trains (Knappe et al., 2016). This brings us to other treatment processes like granular activated carbon, packed tower aeration and reverse osmosis, all of which are ineffective in the treatment of this compound. Additionally, 1,4-dioxane to RO makes it essential for the treatment of the RO permeate by other remediation techniques to remove 1,4-dioxane (Knappe et al., 2016). Irradiation by UV and AOP used in certain studies

have shown promising results but none of the studies use peracetic acid to enhance the formation of hydroxyl radicals which has known to be effective in the remediation of 1,4-dioxane in water.

2.6 Microorganisms of concern in Water

The microorganisms used in this study are *E. coli*, *Legionella pneumophila*, *Mycobacterium avium* and *Aspergillus niger* spores. These OPs were selected based on the associated human health concerns, the challenges associated to their disinfection in water and their vastly varied UV susceptibility.

E. coli. *Escherichia coli* is a gram-negative rod-shaped bacterium and belongs to the *Enterobacteriaceae* family within the class *Gammaproteobacteria*. *E. coli* is one of the most well-studied bacteria and under optimal conditions it is known to replicate in about 20 mins. Since it's often found in the low gastro-intestinal system of warm-blooded animals and human beings, this microorganism is frequently utilized as a fecal indicator bacterium (FIB) for assessing the water quality. Pathogenic *E. coli* strains are known to cause multiple human diseases, resulting in approximately 2 million deaths every year (Kaper et al., 2004). Waste waters from slaughterhouses, wastewater treatment plant effluents, manure and animal wastes are some of the common entry pathways of pathogenic *E. coli* in the environment (Baliere et al., 2015). Specifically, the pathogenic strains of this microorganism can persist in the environmental due to their ability to acquire nutrition by forming filamentous structures and using them to attach to surfaces and thereby colonize within a short period of time (Solomon et al., 2002). Their ability to colonize internally presents a challenge to wash them off from water treatment plants. Certain pathogenic strains pose a big threat in food production/supply chains and

approximately 76 million illnesses, 325,000 hospitalizations and 5,000 deaths are associated with food borne illnesses every year caused by pathogenic strains of *E. coli* (Mead et al., 2000). Since this a microorganism which commonly resides in the intestinal tract of humans, it is often exposed to several types of antibiotics that we consume. This has led to the hypothesis that the antibiotic resistance of some *E. coli* strains might be connected to their origin source (Harwood et al., 2014). The U.S. EPA guidelines state a Maximum Contaminant Level Goal (MCLG) and Maximum Contaminant Level (MCL) of <1 CFU/100 mL of water for *E. coli* (U.S. EPA, 2013a).

Legionella pneumophila. One of the most significant waterborne opportunistic pathogen which is responsible for a large portion of waterborne disease in the U.S. is *Legionella* (Beer et al., 2015). Chronic exposure of this microorganism is associated with pneumonia like illnesses called Legionnaires' disease (LD) and in cases of minor exposure it leads to Pontiac fever (Kerbel et al., 2015). Although we have known about the health concerns associated with this microorganism, the case associated with LD is on the rise from a global perspective. For example, in Europe the notified cases of LD increased from 4921 in 2011 to 11,343 in 2018 (ECDPC, 2019). In the U.S the number of cases has increased from 2301 in 2005 to 7104 in 2014 which is roughly a 300% increase (CDC, 2018). The *Legionella* genus comprises of 60 species and 80 very distinct serogroups (Miyashita et al., 2020). *L. pneumophila* is known to be the primary aetiological agent of LD. The microorganism is known to be ubiquitous in water distribution systems. Common *Legionella* occurrences can be tracked to cooling towers, wastewater treatment facilities, soils, and ambient water environments (Ahmadrajabi et al., 2016; Allestam et al., 2006; Walser et al., 2017; Amemura-Maekawa et al., 2012;

Fliermans et al, 1979). It's known to survive in unfavorable conditions like high temperature environments. Like other OPs like NTM, *Legionella* can be incorporated into protozoan hosts and their biofilms for nutrition and survival in water distribution systems. Important factors like water stagnation, moderate temperature and increase in the organic carbon of water can accelerate the rate of biofilm formation (Abdel-Nour et al., 2013; Liu et al., 2006). The biofilm protects *Legionella* from residual disinfectant concentrations present in the public water distribution systems. They are continuous financial challenge with hospitalizations costing nearly 434 million dollars annually in the United States (Collier et al., 2012). The infection is mostly associated with man-made systems like premise plumbing and water distribution systems associated with that, cooling towers, mist blowers, decorative fountains etc. (CDC, 1990).

Nontuberculous *Mycobacterium* (NTM). NTM is another set of OPs which proliferate in drinking water systems and therefore, are a growing public health concern. NTM are known not only to predominantly cause pulmonary infection but also for soft tissue, skin, and post-operative infections. There are certain species of NTM which are opportunistic pathogens and are characterized by pulmonary infections and lymphadentis, skin, soft tissue, and bone infections (Hosker et al., 1995). Recent studies reported $194 million to be the cost of annual hospitalizations in the United States of America (Falkinham, 2016; Misch et al., 2018; Schnabel, 2016; Allen et al., 2017; Collier et al., 2013). Although the health and economic factors associated with NTM infections are well documented, the source of NTM exposure remains relatively unstudied. Recent studies believe the regular presence of NTM is drinking water and biofilms in water distribution prove that drinking water might be one of the important sources of

pulmonary infections associated with NTM (Donohue et al., 2015; Gerbert et al., 2018). Furthermore, high concentrations of *Mycobacterium avium* (*M. avium)* have been found in high turbidity and particulate matter which is probably associated to the attachment of NTM to the particulate matter in water (Fang et al., 2018). Higher rates of NTM infections are linked to the usage of tap water which is derived from surface water when compared to groundwater (Kotlarz et al., 2019). Pure cultures of *M. avium* (similar to inoculum used in this study) are known to require disinfection doses upto 2300-fold and 50-fold for chlorine and ozone respectively to achieve 3-log inactivation when compared to disinfection doses for microorganisms like *E. coli* (Taylor et al., 2000). Additionally, NTM are known as biofilm pioneers because of their inherent capabilities of parasitizing protozoan cells. They are known to thrive in these biofilms which keep them safe from residual disinfectant doses in the water distribution systems (Delafont et al., 2017).

***Aspergillus niger* spores.** Mass propagation of fungal spores is an issue threatening the drinking water safety and thereby cannot be ignored (Pereira et al., 2009). Under normal circumstances, even low concentrations of metabolic products from fungi populations can lead to variety of problems to the aquatic environment. For example: *Fusarium gramineaurm* which comprises of red pigments has been listed in water drinking water guidelines as a nuisance organism that leads to odor problems (Babič et al., 2017). Immuno-compromised patients are known to be at higher risk of suffering from mycosis and allergic reactions once mycotoxins come in contact with the human body through water and food (Marr et al., 2002; Curtis et al., 2004). *Aspergillus* species are responsible for different types of aspergillosis, totaling to more than 13.5 million cases worldwide every year (Richardson et al., 2012; Kosmidis et al., 2015). Thus, the

fourth microorganism selected in this study is *Aspergillus niger* spores. Harmful health effects of this mainly include asthma symptoms, skin irritation and hypersensitivity pneumonitis (Al-Gabr et al., 2014; Green et al., 2003). UV irradiation of *Apergillus* spores presents a resilient challenge due to its cell structure. In general, the survival of fungal spores depends on two basic components: spore cell wall and pigments. The spore cell wall is usually comprised of polysaccharides like chitin, glucan and pigments like melanin. Thus, the cell wall is highly hydrophobic and pigmented (Beauvis et al., 2014). Pigments like melanin are involved in cell processes ranging from adhesion to virulence while protecting them from the stress induced by radiation and thereby presenting a tough challenge to inactivation by UV irradiation (Eisenman & Casadevall, 2012; Cordero & Casadevall, 2017). But the pigmentation of *A. niger* spores are still puzzling and is yet to be studied in depth. Two different pigments were shown to have two different absorption peaks: green (575 nm) and brown (425 nm). This is reason for the black coloration of these spores and also the reason for their resistance to UV 254 nm irradiation (Jorgensen et al., 2011). Future studies focusing on identifying the different fungal pigments, their absorption peaks will provide a better understanding of the processes that are required to better remediate them from drinking water sources.

3 NDMA: A THREAT AND AN EMERGING CONTAMINANT – CONTROL STRATEGIES USING PERACETIC ACID WITH LOW PRESSURE UV AND REFELCTIVE TECHNOLOGY

3.1 Abstract

NDMA is an important emerging contaminant which belongs to the family of highly potent carcinogens known as N-Nitrosamines. In 1998, the U.S. EPA excogitated the first Contaminant Candidate List (CCL) which contained a list of drinking water contaminants that were known or anticipated to occur in our water systems and were not subject to EPA drinking water regulations. With high potency at low concentrations of 0.7 ng/L and acute hepatotoxic characteristics, NDMA is rightly among the compounds listed in CCL3 and CCL4 by the U.S. EPA in 2009 and 2016. It is a by-product of several industrial processes and its list of precursors include personal care products, herbicides, fungicides, pesticides and chloramination processes used in wastewater treatment plants (WWTPs).

Advanced Oxidation Process (AOP) involving different oxidants have been applied along with UV for the treatment of NDMA. The limitations related to most of these remediation systems arise trying to maintain practical achievability and preventing contaminant recurrence. This study focuses on the development of alternate enhanced NDMA treatment technologies under dynamic flow conditions using AOP involving peracetic acid (PAA) with 220 and 254 nm reflective UV technology.

Experiments were performed with the following variables under dynamic flow conditions: a) NDMA concentration b) PAA dose c) UV wavelength (220 or 254 nm) d) UV dose. The influent and effluent samples were analyzed for NDMA in accordance with

the EPA 521 method for analyzing nitrosamines. While using UV 220 nm employing an excimer lamp; a maximum of 98% remediation was achieved at an optimum PAA dose of 1.5 mg/L and UV dose of 5.5 mJ/cm^2. Decrease in the percent remediation was observed with decrease in the UV dose and increase/decrease in the PAA when compared to its optimum concentration. Meanwhile the UV 254 nm which employs a low-pressure mercury achieved a maximum of 98% remediation at a high UV dose of 1,183 mJ/cm^2. It was observed that while the results were independent of the oxidant concentration, they were highly dependent on the UV dosage.

Since the UV absorption spectrum of NDMA peaks at 227 nm in comparison to UV 254 nm, the highest level of remediation was achieved at the lower UV 220 nm doses. The remediation showed a high dependency on the PAA dose while using UV 220 nm. This study confirmed the ability of both wavelengths to remediate NDMA by optimizing the above-mentioned factors while maintaining practical achievability of the remediation process.

3.2 Introduction

With continued population growth, deteriorating climate and a decrease in the aquifer levels across the globe; potable reuse of wastewater has been gaining importance. Thus, there has been increasing focus on application of water reuse technologies, advances in the field of water engineering and identifying emerging contaminants in public water systems. The U.S EPA published its first Contaminant Candidate List (CCL 1) in 1998 that entailed a list of drinking water contaminants which were known to or anticipated to occur in public water systems and were not subject to the EPA drinking water regulations. One of the compounds considered as an emerging contaminant was N-Nitrosodimethylamine (NDMA) which was included in the CCL 3 and CCL 4 (U.S. EPA, 2016). A Federal Maximum Contaminant Level (MCL) has not been established even though NDMA is a suspected human carcinogen and a known hepatotoxin.

N-Nitrosodimethylamine is a semi-volatile organic compound which belongs to a family of extremely potent carcinogens called N-Nitrosamines. Their potency to cause cancer is known to surpass trihalomethane (Mitch, Gerecke et al., 2003). The U.S. Department of Human Health Services (DHHS) states that NDMA was found to cause tumors in various species of experimental animals. Liver, kidney, trachea and blood vessels were observed to be the primary sites of tumor occurrence (IARC, 1999). There has been an increase in the focus on NDMA since a rocket engine testing facility in Sacramento County, California used rocket fuel with an unsymmetrical dimethylhydrazine (UDMH) base.

While the offsite ground water NDMA concentrations were found to be 20,000 ng/L, the onsite concentrations were measured to be as high as 400,000 ng/L which led to the closure of down gradient drinking water wells (Mitch, Gerecke et al., 2003, U.S. Department of Homeland Security, 2002). Further NDMA concentrations as high as 3,000 ng/L were discovered proximal to another rocket testing facility in San Gabriel Valley, California, which lead the Colorado department of human services (CDHS) to conduct a survey for NDMA in the state's drinking water (Mitch, Gerecke et al., 2003; U.S. Department of Homeland Security, 2002). It was found that there were high levels of NDMA at sites where the wastewater was subjected to chlorine disinfection and later released into the aquifers. This showed that the issue of NDMA was not limited to just regions proximal to a rocket engine testing facility. Ever since the 1970s, there have been concerns about the occurrence of NDMA in consumer products like beer, cured meat, rubber products and cigarettes. Based on these findings, some scientists suggested that NDMA could be one of the reasons for increased cancer rates in urban areas (Shapley, 1976; Mitch, Sharp et al., 2003)

An elucidated a two-step mechanism which helps us understand the increase in formation of NDMA when monochloramines were used in water treatment (Choi & Valentine, 2002). To this day water treatment facilities use chloramines/hypochlorites to maintain chlorine residual in water distribution systems. As a result of the slow rate of formation of NDMA, the use of chloramines increases the concentrations of NDMA within the distribution systems. In the absence of chloramines, hypochlorite can react with secondary amines and form NDMA. The rate of formation of NDMA by this reaction is a magnitude lesser than the one observed with chloramines. The research done

on the topic, documents the increased formation of NDMA when the water was treated with ion exchange resins with quaternary amine groups which could serve as NDMA precursors (Fiddler et al., 1977; Kimoto et al., 1980). The reactions shown in Figure 1 along several other studies conducted to achieve remediation of precursors of NDMA, show us the importance of dealing with the precursors and also the need for new and emergent technologies for the remediation of NDMA (Mitch, Gerecke et al., 2003; Wang et al., 2017).

AOPs are widely used treatment technologies for the remediation of NDMA. They can widely be classified into five categories: Ozone – based AOP, UV- based AOP, Electrochemical AOP, Catalytic AOP and Physical AOP. According to a study, the general concepts of AOPs are based on the in-situ generation of radicals for the oxidation of organic compounds. A majority of the AOPs are based on the generation of hydroxyl radicals (¬.OH) which act as the oxidant in the reaction. In this study we used UV-based AOP method for the remediation of NDMA in water (Miklos et al., 2018).

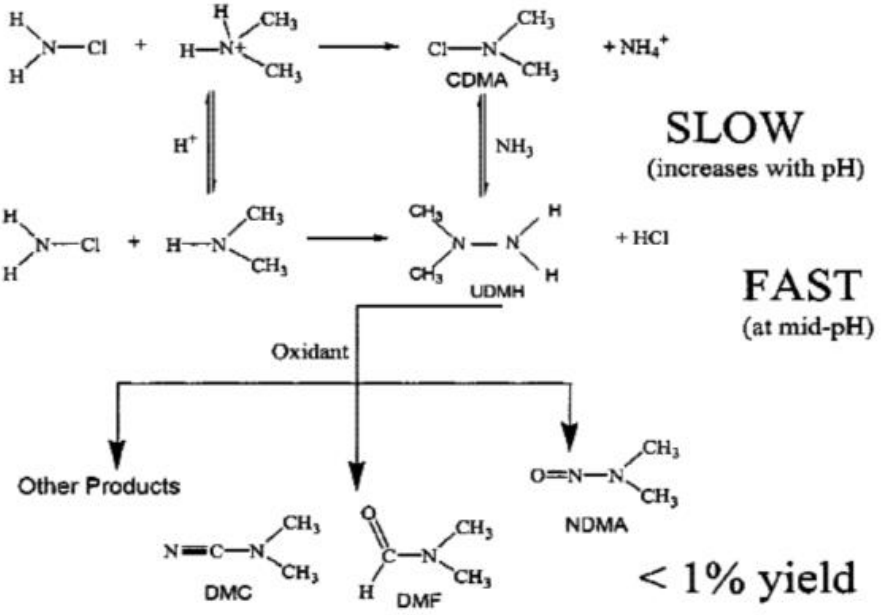

Figure 1: Pathway for NDMA Formation During Chloramination of Dimethylamine via a UDMH Intermediate.

There are different UV-based AOPs to enhance the formation of radials from an oxidant. The AOPs with UV produces different radical promoters which are responsible for breaking the contaminant into smaller fragments. One such process is UV/H_2O_2. Here UV irradiation cleaves hydrogen peroxide (H_2O_2) to form two $^{\cdot}OH$ radicals. Different applications of this technology have been studied for water qualities ranging from ultrapure water to landfill leachate (Miklos et al., 2018; Sgroi et al., 2018; Beita-Sandi et al., 2016). A study conducted in 2018, used this technique for the treatment of secondary and tertiary wastewater effluents. But due to factors such as low UV transmittance and high scavenging capacity of the water matrix, the study rightly stated that UV/H_2O_2 can be applicable for certain potable reuse trains where integrated membrane systems are employed (Miklos et al., 2018). In accordance with this, a review paper clearly states the conversion of H_2O_2 to free radicals is not more than 20% in normal plant conditions (Fujioka et al., 2013).

An alternative to using UV/H_2O_2 which is now being studied is the usage of UV along with primary sulfate radicals (Lutze, 2013). Here UV-C is used to homolytically cleave peroxydisulphate (PDS) resulting in stronger and more selective sulfate radicals. Even though it was also found that PDS results in 0.4 times higher quantum yield than H_2O_2, the fact that sulfate radicals have higher sensitivity to water matrix changes limits the applications of this treatment technology (Lutze, 2013; Feng et al., 2017). Based on the target contaminant and the water matrix, this method can be considered as an alternative to UV/H_2O_2 method.

UV/O_3 is another type of UV-based AOPs. Ozone is subjected to photolytic cleavage using UV resulting in an oxygen molecule and atomic oxygen. The atomic

oxygen thus produced undergoes a fast reaction with the water molecule resulting in the formation of thermally exited H_2O_2, which then subsequently decomposes to form two $^{\cdot}OH$ radicals (Miklos et al., 2018). However, it was observed that only a minor proportion of the generated H_2O_2 decomposed to free hydroxyl radicals resulting in one of the major drawbacks of this method. Combining this with the issue of low energy efficiency of the process, makes UV/O_3 process less desirable. This might be the reason for the absence of any published data on a full-scale application employing this process.

A more promising AOP technique involving UV is UV/Cl_2. Generally, chlorine compounds like hypochlorite and chlorine dioxide are photolytically cleaved using UV-C resulting in different chlorine radicals that subsequently cleave the water molecules to produce hydroxyl radical which is used to oxidize the target contaminant. However, the usage of hypochlorite is considered ideal only in acidic systems depending on the system's pH dependency. As previously stated, and shown in Figure 1, the possibility of reoccurrence of NDMA in the water distribution systems makes this method undesirable for the remediation of NDMA.

Researchers in the past have tried to employ these AOP techniques in the treatment of NDMA. Certain experiments were conducted using buffered deionized water with varying pH. They used O_3/H_2O_2 in their experiments and found that 7.7 mg/L of ozone led to 25% remediation of NDMA (Lee et al., 2007). However, they could achieve a higher remediation of 50-75% when the 7.7 – 15.4 mg/L ozone was coupled with H_2O_2. They observed an improvement in oxidant utilization efficiency by having multiple injections of ozone. Methylamine was found to be one of the major products from NDMA remediation catalyzed by $^{\cdot}OH$ radical. While they could achieve a high

percentage of remediation using ozone, the practicality for large scale applications and economic limitations (high energy required to produce ozone) of this technique remain as major concerns.

A series of field experiments were conducted in 2009 to see the level of NDMA remediation in groundwater with incidental and active recycled water recharge (Zhou et al., 2009). They monitored the NDMA concentration at 32 production wells for seven-years. Factors such as changes in magnitude, significant variations in the concentration of NDMA in the effluents, seasonal hydro-geologic conditions were taken into consideration and they found 90% mass reduction over seven years. Despite its cost effectiveness this would not be advised for NDMA remediation because of the long degradation time.

An economical alternative to UV systems is the biological treatment techniques for ex-situ removal of NDMA from groundwater. *Rhodococcus ruber* ENV425 was used for NDMA remediation (Webster et al., 2013). These bacteria are capable of co-metabolizing NDMA during growth on propane and they were able to achieve > 99.9% efficiency while treating an NDMA concentration of 12 mg/L with a 30 min hydraulic retention time (HRT). The concentration of NDMA in wastewater treatment facilities post-secondary treatment was found to be as high as 250 - 500 mg/L. While this method is feasible for low concentrations of NDMA, no research was found acknowledging the efficiency of this process for higher concentrations of NDMA. In certain full-scale plants, biological activated carbon (BAC) systems were also considered to be a very effective biodegradation technique for NDMA remediation (Gerrity et al., 2015). But on further research, a recent pilot scale studies conducted, reported only 50% removal while the

reoccurrence of NDMA was also reported through BAC systems with water previously treated by O_3 (Li et al., 2017) or UV/H_2O_2 (Sgroi et al., 2018).

The method of coagulation was also found to be ineffective (Beita-Sandí et al., 2016; Krasner et al., 2012) with only <10% NDMA removal and <10-30% removal of NDMA precursors. In fact, an increase in the formation potential of NDMA was seen in certain circumstances when amine based cationic polymers were frequently included. Adsorption was also deemed ineffective for NDMA (Dai et al., 2009; Krasner et al., 2013) since the hydrophilic nature of NDMA ceases to make it effectively adsorb in the soil.

In this study, the experimental plan was designed for a critical evaluation of UV-C (220 and 254 nm) and peracetic acid (PAA) for the remediation of NDMA at different concentrations in water. Since the UV absorption spectrum of NDMA peaks at 227 and 332 nm, two different wavelengths of UV-C (220 and 254 nm) and PAA was used as the catalyst at different concentrations. PAA (CH_3CO_3H) is photolytically cleaved into $CH_3CO_2^{\cdot}$ and $^{\cdot}OH$ radicals. The hydroxyl radical thus generated remediates NDMA and/or forms other reactive radicals like $^{\cdot}OOH$ and $CH_3CO^{\cdot}$. In addition, H_2O_2 present as a part of PAA also contributes to the generation of highly reactive hydroxyl radicals under UV irradiation. Most reported studies have employed static batch reactions for the NDMA treatment, whereas this study employed dynamic flow conditions to better mimic the real-world applications of this technology and allow to efficiently scale-up the process.

The main objective of this study was to formulate a new and effective AOP technique for the remediation of NDMA in water.

The specific research objectives of the study were: 1) to analyze the effect of UV 254 and 220 nm with reflective technology on the remediation of NDMA in water. 2) to study the effect of PAA on NDMA remediation using two UV wavelengths at varying doses. 3) to optimize UV and PAA dosages to efficiently remediate NDMA under dynamic flow conditions to better mimic real world in-situ/ex-situ applications.

3.3 Materials and Methods

3.3.1 Operational Design

Two different experimental UV devices were employed with wavelengths associated with the absorption spectrum of NDMA to create a comparative study. Both systems employed ReFLeX^{TM} technology in their chambers and they were generously provided by NeoTech Aqua Solutions (San Diego, CA). As a part of the technology, the chamber is lined with a quartz sleeve which ensures more than 99% radiation is reflected back into the reactive chamber, thereby increasing the energy efficiency and the extent of treatment that is achieved by the system.

The first UV device consists of a low-pressure mercury lamp which emits radiations at 254 nm, which is the higher end of the NDMA UV absorption spectrum. This employed a horizontal UV chamber which was designed to manage lab scale experiments with a maximum flowrate of 20 gal/min. The second UV device employs an excimer lamp which emits UV radiations at 220 nm. Since NDMA's UV absorption peaks at 227 nm, this provided a good base to study NDMA remediation. With one gallon of chamber volume, this employed a vertical UV column and was designed to manage a maximum of 1.2 gal/min. In comparison to the low-pressure UV 254 nm system, with an excimer lamp as its UV source, this is much more energy efficient but less UV intense.

3.3.2 Experimental Plan and Analysis

A 55-gallon polyethylene barrel was used as the influent containers. The influent tank was filled with tap water which had a residual chlorine level of 0.5 to 1.2 ppm. To ensure non-reactivity of NDMA with the residual chlorine, sodium thiosulphate was used for neutralization. The tap water UV transmittance (UVT) was 94% and average specific UV absorbance (SUVA) was 1.14 L/mg-m. The influent water was then spiked with the desired concentration of NDMA (Sigma-Aldrich Corporation) and mixed thoroughly to ensure homogeneity. The NDMA spiked influent water was then pumped using AMT® model C63JXGWU-1114 Iwaki Magnetic pump model MD-70RLZT for different flowrates to the UV system with one and half inch piping respectively. PAA (Sigma-Aldrich Corporation) was injected upstream to the influent tank using a peristaltic pump (FMI "Q" Pump, model QG50). Thereby, the water containing NDMA and PAA entered the UV 254 or 220 nm system. The bulbs employed in the 254 nm system are 185/254 nm bulbs.

Duplicate samples of the influent and effluent water were collected and submitted to Scottsdale Water Campus for NDMA analysis. Modified EPA 521 method for analysis of nitrosamines was used. An isotope dilution GC/MS/MS method was developed where the sample was spiked at 50 ng/L with labeled nitrosamines and 200 mL was extracted to final volume of 2 mL dichloromethane. The injection was made in split less mode and the compounds were separated on a capillary column. The target compounds as well as their isotopically labeled standards were detected by ammonia positive chemical ionization and quantitated by using multiple reactions monitoring technique. The practical quantitation limits are <2 ng/L of all eight-nitrosamines listed in the EPA Method 521.

The instruments that were used consisted of AutoTrace Solid Phase Extraction apparatus by Thermo Fisher, Agilent 7890 GC equipped with multimode injector and Agilent 7000C triple quadrupole mass spectrometer equipped with chemical ionization source using anhydrous ammonia.

3.4 Results and Discussions

The experiments were conducted using the four variables summarized in Table 1 below.

Table 1: NDMA Remediation Experimental Variables.

Variables	**Set Points Tested**					
Inf NDMA conc (ng/L)	150 - 650					
UV Dose (mJ/cm^2)	115 - 1,030					
UV Wavelength (nm)	254			220		
PAA (mg/L)	0.5	1	1.5	2	3	4

UV 220 and 254 nm at different dosages were applied separately to investigate their efficacy to remediate NDMA. NDMA concentration range in influent was selected according to the NDMA present in the city of Scottsdale Water Campus, Scottsdale, Arizona in the secondary treatment effluent. The PAA concentration was initially set to 0.5 mg/L and then systematically increased until the remediation decreased drastically suggesting the system to be overpowered with the UV reacting with PAA.

Since the UV absorption spectrum of NDMA was closer to 220 nm, UV device consisting of an UV excimer lamp was initially employed at 5.5 and 4.4 mJ/cm^2 with influent NDMA concentration range between 140 to 330 ng/L.

Irrespective of the influent NDMA concentration, the common trend observed was that increasing the UV dosage from 4.4 to 5.5 mJ/cm^2 corresponded to an increase in the NDMA remediation. As depicted in Figure 2, average influent NDMA concentrations

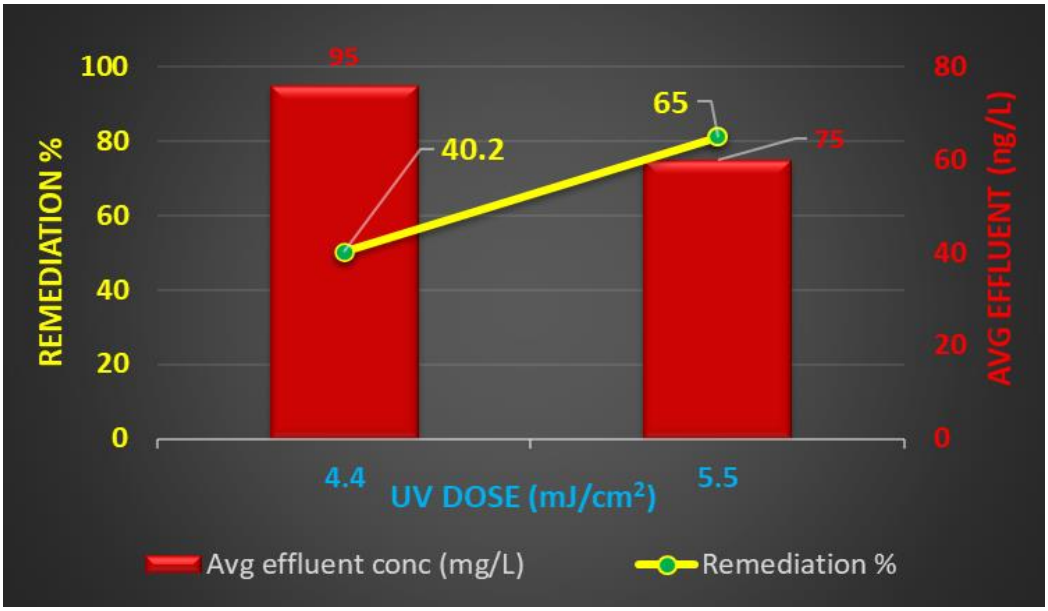

Figure 2: AOP of NDMA Using 220 nm with Different UV Doses.
Note : The effluent values are an average of 4 replicates.

of 220.6 ng/L and 231.6 ng/L were irradiated with 4.4 and 5.5 mJ/cm^2 UV respectively, which resulted in remediation percentages of 40.3% and 65.16%, respectively.

This set of experiments employing <10 mJ/cm^2 UV dose and remediating a high level of the influent NDMA in dynamic flow conditions confirmed the effectiveness of applying UV similar to its UV absorption peak. The results obtained provided a baseline to further investigate AOP using UV 220 nm and PAA.

The next step in the study was to observe the effectiveness of UV 254 nm alone in the remediation of NDMA. The UV system used in this study employed a low-pressure mercury lamp to achieve higher UV doses. Influent NDMA concentrations ranged between 180 to 538 ng/L to observe and establish a performance baseline for UV 254 nm with reflective technology. To obtain different UV doses, the flowrate of the system was adjusted between 20 to 1 GPM to obtain UV doses between 120 to 1,060 mJ/cm^2.

Although 254 nm wavelength is higher on the NDMA UV absorption spectrum, we observed a positive remediation trend with systematic increase in the UV dose.

As shown in Figure 3, using a low UV dose of 120 mJ/cm^2 remediated 15.8% of the influent NDMA and as we increased the dose to 452 mJ/cm^2 we observed the remediation reached 91.4% and flattened out to 94.2% when irradiated with 1,060 mJ/cm^2 UV dose. This set of experiments confirmed the applicability of UV 254 nm with reflective technology, however, for high remediation, it requires higher doses of UV which might not be practical for real world applications.

The remediation experiments conducted using just UV 220 nm and 254 nm concluded the capability of both the wavelengths to remediate NDMA under different conditions. This was followed by investigations employing these two different UV setups and PAA to formulate an alternative remediation technique for NDMA under dynamic

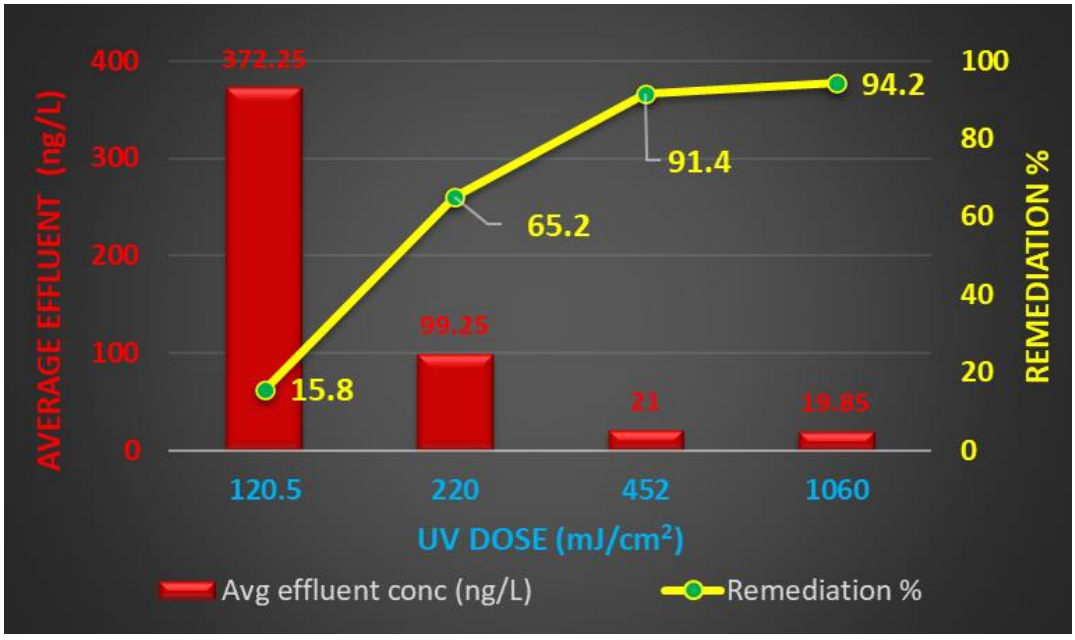

Figure 3: NDMA Remediation Using UV 254 nm at Different Doses.
Note: The effluent values are an average of 4 replicates

flow conditions by optimizing the UV dose, UV wavelength and PAA dose. For the first

set of AOP experiments, the UV 220 nm, emitting an UV dose of 5.5 mJ/cm^2 was used to remediate influent NDMA concentration range of 210 – 370 ng/L. The PAA dose ranging from 0.5 – 4 mg/L was introduced upstream and the respective remediation percentages were noted.

As shown in Figure 4, initially the PAA dose applied was 0.5 mg/L resulting in 60% remediation of NDMA which was 5% less than the value obtained under similar conditions without PAA. As the PAA dosage was systematically increased, an interesting trend in remediation was observed. When the PAA dose was increased to 1 and 1.5 mg/L, the remediation increased to 83.4% and 97.2%, respectively. A negative trend was

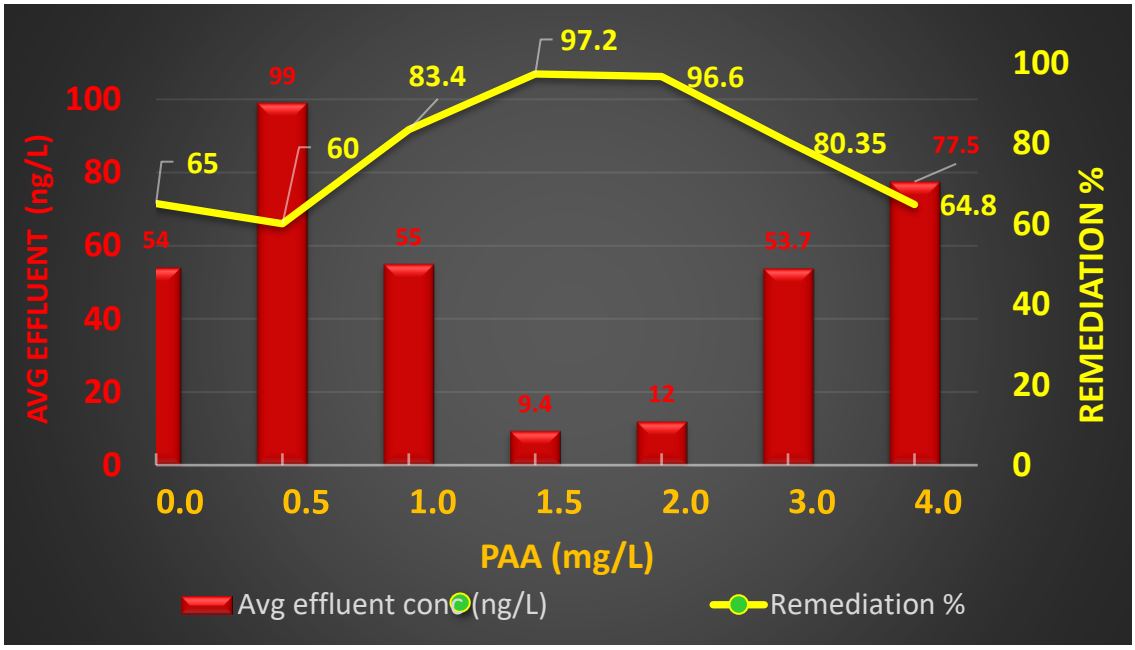

Figure 4: Effect of PAA Concentration on AOP of NDMA Using 5.5 mJ/cm^2 UV Dose of UV 220 nm.
Note: The effluent values are an average of 4 replicates.

observed when the PAA dose was increased beyond 1.5 mg/L. The remediation obtained at 2, 3 and 4 mg/L were 96.6%, 80.3% and 64.8%, respectively. This bell-curve like trend could be explained by the radicals generated under UV light and their scavenging ratios at different concentrations. The reaction of UV/PAA generates multiple radicals which

can react with the contaminant. But the radicals thus generated lack specificity of interaction and without optimization, a high number of radicals can breakdown PAA and react among themselves causing a decrease in the available radicals to remediate the contaminant.

Initially the UV/PAA reaction could have generated enough radicals to enhance the remediation of NDMA until an optimum PAA dose of 1.5 mg/L. But beyond this optimum dose, the remediation observed had a detrimental effect with increase in PAA dose. This could be attributed to the increased in non-specific radicals which could scavenge UV radiation and/or breakdown PAA while interacting with other radicals. This set of data stresses the importance of optimizing the remediation process for practical achievability. Rajala-Mustonen et al., 1997 documented the effects of PAA and UV irradiation on the inactivation of coliphages in wastewater. They explained the reactions that involve injecting PAA upstream to UV to obtain an average of 2-log increase in inactivation which corroborate our hypothesis.

The next step in this study was to investigate the effect of PAA dose on the remediation of NDMA while employing UV 254 nm. The UV doses depicted in Figure 3 were selected while varying the PAA dose. The results obtained while employing UV 254 nm at 115 mJ/cm^2 with varying PAA dose for an average influent concentration of NDMA at 554 ng/L in the remediation of NDMA is shown in Figure 5. Using UV 254 nm independently resulted in 14% NDMA remediation. Low PAA dose of 0.5 mg/L seemed to have a negative impact on NDMA remediation. This could be due to UV radiation being utilized for the breakdown of PAA resulting in lower remediation.

The remediation increased with increasing PAA doses resulting in 18.3% and 34% for 1 and 4 mg/L PAA, respectively. Higher PAA concentration could result in a

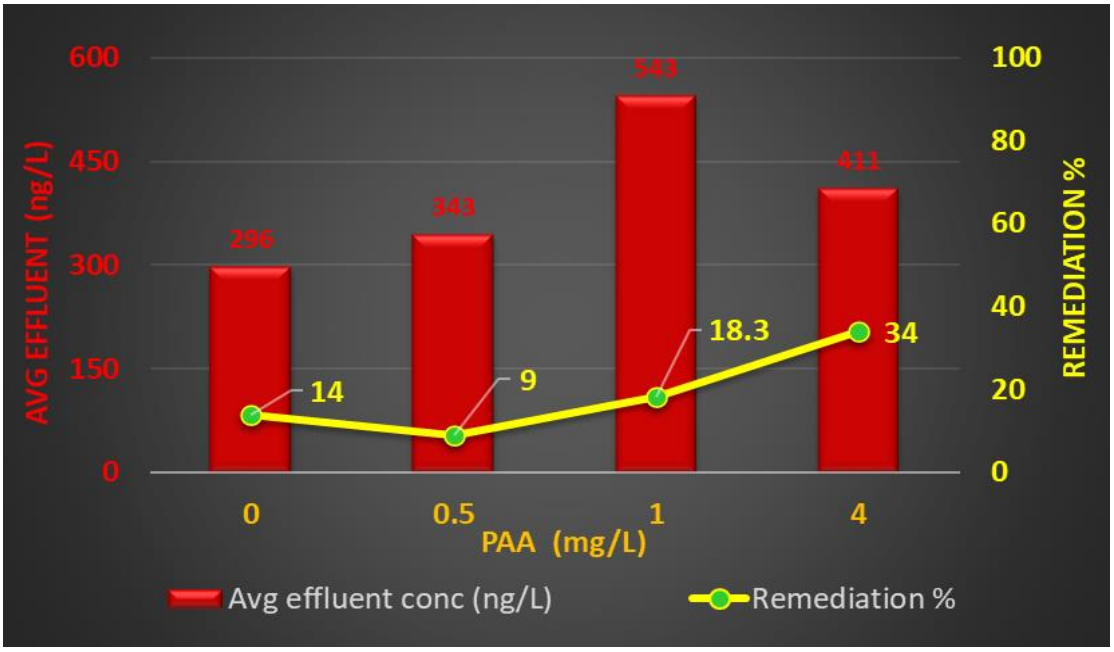

Figure 5: Effect of PAA Concentration on AOP of NDMA Using UV at 254 nm at Average UV Dose of 115 mJ/cm^2.
Note: The remediation value for PAA at 0 mg/L is extrapolated from Figure 3. The effluent values are an average of 4 replicates.

significant radical production and their availability for additional remediation after the initial demand in the system. Remediation of NDMA showed high dependency on PAA dose while employing low doses of UV.

The flowrate of the system was systematically reduced to obtain higher UV dose. UV dose of 354 mJ/cm^2 independently resulted in 81.5% remediation. While using a low PAA dose of 0.5 mg/L the remediation decreased to 60.5% remediation (Figure 6). The remediation decreased to 45% when the PAA dose was increased to 1. 5 mg/L and increased to 69.5% when the PAA dose was further increased to 4 mg/L.

The flowrate was further reduced to increase the UV 254 nm dose to 421 mJ/cm^2 and UV 254 nm independently resulted in high remediation of 85%. Although the trend

obtained in this set of experiments is similar to the one depicted in Figure 6, we observed higher remediation with higher doses of UV. For average influent NDMA concentration

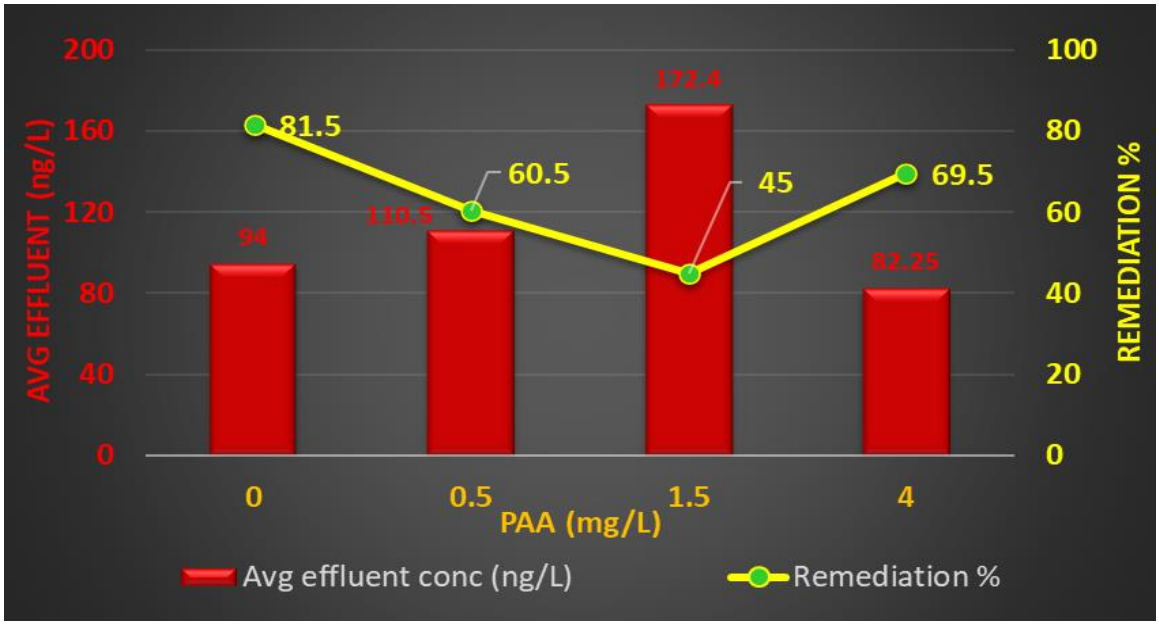

Figure 6: Effect of PAA Concentration on AOP of NDMA Using UV at 254 nm at Average UV dose of 354 mJ/cm^2.
Note: The remediation value for PAA at 0 mg/L is extrapolated from Figure 3. The effluent values are an average of 4 replicates.

of 225 ng/L, low PAA dose of 0.5 mg/L resulted in 51.15% remediation. However, increasing the PAA dose to 1.5 mg/L observed a negative effect on NDMA remediation, further increasing the PAA dose to 4 mg/L resulted in 62.5% remediation.

The similarities observed in the remediation trend depicted in Figures 6 and 7 are noteworthy and important in understanding the dependency and relationship between AOP doses and NDMA remediation. The mid-range UV doses employed, shows a drop in the NDMA remediation when the PAA concentration was increased from 0.5 to 1.5 mg/L and then the remediation increased with an increase in PAA concentration to 4 mg/L. At 0.5 mg/L, it is possible that the resulting reactive radicals are utilized for the

remediation of the target contaminant and when the PAA dose was increased to 1.5 mg/L, the scavenging of UV may have had a negative effect on the remediation.

As previously observed, when the PAA concentration was increased to 4 mg/L, the system might have been overpowered with PAA and thus the sheer quantity of

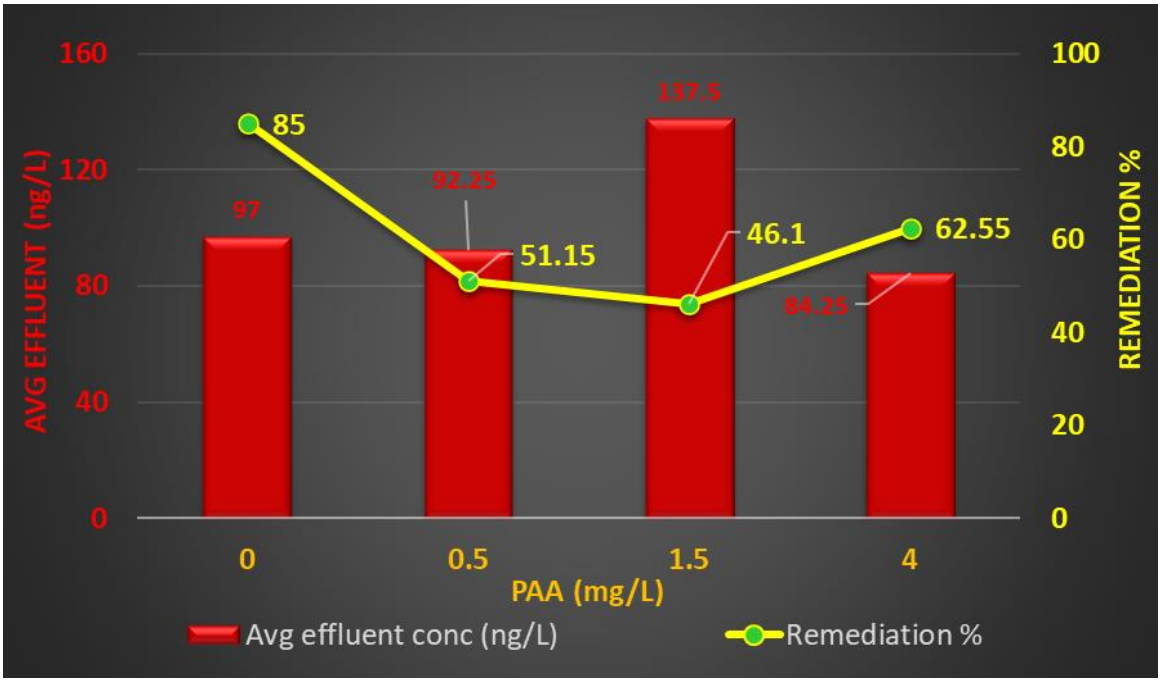

Figure 7: Effect of PAA Concentration on AOP of NDMA Using UV at 254 nm at Average UV Dose of 421 mJ/cm^2.
Note: The remediation value for PAA at 0 mg/L is extrapolated from Figure 3. The effluent values are an average of 4 replicates

radicals produced in the system resulted in a relatively higher NDMA remediation. The results depicted in Figures 6 and 7 proves the intricate relationship between NDMA remediation and PAA concentration at UV dosages.

Future research pertaining the measurement of the radicals formed during this process and their characterization would provide deeper knowledge of the reactions taking place in the reflective UV chamber.

Although the relationship of PAA and UV on NDMA remediation was established, the addition of PAA with UV 254 nm at a mid-range UV dosage of 300 –

421 mJ/cm^2 seemed to have a negative effect on the remediation of NDMA. The flowrate of the system was reduced to its minimum to investigate the PAA dose with a high

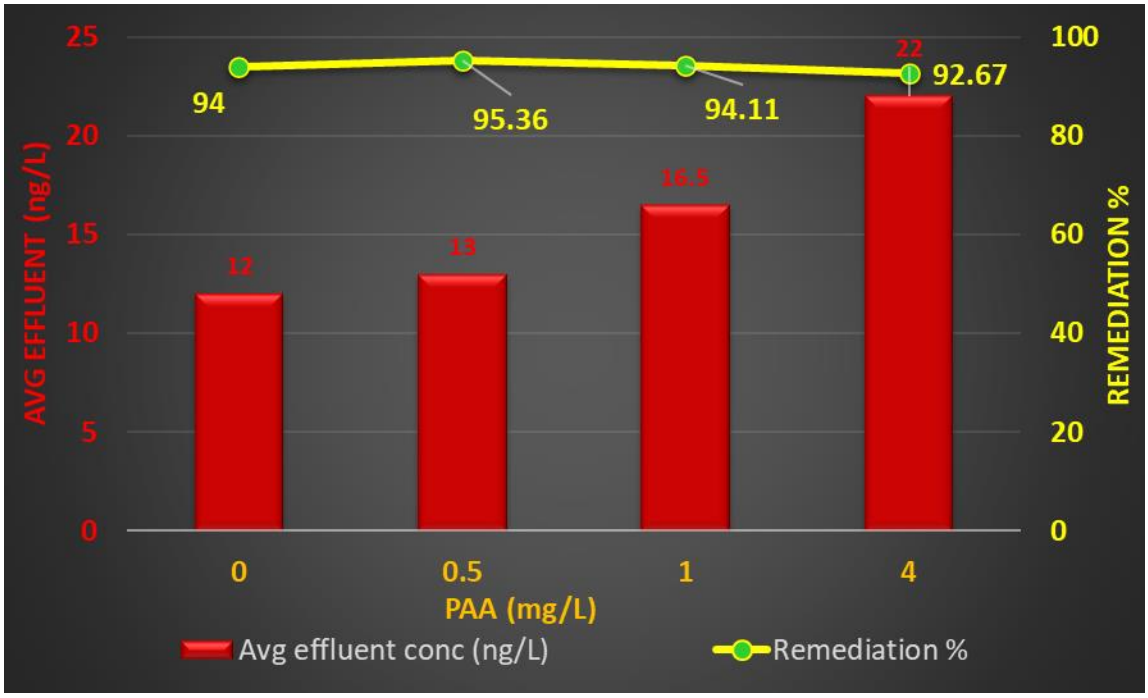

Figure 8: Effect of PAA Concentration on AOP of NDMA Using UV at 254 nm at Average UV Dose of 1,031.3 mJ/cm^2.
Note: The remediation value for PAA at 0 mg/L is extrapolated from Figure 3.
The effluent values are an average of 4 replicates.

average UV at 1,031.3 mJ/cm^2. This high UV 254 nm dose independently obtained 94% remediation. The results obtained while introducing PAA doses between 0.5 to 4 mg/L is shown in Figure 8.An average influent NDMA concentration of 286.6 ng/L was treated with UV at 1,031.3 mJ/cm^2 and varying PAA concentration. Irrespective of the PAA concentration, the experiments resulted in >90% remediation. At high UV of >1,000 mJ/cm^2, PAA had negligible effect on the remediation process.

NDMA was successfully remediated using UV at 254 and 220 nm. Different AOP approaches have been used in an attempt to obtain high NDMA remediation but most of the studies are conducted in a batch reaction condition which does not mimic the real-world application of the process. The combination of ozone and hydrogen peroxide by

Lee et al., 2007; obtained a highest remediation percentage of 75% when 7.7-15.4 mg/L of ozone was coupled with hydrogen peroxide. The issue of ozone handling, economic, production and the dose to achieve >70% remediation makes this process impractical to use in large scale applications.

A few bioremediation techniques have been studied for the remediation of NDMA. *Rhodococcus ruber* ENV425 is bacteria capable of co-metabolizing NDMA when grown on propane and was found to remediate >99.9% of NDMA with an ex-situ concentration of 12 µg/L and 30 min hydraulic residence time (HRT) (Webster et al., 2013). This technique is a good alternate treatment technology for select applications with low NDMA influent concentrations. Future studies on modifying organisms to metabolize higher concentrations of NDMA with lower HRT is necessary to make this process a strong practical alternate treatment technology.

The use of UV 254 and 220 nm with PAA resulted in a higher NDMA remediation. Using UV with reflective technology along with PAA resulted in higher remediation when compared to UV/O3/H2O2. The results obtained while using UV 254 nm indicated the ineffectiveness of PAA on the remediation while using UV higher than 500 mJ/cm^2. The remediation process consistently showed more dependency on PAA at lower UV doses while using UV 254 and 220 nm. Beyond a threshold PAA dose, the remediation decreased with increase in the PAA dose.

3.5 Conclusion

The dynamics of the results obtained using UV 220 nm /PAA was different from the ones obtained using UV 254 nm/PAA. The usage of an excimer lamp emitting UV at 220 nm with maximum UV dose of 5.5 mJ/cm^2 clearly showed the interdependency of UV and PAA. Even though the UV 220 nm with an excimer lamp is a lower powered UV system, the fact that its wavelength is similar to NDMA's UV absorption peak might have contributed to a high transformation efficiency of >95% at 1.5 mg/L of PAA and 5.5 mJ/cm^2 UV dose. The UV 254 nm on the other hand employed a low-pressure mercury lamp, capable of emitting an UV dose of more than 1,000 mJ/cm^2. Independently, UV 254 nm system was able to remediate 94.2% of the influent NDMA with a high UV dose of 1,060 mJ/cm^2. The effect of PAA dose on the remediation of NDMA while UV at higher than 400 mJ/cm^2 was either minimal or in some cases had a negative effect. Nonetheless, high remediation percentages of >90% were obtained while using UV dose of 450 mJ/cm^2.

Although, both UV 220 and 254 nm systems employing ReFLeX^{TM} technology resulted in more than 90% NDMA remediation, there are other factors such as energy efficiency, and type of application should be considered before choosing a remediation system. For point applications which are focused on in-situ remediation of NDMA, AOP involving UV 220 nm with reflective technology and optimized dose of PAA might prove to better suited. Applications which target multiple contaminants with a high-volume flow should consider UV 254 nm with reflective technology. Adding optimized PAA dose to applications with multiple target contaminants is a critical factor for a positive effect on remediation.

Although a majority of PAA studies are lab scale and stationery, they have promising results in the remediation of pharmaceutical products and emerging contaminants in water. Due to the hydroxyl stability and the additional radicals formed when it is activated by UV irradiation, PAA could be new alternative to H2O2 or O3¬ or Cl2. But before any practical application of PAA based remediation processes, studies focusing on determining factors like operational and design variables such as PAA dose and its effect on different water matrices should be performed.

While most of the UV studies on this topic are conducted under stationary conditions or in batch reactors, this study was conducted under dynamic flowing conditions which is an attempt to precisely depict the real-world application while conducting lab scale research for easier industrial scale-up of the remediation process.

4 AOP INVOLVING REFLECTIVE UV TECHNOLOGY AND PERACETIC ACID: A PROMISING ALTERNATE TECHNOLOGY IN THE TREATMENT OF 1,4-DIOXANE IN WATER

4.1 Abstract

1,4-Dioxane, a two-decade old emerging contaminant of concern in water systems has been continuously used in several industrial applications, personal care products and cosmetics. In 1999, IARC classified 1,4-dioxane as Group 2B - possible carcinogen with insufficient evidence of its effect on human health. In 2013, the U.S. EPA classified 1,4-dioxane as a likely carcinogen to humans by all routes of exposure. Physical remediation systems have largely been inefficient in the remediation of 1,4-dioxane in water and this is due to physical properties like high solubility, boiling point of 101°C and low Henry's constant. A few chemical/ AOP remediation strategies that have been explored for the treatment of 1,4-D in the past, have conducted experiments employing static batch reactions as their operational design. To improve the efficiency and scalability of the remediation systems, there is a requirement for remediation studies employing dynamic flow conditions to better mimic the real-world applications.

In this study, a chemical AOP system employing UV 254 nm with reflective technology and Peracetic Acid (PAA) was used in the remediation of 1,4-D in water under dynamic flow conditions. The remediation system was tested by applying varied UV and PAA doses independently which then led to optimized UV and PAA doses while employing AOP in the remediation of 1,4-D. Using an optimum PAA dose of 5 mg/L and UV doses of 460 and 780 mJ/cm^2, 1,4-D remediation of 76.9% and 96.2% respectively was obtained.

4.2 Introduction

1,4-Dioxane (1,4-D) is an aliphatic compound with a six membered carbon ring with oxygen atoms at 1 and 4. This belongs to the super class of Organoheterocyclic compounds and is used as a stabilizer while using chlorinated solvents, especially 1,1,1 – trichloroethane (TCA) and as a solvent (Mohr, 2010). Even though the use of TCA decreased in the 1990s, 1,4-D has been continued to be used as solvent for oils, paints, coatings, and plasticizers and in residues of personal care products (PCPs), cosmetics (Mohr, 2010).

The International Agency for Research on Cancer (IARC) classified 1,4-D as a Group 2B agent or a possible carcinogen. Even though its effect on humans is not studied adequately, carcinogenicity studies conducted on experimental animals provide strong evidence as a carcinogen (IARC, 1999). In 2009, studies which chose rats and mice as test subjects observed 1,4-D exposure increased the occurrence of tumors (Kasai et al., 2009; Kano et al., 2009). The U.S. EPA's Integrated Risk Information System (IRIS) determined the toxicity profile of 1,4-D and recorded different reference values based on modes of ingestion. Accordingly, based on toxicity studies on liver and kidneys, the chronic reference dose reported for oral ingestion (RfD) is 0.03 mg/kg/day; based on the atrophy and respiratory metaplasia in the nasal cavity of experimental animals a chronic reference dose for inhalation (RfC) of 0.03 mg/m^3 is reported (ASTDR, 2012). In 2013, even the U.S. EPA recognized and classified this compound as a likely carcinogen to humans and provided a Health Advisory Level (HAL) of 0.35 µg/L for 1,4-D in drinking water (U.S. EPA, 2013c).

1,4-D has a low Henry's constant (4.80 * 10^{-6}atm-m^3/mol at 25°C), low K_{ow} (Log K_{ow}: -0.27) and low K_{oc} (Log K_{oc}: 1.23) which restricts the efficiency of highly sensitive, rapid analytical approaches and remediation technologies like air stripping, soil vapor extraction and thermal desorption for 1,4-D polluted waters (U.S. EPA, 2013c). The historical usage of 1,4-D and improper storage and disposal of 1,4-D has resulted in mixed matrices of 1,4-D along with other common contaminants in ground and industrial waste waters.

1,4-D is not only produced as a by-product of industrial processes but also widely used at various stages in production facilities especially associated with tricholoroehtylene (TCE). In 2012, a study reported 94% of the groundwater monitoring wells containing detectable levels of 1,4-D along with trichloroacetic acid (TCA) and TCE (Anderson et al., 2012). However, most of the ground water studies for 1,4-D fail to consider its presence independent of its association to TCE and TCA. In 2010, a study report 64% of the detected 1,4-D in groundwater wells were independent of TCA and TCE (Mohr, 2010). This not only presents 1,4-D at an increased threat to human life but also warrants further investigation with regards to the association of 1,4-D with TCE in identified TCE plumes and other plumes with mixed chlorinated solvents. An example of this is: 1,4-D (1.1 to 340 mg/L) was found with TCE (0.72 to 650 mg/L) at United States Air Force Plant No. 44 (AFP 44) aquifers (Chiang et al., 2012). Poly- and per-fluorinated compounds were found at 1,4-D contaminated sites (Zhang et al., 2017).

4.2.1 Physical treatment of 1,4-Dioxane

The difficulties for employing physical remediation systems for 1,4-D can be attributed to certain properties of the compound. 1,4-D as a compound has high solubility

and low Henry's constant which make physical treatment techniques like thermal destruction and air stripping, which are usually applied to remediate highly volatile non-aqeuous phase liquids, unlike 1,4-D ineffective (Triplett-Kingston et al., 2010). The high energy consumption associated with treating large volumes of 1,4-D contaminated water renders this technology economically non-viable. Distillation is another physical treatment technology which can be used to separate compounds with different boiling points, but 1,4-D has a boiling point of 101°C and due its proximity to the boiling point of water, which is 100°C, distillation is non-feasible in the treatment of 1,4-D in water (Vescovi et al., 2010; Mohr, 2010).

The usage of activated carbon to adsorb 1,4-D from water is another alternate physical treatment technology which is successfully used to treat organic compounds like TCE, inorganic metals like copper and zinc which can be adsorbed using granular activated carbon (GAC) (Nakano et al., 2000). Until recently, air stripping and GAC were not even considered as viable treatment techniques for 1,4-D. In the year 2014, there was a study which used unique sorbents, in particular Ambersorb™560 which was a polymeric adsorbent synthesized by the Dow Chemical Company with high surface area, hard, high porosity, spherical in shape with high removal efficiency for 1,4-D, along with other organic contaminants (Woodard et al., 2014). Even though this ensured efficient adsorption of 1,4-D, this technology results in concentrating 1,4-D on the sorbent rather than remediating it to less harmful by-products. Thus, the usage of this technology raises questions of the long-term stability of the adsorbent and risk of contamination in the ground water plumes.

4.2.2 Chemical Treatment of 1,4-Dioxane

1,4-D is a persistent contaminant in the environment (Zenker et al., 2000). Therefore, aggressive strategies involving strong chemical oxidants are considered for the treatment of 1,4-D. The UV absorption spectrum of 1,4-D peaks at 165 nm to 191 nm because of which conventional direct photolysis has reduced effect on the treatment of this compound (Pickett et al., 1951; Kruithof et al., 2007). In-situ photolysis of 1,4-D has been reported to have operational challenges (Mohr, 2010). The focus shifted to Advanced Oxidation Processes (AOPs) using UV with Hydrogen peroxide (H_2O_2) in the 1960s to increase the effectiveness of chemical treatment technologies for this compound. These systems relied on the formation of photon induced highly reactive species which significantly increased the efficacy of treatment of organic chemicals in water (Matsushita et al., 2015; Omura & Matsuura., 1968). H_2O_2 was irradiated with UV light to form hydroxyl radicals which are non-selective highly reactive species. These radicals then acted on the target organic pollutant which in this case 1,4-D and oxidized it through different pathways (Stefan & Bolton., 1998) to result in the release of carbon dioxide at the end of the reaction chain. Formation of reactive radicals is the first step in the remediation reaction mechanism. These radicals then react with 1,4-D to result in 1,4-D radicals which undergo the tetroxide reaction to form 1,4-Dioxan-α-oxy radical. The cyclic structure is then broken down to form ethylene glycol diformate and methoxyacetaldehyde. Ethylene glycol diformate turns into ethylene glycol, which is then converted to glycolic acid, oxalic acid and then finally to carbon dioxide. Methoxyacetaldehyde is converted to formaldehyde which gets converted to formic acid

which then finally gives out carbon dioxide (Zhang et al., 2017). 1,4-D is remediated in this pathway to result in the release of carbon dioxide and water by using UV/H_2O_2.

Due to the short exposure times and high remediation capabilities, AOP is usually the selected method for the treatment of 1,4-D. Studies reported 96% of 1,4-D in a 2h reaction time using H_2O_2 (Kim et al., 2006); over 99% remediation in a 10h reaction time involving both H_2O_2 and ferrous ions (Klecka & Gonsior, 1986); and a 12.2h half-life was reported when peroxone activated persulfate was used in the remediation of mixtures containing 1,4-D and chlorinated compounds (Eberle et al., 2016).

To explore different AOP possibilities, there was a study in 2016 which used multiple oxidative agents in the remediation of 1,4-D (Ikehata et al., 2016). This study employed ozonation along with four other AOPs: O_3/H_2O_2, O_3/UV, O_3/ H_2O_2/UV and UV/H_2O_2, which were used to evaluate the treatment of polluted groundwater at a Superfund site in Simpsonville, SC. They recorded highest remediation when O_3/H_2O_2 with doses 6mg/L and 1.5 mg/L respectively, UV/H_2O_2 with doses of 1,000 mJ/cm^2 and 20mg/L, respectively were employed in the remediation of 1,4-D. An influent concentration of 200 µg/L was remediated down to performance standard concentration of 10 µg/L of 1,4-D using the above-mentioned doses.

The ever-increasing number of 1,4-D contaminated sites have led the investigation of other remediation processes involving zero valent iron, H_2O_2, ozone, persulfate and peracetic acid which are known to enhance the remediation of 1,4-D in water systems. These compounds can directly generate highly reactive species like hydroxyl radicals and sulfonate radicals which are known to decompose organic contaminants on their own (Zhou et al., 2015; Merayo et al., 2014). These oxidation

reactions in certain applications can also be indirectly activated, such as: the addition of Fe^0 and Fe^{2+} significantly improved the removal of 1,4-D while using sonication (Son et al., 2006). Furthermore, remediation studies using advanced electrochemical oxidation (AEO) during which hydroxyl radicals are generated, has shown promising results in the remediation of 1,4-D (Jasmann et al., 2016). The most important factor which proves that the process of AOP is apt for the treatment of 1,4-D is the fact that the by-products of this reaction are mostly low molecular weight fatty acids like glycolic and formic acids which can easily be subjected to bioremediation systems and effectively handled (Merayo et al., 2014).

Over the years, chemical remediation systems employing UV/AOP have often focused on the usage of just a few specific chemicals like H_2O_2 and ozone in static lab conditions using batch reactors to test the efficiency of the remediation systems. In this paper, we focus on the developing a new treatment system for 1,4-D in water under dynamic/flowing conditions which would mimic the real-world applications. AOP employing PAA will be used along with UV 254 nm with reflective technology to explore an alternative treatment technology. 1,4-D will be subjected to PAA, UV 254 nm and UV/PAA to understand the dependency of the remediation of 1,4-D on each of the conditions, respectively. The objective of this paper is to develop an alternate treatment technique under dynamic flowing conditions employing AOP and report appropriate doses of UV and PAA to achieve the remediation of 1,4-D to acceptable standard concentrations.

4.3 Materials and Methods

4.3.1 UV with Reflective Technology

The UV system consisted of a low-pressure UV lamp which emits radiation at 254 nm/185 nm. This system was uniquely equipped with ReFLeX^{TM} technology in its chambers patented to NeoTech Aqua solutions (San Diego, CA). Unlike the conventional UV systems, the lamp sleeve of this system is lined with reflective quartz coating which is designed to ensure 99% of the UV radiated emitted by the lamp to be reflected back thereby ensuring enhanced remediation and energy efficiency. The low pressure-lamp employed in the system had two output peaks: 254 nm (35% efficient) and 185 nm (7% efficient).

4.3.2 Experimental Plan

The influent tank consisted of a 15 L polyethylene container with tap water having a residual chlorine level of 0.5-1.2 ppm. To ensure non-reactivity of 1,4-D, sodium thiosulphate was used to neutralize the residual chlorine. The tap water UV transmittance (UVT) was 90% and average specific UV absorbance (SUVA) was 1.8 L/mg-m. The influent water was then spiked with realistic concentration of 1,4-dioxane (Sigma-Aldrich Corporation) and was mixed thoroughly to ensure homogeneity. The 1,4-D spiked influent water was then pumped using AMT® model C63JXGWU-1114/Iwaki Magnetic pump model MD-70RLZT at varying flowrates to the UV system with one inch and half inch piping, respectively. PAA (Sigma-Aldrich Corporation) was injected upstream to the influent tank using a peristaltic pump (FMI “Q” Pump, model QG50). Duplicate influent and effluent samples were collected before and after every

experimental run. Multiple experiments were conducted with varying PAA and UV dose for the remediation of 1,4-D in water.

4.3.3 Analysis

The influent samples with 1,4-D spiked tap water and duplicates of effluent samples after the treatment were collected and submitted to Scottsdale Water Campus. These samples were analyzed in accordance with EPA's method 522 – Determination of 1,4-Dioxane in drinking water by Solid Phase Extraction (SPE) and Gas Chromatography/Mass Spectrometry (GC/MS) with Selected Ion Monitoring (SIM). The summary of the method as stated by the U.S. EPA is as follows:

Each 500 mL sample (influent and effluent) was passed through an SPE cartridge containing 2g of coconut charcoal to extract the method analyte and SUR. Then the compounds were eluted from the solid phase with a small amount of dichloromethane (DCM) – 9 mL. The extract volume was adjusted and the IS, tetrahydrofuran-d8 (THF-d8), was added. Then finally, the extract was dried with anhydrous sodium sulfate. The analysis of this extract is then performed using GC/MS. The data provided in this method were collected using split-less injection with a high-resolution fused silica capillary GC column that was interfaced to an MS operated in the SIM mode. The analyte, SUR and IS are separated and identified by comparing the acquired mass spectra and retention times to reference spectra and retention times for calibration standards acquired under identical GC/MS conditions. The concentration of the analyte is determined by comparison to its response in calibration standards relative to the IS. The data thus provided was then analyzed, interpreted and the efficiency of the selected AOP technique was reported (Munch & Grimmett, 2008).

4.4 Results and Discussions

The experiments were conducted using the four variables presented in Table 2.

Table 2: 1,4-Dioxane Remediation Experimental Variables.

Variables	Set Points Tested					
Inf 1,4-D (mg/L)	5 – 45					
UV Dose (mJ/cm^2)	115 – 1,050					
UV Wavelength (nm)	254					
PAA (mg/L)	1	2	3	4	5	7

1,4-D was irradiated with different UV doses by varying the flowrate of the system, to observe and study the effect of varying residence times and UV doses on the remediation process. Once this baseline was established, the new AOP was applied to the remediation process by employing UV 254 nm with reflective technology and PAA. Initially the PAA dose was set to 1 mg/L and then it was systematically increased until a sudden drop in the percent remediation of 1,4-D was observed. This could be explained by the phenomenon of radical scavenging. At a threshold PAA dose, most of the radicals produced act on the contaminant to achieve high remediation. Beyond this PAA dose, part of the radicals produced are scavenged for breaking down the extra PAA in the system which in turn limit the interactions between the target contaminant and the reactive oxidative species. This study was conducted using dynamic flow conditions which is aimed at increasing the ease of scaling up this remediation process to suit real-world applications. The experiments were conducted under three major conditions: UV alone, PAA alone and AOP with UV/PAA. The results of these three conditions are presented below.

Primarily, recording the extent of remediation of 1,4-D with UV irradiation alone was important to understand the capabilities of the new UV system employing reflective technology. As shown in Figure 9, average influent concentrations of 5-7 mg/L 1,4-D were subjected to remediation with varying UV doses.

The efficiency of the reflective UV technology to remediate 1,4-D in water was tested in this set of experiments. Highest remediation of 92% was achieved while irradiating a UV dose of 1,031 mJ/cm^2. The remediation reduced to 54% and further to

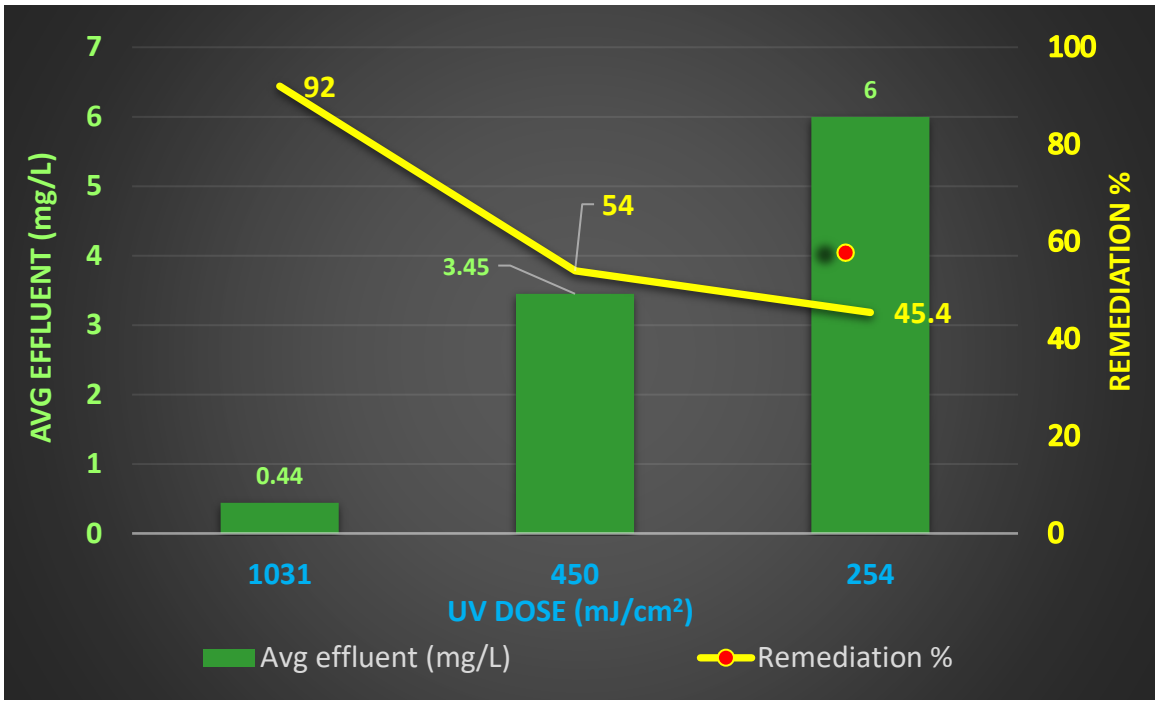

Figure 9: Remediation of 1,4-D with Varying UV Doses.
Note: The effluent values are an average of 4 replicates.

45.4% when the UV dose was reduced to 450 and 254 mJ/cm^2 respectively. In order to achieve varying UV doses, the flow rate of the system was changed for each run. This changed the hydraulic residence time of the influent water which resulted in different percent remediations. The results presented in Figure 9 provided a strong baseline performance of the UV system which was a key factor in designing a new AOP treatment technique for the remediation of 1,4-D.

The next step in the experimental phase was to create a baseline for the remediation of 1,4-D using PAA alone in dynamic flow conditions. For this 2.5 GPM was chosen to be the flowrate and PAA doses of 1-5 mg/L were applied to an average influent 1,4-D concentration range of 11-18 mg/L. We observed an increase in the percent remediation of 1,4-D with an increase in the PAA dose. Remediation of 2.5, 3.6, 5.2, 6.8 and 14.6% were observed for PAA doses of 1, 2, 3, 4 and 5 mg/L, respectively. PAA has a redox potential of 1.78 V which is very comparable to 1.8 V of H_2O_2. The main objective of this set of experiments was to establish PAA as a viable alternative to H_2O_2 in AOPs designed to treat 1,4-D. Most of the studies that use H_2O_2 are conducted in batch reactor conditions and resulted in 90% remediation while having contact times in multiple hours. The results depicted in Figure 10 report 1,4-D remediation of 14.6%

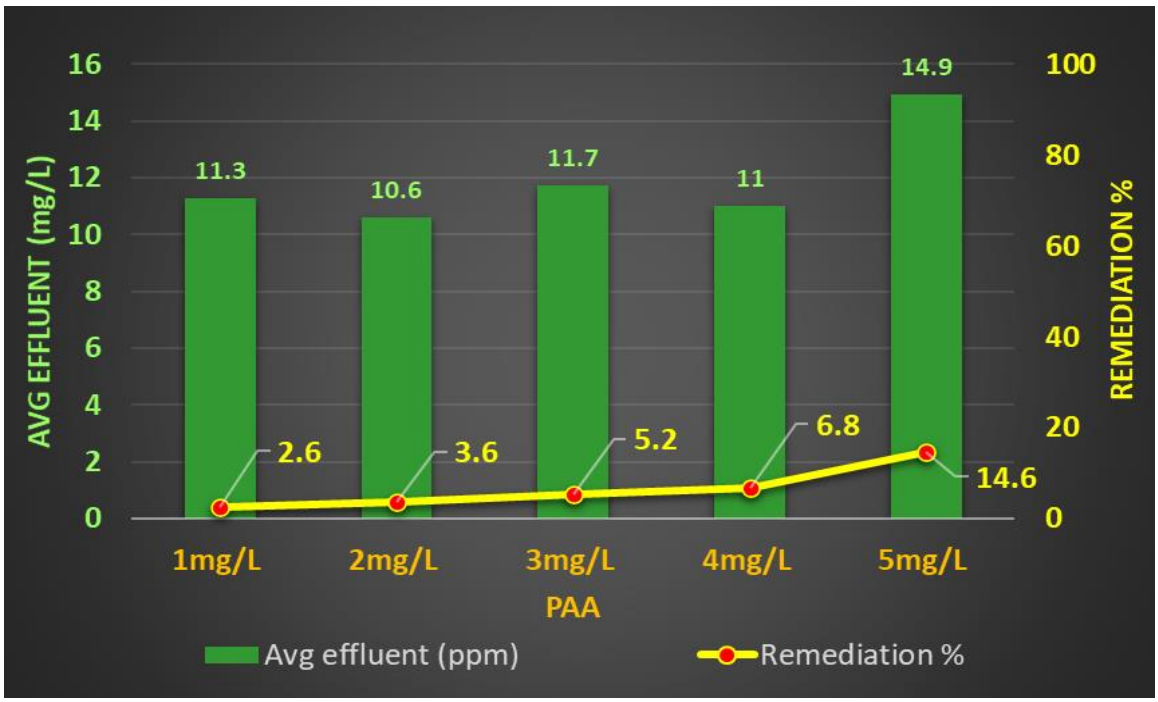

Figure 10: Remediation of 1,4-D Using Varying PAA Doses (2.5 GPM Flowrate). Note: The effluent values are an average of 4 replicates.

while using 5 mg/L PAA dose under dynamic flow conditions. Obtaining a considerable percentage of remediation in a few seconds of contact time establishes the independent

ability of PAA to remediate 1,4-D and further emphasizes on the requirement of future comparative remediation studies for PAA and H_2O_2 under similar conditions.

The last phase of this study was to formulate a new AOP technique using UV 254 nm with reflective technology and PAA for the remediation of 1,4-D by optimizing the PAA dose and UV dose for the remediation system. Varying PAA doses of 1-7 mg/L

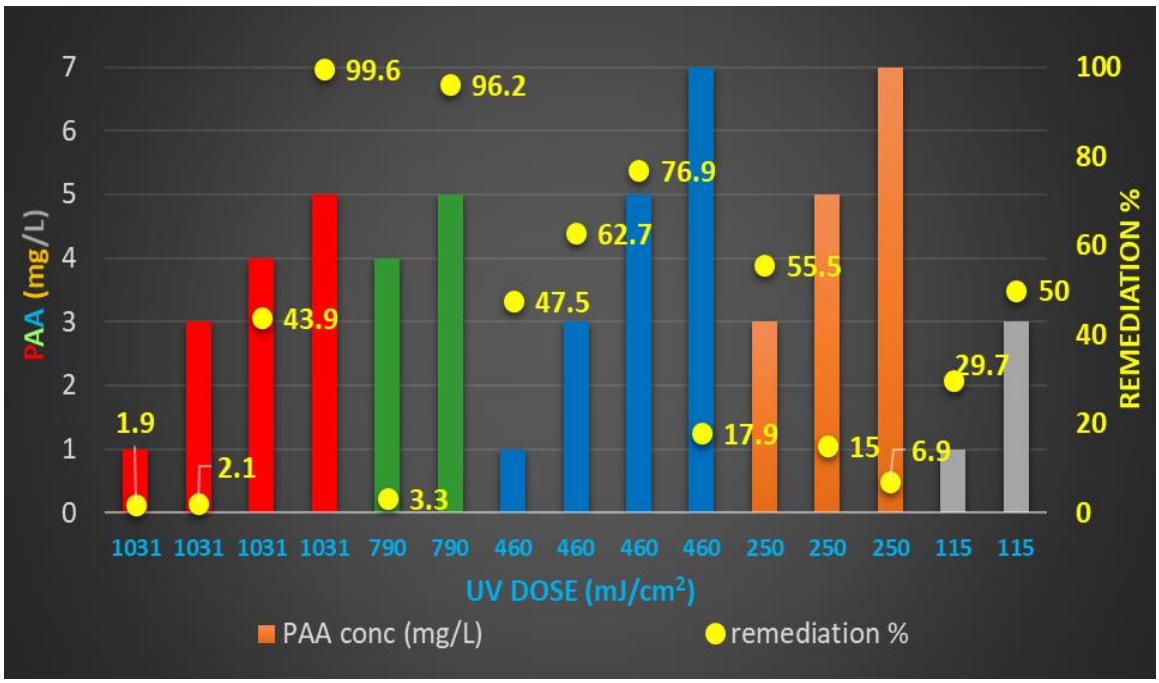

Figure 11: AOP of 1,4-D with Varying UV and PAA Doses.
Note: The remediation values are the average of 4 replicates.

were applied with a range of 115 – 1031 mJ/cm^2 UV doses in the remediation of 1,4-D. The results that were obtained are depicted in Figure 11. While applying an average UV dose of 1,031 mJ/cm^2, four doses of PAA ranging from 1-5 mg/L were administered for the remediation of an average 1,4-D influent concentration of 22.8 mg/L. Varying percent remediations were recorded and is depicted in Figure 11. Systematically increasing the PAA dose from 1 mg/L to 5 mg/L resulted in the remediation to increase from 1.9% to 99.59%. Even though the UV dose used is high, this set of results corroborates our

hypothesis of successfully using AOP involving UV/PAA as an alternate remediation technique for 1,4-D in water.

In order to further optimize the process and study the effect of change in UV dose with similar PAA doses, the UV dose was systematically decreased.

An average UV dose of 790 mJ/cm^2 was used along with 4 and 5 mg/L of PAA to remediate an average influent 1,4-D concentration of 10.45 mg/L. The results of these experiments, as depicted in Figure 11, showed promise for lab scale applications and in the design of in-situ remediation systems for point sources. While application of the lower PAA dose of 4 mg/L resulted in 3.33% remediation, increasing the dose to 5 mg/L resulted in improving the percent remediation to 96.2%. The impact of varying the PAA dose on the remediation was observed and the importance of optimizing UV/PAA doses was established by this set of experiments. Below an optimum dose of PAA, the system might not have been able to generate enough radicals to effectively treat the contaminant. For an average UV dose of 790 mJ/cm^2, an optimum PAA dose of 5 mg/L was established.

The average UV dose was further reduced to 460 mJ/cm^2 and PAA doses ranging from 1-7 mg/L were administered for an average 1,4-D influent concentration of 14 mg/L. The results of this, as depicted in Figure 11, clearly indicate the negative effects of overdosing PAA in the remediation process. The percent remediation increased from 47.5% to 76.9% when the PAA dose was increased from 1mg/L to 5 mg/L. This can be associated with increased radical formation, most of which would have been used to remediate the contaminant. Beyond this optimum PAA dose, the percent remediation reduced to 17.9% when 7 mg/L PAA was applied to the remediation process. At this

PAA dose, the radicals generated might be scavenged to breakdown PAA itself, leaving fewer radicals to destabilize the contaminant and thereby reducing the percent remediation of 1,4-D.

In order to further explore the possibility of using lower UV doses and to record the performance of the UV system with reflective technology, the UV dose was reduced to 250 mJ/cm^2 and was administered along with a PAA dose range of 3-7 mg/L to remediate an average 1,4-D influent concentration of 8 mg/L. The lowest PAA dose of 3 mg/L resulted in the highest percent remediation of 55.5%. The percent remediation steadily decreased to 15% and 6.9% when the PAA dose was increased to 5 and 7 mg/L respectively. Similar results were observed when the UV dose was further dropped to 115 mJ/cm^2 and was applied with PAA doses of 1 and 3 mg/L to remediate an average 1,4-D influent concentration of 4 mg/L. The percent remediation increased from 29.7% to 50% when the PAA dose was increased from 1 to 3 mg/L respectively. Both sets of experiments clearly present the AOP involving low doses of UV with reflective technology along with an optimum PAA dose of 3 mg/L as an effective alternate treatment technique for the in-situ remediation of 1,4-D in water.

Being the first AOP with UV/PAA experiments performed under dynamic flow conditions with reflective UV, this study shows a lot of promise while exposing huge research gaps in the remediation of emerging contaminants such as 1,4-dioxane from water systems.

4.5 Conclusion

1,4-Dioxane (1,4-D) has been an emerging contaminant of interest in water since the year 1999, when the IARC classified it as a group 2B agent which is a potential carcinogen (IARC, 1999). In 2013, the USEPA recognized the threat and classified 1,4-D as a likely carcinogen to humans (U.S. EPA, 2013c). With more than two decades of time and increased number of 1,4-D industrial uses, a RfD of 0.03 mg/kg/day, a RfC of 0.03 mg/m^3 and a Health Advisory Level of 0.35 µg/L; 1,4-D has become a major human health risk in industrial effluents and water systems (ATSDR, 2012). 1,4-Dioxane is an aliphatic compound belonging to the superclass of Organoheterocyclic compounds and is used in several industrial applications till this day for paints, coatings and plasticizers, oils, personal care products and cosmetics (Mohr, 2010). With physical properties like high solubility, low Henry's constant, and boiling point of 101°C, 1,4-D proves to be a challenge and limits the effectiveness of physical remediation systems like thermal destruction, air stripping and distillation (Triplett Kingston et al., 2010; Vescovi et al., 2010).

The requirement of aggressive strategies to deal with the issue of 1,4-D shifted focus to using AOP techniques like UV/H_2O_2, O_3/UV etc. There are studies which used more than 1,000 mJ/cm^2 UV dose (conventional UV system) along with 20 mg/L of H_2O_2 (redox potential of 1.8V) to achieve more than 90% remediation of 1,4-D in water (Ikehata et al., 2016) but alternate AOP approaches to mitigate the risk of 1,4-D in water is relatively unexplored. This study is aimed at exploring other alternative remediation processes employing AOP involving a seldom used chemical compound – PAA (redox potential of 1.7V). Most of the available literature on remediation studies of 1,4-D have

been conducted in static batch conditions which are challenging to translate into real world applications for situ-remediation strategies.

The objective of this paper was exploring an alternate treatment technique under dynamic flowing conditions employing AOP and report appropriate doses of UV and PAA to achieve the efficient remediation of 1,4-D in water. This involves the use of a UV system with reflective technology and a low-pressure mercury lamp which emits radiation at 35% of 254 nm and 7% of 184 nm. To further enhance the remediation of 1,4-D, PAA was introduced to the remediation process as the oxidant radical generator. This is an unexplored alternative, with higher hydroxyl stability in comparison to the frequently used O_3 and H_2O_2.

To develop a baseline performance of the UV system with reflective technology, 1,4-D remediation experiments were conducted using UV alone at three varying levels of UV dose. The highest percent remediation of 92% was obtained while using 1,031 mJ/cm^2 of UV. The percent remediation then decreased with decrease in the UV dose. Percent remediations of 54% and 45.4% were achieved while employing 450 and 254 mJ/cm^2 UV. This set of experiments corroborated the capability of the UV system with reflective technology to remediate a considerable concentration of the 1,4-D independently. To develop an AOP technique using UV/PAA, it was important to explore and study the ability of PAA to remediate 1,4-D independently in dynamic flow operational design.

PAA doses ranging from 1-5 mg/L was applied to 1,4-D containing influent water at 2.5 GPM flowrate. The percent remediation steadily increased from 2.58% for 1 mg/L PAA to 14.57% for 5 mg/L PAA. The gradual increase in the remediation trend showed

promise for the usage of PAA as an effective alternate oxidant radical generator in a new AOP system designed for enhanced remediation of 1,4-D in water.

To optimize the AOP involving UV/PAA varying UV and PAA doses were applied to the remediation of 1,4-D in water. A high UV dose of 1,031 mJ/cm^2 was used along with PAA doses ranging from 1 – 5 mg/L. The highest percent remediation was obtained was 99.6% with 5 mg/L PAA. Reduced UV doses of 790 and 460 mJ/cm^2 were then applied to the remediation process along with PAA doses ranging from 1-7 mg/L resulted in optimized AOP technique for the remediation of 1,4-D in water. High percent remediations of 96.2% and 76.9% was obtained while applying 790 and 460 mJ/cm^2 UV respectively along with an optimized PAA dose of 5 mg/L. These UV and PAA doses are well within practical achievability and remediate a high percentage of 1,4-D in water.

5 MICROBIAL RISK REDUCTION IN SOURCE WATER: INACTIVATION OF *E. COLI, LEGIONELLA , MYCOBACTERIUM* AND *ASPERGILLUS* SPORES USING UV WITH REFLECTIVE TECHNOLOGY AND AOP INVOLVING UV/PAA

5.1 Abstract

Drinking water supply in the U.S. is dependent on surface and ground water. Although the Surface Water Treatment Rules (SWTRs) governs detailed regulations for the treatment of surface water, groundwater is not required to be treated by the water treatment facilities before pumping it into the public water distribution systems. In 2014, a study reported 150 million people in the U.S. primarily depend on groundwater as their water source. Microbial contamination of groundwater has been a growing concern for drinking water safety in the recent years. Opportunistic pathogens (OPs) like *E. coli* and *Legionella* are known to transport through soil and aquifers; thereby entering the drinking water systems and thus, pose potential public health concerns.

Disinfection is the last step in the conventional water treatment process. Disinfection by chlorination and UV irradiation are the most commonly used technologies in conventional treatment trains. Although these disinfection technologies are effective in the inactivation of a wide variety of microorganisms, OPs like Non-Tuberculosis *Mycobacterium* (NTM) and fungal spores are structurally resistant to UV disinfection and chlorination. According to the SWTRs, water treatment facilities are required to achieve 4 log inactivation of viruses, 3 log inactivation of *Giardia lambia* and 2 log inactivation of *Cryptosporidium* before releasing the water into the public water distribution systems. Most of the OPs do not have either a Maximum Contaminant Level Goal (MCLG) or Maximum Contaminant Level (MCL) due to existing inefficient

remediation and quantification techniques or due to the risk assessment studies made by the U.S. EPA. Either way, there is a requirement for studies focusing on developing an effective alternative technology to mitigate public health concerns related to drinking water contamination.

In this study four microorganisms of varying UV susceptibility were selected and applied in the investigation of new disinfection technology involving UV 254 nm with reflective technology and Peracetic Acid (PAA). *E. coli, Legionella pneumophila, Mycobacterium avium* and *Aspergillus* spores were selected for this study based on their UV susceptibility and associated pathogenic health concerns.

The main objective of this study is to develop efficacious methods for the inactivation of selected microbial pathogens of public health concerns from source water. Specific research objectives include: 1) To evaluate the performance of UV with reflective technology involving UV/PAA for the effective inactivation of selected microorganisms. 2) To formulate new AOP technology involving UV/PAA for the effective inactivation of selected microorganisms. 3) To optimize UV and PAA doses to achieve a high inactivation of *E. coli, Legionella , Mycobacterium* and *Aspergillus spores.* This study is the first to use AOP involving UV/PAA in the inactivation of *Aspergillus niger* spores and *Mycobacterium avium* under dynamic flow conditions with reflective UV technology.

E. coli is known to inhibit in the lower gastrointestinal tract of humans and warm-blooded animals. It generally enters the environmental as a result of fecal contamination and pathogenic strains of the selected microorganism is known to be the reason of 2 million deaths every year. Although *E. coli* is considered to be susceptible to

UV irradiation, this microorganism was chosen to create a baseline performance of the UV system with reflective technology. When the microorganism of interest was subjected to varying doses of low-range UV, a highest of 7.4 log inactivation was observed at a UV dose of 150 mJ/cm^2. To record the enhanced remediation obtained by the new AOP technology, 0.5 mg/L PAA was injected upstream and varying doses of UV were applied, highest inactivation of 9.3 log was achieved using UV dose of 150 mJ/cm^2.

Legionella is known to be huge contributor to the issue of waterborne diseases in the U.S. Mild exposure causes Pontiac fever and in cases of major exposure it causes Legionnaires' disease which displays pneumonia like symptoms. Combined with pathogenic capabilities and physical properties which facilitate the survival of *Legionella* in undesirable environments like high temperature make *Legionella pneumophila* an important microorganism of concern. Additionally, they can parasitize protozoan cells and survive as a part of their biofilm, and thereby posing a challenge for their disinfection from drinking water systems. In this study, *Legionella pneumophila* was subjected to enhanced remediation using varying UV dose with reflective technology. A highest of almost 6 log inactivation was achieved with a low range UV dose of 115 mJ/cm^2.

NTM caused pulmonary infections have been cause of growing public health concern, especially in people with pre-existing conditions. In the U.S. a national average of $194 million dollars are spent on hospitalizations related to NTM caused health issues. Researchers have called this organism a biofilm pioneer because of its ability to enter amoeba cells and thrive in protozoan biofilms present in the water distribution systems even in the presence of residual disinfectant concentration. Due to their hydrophobic cell walls, they are resistant to conventional treatment trains, can easily aerosolize.

Mycobacterium avium which is also a part of the NTM family is the third microorganism selected in this study. The microorganism of interest was irradiated with low, medium, and high range of UV 254 nm with reflective technology. The highest of 3.44 log inactivation was achieved using a high range UV dose of 1068 mJ/cm^2.

The fourth microorganism selected for this study is *Aspergillus niger* spores. The issue of mass propagation of fungi has been considered a threat to drinking water safety and has attracted a lot of attention in the recent years. Generally fungal spores are known to be extremely resistant to conventional UV disinfection. The robust characteristics these spores are a direct result of their cell wall composition which is mainly made up of polysaccharides. *Aspergillus* species are known to be the most prevalent genera of fungi in water environments and can cause four different types of Aspergillosis. In this study, *Aspergillus niger* spores were subjected to both UV irradiation and AOP involving UV/PAA. A highest of 0.83 log inactivation was achieved with low range UV dose of 225 mJ/cm^2. AOP of the fungal was conducted under varying doses of UV and PAA. While injecting 2 mg/L of PAA and applying medium range UV dose of 530 mJ/cm^2, a highest of 2.08 log inactivation was achieved. This accurately displayed the efficaciousness of the new AOP technology in achieving enhanced microbial inactivation in water.

5.2 Introduction

Drinking water supply in the United States (U.S.) is derived from both surface water and ground water. Although there are very specific and detailed regulations for the treatment of surface water, water treatment facilities are not required to treat ground water before releasing it to the public water distribution systems. A recent study reported over 150 million people in the U.S. who entirely depend on ground water supply as their water source (Hynds et al., 2014). However, most recent literature on opportunistic pathogens (OPs) transport through soil and aquifer, clearly state ground water contamination can be caused by transport of OPs through the aquifers (McBurnett et al., 2018; Mondal et al., 2020). OPs are also known to be a resilient challenge for pathogen control in the water distribution systems. Even in the presence of certain residual concentration of disinfectants, organisms like *Legionella* and non-tuberculous *Mycobacterium* (NTM) are known survive by growing in biofilms within hosts like protozoa. Such protozoan biofilms not only protect the OPs from disinfection but also facilitate their growth by supplying essential nutrients (Norton et al., 2004; Pryor et al., 2004; Whiley et al., 2014; Donohue et al., 2015). In the last two decades, while there is a recurrent agreement that disinfection can control the presence of OPs in public water systems, the control mechanisms, and their optimal efficiency to treat broad range of microorganisms need further investigation.

Disinfection is the tertiary step in the treatment of water which is designed to control and inactivate microbial pathogens to avoid waterborne diseases (Crittenden et al., 2012). But different disinfection strategies affect OPs differently. For example: chlorination is the most commonly used chemical disinfection technology in drinking

water treatment. Although free chlorine works effectively against microorganisms like *E. coli*, chloramine is a better for the disinfection of *Legionella* and NTM are known to proliferate greater than other biofilm forming bacteria when chloramine is used in the disinfection process (Aggarwal et al., 2008; Luh et al., 2015; Baron et al., 2015; Zhang et al., 2021). Thus, due to chemical disinfection processes reporting high disinfection by-products (DBPs) formation potential and their inability to disinfect certain microorganisms, UV irradiation and the production of highly reactive radicals associated with advance oxidation processes (AOPs) have attracted attention to disinfection processes having a low potential for DBPs formation (Mamane et al., 2007). Ultraviolet irradiation (UV) is one of the most commonly used disinfection techniques in the treatment of drinking water. The effectiveness of this technology was known through a study in the 1990s which reported the ability of UV irradiation to treat *Giardia* and *Cryptosporidium* in water (Hijnen et al., 2006). In addition to its substantial disinfection potential, UV irradiation is also considered an eco-friendly, economically viable method of disinfection of drinking water (Drescher et al., 2001; Hijnen et al., 2006). The germicidal potential of UVC (200 – 280 nm) relies on damaging the cell membranes and cytoplasm of microorganisms (Gupta et al., 2013; Sholtes et al., 2016). But the reliability, efficiency and its disinfection potential depend largely on the type of microorganisms (Shin et al., 2001). For example, while bacterial cells like that of *E. coli* are extremely susceptible to UV, spores (fungal or bacterial) are 10 – 50 times more resistant to UV than cells and thereby require a much higher UV dose to achieve target inactivation (Coohill and Sagripanti, 2008; Zhang et al., 2014).

In this study, four microorganisms with varying UV susceptibility were irradiated to UV with reflective technology and AOP involving UV and Peracetic Acid (PAA). *E. coli, Legionella pneumophila, Mycobacterium avium* and *Aspergillus* spores were selected for this study based on their UV susceptibility and associated pathogenic health concerns.

E. coli is believed to be a part of the microflora in the lower intestinal tract of warm-blooded animals, humans, and is introduced to the environment through feces and wastewater treatment plants (Berthe et al., 2013). Epidemiological studies conducted in the 1980s showed a correlation between *E. coli* in contaminated recreational water and occurrences of gastrointestinal illnesses (Edberg et al., 2000; U.S. EPA, 1986). This then led to the utilization of *E. coli* as an indicator of fecal contamination in recreational water (U.S. EPA, 1986). Pathogenic *E. coli* strains are known to cause multiple human diseases, resulting in approximately 2 million deaths every year (Kaper et al., 2004). Waste waters from slaughterhouses, wastewater treatment plant effluents, manure and animal wastes are some of the common entry pathways of pathogenic *E. coli* in the environment (Balière et al., 2015).

One of the most significant waterborne opportunistic pathogens responsible for a major portion of waterborne diseases in the United States is *Legionella* (Beer et al., 2015). *Legionella* can cause Pontiac fever in the case of mild infection and Legionnaires' disease, which is a pneumonia like illness, from major exposure (Fields et al., 2002). Common *Legionella* occurrences can be tracked to cooling towers, wastewater treatment facilities, soils, and ambient water environments (Ahmadrajabi et al., 2016; Walser et al., 2017; Amemura-Maekawa et al., 2012; Fliermans et al, 1979). Additionally, *Legionella*

can survive in high temperatures and can parasitize, multiply in protozoa present in the environment; thereby increasing the difficulty of efficient disinfection.

Pulmonary infections from NTM have been of increasing concern worldwide especially in people with pre-existing health conditions (Dowdell et al., 2019). The frequent presence of NTM in treated drinking water systems and in plumbing pipelines have led to the hypothesis that drinking water is one of the major sources of NTM exposure (Dowdell et al., 2019). NTM generally possess hydrophobic cell walls which allow them to be more prone to aerosolization than other bacteria. Previous studies have called them biofilm pioneers because NTM possess the ability to attach to variety of surfaces, like water distribution pipelines, and establish biofilms. They, like *Legionella* , can enter and survive within amoeba (Delafont et al., 2014; Drancourt et al., 2014). With the combination of such properties, NTM offer high resistance to conventional water treatment systems and survive in water distribution systems despite residual disinfectants (Falkinham, 2018; Greub & Raoult, 2004). NTM are known not only to predominantly cause pulmonary infection but also for soft tissue, skin, and post-operative infections. In 2012, a study reported $194 million to be the cost of annual hospitalizations in the United States of America (Falkinham, 2016; Misch et al., 2018; Schnabel, 2016; Allen et al., 2017; Collier et al., 2013). The third organism, which is also a member of the NTM family, selected for this study is *Mycobacterium avium*.

Mass propagation of fungi have been an emerging problem in the recent years (Novak Babič et al., 2017). This is considered a threat to drinking water safety and has attracted a lot of attention from the field of water treatment (Wen et al., 2017). Fungal metabolic products are known to pose a range of problems despite their low

concentrations in aquatic environments (Mhlongo et al., 2019). Humans, especially the ones who are immunocompromised, suffer an elevated risk of mycosis and allergic reactions when the mycotoxins come in contact with the human body through water or food (Curtis et al., 2004; Marr et al., 2002). *Aspergillus* is among one of the most prevalent fungal genera in the water environment (Richardson et al., 2019; Afonso et al., 2021). *Aspergillus* species are responsible for different types of aspergillosis, totaling to more than 13.5 million cases worldwide every year (Richardson et al., 2012; Kosmidis et al., 2015). Thus, the fourth microorganism selected in this study is *Aspergillus niger* spores. Harmful health effects of this mainly include asthma symptoms, skin irritation and hypersensitivity pneumonitis (Al-Gabr et al., 2014; Green et al., 2003). Despite the wide prevalence of *Aspergillus* spores in the environment and numerous inactivation studies, these remain a challenge to effectively inactivate using conventional UV technology. The robust characteristics of these spores are mainly because of their cell wall – made of polysaccharides (mainly chitin and glucans) which protect it from UV radiation. This cell wall is then covered by an outer layer made up of rodlets (hydrophobins) and pigments like melanin which make it highly hydrophobic and pigmented (Beauvais et al., 2014). Pigments like melanin not only protect these spores from UV radiation induced stress but also help in various cellular process from virulence to adhesion (Eisenman & Casadevall, 2012; Cordero & Casadevall, 2017).

This study evaluated an improved UV system with reflective technology for enhanced exposure and inactivation of the test microorganisms. With a quartz inner coating in the lamp sleeve, the UV system is able to reflect 99.99% of the radiation emitted from the low-pressure mercury lamp back into the reaction chamber. This is

designed to increase the efficiency of the system and enhance the remediation of the treatment process.

A new AOP technology involving UV with reflective technology and Peracetic Acid (PAA) was also applied to the microorganisms. *Mycobacterium avium* and *Aspergillus niger* are known to be resistant to conventional UV irradiation. The addition of PAA, a radical oxidant generator, to the inactivation process was designed to elevate the production of reactive species when irradiated with UV. The main radical species generated by this AOP are highly reactive hydroxyl radicals ($HO^{\cdot}$) which are known to destabilize cell walls and membranes of microorganisms. PAA is known to have higher hydroxyl stability when compared to the commonly used H_2O_2. This translates into slower breakdown of PAA in the UV system, thereby allowing lower concentrations of PAA yielding higher inactivation efficiency. The main objective of this study is to develop efficacious methods for the inactivation of selected microbial pathogens of public health concerns from source water. Specific research objectives include: 1) To evaluate the performance of UV with reflective technology involving UV/PAA for the effective inactivation of a range of microorganisms with varying UV susceptability. 2) To optimize UV and PAA doses to achieve a high inactivation of *E. coli, Legionella , Mycobacterium* and *Aspergillus spores.* This study is the first to use AOP involving UV/PAA in the inactivation of *Aspergillus niger* spores and *Mycobacterium avium* under dynamic flow conditions with reflective UV technology.

5.3 Materials and Methods

5.3.1 UV system with reflective technology

The UV system used for inactivation of microorganisms in this study was provided by NeoTech Aqua solutions (San Diego, CA). The NeoTech UV system employed a low-pressure mercury lamp and the patented ReFLeX^{TM} technology in its reaction chamber unlike any other conventional UV systems. The uniqueness of this system is attributed to its lamp sleeve which is coated with quartz inner lining. This was designed to ensure 99.99% of the UV radiation emitted by the UV lamp is bounced back into the system. This operational design is supposed to reduce energy consumption of the system while attaining an enhanced remediation of the contaminants. This lab scale UV system was graded for 20 – 25 gal/min flowrate. The UV doses were recorded using a dosimeter provided by the company.

5.3.2 Operational design

The design consisted of an influent tank in the form of a 15L polyethylene container connected with the UV system through one-inch PVC piping. The effluent water is collected in a polyethylene container. Water is pumped though the system using Magnetic pump (model C63JXGWU-1114/Iwaki). Muncipal tap water having a residual chlorine level of 0.5 – 1.2 ppm was used for the experiments. To ensure the non-reactivity of residual chlorine and the microorganism of interest, the influent tank was neutralized with the appropriate concentration of sodium thiosulphate before any microbial contaminant was introduced. The microbial culture of the desired concentration was then individually added to the influent tank and thoroughly mixed. Approximately 1L of influent water was collected as the influent sample for each experimental run. The

influent water was then pumped to the UV system at the desired flowrate to achieve target UV exposure dose. For experiments which involved the use of AOP, PAA (Sigma-Aldrich Corporation) was injected to the remediation system upstream to the influent tank, prior to UV, using a peristaltic pump - FMI "Q" Pump, model QG50. Approximately 1L of effluent samples were collected after each experimental run. These samples were then subjected to specific microbial assays for each of the target microorganism selected for the study. CFUs were counted and the log inactivation was calculated.

5.3.3 Microbial Inactivation

***E. coli* Culture Preparation.** The pure culture of *Escherichia coli* (ATCC 25922) was obtained originally from American Type Culture Collection (ATCC, Manassas, Virginia). The working culture of *E. coli* was started from the frozen stock kept at -80^{o}C by streaking onto a tryptic soy agar (TSA) plate (MilliporeSigma #22091). The TSA plate was then incubated 24 hours at 37^{o}C. Following day, a single colony from the plate was transferred into 10 mL tryptic soy broth (TSB) (MilliporeSigma #22092) and incubated for 24 hours at 37^{o}C. The overnight TSB culture was used as the stock solutions and was diluted to desired concentrations for the following experimental runs.

UV Exposure of *E. coli* overnight culture. The overnight culture was diluted to an average influent concentration of 7.3 $\log_{10}$CFU/mL by adding to the influent tank containing 15 L of neutralized tap water. After thorough mixing, 1 L of the influent water was collected in a sterilized polypropylene bottle for pre-treatment microbial assay. The influent water was pumped through to the UV system. Desired doses of PAA was injected upstream to the influent tanks for experimental runs employing AOP. UVC

doses ranging from 35 – 150 mJ/cm^2 used in separate experimental runs to test and optimize the inactivation process. Approximately 1 liter of effluent water was collected in a sterilized polypropylene bottle for post treatment microbial assay.

E. coli Assay. The influent samples collected pre-treatment were serially diluted using phosphate buffered saline (PBS). The PBS consisted of NaCl, KCl, Na_2HPO_4, KH_2PO_4 (0.0684, 0.00134, 0.005, 0.0009 molarity respectively) with a final pH of 7.4. Selected diluted influent samples and effluent samples collected post treatment were then assayed in triplicates using spread plate method onto TSA plates. TSA was prepared according to the manufacturer's instructions. Triplicate 100 mL effluent samples were also subjected to membrane filtration (membrane: Thomas Scientific #1217D62) and the membrane was placed on fresh TSA plates. All the influent and effluent assay plates were incubated overnight 24 to 48 hours at 37^{o}C and data was recorded in colony forming units (CFU) per mL. The inactivation efficiency of the UV system was calculated as average log inactivation for *E. coli*.

Legionella **Culture Preparation.** The pure culture of *Legionella pneumophila* (ATCC 33152) was previously obtained from ATCC and stored at -80^{o}C. The frozen stock was thawed to room temperature and plated on petri dishes containing buffered charcoal yeast extract with 0.4 g/L of L-cystein (BCYE from Hardy Diagnostics #G08) using spread plate method. The selective BCYE media was ordered pre-made with antibiotics colistin, vancomycin and anisomycin to suppress the growth of gram-negative, gram-positive, and eukaryotic cells respectively. The petri dishes containing the culture was incubated at 37^{o}C for 8 – 10 days. *Legionella* lawn formation on the surface of the media was observed after the incubation period. This was carefully washed off the plates using 5 – 10 mL PBS per

plate. The *Legionella* stock solution was stored and diluted to desired concentrations for the following experimental runs.

UV Exposure of *Legionella pneumophila* culture. The incubated stock solution was diluted to an average influent concentration of 7 $\log_{10}$CFU/mL by adding to the influent tank containing 15 L of neutralized tap water. After thorough mixing, 1 L of the influent water was collected in a sterilized polypropylene bottle for pre-treatment microbial assay. The influent water was pumped through to the UV system through 1-inch PVC piping. UVC doses ranging from 70 – 125 mJ/cm^2 were applied in separate experimental runs to test the efficiency of low UVC doses in the inactivation process. Approximately 1 L of the effluent water was collected in sterilized polypropylene bottles for post treatment microbial assays.

***Legionella pneumophila* Assay.** The influent samples were serially diluted to quantifiable concentrations using PBS. Selected influent dilutions and effluent samples were subjected to membrane filtration in quadruplicates. The membranes were then placed face down on fresh BCYE plates and were incubated for 24 hours at 37^{o}C. The following day each plate was rid of the membrane and incubation period was continued for 8 – 10 days. The efficiency of the UV system with reflective technology in the inactivation of the target microorganism was quantified in CFU/mL. The inactivation was then calculated in terms of average log inactivation.

***Mycobacterium* Culture Preparation.** The pure culture of *Mycobacterium avium* (ATCC 25291) was obtained from ATCC. The working culture was started by resuspending the frozen stock kept at -80^{o}C, in 50 mL of Middlebrook 7H9 broth base (MilliporeSigma #M0178) which was prepared according to the company's instructions.

The resuspended culture broth was incubated at 37°C for 3 – 4 weeks. After the incubation period, the working bacterial stock solution was used for the following experimental runs.

UV exposure of *Mycobacterium avium* culture. The incubated stock solution containing was diluted to an average influent concentration of 3.4 $\log_{10}$CFU/mL by adding to the influent tank containing 15L of neutralized tap water. After thorough mixing, 1 L of the influent water was collected in sterilized polypropylene bottle for pre-treatment microbial assays. The influent water was pumped through to the UV system through 1-inch PVC piping. UVC doses ranging from 125 – 1,068 mJ/cm^2 were applied to test the efficacy of UV with reflective technology in the inactivation process. Approximately 1 L of the effluent water was collected in sterilized polypropylene bottles for post treatment microbial assays.

***Mycobacterium avium* Assay.** The influent samples were initially subjected to serial dilution using PBS to attain quantifiable concentrations. Select influent dilutions and effluent samples were filtered onto a membrane in quadruplicates and the membrane was placed on freshly prepared agar plates containing Middlebrook 7H10 agar base (MilliporeSigma #M0303). The plates were then incubated at 37°C for 3 – 4 weeks. The results following the incubation period was quantified in CFU/mL and the inactivation was calculated in terms of average log inactivation.

***Aspergillus niger* Culture Preparation.** Pure dehydrated culture of *Aspergillus niger* (ATCC 10582) was obtained from ATCC and was stored at -80°C. The frozen stock was thawed to room temperature and mixed thoroughly in PBS+10% tween solution. The stock culture was then spread on petri dishes containing potato dextrose agar media (MilliporeSigma 1101300500) which were made according to the company

instructions. The plates were incubated for 8 – 10 days at room temperature (21 +/- 2^{o}C). At the end of the incubation period, the black fungal spore lawn growth on the petri plates were washed with PBS+10% tween solution and was stored as the stock solution for the following experimental runs.

UV Exposure of *Aspergillus niger* culture. The incubated stock fungal solution was diluted to an average influent concentration of 4 $\log_{10}$CFU/mL by adding to the influent tank containing 15 L of neutralized tap water. After thorough mixing, 1 L of the influent water was collected in a sterilized polypropylene bottle for pre-treatment sample microbial assays. While the influent water was being pumped to the UV system, PAA was injected upstream to the influent tank using a peristaltic pump for experimental runs involving AOP in the inactivation process. UVC doses ranging from 125 – 530 mJ/cm^2 was applied. Approximately 1 L of the effluent water was then collected in sterilized polypropylene bottles for post treatment fungal assays.

***Aspergillus niger* Assay.** The influent samples collected pre-treatment were serially diluted using PBS to achieve quantifiable concentrations. Selected influent dilutions and effluent samples collected post-treatment were then subjected to membrane filtration in triplicates. The membranes were then placed individually on freshly prepared petri dishes containing potato dextrose agar media and incubated at room temperature (21+/-2^{o}C) for 8 – 10 days. The inactivation of fungal spores using UV with reflective technology and AOP involving UV/PAA was quantified in terms of average log inactivation.

The selected microorganisms for the study were subjected to inactivation using a defined set of variables as shown in Table 3.

Table 3: Microbial Inactivation Experimental Variables.

Microorganism	**Average Influent (Log_{10}CFU/mL)**	**UV Dose Range (mJ/cm^2)**	**PAA Dose (mg/L)**
Escherichia coli	7.3	35 - 150	0.5
Legionella pneumophila	7	70 - 125	N/A
Mycobacterium avium	3.4	125 – 1,068	N/A
Aspergillus niger spores	4.28	125 – 530	1 – 2

5.4 Results and Discussions

5.4.1 Inactivation of E. coli using UV with reflective technology and AOP involving UV/PAA

Experiments were performed to obtain a baseline of the new UV technology in the inactivation of a range of microorganisms and results are presented in this section. The inactivation efficiency of the UV system alone for *E. coli* was initially tested. Since *E. coli* is known to be susceptible to UV irradiation, low UV doses of 35 – 150 mJ/cm^2 was employed and the inactivation obtained is reported in Figure 12.

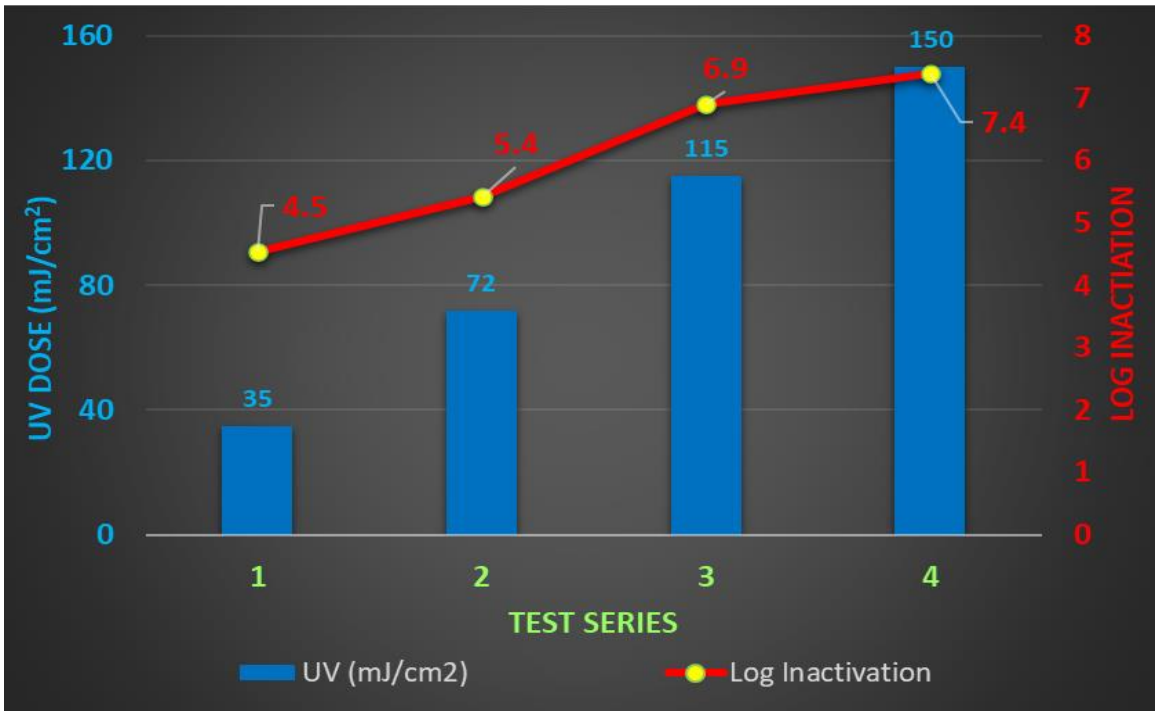

Figure 12: UV Inactivation of *E. coli* with Varying Low Range UV.
Note: The inactivation values are an average of 4 replicates.

A low UV dose was 35 mJ/cm^2 was initially employed and resulted in an average of 4.5 log inactivation of *E. coli*. The UV dose was then systematically increased up to 150 mJ/cm^2 which resulted in a maximum of 7.4 log inactivation on average. A common trend of higher inactivation was recorded with increase in the UV dose. The results obtained from this set of experimental runs demonstrated the potential and high efficiency of UV with reflective technology in the inactivation process of indicator bacteria like *E. coli*.

The next step in the study was to further achieve enhanced inactivation and to test the effectiveness of the AOP technology. Thus, an average *E. coli* influent concentration of 9.7 $\log_{10}$CFU/mL was irradiated with comparable UV dose while introducing 0.5 mg/L PAA upstream to the influent tank and the set of results are depicted in Figure 13.

The addition of a low PAA dose of 0.5 mg/L resulted in inconsistent increase in the inactivation when the UV dose was increased from 35 - 150 mJ/cm^2. Although the inactivation trend remained similar to Figure 12, enhanced inactivation of 7.1, 8.3 and 9.3 log inactivation was achieved while irradiating UV doses of 35, 72 and 150 mJ/cm^2

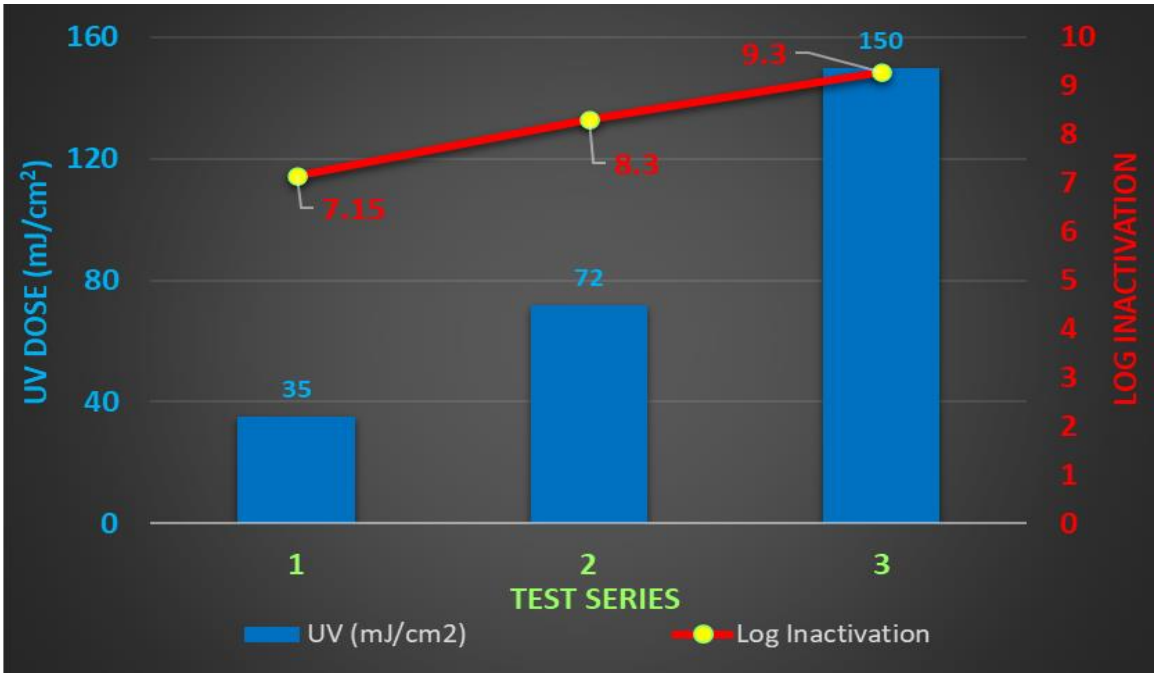

Figure 13: AOP of *E. coli* Using Varying Doses of UV with Reflective Technology and 0.5 mg/L PAA.
Note: The inactivation values are an average of 4 replicates.

respectively. Highly reactive oxidant species are known to be released when a chemical oxidant is irradiated with UV light. The most important and reactive species released when PAA is irradiated with UV light is hydroxyl radicals ($OH^{\cdot}$) (Caretti and Lubello, 2003; Lubello et al., 2002). Hydroxyl radicals are known to destabilize microbial cell walls and membranes which are primarily made of lipids (Yin et al., 2011). Thus, the additional inactivation obtained while employing AOP technology in this study are believed to the result of highly reactive radicals generated during UV irradiation of PAA. This set of inactivation experiments involving *E. coli* sets a baseline performance of the

UV system while displaying the potential of AOP technology to achieve enhanced inactivation of microorganisms in water.

5.4.2 Inactivation of Legionella pneumophila using UV with reflective technology

*Legionella (*7.5 $\log_{10}$CFU/mL) was subjected to a low range (from 70 – 125 mJ/cm^2) of UV with reflective technology and the results obtained are presented in Figure 14. Increase in the inactivation was observed with increase in the UV dose. UV

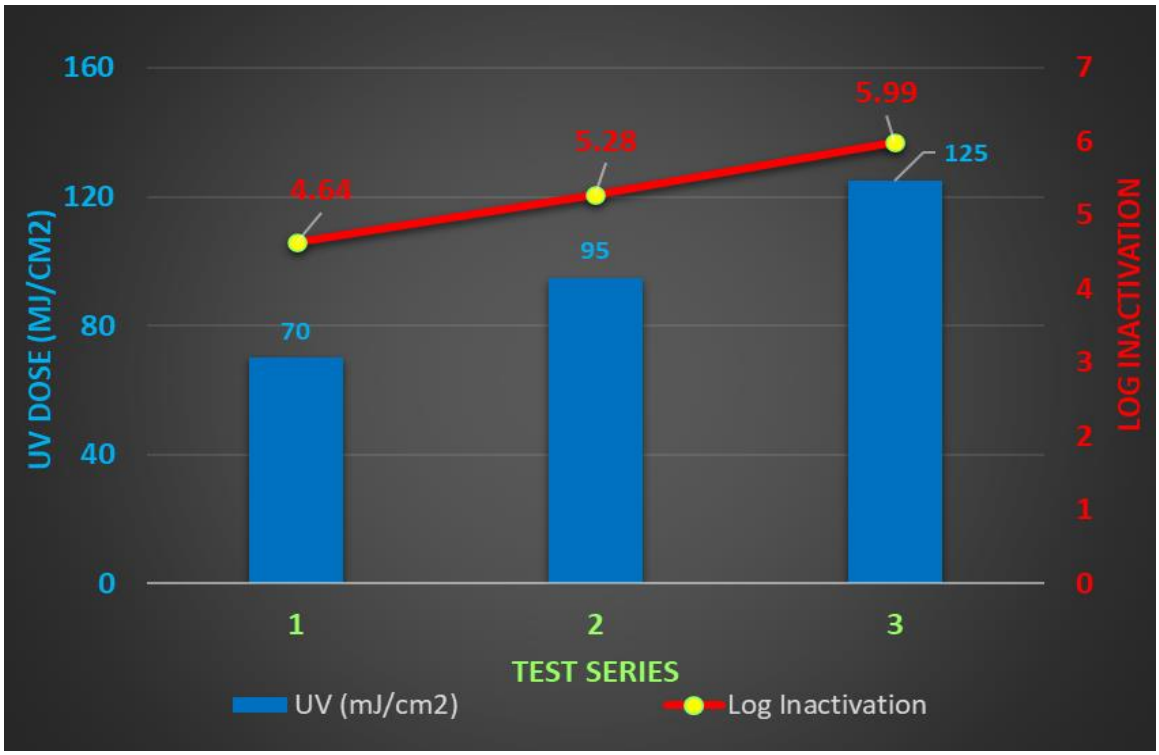

Figure 14: Inactivation of *Legionella Pneumophila* Using Varying UV Doses.
Note: The inactivation values are an average of 4 replicates.

dose of 70 mJ/cm^2 resulted in 4.64 log inactivation and further increased to 5.28 and 5.99 log inactivation when the UV dose was increased to 95 and 125 mJ/cm^2 respectively. The inactivation results of *E. coli* and *Legionella* obtained while using UV alone showed promise for the application of this new UV technology to other microorganisms like *Mycobacterium* which are known to be more resistant to UV irradiation.

5.4.3 *Inactivation of Mycobacterium avium using UV with reflective technology*

Experiments were conducted using an average influent concentration of 3.4 log_{10}CFU/mL of *M. avium* was irradiation with low (125 mJ/cm^2), medium (260 and 554 mJ/cm^2) and high (1068 mJ/cm^2) doses of UV with reflective technology and the results obtained are depicted in Figure 15. The UV doses were varied to test the efficacy of the new UV system to achieve enhanced inactivation.

Low UV dose achieved 0.82 log inactivation and as the UV dose was increased to

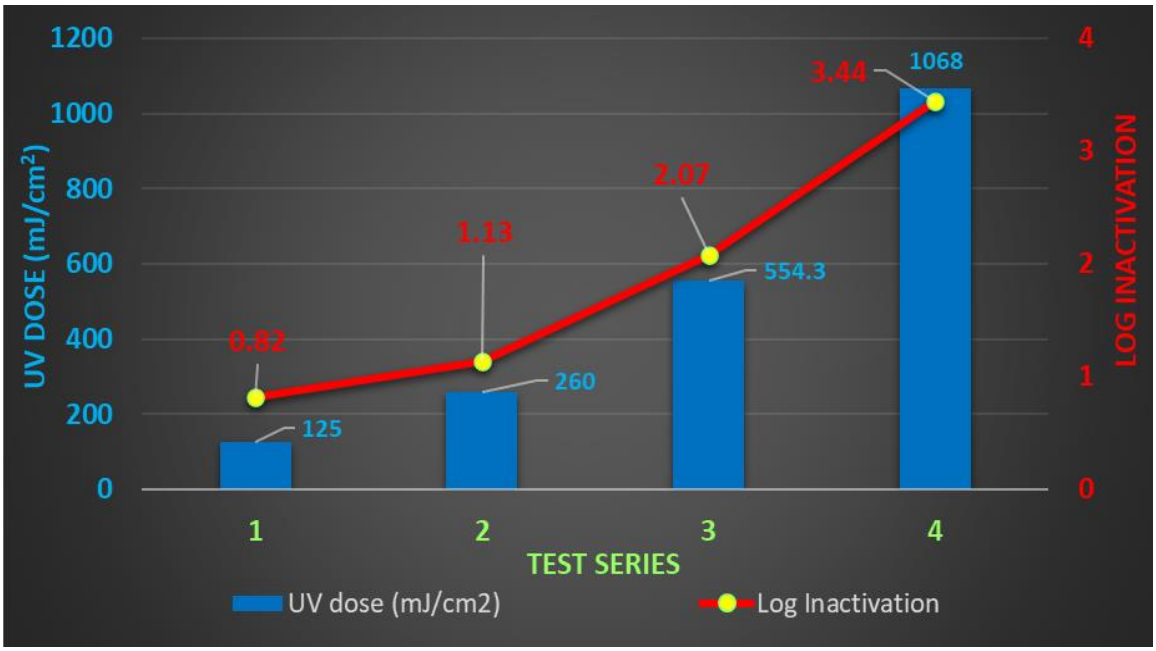

Figure 15: Inactivation of *Mycobacterium Avium* Using UV with Reflective Technology. Note: The inactivation values are an average of 4 replicates.

mid-range, 1.14 and 2.07 log inactivation was achieved using 260 and 554 mJ/cm^2 respectively. The last set of experiments which were performed using high range UV dose of 1,068 mJ/cm^2, resulted in complete inactivation of *Mycobacteruim:* the influent microorganism and thus resulted in >3.44 log inactivation.

Future AOP studies involving UV with reflective technology and oxidant species like PAA and H_2O_2 are necessary to explore and optimize the potential of this technology in the activation of *Mycobacterium* in surface waters.

Mycobacterium avium is known to be highly resistant against chemical disinfectants like chlorine, chloramine, chlorine dioxide and ozone (Taylor et al., 2000; Luh & Marinas, 2007). Furthermore, studies made in 2000 reported *M. avium* to be 50 times more resistant to disinfect exposure than *E. coli* at the same experimental conditions that were studied (Taylor et al., 2000).

5.4.4 *AOP and UV inactivation of Aspergillus niger spores using UV with reflective technology and PAA*

The initial experiments were performed using an average influent concentration of 4.28 $\log_{10}$ CFU/mL of *A. niger* spores and irradiated with UV doses of 130 – 225 mJ/cm^2.

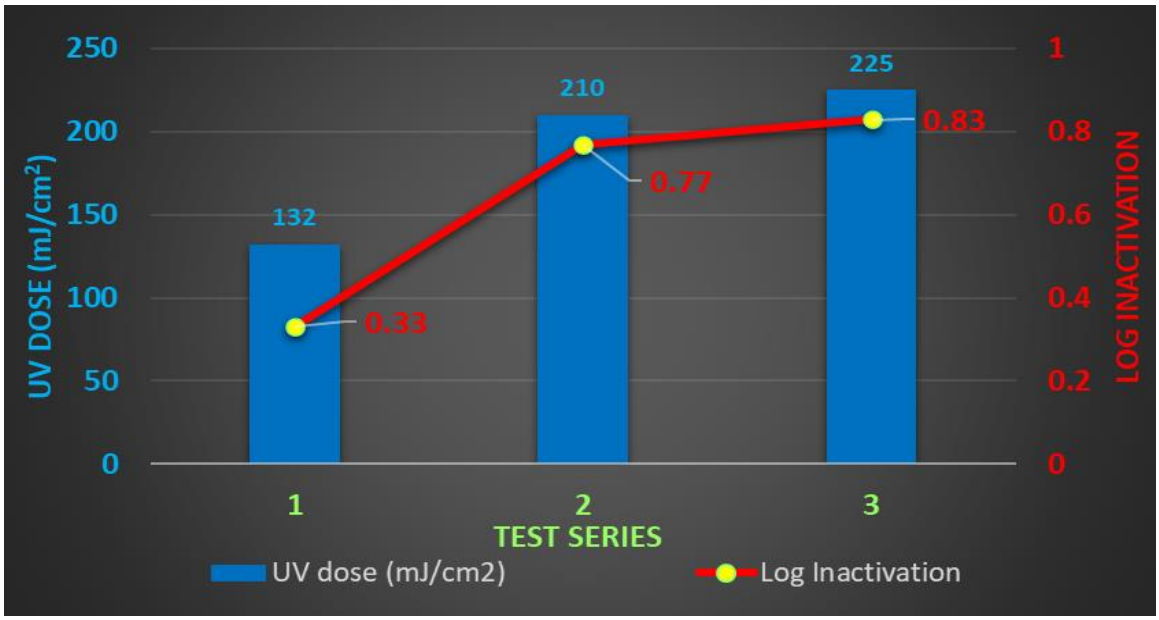

Figure 16: Inactivation of *Apergillus Niger* Spores Using UV with Reflective Technology.
Note: The inactivation values are an average of 4 replicates.

This was done to achieve a baseline performance of the new UV system with reflective

technology in the inactivation of fungal spores. A lowest of 0.33 log inactivation was obtained using 132 mJ/cm^2 UV and the highest was 0.83 log inactivation while employing 225 mJ/cm^2 (Figure 16). To further achieve enhanced inactivation, AOP involving UV/PAA was employed. An average influent concentration of 4.18 $\log_{10}$ CFU/mL was irradiated with varying doses of UV while PAA was injected upstream to the influent tank (Figure 17).

Average UV dose of 122.5 was applied with PAA doses of 1 and 2 mg/L to the target microorganism and obtained 0.16 and 0.36 log inactivation respectively. The increase in log inactivation value is a direct result of increased reactive radical generation because of the increase in PAA dose. Thus, 2 mg/L of PAA was employed along with 470 and 530 mJ/cm^2 and this resulted in 1.29 and 2.08 log inactivation respectively. This

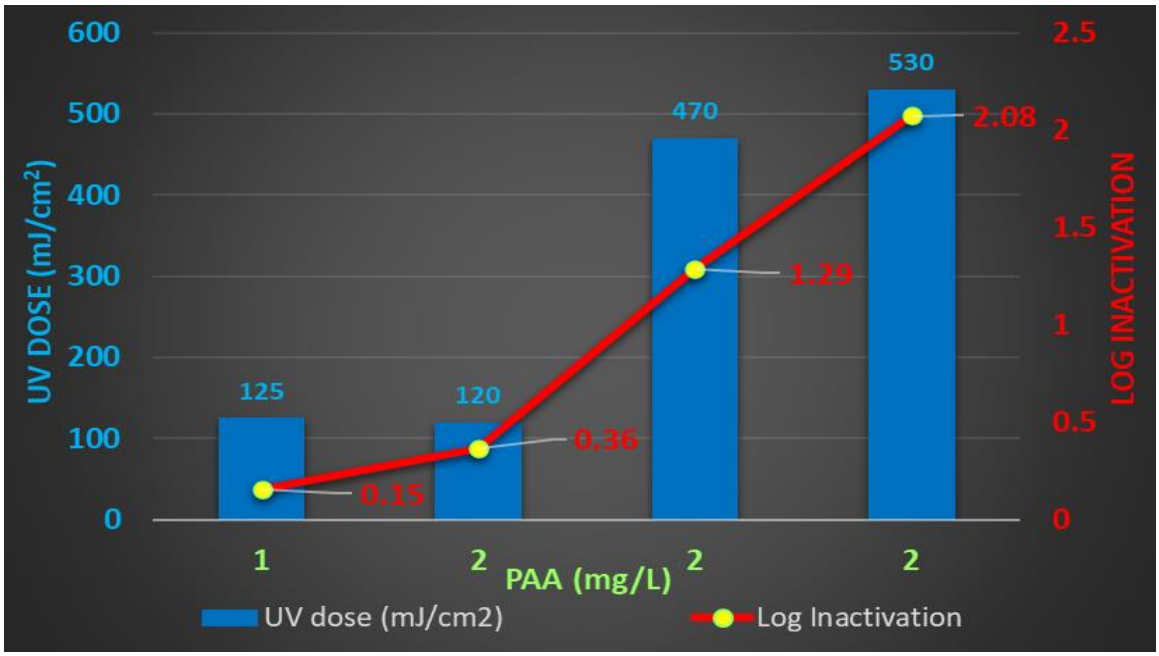

Figure 17: AOP of *Aspergillus Niger* Spores Using UV with Reflective Technology and PAA.

Note: The inactivation values are an average of 4 replicates.

clearly displayed the potential of AOP involving UV with reflective technology and PAA in the inactivation of fungal spores.

Although UV technology has proved to be effective against microorganisms like *E. coli* and *Legionella* , some pathogenic microorganisms like *Mycobacterium* and fungal spore remain resistant to UV disinfection. The performance of new UV system with reflective technology was comparable to the microbial inactivation by conventional UV systems. An inactivation study of *E. coli* obtained 4 log inactivation using 20 – 30 mJ/cm^2 UV (Sommer et al., 2000). For the inactivation of fungal spores, different treatment strategies in the past have obtained comparable results to this study. For example: 2 and 4 log inactivation of *A. niger* spores were reported by studies using 5.63 mgmin/L of ozone and 220 mJ/cm^2 pulsated UV respectively (Wen et al., 2020; Wan et al., 2020). But both of these studies were conducted under static batch reactor conditions which is different from the operational design of this study employing dynamic flow conditions. *Mybacterium* strains are known to need 700 times more UV dose to achieve 3 log inactivation when compared to that of *E. coli* (Le Dantec et al., 2002). A study using medium pressure UV lamp reported 3 log inactivation of *E. coli* and *M. avium* while using 10 and 100 mJ/cm^2 respectively and displayed the relative UV resistance of *Mycobacterium* species (Lee et al., 2010). In summary, although the new UV with reflective technology did not lead to the enhanced remediation of microorganisms, considerable microbial inactivation was obtained which was consistent with the existing literature. The use of PAA had a positive effect on the inactivation and lead to reduced requirement of UV dosage. AOP technologies employing UV and a chemical compound as the radical oxidant generator species are becoming popular in the treatment of water.

AOPs involving UV primarily depend on the generation of highly reactive hydroxyl radicals to achieve enhanced remediation. Studies reported a linear correlation between the concentration $HO^{\cdot}$ Radicals and the inactivation of *E. coli* (Chen et al., 2009). Titanium dioxide (TiO_2), hydrogen peroxide (H_2O_2) are among the commonly used chemical oxidants in AOP involving UV. But TiO_2 based AOPs are largely lab-scale based due to their low efficiency of utilizing UV light. While AOPs involving UV/H_2O_2 have proved to be an effective disinfection technology against microorganisms of concern in water, AOP technology used in this study provides a new alternate treatment technology for enhanced inactivation. The advantages of using PAA in comparison to the other existing conventional technologies are reduced toxic by-product formation in effluent waters, easy technical implementation, lower pH dependence, high oxidation potential and higher hydroxyl stability when compared to H_2O_2 which essentially leads to longer sustained reactive radical formation (Zhang et al., 2017). The use of AOP involving UV with reflective technology and PAA present a viable alternate disinfection technology to achieve considerable microbial inactivation of OPs.

5.5 Conclusion

In conclusion, this study achieved its main objective of developing an efficacious method for the inactivation of the selected microbial pathogens of public health concerns. The performance of the new UV system with reflective technology for broad types of microorganisms was evaluated and a new AOP technology involving UV/PAA was developed. For *E. coli,* 9.3 log inactivation was recorded while applying 150 mJ/cm^2 UV dose and 0.5 mg/L PAA. Low UV doses of 125 mJ/cm^2 resulted in almost 6 log inactivation of *Legionella pneumophila.* Although *Mycobacterium avium* is known to be

resistant to UV disinfection, high UV doses of 1,068 mJ/cm^2 achieved more than 3.44 log inactivation. *Aspergillus niger* spores when irradiated with a mid-range UV dose of 530 mJ/cm^2 and 2 mg/L PAA, resulted in the highest of 2.08 log inactivation. This study presents a strong alternative treatment system for the efficient disinfection of a broad spectrum of microorganisms of public health concern in drinking water.

6 CONCLUSION

A new UV/AOP technology for the enhanced remediation of contaminants of public health concerns including chemicals and broad-spectrum microorganisms in water was successfully developed. Thus, the main objective of this study was achieved and each specific objective was investigated and optimized conditions were identified. Due to factors such as physical properties, chemical reactivity with disinfectants and UV absorption, the selected chemical contaminants present a challenge to conventional treatment processes. Most of the existing AOP studies have employed static batch reactions as their operational design, therefore scalability do not represent real-world application conditions. The microorganisms selected for this study are meant to represent a broad range with varied disinfection susceptibilities and public health concerns. *E. coli* which is an indicator organism with high UV susceptibility was selected to obtain a baseline performance of the new technology. Opportunistic pathogens prevalent in surface and groundwater systems such as *Legionella pnemophila* and *Mycobacterium avium* with known resistance to UV disinfection were selected because of the threat they pose to drinking water safety. *Aspergillus* spores are known to be resistant to UV and are public health concerns, high resistance to conventional disinfection technologies and are the most prevalent genera of fungi in the environment. Thus, *Aspergillus niger* spores were selected for this study to challenge the disinfection potential of the new UV device with reflective technology.

Initially the efficacy of the new UV device was tested separately for each of the contaminants. The highest NDMA remediation of 65% with 5.5 mJ/cm^2 UV 220 nm and >90% remediation using UV 254 nm at ~450 mJ/cm^2 was achieved. Since the UV

absorption spectrum of NDMA peak is at 227 nm, a high remediation resulted using UV 220 nm at lower UV dose. Photolysis of 1,4-Dioxane using the UV 254 nm device employing low-pressure mercury lamp showed a consistent trend. A 92% remediation was achieved with a high UV dose of 1,031 mJ/cm^2. Since the UV absorption peak of 1,4-Dioxane are at 165 and 191 nm, high-range UV doses had to be applied to achieve >90% remediation. The remediation consistently decreased with lower UV doses. *E. coli*, as expected, displayed the highest UV susceptibility by resulting in 7.4 log inactivation with 150 mJ/cm^2 using UV 254 nm. UV irradiation of *Legionella pnemophila* resulted in a considerable inactivation of 5.9 log with low range UV dose of 115 mJ/cm^2. *Mycobacterium avium* displayed high UV resistance and therefore high range UV dose of 1,068 mJ/cm^2 had to be applied to achieve >3.44 log inactivation. *Aspergillus niger* spores displayed the highest resistance to UV disinfection with the highest of 0.83 log inactivation using mid-range UV dose of 225 mJ/cm^2. Although the UV irradiation of the selected microbial contaminants showed considerable inactivation, application of the AOP technology reduce the required UV dose to achieve a similar inactivation.

PAA dose had a significant impact on the remediation of NDMA using UV 220 nm. Until an optimum PAA concentration of 1.5 - 2 mg/L was reached, the remediation consistently increased and then decreased beyond the optimum PAA concentration, suggesting the increase in radical demand to breakdown the extra PAA in the reaction chamber. While using UV 254 nm, PAA dose had a net negative effect on the NDMA remediation for UV <450 mJ/cm^2 and had little to no effect for high-range UV doses. Approximately, 90% remediation was achieved for UV doses >1000 mJ/cm^2 irrespective

of the PAA concentration. While remediating 1,4-D using varying doses of PAA, the highest remediation of 14.6% was achieved using 5 mg/L PAA at flowrate of 2.5 GPM. This displayed the effectiveness of PAA in the remediation of 1,4-D with significantly short contact time. PAA had a considerable positive impact in achieving enhanced inactivation of *E. coli* and *Aspergillus niger* spores due to the production of highly reactive radicals in the UV reaction chamber.

AOP of NDMA using UV with reflective technology and PAA displayed enhanced remediation while using UV 220 nm. A low UV dose of 5.5 mJ/cm^2 and optimum PAA dose of 1.5 mg/L resulted in 97.2% remediation. While using UV 254 nm, AOP of NDMA did not have a positive impact on the remediation. This might be due to the use of high UV dosages. Optimum PAA dose of 5 mg/L along with 460 and 790 mJ/cm^2 resulted in 76.9% and 96.2% remediation, respectively. Any PAA dose other than the optimum concentration had a negative impact on the remediation irrespective of the UV dosage.

AOP of *E. coli* using 0.5 mg/L PAA and varying UV doses consistently displayed enhanced inactivation. A 9.3 log inactivation was achieved with UV dose of 150 mJ/cm^2. AOP of *Aspergillus niger* resulted in slightly higher inactivation. A 2.08 log inactivation was achieved with 530 mJ/cm^2 UV and 2 mg/L PAA.

The results obtained through this study clearly displays the ability of UV with reflective technology to achieve enhanced remediation of emerging chemicals and broad-range microbial contaminants in water. UV 220 nm employing a low powered excimer lamp with reflective technology can be an excellent addition to in-situ remediation of specific chemical contaminants and TOC compounds with relatable UV absorption

peaks. UV 254 nm using a low-pressure mercury lamp with reflective technology can independently achieve considerable remediation of the selected emerging contaminants. Future studies using the technology is required to better understand the inactivation mechanisms. This study is among the first to develop a new AOP technology involving UV with reflective technology and PAA for remediation of chemical contaminants like NDMA and 1,4-D under dynamic flow conditions to better mimic the real-world applications.

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