Removal of 1,4-Dioxane from Water by UV/TiO2 Advanced Oxidation

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Removal of 1,4-Dioxane from Water by UV/TiO₂
Advanced Oxidation

A Major Qualifying Project Report:
Submitted to the Faculty
Of the
WORCESTER POLYTECHNIC INSTITUTE
In partial fulfillment of the requirements for the
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Submitted By:

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Approved By:
Professor John Bergendahl, Major Advisor
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Design Statement

The design portion of this project was intended to take information gathered from the bench scale study and scale it up to a larger pilot system. This pilot system can be used to further investigate the Advanced Oxidation Process (AOP) of TiO₂ impregnated on fiberglass in tandem with UV light to remove 1,4-dioxane from water on a larger scale. The problem that this design is intended to solve is to remove 1,4-dioxane from water with a starting concentration of 2 mg/L to an effluent concentration of 50 μg/L.

The designed pilot scale system includes a plug flow reactor (PFR) with a flow rate of 0.05 m³/min. The velocity of the water in the inlet and outlet piping of the PFR is 2 m/s. The diameter of the PFR is 0.5 m, and the diameter of the UV lamps chosen is 0.05 m. Because four lamps were needed per reactor, the total diameter of the PFR is 0.7 m. These were the chosen parameters to base all the calculations on. The PFR design equation used was as follows:

\[ \ln \frac{C_e}{C_0} = \frac{-k \pi d^2 L}{4Q} \]

Using this equation, the required length of the PFR was calculated.

The limiting design constraint was the low reaction rate constant. Due to the low amount of TiO₂ on the glass fibers, the degradation of 1,4-dioxane was relatively slower than other AOP methods. As a result, the design has a relatively low first order reaction rate constant of 0.042 min⁻¹. Because of this, the length of the PFR is quite long for a pilot scale reactor. Decreasing the flow rate helped make the length short enough to be viable, but this constraint had to be overcome by having four separate PFRs in series. These PFRs are approximately 5.5 meters in length each.

The total volume of the PFRs was found by multiplying the length of the PFRs by the cross sectional area. It was found that the volume of the pilot scale system is approximately 8,600 times larger than the bench scale study. This means that the power for the UV light has to be scaled up by the same amount. This was also a constraint because the calculated power was approximately 40 kW. This is a relatively high amount for a pilot system, but again necessary due to the low reaction rate constant. This was made viable by implementing four 10 kW UV
lamps in each PFR, which would achieve the appropriate power necessary for 1,4-dioxane degradation.

In order to reach the required retention time in the PFRs and maintain a velocity of the inlet and outlet piping of 2 m/s, the diameter of the piping had to be relatively small. The calculated inner diameter of the inlet and outlet piping is 2.3 cm, which ends up being a lot smaller compared to the diameter of the PFRs. Though this is the case, this size is required in order to have the desired degradation. This size piping is not currently manufactured, so a 2.5 cm CPVC pipe must be used instead. CPVC piping is resistant to many contaminants, 1,4-dioxane being one of them (The Engineering Toolbox).

A pump was chosen based on the total head and flow rate of the system. The head was calculated by adding the elevation head of the system to the head loss due to friction in the piping. It is assumed that there is negligible frictional head loss in the PFR reactors. The specific pump was chosen based on its pump curve to meet this system’s needs.

Another issue that was encountered during the bench scale study was the cloudiness and turbidity of the water after repeated runs using the same fiberglass sample. This was addressed in the pilot scale design by adding a bag filter at the end of the PFRs in series to remove any particulates that may be in the water from the fiberglass. After the water passes through the bag filter, it flows into a tank for either distribution or temporary storage.

This project meets the design requirements because it achieves the desired removal of 1,4-dioxane using the information gathered in a bench scale study. This is a viable option for a pilot study that can be used to gather more information about this specific type of AOP, and to possibly design a larger scale system.
Professional Licensure Statement

Professional licensure in the engineering field is required in order to protect the public by only allowing qualified individuals to practice engineering. These individuals must adhere to a high standard of education, work experience, qualification exams, and continuing education after licensure.

The first step to becoming a licensed engineer is to attend an ABET accredited engineering program and earn a degree at that school. ABET, which stands for Accreditation Board for Engineering and Technology, accredits college and university programs in fields such as engineering, science, computing, and technology at varying levels of degrees. This ensures students, employers, and the general public, that students in these programs will leave their school ready to take on the workforce with the proper knowledge needed in these fields.

The next step to becoming a licensed engineer is to pass the FE exam. The Fundamentals of Engineering exam is typically taken by recent graduates of an ABET accredited program, or students who are about to earn their degree. This exam is administered by NCEES, which is the National Council of Examiners for Engineering and Surveying. Students wishing to take the exam must first register with their state licensing board, as well as with NCEES. Once all of the board registrations go through, they can register for the FE exam.

After passing the FE exam, a licensure candidate must gain experience working in their field, usually for at least four years. This work is typically done under the guidance of a Professional Engineer (P.E.). This is a very important step, as candidates will become familiar with the type of work real engineers do, and will gain the experience needed to succeed in the final step, which is to take the PE exam.

The last step to becoming a licensed engineer is to pass the Professional Engineering exam. Candidates must take the exam in their practiced discipline. Once they pass this exam, they are officially licensed Professional Engineers. After this licensure is gained, PE’s must maintain it through continuing education credits.

Continuing education requirements for PE’s are different for every state. Each state requires a certain amount of continuing education hours to be completed each year. These hours can be accomplished through engineering seminars, independent studies, and events such as
industry-wide meetings and conferences. Continuing education is very important in the engineering field because engineers must maintain a high level of education and experience in their fields. This will ensure that practicing engineers are always at the high standard that is needed to protect the public.

Licensure is extremely important to the engineering profession, the individual, and to the public. It ensures that only qualified individuals can practice engineering, which affects the public every day. Since engineering decisions greatly affect the public and the environment, licensure must be taken very seriously, as to only allow those who have taken the proper steps to become a qualified, competent engineer.
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Background

1,4-Dioxane

Introduction

1,4-Dioxane (C₄H₈O₂ – see Figure 1) is an emerging contaminant in drinking water and is classified by the EPA as a likely human carcinogen (United States Environmental Protection Agency, 2014b). This contaminant is also thought to be possibly carcinogenic to humans by the International Agency for Research on Cancer and a reasonably anticipated human carcinogen by the National Toxicology Program (International Agency for Research on Cancer, 1987; National Toxicology Program). 1,4-Dioxane is a clear, flammable liquid that is understood to have a faint, pleasant odor (United States Environmental Protection Agency, 2014b). It is formed as a by-product during the synthesis of certain industrial compounds and also is used as a stabilizer for chlorinated solvents (United States Environmental Protection Agency, 2014b; Zenker et al., 2003). 1,4-Dioxane is a cyclic ether and is classified as a Lewis base (Mohr et al., 2010). Its symmetric structure with two ether groups results in high miscibility with water and resistance to biodegradation in the environment (Zenker et al., 2003).

![Figure 1: Molecule of 1,4-Dioxane](image)

General Information and Hazards

1,4-Dioxane can be considered a hazardous material and caution must be used when handling this substance (Sigma-Aldrich, 2015). As an eye and respiratory irritant, proper equipment and safety gear must be used and worn while in contact (Sigma-Aldrich, 2015).
Because it is a flammable substance, explosion-proof equipment should be used to avoid any fire hazards due to equipment malfunctions (Sigma-Aldrich, 2015). When exposed to light or air, 1,4-dioxane may become explosive (United States Environmental Protection Agency, 2014b). If a fire does occur with 1,4-dioxane, dry sand or alcohol-resistant foam should be used to extinguish it (Sigma-Aldrich, 2015).

To avoid breathing in 1,4-dioxane, a fume hood should be used to draw any gaseous phase contaminant out of contact (Sigma-Aldrich, 2015). If 1,4-dioxane comes into contact with skin, the area should be thoroughly washed with soap and water to prevent irritation and dryness (Sigma-Aldrich, 2015). If 1,4-dioxane gets into the eyes, rinse thoroughly with water and be sure to remove contact lenses, if any (Sigma-Aldrich, 2015). 1,4-Dioxane may cause symptoms such as nausea, vomiting, dizziness, loss of appetite, kidney injury, or liver injury (Sigma-Aldrich, 2015). When using this substance in a laboratory setting, one must be aware of these hazards and be cognizant of the risks it poses.

Regulations

1,4-Dioxane is regulated by the EPA under the Clean Air Act, the Comprehensive Environmental Response, Compensation, and Liability Act, The Food, Drug, and Cosmetic Act, The Resource Conservation and Recovery Act, and The Superfund Amendments and Reauthorization Act to some extent, but the EPA does not currently regulate 1,4-dioxane in drinking water (Morrison et al., 2004; United States Environmental Protection Agency, 2014b). Through the Integrated Risk Information System (IRIS), an EPA database, chronic oral reference doses (RfD) for contaminants are defined. In the case of 1,4-dioxane, the RfD is 0.03 milligrams per kilogram per day, which was determined based on how it is thought that this contaminant would affect the human liver and kidney from animal testing results (United States Environmental Protection Agency, 2014b). IRIS also includes a chronic inhalation reference dose (RfC) of 0.03 milligrams per cubic meter for humans, which was also determined from animal testing (United States Environmental Protection Agency, 2014b).

Although the EPA has defined both the RfD and RfC for 1,4-dioxane, there is no national maximum contaminant level (MCL) for this contaminant (United States Environmental Protection Agency, 2014b). Some states have somewhat of a regulatory limit, such as Massachusetts, who has an Office of Research and Standards Guideline Level limit of 0.0003.
mg/L (0.3 ppb), but 1,4-dioxane is not currently federally regulated (Mass.Gov, 2015). Recently, 1,4-dioxane has been included on EPA’s Contaminant Candidate List 3 (CCL 3), which is a list of contaminants known or thought to be present in drinking waters that are not currently regulated, but may eventually require federal regulation under the Safe Drinking Water Act, and has also been placed on the newest list, the Contaminant Candidate List 4, in 2015 (United States Environmental Protection Agency, 2014a, 2014b, 2015a). The process to create the CCL 3, which was the first CCL to contain 1,4-dioxane, began by listing potential drinking water contaminants, which totaled to about 7,500 initial contaminants for the EPA to consider (United States Environmental Protection Agency, 2014a). This was then narrowed down to the final CCL 3, which included 116 contaminants, of which, 1,4-dioxane was included (United States Environmental Protection Agency, 2014a). The fact that 1,4-dioxane remained on CCL 3 amongst over 7,000 other contaminants, and was again put on CCL 4, indicates its emerging danger within our drinking water.

Use

1,4-Dioxane is used commercially and in the manufacturing industry. It has been detected in paint strippers, dyes, greases, varnishes, and waxes and can also be found in antifreeze and aircraft deicing fluids, as well as consumer products such as deodorants, shampoos, and cosmetics (United States Environmental Protection Agency, 2014b). In many of these occurrences, 1,4-dioxane is not directly used, but formed as a by-product or impurity. The resins used in paint production often contain methyl chloroform and dichloromethane, which may form 1,4-dioxane as a by-product (Mohr et al., 2010). There is typically no direct use of 1,4-dioxane in printing inks, yet the contaminant is again a possible by-product of methyl chloroform and/or propylene glycol in this industry (Mohr et al., 2010). When producing antifreeze and aircraft deicing fluids, 1,4-dioxane is created as an impurity from the manufacturing of glycol (Mohr et al., 2010). In the cosmetic industry, it was not originally known that 1,4-dioxane was present in many products (Mohr et al., 2010). It has since been discovered that 1,4-dioxane was produced as a by-product from surfactants used in the manufacturing processes of many cosmetics, before the risks of the contaminant were known and studied (Mohr et al., 2010).

Because of its use and by-product formation in manufacturing, 1,4-dioxane is commonly found in wastewater from industrial plants and landfill leachate (Mohr et al., 2010). Improper
disposal and spills have resulted in the spread of 1,4-dioxane to surface water, groundwater, soil, and the air (Mohr et al., 2010). 1,4-Dioxane also has been detected in many foods, most probably because the water used in food production may have trace amounts of the contaminant (Mohr et al., 2010). Since it is used as a stabilizer for chlorinated solvents, such as 1,1,1-trichloroethane (TCA), it is expected that 1,4-dioxane will be found where these solvents are also known to be polluting (United States Environmental Protection Agency, 2014b).

Fate and Transport in the Environment

1,4-Dioxane is currently not typically released into the environment because of regulations on wastewater, but it can be introduced into the environment from the effluent of treated water in which 1,4-dioxane was not efficiently removed, or from accidental spills and improper disposal (Mohr et al., 2010). 1,4-Dioxane is highly soluble in water, is not found to be biodegradable, does not readily volatilize, is not adsorbed easily, and is highly mobile within the environment (Zenker et al., 2003).

When introduced into surface water, 1,4-dioxane is altered and transported due to the movement of the water, biological processes, sunlight, sedimentation, and various chemical reactions (Mohr et al., 2010). Movement of 1,4-dioxane in surface water can further contaminate the environment, end up in drinking water, or also end up in groundwater. When in groundwater, 1,4-dioxane is very mobile and will persist in that environment due to the fact that it does not normally adsorb onto sediment and because it is very soluble in water (Morrison et al., 2004). Groundwater contamination including 1,4-dioxane is expected to become quite large in area and volume, especially due to this contaminant’s mobility (Morrison et al., 2004).

Treatment of 1,4-Dioxane

Typical water treatment processes include precipitation-coagulation, volatilization through air stripping, carbon adsorption, and conventional biological treatment (Zenker et al., 2003). 1,4-Dioxane has been detected in drinking water as early as the mid-1970s, and because of all the aforementioned characteristics, is not efficiently removed by these conventional water treatment processes (Zenker et al., 2003). Advanced oxidation processes have been proven to successfully remove 1,4-dioxane and are a more practical approach than the conventional, less effective methods previously listed (Zenker et al., 2003).
Occurrences and Case Studies

Stanford Linear Accelerator Center

The Stanford Linear Accelerator Center (SLAC) is a laboratory and research facility owned by Stanford University and used by both the university and the United States Department of Energy (Mohr et al., 2010). SLAC is known for the Stanford Linear Collider, which is the largest linear particle accelerator in the world (Mohr et al., 2010). SLAC has previously stored solvents, specifically methyl chloroform with 1,4-dioxane as a stabilizer, that were then used to clean parts and for painting (Mohr et al., 2010). In 1984, it was discovered that the soil and groundwater around the area were contaminated with these solvents, and as a result, the California Regional Water Quality Control Board required a cleanup of the contaminated areas around the facility, as well as the installation of over 100 groundwater monitoring wells (Mohr et al., 2010).

1,4-Dioxane has been used primarily as a stabilizer for methyl chloroform at SLAC (Mohr et al., 2010). Four contaminant plumes containing volatile organic compounds (VOCs) have been identified from the SLAC facility, three of which contained both 1,4-dioxane and methyl chloroform (Mohr et al., 2010). These three plumes originated from the Former Solvent Underground Storage Tank (FSUST), the Plating Shop Area, and the Former Hazardous Waste Storage Area (FHWSA) (Mohr et al., 2010). At all three of these locations, there was never any reported direct disposal of solvents (Mohr et al., 2010). The cause of the contamination was from spills and leaks in these areas (Mohr et al., 2010).

As of 2010, all of the SLAC plumes containing 1,4-dioxane were less than 200 feet long and traveled at less than 10 feet per year (Mohr et al., 2010). The remediation for the FHWSA site included a duel-phase extraction system in which groundwater and soil vapor was sent to an air stripper to remove VOCs (Mohr et al., 2010). The air stripper influent had a 1,4-dioxane concentration range of 1.8 to 2.2 μg/L, and approximately 50.6 pounds of VOCs have been removed since December 2003 (Mohr et al., 2010).

In the FSUST area, another dual-phase groundwater and soil vapor extraction process was installed, but instead discharged to granular activated carbon (GAC) vessels (Mohr et al., 2010). 1,4-Dioxane concentrations in this area were as high as 3,100 μg/L, but have ranged from
75 to 480 μg/L in 2006 and 2007 for combined extraction wells (Mohr et al., 2010). The GAC effluent has been nondetect for 1,4-dioxane, meaning at a concentration below the instrument’s detecting capabilities, which may have been because the right bacteria capable of 1,4-dioxane biodegradation were present in the low flow, possibly warmer, treatment system (Mohr et al., 2010). Another reason for the nondetect effluent conditions using GAC may have been due to the very slow flow rate (0.2 gpm) through the vessels, allowing for adsorption into GAC pores instead of onto GAC surfaces (Mohr et al., 2010). The last theory for 1,4-dioxane removal using GAC was that some of the contaminant was oxidized by chlorine, while the rest was biodegraded by microbial life that thrived in the right conditions within the GAC vessels (Mohr et al., 2010). It is important to note that under normal conditions, 1,4-dioxane is not typically fully removed by GAC treatment, and that this case was quite unique (Zenker et al., 2003).

Orange County Water District

The Orange County Water District (OCWD) implemented a groundwater replenishment system in which the district thoroughly treats wastewater before pumping it back into the ground (Mohr et al., 2010). It has been found that 1,4-dioxane was present in the recycled, treated water, which contributes to 70% of the water serving 2.3 million people in 20 cities (Mohr et al., 2010). OCWD utilizes the groundwater replenishment system to maintain the groundwater table and to also prevent saltwater intrusion (Mohr et al., 2010). Injection wells were implemented in 1965 to initially prevent saltwater intrusion, and in 1971, the California Department of Health Services approved the full-scale project to add additional injection wells and use 100% treated wastewater in the process (Mohr et al., 2010). Water Factory 21, which is the advanced wastewater treatment facility, opened in 1976 and utilized chemical clarification, air stripping, recarbonation, filtration, GAC adsorption, and chlorination to treat 15 million gallons per day (Mohr et al., 2010).

Water Factory 21 had concentrations of 1,4-dioxane, detected in both the influent and effluent water in December 2001 (Mohr et al., 2010). Concentrations ranged from 1 to 75 μg/L, with two outlier concentrations of 150 and 200 μg/L (Mohr et al., 2010). Nine out of 19 sampled wells tested positive for 1,4-dioxane with concentration levels between 4 and 20 μg/L, while California’s action level for 1,4-dioxane is 3 μg/L (Mohr et al., 2010). Even though California does not require shutting down well service unless the concentration level reaches 100 times the action level, the affected wells were put off line (Mohr et al., 2010). The discovery of 1,4-
dioxane in OCWD’s Water Factory 21 has led to the continued testing of 1,4-dioxane within the factory, as well as refining the methods in which it is tested for (Mohr et al., 2010).

The fluctuations in 1,4-dioxane concentrations suggested that there was point source pollution from specific industrial wastewater effluents (Mohr et al., 2010). Once the responsible party was found, which was a cellulose acetate membrane manufacturer, they stopped releasing 1,4-dioxane into their wastewater, and the concentrations of the contaminant in Water Factory 21 influent water dropped to 1 μg/L (Mohr et al., 2010). This manufacturer released 48,000 to 87,000 lbs/year of 1,4-dioxane into the sewer, which accounts for the diluted concentrations that were detected at Water Factory 21, located about five miles away (Mohr et al., 2010).

In 2002, UV and 5 mg/L of hydrogen peroxide treatment was added to Water Factory 21 in order to remove increased concentrations of NDMA, but these levels were not sufficient enough to remove 1,4-dioxane (Mohr et al., 2010). If 1,4-dioxane concentrations were not lowered after point source investigation, a hydrogen peroxide dose of about 10-15 mg/L would have been sufficient to remove the contaminant (Mohr et al., 2010).

Army Creek Landfill

Army Creek Landfill, formally known as Llangollen Landfill, is located southwest of Wilmington, Delaware (DeWalle et al., 1981). The landfill is approximately 4,000 feet long and 900 feet wide, and is a total of 47 acres (DeWalle et al., 1981). It was used between the years 1960 and 1968 by New Castle County as the main disposal location for both municipal and industrial solid wastes (DeWalle et al., 1981). With about 30% of the landfill’s volume being beneath the seasonal high water table, the waste was dumped in standing water until it was covered with sand in 1970 and purchased by the county to be turned into a future park (DeWalle et al., 1981).

Contaminants from the landfill, one of which was 1,4-dioxane, were already in contact with the groundwater table, and were thus able to travel through the groundwater and pollute downstream from the landfill (DeWalle et al., 1981). Leachate from the Army Creek Landfill was analyzed and numerous volatile organics were identified (DeWalle et al., 1981). Due to the removal of a clay layer in the area, the Upper Potomac Aquifer was exposed to landfill leachate (DeWalle et al., 1981). Major well fields were tapped into the Upper Potomac Aquifer, supplying
approximately 6.5 million gallons per day to the public (DeWalle et al., 1981). Eventually, contaminants began affecting some households in the area, so a contaminant control program was put in place in order to prevent the plume from further affecting the well fields (DeWalle et al., 1981). Seven recovery wells were installed in 1973 to pump about 3.5 million gallons per day in between the landfill and the well fields, creating additional cones of depressions, and pumping contaminated water elsewhere before reaching the public supply wells (DeWalle et al., 1981).

Of the eight wells sampled as part of this study, three were positive for 1,4-dioxane with concentrations between 0.1 and 2.4 μg/L (DeWalle et al., 1981). 37% of the groundwater samples contained 1,4-dioxane (DeWalle et al., 1981). It was shown that the contaminant control program effectively averted the leachate from reaching the public supply wells (DeWalle et al., 1981). Though this program was somewhat successful, the contaminated water was not treated, but instead discharged into Army Creek and the Delaware River. This means that the contaminants, such as 1,4-dioxane were still able to persist in the environment, just not where they were originally located. This can cause contamination problems for other communities in the future, downstream of Army Creek and the Delaware River.

Landfill Leachate Testing in Japan

In Japan, wastes can be put into three different kinds of landfills, depending on their toxicity: open landfills, controlled landfills, and closed landfills (Yasuhara et al., 1999). Open landfills are for lower risk materials, controlled landfills are for semi-toxic wastes, and closed landfills are enclosed and protected from the environment for more dangerous materials (Yasuhara et al., 1999). Of the hazardous wastes disposed of in Japan, approximately 30% of them are buried in landfills (Yasuhara et al., 1999). A 1995 study in Japan tested 11 landfill leachates for both organic and inorganic contaminants (Yasuhara et al., 1999). With the use of gas chromatography and mass spectrometry, about 190 organic compounds alone were identified in the leachate samples (Yasuhara et al., 1999).

1,4-Dioxane was one of the contaminants detected in 10 of the 11 landfills, with concentrations ranging from 0.8 to 190 μg/L with a median concentration of 31.7 μg/L (Yasuhara et al., 1999). The median concentrations of multiple identified contaminants had increased since a similar study done the year before (Yasuhara et al., 1999). It was found that waste plastics were a possible origin of many of the contaminants and that sewage sludge that
was disposed of in Japanese landfills was high in chlorinated organic compounds, thus releasing these compounds into the landfill leachate (Yasuhara et al., 1999). As stated before, 1,4-dioxane is used as a stabilizer for chlorinated solvents, so it is no surprise that 1,4-dioxane was found amongst these chlorinated compounds. “The detection of 1,4-dioxane at high concentrations in most of leachates is serious because of its toxicity and resistance to biodegradation,” (Yasuhara et al., 1999).

Advanced Oxidation Processes

Introduction

An Advanced Oxidation Process (AOP) is an oxidation process in which the dominant reactive species are hydroxyl radicals. AOPs effectively achieve two goals: making substances more biodegradable, and converting organics to simple products, such as water and carbon dioxide (Jia et al., 2011). According to the transition state theory, hydroxyl radicals have the potential to accelerate oxidation rates of organic compounds, which in turn, degrades them faster (Tang, 2004). A catalyst is a substance added to a reaction to increase the production rate of a desired product. A photocatalyst is a substance that produces hydroxyl radicals when it interacts with photons (Tang, 2004). Some of the most effective AOPs studied so far include UV/H₂O₂, UV/O₃, and UV/TiO₂ (Tang, 2004). All of these AOPs rely on UV light producing photons that decompose a photocatalyst into hydroxyl radicals (Tang, 2004). Since the efficiency of AOPs is compound specific, each of these must be studied to determine their validity as a contaminant treatment option (Munter, 2001).

Fundamentals

UV/H₂O₂, UV/O₃, and UV/TiO₂ all rely on the production of hydroxyl radicals to degrade contaminants in water. In the case of UV/H₂O₂, the ultraviolet light cleaves the oxygen-oxygen bond within the hydrogen peroxide, thus creating two hydroxyl radicals (United States Environmental Protection Agency, 2015b). When UV/O₃ is used, ozone is converted into oxygen and hydrogen peroxide in the presence of water and UV radiation (Spartan Environmental Technologies). Next, ozone interacts with the created H₂O₂ to produce hydroxyl radicals and oxygen (Spartan Environmental Technologies). As a photocatalyst, TiO₂’s surface first needs to be exposed to light that carries energy greater than or equal to its bandgap energy (ΔEbg)
(Thiruvenkatachari et al., 2008). This gives the electrons enough energy to jump from the valence band to the conduction band, which forms a positive hole in the valence band (Thiruvenkatachari et al., 2008). The electron in the conduction band reduces oxygen adsorbed to the photocatalyst, while the positive hole either oxidizes contaminants directly or oxidizes water to produce hydroxyl radicals (Thiruvenkatachari et al., 2008). The key factors for an efficient advanced oxidation process are the reactor, the light source, and the photocatalyst used (Thiruvenkatachari et al., 2008).

Titanium Dioxide

TiO$_2$ is an odorless and tasteless solid white powder and can be slightly hazardous if inhaled or ingested (Sciencelab.com, 2013). It is chemically and biologically inert, as well as resistant to photo and chemical corrosion (Alvarez Corena, 2015). It is used in a variety of production processes, including the production of plastics, enamels, artificial fibers, electronic materials, and rubber (Tang, 2004).

TiO$_2$ is classified as a semiconductor, which are characterized by their band structures. The valence band (VB) is an electron-rich band of closely bonded atoms in a series of closely packed energy levels. The conduction band (CB) is an electron-deficient band consisting of a series of spatially diffuse atoms with similar energy levels at a higher energy (Tang, 2004). The difference between the VB’s and CB’s energies results in the thermal distribution of the CB, which is responsible for the overall particle’s electrical conductivity. This gap also defines TiO$_2$’s sensitivity to irradiation by photons at different wavelengths (Tang, 2004).

TiO$_2$ has both amorphous and crystalline phases, with its crystalline phases being the most important factor for its photocatalytic performance. It exists as crystalline in three different phases: rutile, brookite, and anatase (Alvarez Corena, 2015). Anatase has been shown to have the greatest photocatalytic activity, but this does not mean that pure anatase is the best option for AOPs. In studies, a mixture of anatase and rutile has shown to be most effective because of a wider pore size distribution along with the introduction of mesoporosity (Thiruvenkatachari et al., 2008). A mixture of anatase and rutile, called Degussa P25, has been shown to have a higher photocatalytic effectiveness than other forms of TiO$_2$. This is because the synergistic combination of anatase-rutile makes this form very effective at absorbing light, and the rutile gives its carrier electrons a longer lifespan (Alvarez Corena, 2015).
Ultraviolet Light

Ultraviolet light as a photolysis treatment has low organic contaminant removal (Alvarez Corena, 2015). However, when combined with a photocatalyst, the interaction of the two produce photons, which are key in AOPs. The source of UV light and the properties of the UV light itself can affect the production of these photons (Tang, 2004). Because of this, it is important to know the fundamentals of how UV light-based treatment works, and where different sources of UV light can come from.

UV light can exist in wavelengths between 100 nm to 400 nm and energies between 3 eV to 124 eV (Alvarez Corena, 2015). The characteristics of the UV light that affect the photocatalyst include wavelength, quantum yield, photon flux rate, and UV irradiance (Alvarez Corena, 2015). The AOP process relying on TiO$_2$ as the photocatalyst requires wavelengths less than 400 nm (Alvarez Corena, 2015).

UV light can be produced by UV lamps, of which there are a variety. Although there are other technologies available, the most common lamps rely on mercury (Masschelein et al., 2002). Mercury based lamps come in three common varieties based on the inside pressure, which are low-pressure, medium-pressure, and high-pressure (Masschelein et al., 2002). These lamps rely on a filler gas, most commonly argon, which is responsible for starting the activation-ionization of the mercury as well as starting the discharge of light (Masschelein et al., 2002). This technology uses mercury by activating its electrons through collisions with the filler gas, creating emissions of light (Masschelein et al., 2002). The activation of mercury in the gas phase is done at temperatures compatible with the lamps, and it is the most volatile metal element that has this characteristic (Masschelein et al., 2002). Because mercury is hazardous to human health, care must be taken when using this technology so that the water is not contaminated further (Masschelein et al., 2002).

Each type of lamp has its own properties that need to be considered, such as wavelength produced, lifetime, operating temperature, and cost to maintain, operate, and dispose of (Masschelein et al., 2002). The outer shell of most UV lamps are made of quartz, which age due to a loss in transmission, scaling deposits, and slime-building effects (Masschelein et al., 2002). Factors such as these need to be considered when deciding which lamp to use, as some lamps
might produce a favorable wavelength, but due to a low lifetime, make it too expensive to be a viable option.

Low-pressure mercury lamps are operated at total gas pressures between $10^2$ to $10^3$ Pa, with the filler gas being in excess of the mercury by 10 to 100 times (Masschelein et al., 2002). At thermic equilibrium conditions, liquid mercury is always present. Medium-pressure mercury lamps operate at a total gas pressure between 10 to 30 MPa. Both low-pressure and medium-pressure have an inside lamp temperature of 5,000 to 7,000 K and are based on plasma emission. High-pressure mercury lamps operate at total pressures of up to $10^6$ Pa, and are not suitable for photochemical reactions because they emit continuous spectra not useful for the reactions (Masschelein et al., 2002). Medium-pressure lamps age faster than low-pressure lamps, having a lifetime of about 4,000 hours compared to 10,000 hours. Medium-pressure lamps also require 3-5 kV depending on the wavelength and intensity desired, while low-pressure lamps operate at low voltages close to 220 V. Medium-pressure mercury lamps generally produce higher wavelengths between 250-580 nm with higher intensities than low-pressure lamps, which produce wavelengths between 180-360 nm (Masschelein et al., 2002). This makes the wavelength and intensity needed for a system the deciding factor in choosing which lamp will be the most economically feasible.

Advanced Oxidation Process using UV and TiO$_2$

TiO$_2$ can be added to water and activated by UV light to produce hydroxyl radicals in a heterogeneous photocatalytic oxidation process. The UV light excites the TiO$_2$, which produces hydroxyl radicals, which then perform redox reactions that have the potential to degrade organic contaminants. This process degrades many types of organics, and with its low amounts of toxic byproducts, large availability, and low operational costs, it is a viable AOP option (Alvarez Corena, 2015). The use of this technology was first commercialized in the 1990s, and has steadily grown in popularity as it continues to be studied for treating various emerging organic contaminants present in wastewater (Tang, 2004).

There are two ways to introduce the TiO$_2$ to the wastewater, the first of which is by adding the powdered form in the water and completely mixing it in what is called a slurry reactor (Alvarez Corena, 2015). This is effective in degrading organic materials, however, the TiO$_2$ must be separated from the water after the contaminant has been degraded. Doing this is difficult and
expensive, and is therefore not a practical process (Thiruvenkatachari et al., 2008). The second method involves attaching the TiO₂ to a medium, such as silica gels, glass beads, ceramic membranes, or fiberglass. This eliminates the need for separation of TiO₂, but has also been shown to slow the organic degradation rate by 2-6 times (Tang, 2004). This is because the degradation reaction relies on many factors, with one of the most important being surface area of TiO₂. If TiO₂ is fixed on a medium, it does not come in contact with as much organic material as it would in a slurry reactor.

Uses

UV/TiO₂ has been studied to treat a variety of substances. Attached to a membrane, it has been shown to effectively decrease the concentrations of pharmaceuticals, endocrine disrupting compounds, and estrogenic activity in wastewater (Benotti et al., 2009).

Wuhan, China

Macromolecular organic substances are commonly found in landfill leachate (Jia et al., 2011). A study was conducted by Jia Chenzhong, Yanxin Wang, Ciaxiang Zhang, and Qiaoyan Qin to determine the effectiveness of UV/TiO₂ in removing these organic substances (Jia et al., 2011). This was done by testing the chemical oxygen demand (COD), biological oxygen demand (BOD), dissolved organic carbon (DOC), and color both before and after treatment (Jia et al., 2011). Their system used a slurry reactor that utilized TiO₂ consisting of 70% anatase (Jia et al., 2011).

The COD content in wastewater is an indicator of the organic matter in the water, and a reduction in COD would mean the organics have been converted to simple final products, such as water and CO₂ (Jia et al., 2011). The BOD/COD ratio is also an indicator of the biodegradability of wastewater (Jia et al., 2011). When the ratio is above 0.4, the wastewater is considered completely biodegradable, and between 0.3-0.4, it is considered partially biodegradable (Jia et al., 2011).

The UV/TiO₂ system used was able to increase the BOD/COD ratio up to 0.39, as well as removed 60% COD and 72% DOC content (Jia et al., 2011). These results show that complete mineralization by only a photocatalytic treatment was difficult, but it was able to increase the biodegradability enough that it could be feasible to use as a pretreatment (Jia et al., 2011). This
means that a secondary biological treatment would be effective if used after a pretreatment of UV/TiO₂ (Jia et al., 2011). Biological treatment would be able to degrade leftover organics that were not mineralized by the photocatalytic process.

Challenges

Although UV/TiO₂ is a promising method for contaminant degradation, it does have its challenges. Because of the need for separation in some instances, it can be too expensive to be used as a sole treatment (Jia et al., 2011). But, because biodegradability has been shown to increase with photocatalytic process, it can be used as a pretreatment process for water with organic contaminants (Jia et al., 2011). Not much is known about the UV/TiO₂ process's effectiveness as a pre-treatment, and there are a variety of factors that can affect the effectiveness of AOPs in the water under consideration.

As discussed earlier, one of these factors is the type of reactor used. Fixed-media reactors are beneficial compared to slurry reactors because they eliminate the need for post-treatment to separate and remove the TiO₂ (Thiruvenkatachari et al., 2008). However, some studies have reported both scouring and detachment of the TiO₂ powder (Thiruvenkatachari et al., 2008). Fixing TiO₂ on the media also requires heating, which decreases its porous structure. These combine and reduce the area-to-volume ratio of the TiO₂, which results in ineffective mass transfer (Thiruvenkatachari et al., 2008). This makes fixed-media reactors much less effective at photocatalytic degradation by decreasing the degradation rate by up to a factor of ten compared to slurry reactors (Thiruvenkatachari et al., 2008).

The pH of the water is also an important parameter for the process. The pH can change the TiO₂'s surface charge, which can alter the reaction rates and TiO₂'s tendency to aggregate (Alvarez Corena, 2015). Also, if the water has a high alkalinity concentration, it can react with the hydroxyl radicals produced, decreasing the effectiveness. Because of these, the UV/TiO₂ process has been found to be more effective at acidic pH levels (Jia et al., 2011). To adjust the pH, HCl and NaOH can be added. A pH of 5.0 has been shown to result in the highest degradation rate constants (Alvarez Corena, 2015).

The concentration of TiO₂ affects the degradation rate during the AOP process. Generally, larger concentrations result in larger degradation rates, meaning that the organic
contaminant is broken down faster (Jia et al., 2011). This is because an increase in TiO$_2$ means more surface area and active sites for oxidation (Alvarez Corena, 2015). However, a study by Jia Chenzhong, Yanxin Wang, Ciaxiang Zhang, and Qiaoyan Qin showed that the degradation rate only increased up to a TiO$_2$ concentration of 2.0 g/L (Jia et al., 2011). After this, the addition of more TiO$_2$ decreased the UV transmittance, ultimately decreasing contaminant removal (Alvarez Corena, 2015).

Photocatalytic Oxidation of 1,4-Dioxane

There are many advanced oxidation process options when trying to degrade 1,4-dioxane in water. Some oxidants include ozone, hydrogen peroxide, and titanium dioxide with the use of UV light (Tang, 2004). The use of UV/H$_2$O$_2$ to degrade 1,4-dioxane has been thoroughly researched by Stefan and Bolton. They have concluded that because 1,4-dioxane is very soluble in water and has a low vapor pressure, adsorption by activated carbon and volatilization through air stripping is not practical (Stefan et al., 1998). Their research showed that through oxidation, intermediate substances were created from 1,4-dioxane’s degradation, and ultimately mineralized and removed (Stefan et al., 1998). Intermediates that were characterized in these experiments included aldehydes such as formaldehyde, acetaldehyde, and glyoxal, organic acids, including formic, methoxyacetic, acetic, glycolic, glyoxylic, and oxalic acids, and mono- and diformate esters of 1,2-ethanediol (Stefan et al., 1998).

1,4-Dioxane reacts very rapidly with hydroxyl radicals because of its high rate constant (Stefan et al., 1998). The process first turns 1,4-dioxane into hydroxylated 1,4-dioxane, which opens rings and forms organic acids, and then is ultimately converted to CO$_2$ and H$_2$O (Zenker et al., 2003). The most significant byproduct of this reaction is ethylene diformate (Zenker et al., 2003).

The amount of the organic contaminant adsorbed on the TiO$_2$ surface can give us an estimate of the kinetic rate of the photocatalytic process (Alvarez Corena, 2015). A first order reaction rate equation has been developed, the final form of which is:

$$C = C_0 e^{-kt}$$  \hspace{1cm} (Equation 1.1)

$C_0$ is the initial 1,4-dioxane concentration, $C$ is the final 1,4-dioxane concentration, $t$ is the reaction time elapsed, and $k$ is the first order reaction rate constant. These values can be found
from experimentation and then used to solve for k. The first order reaction rate constant will differ depending on the AOP method used because it is influenced by a variety of factors including properties of the photocatalyst, number of adsorption sites, reaction mechanisms, intermediate formations, concentration of oxygen, and irradiation (Alvarez Corena, 2015). Studying the results of the first order model is important in designing scale-up reactors based on experimental data (Alvarez Corena, 2015).
Experimental Material and Methods

Calibration Curve
Before testing in the reactor, a gas chromatograph (GC) calibration curve was created, using the Agilent Technologies 6890N Network GC System. A 200 mg/L stock solution of 1,4-dioxane was prepared. From this stock solution, various dilutions were prepared to create the following concentrations to test: 1 mg/L, 2 mg/L, 3 mg/L, 4 mg/L, and 5 mg/L. 10 mL of each concentration was pipetted into GC vials. 4 grams of NaCl was added to each vial to promote volatilization, along with 50 μL of 0.0013 M chlorobenzene, which was used as an internal standard. These five concentrations were run on the GC, and the area under the 1,4-dioxane peak for each concentration (located at approximately 12 minutes) was recorded and used to create a concentration versus area curve, which was used as the calibration curve to determine unknown concentrations.

Peak Area to Concentration
The areas under the peaks for 1,4-dioxane and the internal standard were used to determine the concentration of 1,4-dioxane. The following relationship was used:

\[
\frac{\text{Area}_{1,4\text{-dioxane}}}{\text{Area}_{\text{chlorobenzene}}} = mC + b
\]  
(Equation 3.1)

Where \( m \) is the slope determined from the calibration curve, \( b \) is the y-intercept also determined from the calibration curve, and \( C \) is the concentration of 1,4-dioxane.

Chemicals and Reagents
Titanium dioxide (TiO₂) impregnated on glass fibers was the photocatalyst used in this experiment. The phase and distribution of the TiO₂ was found using Raman Spectroscopy (Horiba Xplora). Glass fibers were taken off of a larger sample using tweezers and put under the Raman microscope. These fibers were analyzed by the spectroscope and produced a unique spectrum for the phase of TiO₂ on the glass fibers that helped identify it.

Bench Scale Batch Reactor
A 1 L water-jacketed batch photoreactor (Ace Glass, Vineland, NJ, USA) was used for the photocatalytic experiments. This photoreactor consisted of a double-walled quartz immersion
well with a removable inner cooling tube, as well as a medium-pressure mercury 100 Watt lamp that produced between 40-48% of its radiated energy in the range of ultraviolet light. In order to keep a constant water temperature, a refrigerator bath circulator unit (NESLAB™, RTE-111) was used. To obtain a complete mixture of the aqueous solution, a Fisher Scientific magnetic stirrer was used at 350 rpm during experiments. Oxygen was supplied at a constant rate of 3 ft³/min.

Controls
Multiple controls were tested to ensure that no one variable influenced the results without our knowledge. These controls included running a 5 mg/L sample with the original pH of about 5.4, with a constant oxygen supply, and being constantly stirred. The controls tested were the following:

1. No UV light and no TiO₂
2. UV light and no TiO₂
3. No UV light and TiO₂
4. Using the same TiO₂ for multiple runs

Factors Affecting the Photocatalytic Degradation
Different variables were changed during different experiments in order to determine their effect on degradation and the extent of their effect. The variables tested were pH and time. Other factors that could have an effect on the degradation, but were kept constant included TiO₂ concentration (taken as the mass of the fiberglass), the type of photocatalyst, temperature, UV wavelength and radiant flux, and the initial 1,4-dioxane concentration.

Effect of Time
A series of experiments were conducted with varying reactor run times. The samples were run in the reactor for the following amounts of time: 1 minute, 5 minutes, 10 minutes, 15 minutes, 30 minutes, and 45 minutes. All other variables remained the same during these runs.

Effect of pH
In order to adjust the pH of the 5 mg/L 1,4-dioxane sample, 0.01 N hydrochloric acid (HCl) and 0.1 N sodium hydroxide (NaOH) were used. Samples were adjusted separately to a pH of 3, 5, 7,
and 9 and ran in the reactor. All other variables remained constant, including the TiO₂ concentration.

Sample Preparation
A stock solution of 200 mg/L was prepared each week by mixing 39 µL of 1,4-dioxane with 200 mL of pure water, and stored at 4°C in the refrigerator. This stock was used to create 5 mg/L solutions to use in the reactor. The sample was then transferred to the photoreactor and exposed to the UV light for the designated reaction time. For each run, three samples were taken and analyzed using the GC. The peak area results were compared to the calibration curve that was created in order to deduce the concentration of 1,4-dioxane remaining in the sample. For each batch of samples that were run using the GC, a 5 mg/L spike was created and tested at the end of the run to ensure the machine stayed consistent.

First Order Reaction Rate Constant
The reaction rate constant (k) is found by plotting the natural logarithm of the concentration at different recorded times during the photocatalytic reaction versus the related time (ln C vs. t) at specific conditions of pH, UV irradiation power, and TiO₂ concentration.

\[
\frac{dc}{dt} = -kC \quad \text{(Equation 3.2)}
\]

\[
C = C_0 e^{-kt} \quad \text{(Equation 3.3)}
\]

Normalization of First Order Kinetic Rate to Energy Delivered per Volume
Design parameters such as the energy delivered by the UV lamp and volume of the reactor chamber were used to normalize the first-order kinetic constants. This normalized rate (k') is shown in Equation 3.4:

\[
C = C_0 e^{-(k')(\frac{P}{V})} \quad \text{(Equation 3.4)}
\]

Where P is the net power of the lamp in the UV range and t is the exposure time in minutes. These two values multiplied together make Ed, which is the energy delivered.
Results

TiO₂ Impregnated Glass Fibers

With the use of a Raman Spectrometer (Horiba Xplora), the phase of the TiO₂ was determined. The spectrometer had a 532 nm laser, operated at 25 mW of power, with 1800 grating and a lens that magnified 100 times. Typical Raman spectra for three isotopes of the anatase form of TiO₂ are shown in Figure 2.

As seen in Figure 2, the typical peaks for anatase are located at Raman Shifts of about 150 cm⁻¹, 390 cm⁻¹, 520 cm⁻¹, and 640 cm⁻¹. The spectra obtained from our first two samples are shown in Figure 3.
These spectra obtained in the lab very closely resemble the typical spectrum for anatase, resulting in the conclusion that the TiO$_2$ impregnated glass fibers are in fact impregnated with the anatase form of TiO$_2$. 

Figure 3a: Anatase Spectrum from First Run

Figure 3b: Anatase Spectrum from Second Run
Images of the TiO\textsubscript{2} impregnated glass fibers obtained from the microscope in the Raman spectrometer are shown in Figure 4 Figure 5.

![Figure 4: Magnified Image of Glass Fiber (1)](image1)

![Figure 5: Magnified Image of Glass Fiber (2)](image2)

When the spectrometer laser was focused on the “globs” shown in the figures, the spectra in Graph 1 and Graph 2 were typical results, meaning that the “globs” on the fibers are pure anatase. When focused on the actual fiber, a different spectrum emerged, as shown in Figure 6.
This is due to the fact that the anatase is not evenly distributed on the glass fibers, and contained both large and small TiO$_2$ concentrations at different locations along the tested fibers. The spectrum shown in Figure 6 is different from the spectra obtained from the anatase globs. The spectrum in Figure 6 very closely resembles the spectra from a study on silica nanoparticles, shown below in Figure 7, further validating that the anatase is impregnated on glass fiber. The silica nanoparticles have peaks at Raman shifts leading up to 500 cm$^{-1}$ and at 600 and 800 cm$^{-1}$, which is also true for the Raman spectrum obtained on the fiberglass sample that was tested.

Figure 6: Spectrum when Focused on Glass Fiber

Figure 7: Raman Spectra of Silica Nanoparticles (Alessi et al., 2013)
Based on Figure 4 and Figure 5, it was approximated that 11%-22% of the fiberglass/TiO₂ complex volume is strictly TiO₂, based on the amount of “globs” to length of fiberglass. For calculation purposes, it was estimated that 16.5% of the total fiberglass/TiO₂ volume was TiO₂. Using the densities of glass (~2.5 g/cm³) and titanium dioxide (~4.23 g/cm³), and a theoretical volume of the fiberglass/TiO₂ complex, it was found that the approximate mass fraction of TiO₂ for this sample was 0.25. These calculations can be found in Appendix E. Of the 0.45 g of fiberglass/TiO₂ used for each reactor run, approximately 0.1125 g of it was titanium dioxide, while the remaining 0.3375 g was glass.

Calibration Curve

In order to use the internal standard when creating the calibration curve for 1,4-dioxane using the GC instrument, the chromatograph peak area of the 1,4-dioxane was divided by the peak area of the chlorobenzene. This was done in order to normalize the 1,4-dioxane peak area to the chlorobenzene peak area, which was the purpose of using an internal standard. An issue was encountered while using this method, as the peak areas of the chlorobenzene varied so greatly from sample to sample. This made some results inconclusive. In some cases, dividing the area of the 1,4-dioxane by the area of chlorobenzene made the concentration of the sample greater than the initial concentration, which was impossible.

The calibration curve that was created for 1,4-dioxane using the GC, without taking into account the internal standard because of this issue, is shown in Figure 8.

![Figure 8: 1,4-Dioxane Calibration Curve](image_url)
The R² value from the linear trend line of this data is greater than 0.99, which shows an almost perfect linear relationship. This calibration curve is the one that was used for each run because of its high R² value, even though the internal standard was not taken into account. So, instead of using Equation 3.1, the concentration of 1,4-dioxane was calculated using the following equation and information from the line of best fit of the calibration curve:

\[ C_{1,4\text{-dioxane}} = \frac{A_{1,4\text{-dioxane}+23.71}}{119.85} \]  

(Equation 4.1)

Experimental Controls

Multiple control experiments were ran to ensure that the degradation of the 1,4-dioxane was due to the combination of UV and the TiO₂ impregnated fiberglass. All control experiments were run with 5 mg/L samples for 15 minutes at constant temperature (20-25°C). These controls included running the sample in the reactor exposed to UV, but with no TiO₂ fiberglass, running the sample in the reactor with neither UV nor TiO₂ fiberglass, running the sample in the reactor with TiO₂ fiberglass, but no UV, and the last was using the same fiberglass sample for multiple runs. The control experiments showed little to no degradation of 1,4-dioxane. This illustrated that the combination of both UV and TiO₂ was needed for the reduction in concentration of 1,4-dioxane present. Due to the increase in turbidity of the water as a result of continued use of the same fiberglass sample for multiple runs, each fiberglass sample was only used for a total of about 45 minutes to 1 hour of run time to avoid elevated turbidity in the samples used for the GC analyses.

Effect of Time

When testing different time intervals, it was discovered that time has a linear inverse relationship with respect to 1,4-dioxane concentration. The graph depicting this relationship is shown in Figure 9.
As can be seen by the line of best fit for this graph, as well as an $R^2$ value of 0.986, the effect of time on the concentration of 1,4-dioxane can be described as linear. As the time that the sample is exposed to UV and TiO$_2$ is increased, the concentration of 1,4-dioxane decreases linearly.

Effect of pH

The pH of each prepared 5 mg/L sample to use in the reactor was about 5.4. After preparing four separate samples and changing this pH to 3, 5, 7, and 9, the data in Figure 10 was collected to compare the degradation of 1,4-dioxane at varying pH levels.
The most degradation of 1,4-dioxane was experienced at a pH of 7. At this point, approximately 30.6% of the 5 mg/L of 1,4-dioxane was degraded, while at the other pH values, the percent removal was quite lower. 1,4-Dioxane removal increased as the pH approached 7 and decreased after as the pH continued to become basic past 7.

**First Order Reaction Rate Constant**

The first order reaction rate was found to be approximately 0.042 min⁻¹. This was achieved by graphing the natural logarithm of the concentration of 1,4-dioxane versus various reaction run times. The resulting slope of the line of best fit is the first order reaction rate constant. The fact that the rate constant is negative in the equation means that the 1,4-dioxane is being degraded. The graph is shown in Figure 11.
Normalization of First Order Kinetic Rate to Energy Delivered per Volume

The first order reaction rate was normalized to the energy delivered per volume. The graph used to distinguish this pseudo-first order rate constant normalized to energy per volume, which is denoted as $k'$, is shown in Figure 12. $k'$ was found to be 0.28 m$^3$/kW·h.

Figure 11: Natural Log of 1,4-Dioxane Concentration versus Time

Figure 12: Natural Logarithm of 1,4-Dioxane Concentration versus Energy Delivered Per Unit Volume (E)
Discussion

TiO₂ Impregnated Glass Fibers

Since anatase has been shown to have the greatest photocatalytic activity out of all three crystalline phases of TiO₂, it is expected that this phase of titanium dioxide on the fiberglass would have the best results, as compared to brookite and rutile. Further studies can be done to confirm this, but based on prior research, it is predicted that anatase would be the best phase for photocatalytic activity (Thiruvenkatachari et al., 2008). It has also been shown that an anatase/rutile mixture can outperform pure anatase (Thiruvenkatachari et al., 2008). This can be further researched to determine if an anatase/rutile impregnated glass fiber would be a better option for this AOP.

As the mass percent of TiO₂ in the fiberglass complex is estimated to only be 25%, there is room for improved 1,4-dioxane degradation by increasing the ratio of TiO₂ to fiberglass mass. As seen in Figure 4 and Figure 5, the so-called “globs” of anatase are quite scarce and spread out. Greater contaminant degradation can be achieved if the TiO₂ was impregnated on the fibers to a greater extent. Approximately three-quarters of the fiberglass/TiO₂ mass sample is simply glass, which is why the reaction rate constant may have been so low as compared to other experiments using just titanium dioxide.

Future work can also be done to find a more accurate mass of TiO₂ in our fiberglass sample. The calculations done were based on an approximate volume percent from a magnified photo of the fiberglass. The titanium mass can be determined using a hydrofluoric acid digestion followed by an analytical technique such as AA or ICP.

Effect of Reaction Time

As the time of the UV exposure increased during reaction runs, the 1,4-dioxane concentration decreased linearly. For the initial 5 mg/L samples in this bench scale study, it is theoretically expected that 100% removal would take approximately 51.4 minutes. In reality, it was nearly impossible to have complete contaminant removal. For the final pilot scale design, the treatment was designed for an effluent 1,4-dioxane concentration of 50 µg/L (a local drinking water MCL) (Bethpage Water District, 2015). Given a starting concentration of 5 mg/L, one would expect it to take approximately 50.9 minutes to achieve a final concentration of 50 µg/L in
this bench scale study. Though these reaction run times are very close, it would be nearly impossible to reach 100% removal.

Effect of pH

The pH that promoted the greatest 1,4-dioxane removal was at pH 7. Previous studies using UV and a TiO2 slurry experienced the greatest 1,4-dioxane degradation at a pH of 5 (Alvarez Corena, 2015). A neutral pH may have experienced the greatest degradation because of the interaction between the hydroxyl radicals produced and the H+ ions and OH− ions associated with an acidic solution and a basic solution. Further testing can be done to determine a more exact pH that results in the best 1,4-dioxane degradation. Though it was found in this study that a pH of 7 was most effective, although the optimal degradation could, in reality, be experienced anywhere between a pH of 5 to 9 because of the chosen testing values.

First Order Reaction Rate Constant

The first order reaction rate constant derived from these experiments is much lower than found in other experiments (Alvarez Corena, 2015). This is most likely due to the fact that the actual mass of TiO2 on the fiberglass used in this study was so low in comparison to the total mass. In order to have a better rate of contaminant removal, the mass of TiO2 impregnated on the fiberglass can be greatly increased. Also, a greater total mass of the fiberglass/TiO2 complex could be used in the reactor. The downside to this method would be that there would be more glass in the water, increasing the possibility for some of the fibers to contaminate the water. The best option would be to increase the TiO2 to fiberglass ratio as much as possible to minimize the material used, and increase the availability of hydroxyl radicals in the reactor, thus increasing the first order reaction rate constant.

Normalization of First Order Kinetic Rates

In this study, the first order reaction rate constant was able to be normalized to the energy delivered per volume. It is also possible to normalize a reaction rate to TiO2 surface area, and then further, normalized to energy and TiO2 surface area. Due to the nature of the fiberglass sample, we were unable to analyze the TiO2 to the extent to normalize the reaction rate to the surface area. In the future, it would be beneficial to determine both the exact mass of TiO2 on the
fiberglass, as well as the specific surface features, such as surface area, of the TiO₂ in this sample.
Pilot System Design

This section describes the design process of a pilot scale system that treats drinking water contaminated with 1,4-dioxane. This pilot system can be used to determine parameters for a larger scale drinking water treatment system. The chosen design consists of a plug flow reactor (PFR) with a feed inlet pipe and outlet pipe velocity of 2 m/s. The diameter of the inlet and outlet piping was calculated based on this velocity and the chosen flow rate of 0.05 m³/min (13.2 gpm). The PFR reactor diameter was chosen to be 50 cm. The diameter of the UV lamp, which was to be scaled up from the batch reactor, must be added to this diameter to calculate the total PFR diameter. The chosen influent contaminant concentration is 2 mg/L. This system was designed to achieve a 1,4-dioxane effluent concentration of 50 µg/L.

The PFR design equation is shown in Equation 6.1.

\[
\ln \frac{c_e}{c_0} = -\frac{k_d d^2}{4L} \frac{Q}{Q} \quad \text{(Equation 6.1)}
\]

With the chosen and known parameters (influent concentration, effluent concentration, first order reaction rate constant, diameter in which water will flow in the reactor, and flow rate), the length of the PFR was calculated using Equation 6.1. This length was calculated to be approximately 22 m. This can be split into four 5.5 m reactors in series. The volume of each reactor was calculated to be 4.4 m³. Since this volume is scaled up approximately 8,600 times from the bench-scale study, the power required for the UV lamp will have to be scaled up the same amount. Using this, the power required would be approximately 40 kW of total UV radiated from the lamp. This can be accomplished by using four lamps, each with a UV power of 10 kW, in each of the four reactors. If each of these lamps has a diameter of approximately 5 cm, the total diameter of the PFR will be 70 cm.

The diameter of the inlet and outlet piping was calculated using the following equation:

\[
d = \sqrt{\frac{Q}{3600 \times v}} \times \frac{4}{\pi} \quad \text{(Equation 6.2)}
\]

Using the selected parameters, the inner diameter of the piping was found to be 2.3 cm. Since this exact size piping is not currently manufactured, Schedule 80 1 inch CPVC pipe with an average inner diameter of 0.936 inches (2.38 cm) will be used instead (Harvel, 2016).
The fiberglass required for this amount of treatment was scaled up in the same way the power was scaled. Since the bench scale study used approximately 0.45 g of fiberglass, the pilot study would require 3,870 g of fiberglass. When this is divided among the four reactors, 967.5 g of fiberglass is used per reactor. The fiberglass would be wrapped around the quartz sleeve of each UV lamp in the reactors, similarly to the bench scale study, as to allow for the greatest contact between the TiO₂ on the fiberglass with the UV light. In order to insure that no fiberglass or TiO₂ remains in the water after treatment, a bag filter will be used at the end of the process to remove any of these particulates.

Depending on the water quality, pH adjustments may need to be made to ensure the desired degradation. Because the bench scale study was done at a pH of ~5.4, the pH of the water should be adjusted to this value before entering the reactors. A peristaltic pump will be used to inject HCl or NaOH at the desired flow rate, depending on what is necessary to get the pH to a value of 5.4 for the specific water sample.

Valves are also necessary for this design. Isolation valves will be used so that their operation is automatic and not manual. Isolation valve placement can be seen in the process flow diagram (Figure 15). The valves are placed in each of their respective locations for maintenance purposes and emergencies. If maintenance is needed at any part of the system, valves can be shut to isolate any portion in order to drain water and perform necessary work on the equipment.

The head loss due to friction in the CPVC piping was calculated. These calculations can be found in Appendix F. First, the Reynolds number was calculated, followed by the relative roughness of CPVC piping. Using these two calculated values, the friction factor was determined from the Moody Chart. Next, the Darcy-Weisbach equation was used to calculate head loss due to friction, which is 0.77 m. For this design, the water source is a well, approximately 35 m deep. The depth of the well, as well as the change in head of the design, which is 2.1 m due to the height of the reactors above the pump, was added to the friction loss for a total head of 37.87 m. The pump chosen that has enough power to deliver water from the well, through the reactors, to a storage tank is a 0.5 HP 4” submersible, stainless steel pump by Pentair. The pump performance curve is shown in Figure 13.
The designed PFR reactor set up is shown in Figure 14. To accommodate for using four reactors, they will be stacked to save space.

The process flow diagram is shown in Figure 15. The total length of pipe from the pump to the storage tank is 10.5 m. There is enough space to the left of the reactors to allow for...
changing out the lamps, changing the TiO$_2$ fiberglass and for other miscellaneous maintenance within the reactors.
Conclusions and Recommendations

After studying the sample of fiberglass/TiO$_2$ and designing a pilot scale study, it has been concluded that there should be a higher concentration of TiO$_2$ on the fiberglass in order to have a higher reaction rate constant and a more reasonable pilot scale system size. It is recommended that the TiO$_2$ concentration on the fiberglass be increased, or the TiO$_2$ be fixed on another type of media so that there may be a greater production of hydroxyl radicals. Also, an anatase/rutile mix impregnated on fiberglass should be researched to see if it would be more effective than anatase.

Due to the relatively low first order reaction rate constant, the PFR reactors had to be quite large. In reality, if this pilot scale design were to be scaled up to a sizable full-size system, it would be economically and spatially overwhelming due to the size of the reactors required to achieve the desired degradation. Also, the power needed for the UV lamps would also be economically undesirable. These lamps also have to fit within the reactors and still maintain a feasible reactor diameter.

It is recommended that other designs be explored in utilizing TiO$_2$/UV as an AOP process. Though the PFR is a very common design to implement UV treatment, other options may be feasible, such as open channel flow with UV lamps overhead. This design should be further studied to see if it can be used with the TiO$_2$ fiberglass in a more efficient configuration than the PFR design.

Overall, we recommend that more testing be done with TiO$_2$ impregnated on glass fibers. We are still uncertain of the exact amount of TiO$_2$ on this sample of fiberglass. It would be beneficial to quantify this amount during further studies, especially to determine whether or not increasing this amount would help in the AOP process of degrading 1,4-dioxane.

From the work completed in this study, it has been shown that TiO$_2$ impregnated on fiberglass and exposed to UV light reduces the concentration of 1,4-dioxane in water. This AOP process follows a first order reaction rate. The greatest degradation occurs at a pH value of 7 and the contaminant concentration is decreased linearly with time. This method of treatment shows promise and should be further researched in order to apply this process to its fullest extent.
Appendix A: Sample Preparation and Analytical Techniques

A.1. Experimental Procedure: Reactor Operation and Sample Preparation
200 mL of purified water and 39 µL of 1,4-dioxane were combined in a 500 mL beaker and stirred for at least 30 minutes to obtain a solution of 1,4-dioxane at 200 mg/L. This solution was used as a stock solution. This stock solution was stored in a refrigerator and disposed of after a week.

1. 12.75 mL of the stock solution prepared in step 1 was diluted with 497.25 mL of pure water in a 600 mL beaker to obtain a solution at 5 mg/L 1,4-dioxane. This solution was prepared as needed for each run and only used on the same day.

2. The TiO\textsubscript{2} impregnated glass fiber used for each run was cut to approximately a 6” x 6.5” rectangle, one layer thick, and measured on a scale. It was ensured that each sample used was approximately 0.45 g.

3. The solution prepared in step 1 along with the desired amount of TiO\textsubscript{2} impregnated fiberglass was added to the reactor. The fiberglass was attached to the quartz glass surrounding the UV light using electrical tape, so that the fiberglass was in the solution and would stay in place. The height of the fiberglass was also ensured to cover the height of the UV lamp and submerged in the solution.

4. The oxygen supply valve was adjusted to a rate of 3 ft\textsuperscript{3}/min, the stir bar set to 350 rpm, and the UV lamp was powered on for the desired time.

5. The UV lamp was turned off after the desired reaction time.

6. The total volume from the reactor was transferred to a beaker. 10 mL of the solution was transferred to the GC vials. This was done three times for each sample.

7. 50 µL of internal standard was added to the 10 mL vials. 4 g of sodium chloride was also added to the 10 mL vials. These vials were then analyzed using the GC-FID technique.

8. Steps 1-7 were repeated every time a sample was prepared to analyze samples at different times and pH levels.
A.2. GC-FID Analysis

An Agilent 6890 gas chromatograph equipped with Agilent 7863 automatic sampler controlled by a computer running Agilent Chemstation software, equipped with flame ionization detector (FID) was used to conduct GC analysis.

- Configuration Details:
  - Injector Volume = 1.0 to 2.0 µL
  - Inlet Mode: Splitless
    - Gas: N₂
    - Heater: 290 °C
    - Pressure: 8.91 psi
    - Total Flow: 45.6 mL/min
    - Purge flow to split vent: 38.9 mL/min at 0.40 min
  - Column
    - Mode: constant pressure
    - Model No.: Restek RTX-5Sil MS – Capillary 30.0 m x 320 µm x 0.5 µm nominal
    - 350 °C max temp
    - Flow: 2.2 mL/min
    - Velocity: 35 cm/s
  - Oven Configuration:
    - Oven Ramp | °C/min | Next °C | Hold min | Run time
      Initial   | ---    | 32     | 4.00     | 4.00
      Ramp 1    | 3.00   | 50     | 0.00     | 10.00
      Ramp 2    | 8.00   | 290    | 3.00     | 43.00
  - FID Detector
    - Heater: 300 °C
    - H₂ flow: 40.0 mL/min
    - Air flow: 450 mL/min
    - Makeup N₂: 45 mL/min
  - Signals
    - Signal 1: 50 Hz – 0.004 min
    - Signal 2: 20 Hz – 0.01 min
Appendix B: Calibration Curve Data Points

<table>
<thead>
<tr>
<th>1,4-Dioxane Concentration (mg/L)</th>
<th>1,4-Dioxane Peak Area</th>
<th>Chlorobenzene Peak Area (Not Used)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>175.3</td>
<td>1104.1</td>
</tr>
<tr>
<td>2</td>
<td>345.4</td>
<td>606.1</td>
</tr>
<tr>
<td>3</td>
<td>430.4</td>
<td>1242.5</td>
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<tr>
<td>4</td>
<td>504.2</td>
<td>1405.7</td>
</tr>
<tr>
<td>5</td>
<td>590.9</td>
<td>1650.8</td>
</tr>
</tbody>
</table>
## Appendix C: Concentration vs. Time Data

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>1,4-Dioxane Peak Area Average</th>
<th>Concentration (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>512.70</td>
<td>4.48</td>
</tr>
<tr>
<td>5</td>
<td>466.13</td>
<td>4.09</td>
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<td>10</td>
<td>423.80</td>
<td>3.73</td>
</tr>
<tr>
<td>15</td>
<td>317.33</td>
<td>2.85</td>
</tr>
<tr>
<td>30</td>
<td>191.47</td>
<td>1.80</td>
</tr>
<tr>
<td>45</td>
<td>57.60</td>
<td>0.68</td>
</tr>
</tbody>
</table>
Appendix D: Percent Removal vs. pH Data

<table>
<thead>
<tr>
<th>pH</th>
<th>1,4-Dioxane Peak Area Average</th>
<th>1,4-Dioxane Percent Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>223.43</td>
<td>6.47%</td>
</tr>
<tr>
<td>5</td>
<td>267.53</td>
<td>15.01%</td>
</tr>
<tr>
<td>7</td>
<td>165.83</td>
<td>30.58%</td>
</tr>
<tr>
<td>9</td>
<td>202.87</td>
<td>15.08%</td>
</tr>
</tbody>
</table>

*Percentages based on the 1,4-dioxane peak area result for each run’s 1,4-dioxane 5 mg/L spike, due to the fact that the internal standard was not reliable.*
Appendix E: TiO$_2$ Mass Calculations

Let the volume of fiberglass/TiO$_2$ complex = 100 g

$TiO_2$ volume = $0.165 \times 100 \text{ cm}^3 = 16.5 \text{ cm}^3$

$\text{fiberglass volume} = 100 \text{ cm}^3 - 16.5 \text{ cm}^3 = 83.5 \text{ cm}^3$

$m = \rho V$

$TiO_2$ mass = $\frac{4.23 \text{ g}}{\text{cm}^3} \times 16.5 \text{ cm}^3 = 69.795 \text{ g}$

$\text{fiberglass mass} = \frac{2.5 \text{ g}}{\text{cm}^3} \times 83.5 \text{ cm}^3 = 208.75 \text{ g}$

$\omega_{TiO_2} = \frac{69.795 \text{ g}}{69.795 \text{ g} + 208.75 \text{ g}} = 0.25$

$m_{TiO_2} = 45 \text{ g} \times 0.25 = 0.1125 \text{ g}$

$m_{\text{fiberglass}} = 45 \text{ g} - 0.1125 \text{ g} = 0.3375 \text{ g}$
Appendix F: Design Parameters and Calculations

Given Parameters:

\[ k = 0.042 \text{ min}^{-1} \]

Chosen Parameters:

\[ C_0 = 2 \text{ mg/L} \]
\[ C_e = 0.05 \text{ mg/L} \]
\[ Q = 0.05 \text{ m}^3/\text{min} \]
\[ d_{\text{water flow through reactor}} = 0.5 \text{ m} \]
\[ v_{\text{piping}} = 2 \text{ m/s} \]

Calculations:

\[ \ln \left( \frac{0.05 \text{ mg/L}}{2 \text{ mg/L}} \right) = \frac{-0.042 \text{ min}^{-1} \left( \frac{\pi \times 0.5 \text{ m}^2}{4} \right) L}{0.05 \text{ m}^3/\text{min}}; L = 22.366 \text{ m} \]

\[ A = \frac{\pi \times 0.5 \text{ m}^2}{4}; A = 0.196 \text{ m}^2 \]

\[ V = 22.366 \text{ m} \times 0.196 \text{ m}^2; V = 4.392 \text{ m}^3 \]

\[ V_{\text{each reactor}} = \frac{4.392 \text{ m}^3}{4} = 1.098 \text{ m}^3 \]

\[ \tau = \frac{4.392 \text{ m}^3}{0.05 \text{ m}^3/\text{min}}; \tau = 87.831 \text{ min} \]

\[ d = \sqrt{\frac{Q_w}{3600 \times \nu}} \times \frac{4}{\pi} = \sqrt{\frac{0.05 \text{ m}^3/\text{min}}{3600 \times 2 \text{ m}^3/\text{s} \times \frac{4}{\pi}}}; d = 0.023 \text{ m} = 2.3 \text{ cm} \]

\[ Re = \frac{\rho u L}{\mu} = \frac{1000 \frac{kg}{m^3} \times 2 \frac{m}{s} \times 10.5 \text{ m}}{1 \times 10^{-3} \frac{Ns}{m^2}} = 2.1 \times 10^7 \]

Relative Roughness (CPVC piping), \( r = \frac{\varepsilon}{D} = \frac{0.0025 \text{ mm}}{23.77 \text{ mm}} = 1.05 \times 10^{-5} \)
\[ h_f = f \frac{L v^2}{D 2g} = 0.009 \times \frac{10.5 \text{ m}}{0.02377 \text{ m}} \times \frac{(2 \frac{\text{m}}{s})^2}{2 \times 9.81 \frac{\text{m}}{s^2}} = 0.77 \text{ m} \]

\[ h_{total} = 0.77 \text{ m} + 2.1 \text{ m} + 35 \text{ m} = 37.87 \text{ m} \]
Appendix G: Images

Figure G.1: Bench scale set up, including enclosed reactor and cooling system.

Figure G.2: Bench scale reactor sitting on magnetic stirrer plate, with cooling system piping, thermometer, and oxygen piping.
Figure G.3: GC instrument
References


National Toxicology Program. 1,4-Dioxane (Thirteenth ed.).


Sigma-Aldrich. (2015). Safety Data Sheet *1,4-Dioxane*. St. Louis, MO.


