Safe Discharge of Landfill Leachate to the Environment

Year 2 Final Report

July 2016

Author

Daniel E. Meeroff
Florida Atlantic University
Department of Civil, Environmental & Geomatics Engineering

And

Co-Author

Joseph Lakner, Neil Coffman
Florida Atlantic University
Department of Civil, Environmental & Geomatics Engineering

Hinkley Center for Solid and Hazardous Waste Management
University of Florida
P.O. Box 116016
Gainesville, FL 32611
www.hinkleycenter.org

Report # 11073

ACKNOWLEDGEMENTS

The researchers would like to acknowledge the William W. "Bill Hinkley Center for Solid and Hazardous Waste Management for the funding for this project. The researchers would also like to thank the Technical Advisory Group members for their invaluable advice, feedback, and support of this work.

A special thank you goes to Erin Meeroff and Kitti Lakner for providing unwavering support of our academic careers. Without them, none of this would have been possible.
We also wish to thank Craig K. Jones, Ph.D. for his gracious contributions with respect to the EMOH device, and our hearts go out to his family after he lost his battle with cancer earlier this year. We hope to honor his memory by completing the work he started.

The authors would like to thank all of the reviewers of this report for their valuable comments and feedback.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

FINAL REPORT

12/01/2013 – 06/30/2016

PROJECT TITLE: Safe Discharge of Landfill Leachate to the Environment

PRINCIPAL INVESTIGATOR(S): Daniel E. Meeroff, Ph.D.

AFFILIATION: Florida Atlantic University

EMAIL: dmeeroff@fau.edu **PHONE NUMBER:** 561-297-3099

PROJECT WEBSITE: http://labees.civil.fau.edu/leahcate.html

COMPLETION DATE: 06/30/2016

TAG MEMBERS: Jeff Roccapriore, Damaris Lugo, Joe Lurix, Art Torvela, Ravi Kadambala, Kevin Leo, Fred Bloetscher, Dan Schauer, André McBarnette, Frank Youngman, Mark Bruner, Mark Eyeington, Nate Mayer, Amede Dimmonay

KEY WORDS: Leachate, photocatalytic oxidation, COD, ammonia, alkalinity, centrifugation

ABSTRACT: Some closed or partially closed landfills still produce important quantities of leachate, but instead of blending this material with active Class I leachate for disposal, there may be better alternatives. If a relatively inexpensive way to pretreat the leachate and safely dispose of it onsite can be developed, a giant step toward the potential for zero liquid discharge can be achieved. FAU has pioneered the advancement of landfill leachate treatment systems using photochemical iron-mediated aeration and TiO_2 photocatalysis at laboratory scale in previous research funded by the Hinkley Center, which has led to the development of reactor prototypes for pilot scale testing. The objective of the proposed research is to test a prototype photooxidative reactor at pilot scale for the removal of COD/BOD, heavy metals (i.e. arsenic, lead, and iron), ammonia, color, chlorides, and pathogens to determine the feasibility of safely discharging or reusing this leachate as a resource on-site.

METRICS:

1. List graduate or postdoctoral researchers **funded** by **THIS** Hinkley Center project.

Last name, first name	Rank	Department	Professor	Institution
Lakner, Joseph	MSCE Candidate	CEGE	Meeroff	FAU
Coffman, Neil	MSCE Candidate	CEGE	Meeroff	FAU

2. List undergraduate researchers working on **THIS** Hinkley Center project.

Last name, first name	Department	Professor	Institution
Dacey, Justin	CEGE	Meeroff	FAU

Meyer, Lisandre	CEGE	Meeroff	FAU
Walecki, Eve	CEECS	Meeroff	FAU
Harris, Alyssa	CEECS	Meeroff	FAU

3. List research publications resulting from **THIS** Hinkley Center project.

Meeroff, D. E., J. Lakner, B. Shaha, E. Walecki, A. Harris, and L. Meyer. "Futuristic On-Site Leachate Management." In *World Environmental and Water Resources Congress 2016*, Environmental, Sustainability, Groundwater, Hydraulic Fracturing, and Water Distribution Systems Analysis, pp. 1-10.

4. List research presentations resulting from **THIS** Hinkley Center project

4 TAG meetings

Meeroff, D.E. (2016). World Environmental and Water Resources Conference, Treatment of Landfill Leachate Session, 4:00 pm – 5:30 pm, Palm Beach County Convention Center, West Palm Beach, FL, May 24, 2016.

5. List who has referenced or cited your publications from this project:

None so far

6. How have the research results from **THIS** Hinkley Center project been leveraged to secure additional research funding?

Year two funding from the Hinkley Center for Solid and Hazardous Waste Management was secured. Additional funding is being pursued through the Solid Waste Authority of Palm Beach County and Waste Management. An NSF proposal was submitted to use the technology for fracking fluid treatment. A proposal was submitted to Advanced Technology Group to co-develop the technology.

7.. What new collaborations were initiated based on **THIS** Hinkley Center project?

F. Bloetscher, Ph.D., P.E., LEED AP and Craig K. Jones, Ph.D.

8. How have the results from **THIS** Hinkley Center funded project been used by FDEP or other stakeholders?

To date, the results have not been used by stakeholders.

EXECUTIVE SUMMARY

12/01/2013 – 06/30/2016

PROJECT TITLE: Safe Discharge of Landfill Leachate to the Environment

PRINCIPAL INVESTIGATOR(S): Daniel E. Meeroff, Ph.D.

AFFILIATION: Florida Atlantic University

PROJECT WEBSITE: http://labees.civil.fau.edu/leahcate.html

TAG MEMBERS: Jeff Roccapriore, Damaris Lugo, Joe Lurix, Art Torvela, Ravi Kadambala, Kevin Leo, Fred Bloetscher, Dan Schauer, André McBarnette, Frank Youngman, Mark Bruner, Mark Eyeington, Nate Mayer, Amede Dimmonay

COMPLETION DATE: 06/30/2016

Introduction

The goal of the research was to determine if leachates from closed or partially closed landfills similar to those obtained from Dyer Park could be treated to a level that would allow reuse onsite. At most facilities today, the current leachate management strategies include municipal sewer discharge, deep well injection, hauling offsite, on-site treatment, or a combination approach. Each of these options has its inherent limitations, further complicated by the extremely variable leachate quality, generation rates, and regulatory environment. As a result, it is conceivable that in the future, landfill managers may be forced into considering on-site treatment and disposal to handle their leachate. Thus there will be a major technological need for sustainable, economical options for safe discharge or zero liquid discharge of treated leachate to the environment.

After evaluating over 25 different engineering alternatives for long-term leachate management (Meeroff and Teegavarapu 2010), the ideal leachate management approach will be sustainable, low-cost, site-specific and adaptable to evolving regulations. The preferred strategies for the future will involve technologies that can destroy different classes of contaminants all at once, without producing harmful byproducts or residuals. Advanced oxidation processes, such as photochemical iron-mediated aeration (PIMA), electromagnetic oxygen/hydrogen (EMOH) technology, and TiO_2 photocatalytic oxidation are being developed at FAU for this eventuality. These processes are theoretically capable of: 1) converting refractory organics into more biodegradable constituents, 2) removing heavy metals such as Pb, As, Cd, Hg through co-precipitation, adsorption, and redox mechanisms, 3) dealing with ammonia through stripping of $NH_3(g)$ and also conversion of ammonia to nitrate through aeration, 4) destroying or completely mineralizing recalcitrant organics, 5) stripping VOCs, 6) achieving high levels of disinfection, and 7) addressing color/odor issues. Therefore, advanced oxidation technologies may provide an efficient and sustainable approach to long-term leachate management as well as aquatic water quality protection.

The main focus of this research was to test advanced oxidation methods for the removal of selected pollutants (i.e. COD, ammonia, alkalinity, etc.) in mature landfill leachate using

prototype laboratory reactors. The primary objective was to determine a reactor configuration that meets the water quality goals of one or more of the following: 1) surface water discharge, 2) industrial reuse as cooling water, irrigation, or dust control, or 3) on-site use as dilution water to reduce leachate clogging issues in pipes.

Methodology

In this study, leachate was collected from the Dyer Park Landfill operated by the Solid Waste Authority (SWA) of Palm Beach County, FL. This site was chosen because it generates particularly weak leachate. The Dyer Park Landfill is currently no longer accepting waste, and most of the 80-acre site is being used as a recreational facility (Statom et al. 2004). The lined portion of the landfill has only a top cap with the side slopes closed only with soil and sod. As a result, the leachate produced is on the order of 120,000 gallons per month on average in 2014-15, which is more dilute and of higher than expected quality than a comparable facility. Leachate samples were collected on: May 30, 2014, September 18, 2014, February 19, 2015, July 1, 2015, and August 21, 2015. The samples were taken from a ¼-inch sampling port, which was purged for one minute before collection in a five-gallon HDPE container. The samples were stored in a refrigerator at 4°C until treated and analyzed in the laboratory.

UV/TiO_2 experiments were conducted using a modified CE584 Advanced Oxidation unit operated in two configurations: 1) falling film reactor and 2) flow through reactor. The falling film reactor was converted to a flow through reactor by means of closing a three-way valve and allowing the leachate to completely fill the annular space around the UV lamp to create a reaction zone. Two different light sources with similar radiation flux were used: 1) 450-W medium pressure, quartz, mercury-vapor lamp operating in the UV-A/B band (56 mW/cm^2) and 2) 150-W low pressure mercury lamp operating in the UV-C range (7.2 mW/cm^2). To measure the UV light intensity, a Fisher Scientific Traceable™ UV light meter for UV-A and UV-B and a Sper Scientific 850010 UV-C light meter were used. The lamps were allowed to warm up for 15 minutes to achieve an operating temperature of 90°C. Then the sensors were placed 0.75-inches from the light, and a set of measurements was taken. This was repeated three times for each light source, and an average of the readings in units of mW/cm^2 was taken.

Electromagnetic oxygen/hydrogen (EMOH) experiments were performed using a custom built unit in which leachate is diverted through a magnetic field created by neodymium magnets and copper rods and then is passed through a critical orifice venturi tube, where it becomes pressurized and ejected at a high velocity. This creates a vacuum where the dissolved oxygen comes out of solution and creates a large number of micro-bubbles with a relatively large combined surface area to carry out the oxidation reaction steps.

To initiate an experiment, leachate was added to the reactor reservoir. Then the unit was powered up, and the stainless steel magnetic drive circulating pump was started. Next, the TiO_2 (Degussa Aeroxide P-25) was added in slurry form (dose range: 0 – 30 g/L). Aeration of the reservoir was provided with a 2 cfm blower and aeration stones. Experimental run times varied up to 48 hours with samples collected periodically for kinetics testing. The leachate was maintained at 20-25°C using a stainless steel coil filled with Dynalene HC-50 coolant in a closed loop recirculating chiller. Active lamp cooling by blowing 2 cfm airflow through the annular space of the reactor kept temperatures in the inner lens and the reaction zone from exceeding 40°C.

During kinetics testing, it was observed that the initial exposure of leachate to TiO_2 photocatalytic particles caused a measurable removal of COD. It was hypothesized that this apparent removal was due to a surface adsorption mechanism. Thus, adsorption pre-treatment followed by filtration or settling was attempted. Pretreatment options tested included: 1) TiO_2 pre-adsorption (rapid mixing of 30 g/L TiO_2 with raw leachate for 5 minutes at 100 rpm) followed by 5 micron cloth filtration, and 2) TiO_2 pre-adsorption (rapid mixing of 30 g/L TiO_2 with raw leachate for 5 minutes at 100 rpm) followed by one hour quiescent settling.

Samples were collected from the reactor outlet, centrifuged (6000 rpm for 6 minutes) to remove photocatalyst particles, and analyzed for the following constituents: COD (SM5220D; reactor digestion method), ammonia (EPA methods 350.2 Nessler spectrophotometric method), alkalinity (SM2320B; digital titrator method), pH (SM4500-H^+B), and temperature (SM2550). BOD tests (SM 5210B) were also conducted on selected samples. All water quality data collected was statistically analyzed by first checking for normality, and then performing a student's t-test to determine if treatment effects were significant.

Tests for understanding the potential of photocatalytic particles to be recovered and reused were also conducted. After treatment, it was necessary to: 1) determine the bench scale TiO_2 recovery efficiency of centrifugation, sedimentation, and filtration; 2) characterize the recovered TiO_2 particles; and 3) develop preliminary scale-up parameters for design of each of the recovery technologies for economic analysis purposes. These experiments focused on centrifugation, sedimentation, and filtration. Particle characterization was performed by measuring particle size and zeta potential with a zeta-meter as well as a modified COD test to detect fine particles that evaded capture.

Results and Discussion

The first set of experiments focused on determining which lamp achieved better removal using 5-10 g/L TiO_2. The highest COD removal was found with the 450-W falling film reactor, but the 150-W falling film reactor achieved the highest ammonia and alkalinity removal. However, t-tests showed no statistically significant difference in COD, ammonia and alkalinity removal with lamp type. Tests using both lamps together did not demonstrate any improved process removal efficiency. Therefore, all remaining UV/TiO_2 experiments were conducted with the 150-W lamp.

The next set of experiments focused on determining the process removal efficiency of the EMOH unit. Then experiments were conducted with the 150-W falling film reactor in series with the EMOH unit and with or without pre-treatment. Most experiments were conducted over an 8-hour exposure period with the exception of the 48 hour test, which also used pure oxygen aeration (1 cfm) in the reservoir. The most efficient COD removal occurred in experiment 7 (63%). It is interesting to note that the initial degradation rate is much steeper than the overall reaction rate, which follows a first order trend and suggests that a sequencing batch reactor process would improve removal efficiency.

Previous work (Meeroff et al. 2012) suggested that the COD is converted step-wise to more biodegradable BOD, prior to achieving complete mineralization. This conversion would be expected to have several stages of decomposition, particularly when dealing with complex organics typically found in leachate. Theoretically for complete mineralization to occur, the COD should be converted to CO_2 and H_2O, such that the BOD_5 does not increase in the effluent.

Conversely, if COD is being converted to less complex but more readily biodegradable forms instead, the BOD_5 would tend to increase in the effluent. The raw leachate BOD_5 was measured to be 36 ± 0.3 mg/L, and the final treated effluent was 30 ± 7.6 mg/L. With a 95% level of confidence, COD is not converted to BOD, which provides evidence that complete mineralization is actually occurring.

Taking the results from the experiment with the most efficient performance (experiment number 7), which consisted of pre-treatment with TiO_2 adsorption/settling and UV/TiO_2 in the falling film (150-W) + EMOH reactor, the treatment goals were assessed in **Error! Reference source not found.**. The surface water discharge regulatory goal is the most stringent target and was developed using the following regulations: USEPA primary and secondary drinking water standards, FAC 62-550, and 62-777. The reclaimed water regulatory goal is taken from FAC 62-610. For the dilution water goal, the water quality must complement the Langelier saturation index of other leachates on site to reduce scaling in the collection system and disposal well.

For both COD and ammonia, the dilution water treatment goals were met, but the reclaimed water and surface water discharge goals were not. The combined treatment process came very close to meeting even the most stringent regulatory goals for safe discharge to a surface water body or onsite reclaimed water reuse. With additional modification and cost optimization, the combined process may eventually meet these discharge standards for COD, ammonia, and other contaminants of concern.

Conclusion

The effect of UV spectrum and light density was investigated, and the 150-W lamp showed slightly better removal compared to the 450-W lamp, although not statistically significant. Thus lamp power could be reduced without negatively impacting removal efficiency.

Several different reactor configurations were tested, and each one achieved removal of the parameters of interest. Pretreatment of leachate with TiO_2 adsorption/settling prior to UV/TiO_2 photocatalysis was shown to enhance process removal efficiency. The pretreatment step alone removed 41% of alkalinity, 42% of COD, and 16% of ammonia. If pretreatment is followed by the falling film (150-W) + EMOH reactor, the overall process removal efficiency in 8 hours was 63% of COD removed, 53% of ammonia removed, and 73% of alkalinity removed. With more efficient treatment, discharge to the environment and reclaimed water treatment goals can be achieved. According to the Langelier saturation index (LSI = -0.59, the treated leachate will be corrosive, which would be beneficial as a dilution water for controlling calcium carbonate scale formation in pipes.

Recovery of the TiO2 particles was determined to be feasible with bench scale tests. Centrifugation and membrane filtration with pore size of 1.5 µm achieved recovery efficiencies of 92.5 – 99.5%, which was not affected by pH. Particle characterization studies revealed that TiO_2 agglomerates rapidly in leachate and has an effective diameter that is 100x larger than the photocatalyst particle itself, and the zeta potential is around -20 mV, which is incipiently unstable. Using the COD test as a proxy to analyze for fine photocatalyst particles that escaped recovery, it was shown that centrifugation had no detectable fines break through compared to detectable amounts with filtration.

For these conditions, the kinetics results showed very high initial decomposition rates, suggesting that the use of a sequential batch reactor might improve the overall efficiency and reduce treatment times to eventually allow the technology to achieve all three stated treatment goals.

1. INTRODUCTION

1.1 BACKGROUND

Landfilling is the predominate method of disposing of municipal solid waste with 53.8% of all waste ending up in landfills in the United States (USEPA, 2012a). In 1976, the Resource Conservation and Recovery Act (RCRA) established two key tenants in solid waste management. First, it required that hazardous waste be disposed of separately from non-hazardous waste such that hazardous waste was to be disposed of in a manner that would not pollute the environment, and second, it established the US Environmental Protection Agency as the administrative agency for solid waste. This legislation aimed to halt illegal dumping of waste to protect water supplies from contamination. To further, protect water resources, the Hazardous and Solid Wastes Amendment of 1984 mandated treatment of all surface water runoff from landfills. This act was amended in 1991 to require landfills to protect groundwater by employing a multi-component bottom liner with a system to collect the liquids that seep through the landfill. The liner protects against groundwater intrusion into the landfill and protects against the seepage of precipitation and irrigation that comes in contact with solid waste from entering the groundwater. This liquid is termed *leachate* and results from precipitation or other water that comes in contact with waste after collection, as well as water generated by waste decomposition. This leachate, which contains many potentially harmful contaminants, such as recalcitrant organic material, ammonia, chlorides, heavy metals, and other toxics, must be treated prior to discharge.

Not all leachate is the same. Leachate can be classified into two types by age of the landfill (i.e. young and mature). In young active landfills (<5 years old), leachate is characterized by elevated levels of recalcitrant organic material, high BOD_5, high COD, a BOD_5/COD ratio greater than 0.3, color, ammonia, chlorides, and heavy metals such as arsenic, lead, and iron (de Morais and Zamora, 2005, Sari et al., 2013). In closed or partially closed landfills (>10 years old), mature leachate is characterized as being more stable by a low BOD_5/COD ratio less than 0.1, a lower overall organic content, high concentrations of humic and fulvic acids, salts, and relatively low ammonia levels (Renou et al., 2008; Meeroff and Teegavarapu, 2010; Sari et al., 2013; de Morais and Zamora, 2005; Meeroff and Youngman, 2013). While treatment of young active leachate with conventional treatment processes may be effective on COD and ammonia (Renou et al. 2008), mature leachate's ratio of BOD_5/COD ratio makes mature leachate less biodegradable, rendering conventional treatment largely ineffective. However, if a safe economical treatment option was developed, this leachate could be discharged to the environment or could provide potential benefits to landfills, such as irrigation to maintain the vegetative cover.

The amount of leachate produced from active Class 1 landfills in Florida (FDEP, 2007; Meeroff and Teegavarapu, 2010) can be up to 7000 gallons per day per acre, which must be eventually discharged back into the environment. A major limitation to the sustainable management of landfill leachate has been the lack of effective methods to guarantee safe long-term discharge back into the natural environment. This is further complicated by the extremely variable leachate quality and generation rates, along with the ever-changing regulatory environment, which has caused many conventional technologies to fail to meet this goal.

In partially closed landfills, leachate generation rates can be on the order of 400-700 gallons per day per acre (Eyeington, 2013). This mature leachate is of very different quality, characterized as being more stable by a lower BOD_5/COD ratio, a lower overall organic content, and relatively low ammonia levels (Amokrane et al., 1997; Renou et al., 2008; Meeroff and Teegavarapu, 2010; Meeroff and McBarnette, 2011; see also Table 3 and references therein). One possible way to reduce costs and energy requirements at closed or partially closed facilities would be to treat the mature leachate on-site and reuse or reclaim the water. To do so, the regulatory water quality targets for parameters of concern in the leachate must be determined.

1.2 WATER QUALITY REGULATIONS

For any wastewater, the extent of treatment is based on the final disposal option. If the treated leachate is to be discharged to the environment (canal, stream, or other surface water body) such that discharge will not significantly deteriorate the receiving water quality. The USEPA sets effluent discharge limits for non-hazardous sanitary landfills in 40 CFR 445.21 (Table 1). These limits are the minimum discharge standards. States and local jurisdictions can apply more stringent limits where applicable.

Table 1. USEPA non-hazardous waste landfill effluent limitations (10 CFR 445.21).

Regulated Parameter	Units	Maximum Daily	Maximum Monthly Average
BOD_5	mg/L as O_2	140	37
TSS	mg/L	88	27
Ammonia	mg/L as N	10	4.9
α-Terpineol	mg/L	0.033	0.016
Benzoic acid	mg/L	0.12	0.071
ρ-Cresol	mg/L	0.025	0.014
Phenol	mg/L	0.026	0.015
Zinc	mg/L	0.20	0.11
pH	Standard units	6-9	6-9

Other limits that are important to note are the USEPA Primary and Secondary Drinking Water Standards, since Florida obtains most of its drinking water from either the Floridan or Biscayne aquifers, which are shallow aquifers with direct connections to surface water in most parts of the state. Additionally, the Florida Administrative Code F.A.C. 62-550 sets the Florida-specific drinking water standards that must be met.

In this study, the ultimate disposal options considered were surface water discharge, reclaimed water and dilution water for control of landfill leachate pipe clogging. For surface water discharge in Florida, the USEPA Primary and Secondary drinking water standards must be met. In Florida, the federal guidelines are further regulated by the Florida Administrative Code (F.A.C.) 62-550 that sets the Florida-specific drinking water standards that must be met. Any discharge of leachate beyond these standards could potentially contaminate drinking water supplies. Any landfill that was in use prior to the 1976 enactment of RCRA may also need to apply F.A.C. 62-777, which is the Florida Department of Environmental Protection Cleanup Target Levels for Waste Management, because before this period, there was no separation of hazardous and non-hazardous waste, meaning that arsenic, petroleum, benzenes, chlorides, other

chemicals, acids, lead and other hazards materials were disposed of in the same landfills as the municipal solid waste (MSW). Leachate from these landfills could contain any of those constituents.

The regulations for reclaimed water fall under the Florida Administrative Code F.A.C. 62-610. These standards are based on the type of treatment that the wastewater shall receive. Any reclaimed water must undergo at a minimum conventional secondary treatment plus filtration with high level disinfection. The dilution water option would be for on-site use to control scaling in pipes prior to disposal via deep injection well. Currently the regulatory standards for this option are governed by the disposal permit.

1.3 LEACHATE QUALITY

Several reviews have been conducted with the goal of documenting leachate composition according to the location (i.e. the climate and especially the precipitation rate), the age of the landfill, or the type of wastes. Typical ranges for selected constituents are summarized in Table 2.

Table 2. Typical leachate quality data from young and mature landfills (Tchobanoglous, Theisen, and Vigil, 1993; Metcalf and Eddy, 2003).

Constituent	Units	Young (<5 years old)	Mature (>10 years old)
Ammonia-nitrogen	mg/L as NH_3-N	10 – 800	20 – 40
BOD_5	mg/L as O_2	2000 – 30,000	100 – 200
COD	mg/L as O_2	3000 – 60,000	100 – 500
Iron (Fe)	mg/L	50 – 1200	20 – 200
pH	pH units	4.5 – 7.5	6.6 – 7.5
Alkalinity	mg/L as $CaCO_3$	1000 – 10,000	200 – 1000
TSS	mg/L	200 – 2000	100 – 400

Other important constituents include: i) dissolved organic matter from methane (CH_4) to volatile fatty acids (VFA) to more refractory humics and fulvics; ii) inorganic constituents, such as calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}), potassium (K^{+}), ammonium (NH_4^{+}), iron (Fe^{2+}), manganese (Mn^{2+}), chloride (Cl^{-}), sulfates (SO_4^{2-}) and bicarbonates (HCO_3^{-}); iii) heavy metals (arsenic, cadmium, chromium, cobalt, copper, lead, mercury, nickel and zinc), in the microgram per liter range; and iv) xenobiotic organic compounds from domestic and industrial sources, comprised of a broad variety of aromatic hydrocarbons, phenols, endocrine disrupting compounds (EDCs), pharmaceuticals, personal care products, pesticides, and chlorinated aliphatics.

A review of leachate quality from 128 landfills from different countries and continents, reported in the literature, is summarized in Table 3. The large ranges reported are the result of the high variability among leachates. It is important to note that leachate can have very high concentrations of many different constituents, many of which are known to have deleterious impacts in groundwater and soil. Aside from those listed here, there are numerous other constituents found in leachate ranging from heavy metals (e.g., cadmium, chromium, mercury,

arsenic, nickel, selenium, iron, manganese, silver, copper, lead, thallium, zinc and others), other inorganic components (e.g., ammonium, barium, beryllium, bicarbonate, chloride, magnesium, manganese, nitrate, phosphorus, potassium, sodium, sulfate and others) (Qasim and Chiang, 1994), and an array of organic constituents including xenobiotic organic compounds (XOCs) such as: BTEX (benzene, toluene, ethylbenzene, and xylene), antibiotics and other pharmaceuticals, pesticides, herbicides and endocrine disrupting compounds (EDCs) (Baun et al., 2003). Specific conditions are not indicated here, as the summary serves to point out the wide variety of leachate quality that can be found. Clearly, it would be difficult to define a typical landfill leachate quality because each facility produces varying compositions of leachate at different times depending on waste composition, climate, seasonal variations, rainfall, age of the waste, and solid waste management practices.

Table 3. Summary of extreme values for the composition of leachate developed through review of technical literature.

		Concentration	
Parameter	**Units**	**Range**	**Average**
Ammonia	mg/L as NH_3-N	BDL* – 13,000	1,100
BOD_5	mg/L as O_2	BDL* – 80,800	3,100
COD	mg/L as O_2	0.4 – 152,000	8,750
Conductivity	µS/cm	5.2 – 95,000	15,400
Lead (Pb)	mg/L	BDL* – 5.0	0.41
pH	pH units	2.0 – 11.3	7.73
TDS	mg/L	0.1 – 88,000	11,100
TSS	mg/L	10 – 45,000	1,120
Alkalinity	mg/L as $CaCO_3$	3,300 – 11,000	9,640
Color	Platinum-Cobalt Units	3,530 – 40,000	3,630

BDL* = below detection limit.

Sources: Adapted from Abu Amr and Aziz (2012), Adlan et al. (2011), Åkesson and Nilsson (1997), Al-Yaqout et al. (2005), Amokrane et al. (1997), Anglada et al. (2011), Aziz et al. (2011), Bashir et al. (2010), Bekbölet et al. (1996), Bernard et al. (1997), Bila et al. (2005), Bouhezila et al. (2011), Calli et al. (2005), Cheibub, Campos, and Fonseca (2014), de Morais and Zamora (2005), Deng and Ezyske (2011), Fernandes et al. (2015), Geenens et al. (2000), Gonze et al. (2003), He et al. (2015), Hickman (2003), Iaconi et al. (2010), Imai et al. (1998), Ince (1998), Jia et al. (2011), Kim et al. (1997), Kim et al. (2007), Kjeldsen et al. (2002), Kurniawan and Lo (2009), Li et al. (2009), Lin and Chang (2000), Mahmud et al. (2011), Mohammad et al. (2004), Mohajeri et al. (2010), Moraes and Bertazzoli (2005), O'Leary and Walsh (1995), Oweis and Kehra (1998), Poblete et al. (2012), Reinhart and Grosh (1998), Reinhart and Townsend (1998), Renou et al. (2008), Salem et al. (2008), Silva et al. (2004), Solid Waste Authority of Palm Beach County (2006), Statom et al. (2004), Steensen (1997), Tammemagi (1999), Tamrat et al. (2012), Tatsi et al. (2003), Tchobanoglous and Kreith (2002), Vilar et al. (2011), Ward et al. (2002), Westlake and Phil (1995), Wichitsathian et al. (2004), Wu et al. (2004), Youcai et al. (2002), Zhao et al. (2010).

In this particular study, the Dyer Park Landfill located in Palm Beach County, FL is the focus because it is a partially closed landfill that generates particularly weak leachate. The Dyer Park landfill operated from 1968 to 1992. However, the lined section of the landfill accepted waste from 1984 to 1992. Statom, Thyne, and McCray (2004) investigated the leachate water chemistry of the Dyer Park landfill and monitored the levels of several contaminants, as summarized in Table 4.

Table 4. Selected water quality parameters of interest from Dyer Park Landfill leachate (Statom, Thyne and McCray 2004).

Parameter	Units	No. of Samples	Range	Average	Standard Deviation
pH	Standard units	50	6.56 – 8.01	7.07	0.27
Conductivity	mmhos/cm	49	3.6 – 15	7.64	2.85
Temperature	°C	50	2.16 – 32.8	27.7	2.14
COD	mg/L as O_2	50	222 – 2000	835	383
BOD_5	mg/L as O_2	48	<1 – 184	47	40.2
Ammonia	mg/L as N	50	5.6 – 1350	473	254
Chloride	mg/L	49	63 – 1580	837	330
Sulfate	mg/L	49	<1 – 118	20	26
Alkalinity	mg/L as $CaCO_3$	31	1160 – 3900	2450	597
Bicarbonate	mg/L	4	1900 – 3900	2660	928
Calcium	mg/L	23	132 – 220	176	22
Magnesium	mg/L	20	41 – 63	54	5.7
Iron	mg/L	50	1.6 – 9.7	4.8	2.4
Boron	mg/L	6	2.6 – 4.0	3.2	0.5
Arsenic	µg/L	49	<5 – 25	nr	nr
Chromium	µg/L	49	<5 – 60	20	11
Lead	µg/L	49	<4 – 110	nr	nr
Silver	µg/L	49	<1 – 25	nr	nr
Zinc	µg/L	49	<6 – 488	nr	nr

nr = not reported

Comparing the 2004 Dyer Park study to typical mature leachate values (refer to Table 2) indicates differences in the type of MSW and daily cover within the landfill. The pH of the 2004 study fell within the typical range. The 2004 average alkalinity of 2450 mg/L as $CaCO_3$ is above the typical range of 1000 mg/L as $CaCO_3$. This can be attributed to daily cover of the landfill. The daily cover was local soil, typically pulled from borrow pits dug from limestone. This limestone can add alkalinity to water, particularly with pH changes (Black, Ziemkiewicz, and Skousen, 1999).

The reported ammonia levels from Statom, Thyne and McCray (2004) were 473 mg/L, which is one order of magnitude larger than the typical value of 40 mg/L in this study (refer to Table 5). Ammonia is mainly released from decomposing organic material (Lee, Nikraz, and Hung, 2010). The semitropical climate of Palm Beach County, FL produces a year round growing season that could contribute more vegetative waste than a typical landfill. The newer, lower ammonia values reflect the change of more than 10 additional years of biodegradation since 2004. The BOD_5 value in 2014 of 47 mg/L is below the typical value of 100 mg/L. This lower value indicates the landfill is older than the typical landfills studied and has therefore undergone more waste stabilization. This is supported by the fact that the landfill was created in 1984 with a liner, while liners were not mandated until 1991, potentially making the landfill 7 years older than comparable sites. The iron content of the 2004 study was 4.8 mg/L below the 20 mg/L typical value in this study (refer to Table 5). This indicates that less metals, particularly tin can were

disposed of in the landfill. In fact, Palm Beach County, FL started recycling in 1987, this diverted metals of value away from the landfill, contributing to the reduced iron content of the leachate.

1.4 POLLUTANTS OF CONCERN

Currently there is no pre-treatment process being used prior to deep injection well disposal other than dilution of the mature leachate with younger leachates and various other wastewater flow streams at the site. To determine which pollutants should be targeted at Dyer Park, the Statom, Thyne, and McCray (2004) study and samples collected at the beginning of this study were tested for many constituents typically detected in the Dyer Park Landfill leachate and then compared them to the appropriate maximum contaminant level (MCL) in Table 5. Any constituent that exceeds the MCL requires targeted treatment.

Table 5. Dyer Park constituents selected for treatment.

Parameter	Units	Mean Values from (Statom, Thyne, and McCray, 2004)	Mean Values from this study	Surface Discharge MCL
COD	mg/L as O_2	835	473	nr*
Alkalinity	mg/L as $CaCO_3$	2,453	1,419	nr*
Calcium	mg/L as $CaCO_3$	176	893	nr*
pH	Standard Units	7.07	7.35	6.5-8.5
Ammonia	(NH_3-N) mg/L	473	351	4.9
BOD_5	mg/L as O_2	47	32	20
TDS	mg/L	3,442	2,786	500

***not regulated**

This research focused on the following parameters: chemical oxygen demand (COD) and ammonia and to a lesser extent, BOD_5, TDS, and alkalinity. COD was chosen as a measure of the organic matter in the leachate (USEPA, 2012b). The mean value found by Statom, Thyne, and McCray (2004) was 835 mg/L as O_2, while and the mean for this study (2014-15) was found to be 473 mg/L as O_2 (refer to Table 5), indicating natural reduction over time. There is no specific treatment target for COD per se, but the federal government currently has set limitations for BOD_5 (see Table 1). Local sewer use limitations (for example, Broward County Code Chapter 34 Article VI, Ordinance No. 2001-43 Sewer Use Ordinance) typically charge a fine for high strength wastewater if COD concentration exceeds 800 mg/L. The European Union sets a secondary treatment standard of 125 mg/L COD as O_2 (Frost, 2009). For this study, the COD treatment goal for surface discharge is 125 mg/L as O_2, which was set since no target level exists currently. For reclaimed water treated by conventional secondary methods with biological treatment with disinfection, the typical COD value is 30-60 mg/L as O_2. This is not a standard but a typical value as reported in Metcalf and Eddy (2003). For both reclaimed water and dilution water there is no regulatory COD limit set.

Ammonia (NH_3) is an inorganic form of nitrogen that is created in the natural anaerobic degradation process of many organic compounds (USEPA, 2012b). When ammonia in an aqueous solution is exposed to air, it rapidly becomes a colorless gas with a strong noticeable odor (Commonwealth of Australia, 2010). The amount of ammonia in an aqueous solution has a

direct correlation to temperature and pH (USEPA, 1985). Concentrations of ammonia at levels as low as 0.03 mg/L have been found to be toxic to aquatic life, and the LC_{50} (concentration which is fatal to 50% of the subjects) for freshwater fish occurs at 0.068 – 2.00 mg/L as NH_3-N, during a set exposure time of 96 hours (Eddy, 2005). Taste and odor issues have been reported at levels of 35 mg/L and 1.5 mg/L, respectively (WHO, 2004).

Ammonia concentrations naturally found in groundwater and surface water are usually less than 0.2 mg/L, although anaerobic groundwater may have levels near 3 mg/L. In the state of Florida, ammonia is identified as a "minimum criteria systemic toxicant" and has a groundwater cleanup target level (CTL) of 2.8 mg/L. The CTL is not a regulation or standard, but rather a suggestion for water quality. In fact, the State of Florida may consider to remove the target altogether because of the lack of regulatory authority to enforce it. The concentrations found in leachate, which were shown in Table 2 (20-40 mg/L for mature leachate) and Table 3 (up to 13,000 mg/L as NH_3-N) far exceed these levels. Broward County sewer use limitations stipulate high strength wastewater surcharges if the NH_3-N is above 25 mg/L as NH_3-N, and concentrations exceeding 70 mg/L as NH_3-N are not permissible. For conventional secondary treatment, the average effluent concentration is 20 mg/L as NH_3-N (Pescod, 1992). The Dyer Park leachate historical average was 473 mg/L as NH_3-N, and the 2014-2015 average amount in this study was 351 mg/L as NH_3-N (Table 7). The treatment goal for surface discharge for ammonia is 4.9 mg/L as NH_3-N from EPA 40 CFR 445.21. The treatment goal for reclaimed water is 20.0 mg/L as NH_3-N. There is no ammonia goal set for dilution water, since ammonia does not impact the Langelier Index.

The treatment goals for the three types of discharge options which are the focus of this study are summarized in Table 6. Surface discharge goals have established standards while reclaimed water and dilution water were set from best practices.

Table 6. Summary of target treatment goals for this study.

Parameter	Units	Surface Discharge Treatment Goal	Surface Discharge Source	Reclaimed Water Treatment Goal	Dilution Water Treatment Goal
COD	mg/L as O_2	125	EU Extensive Wastewater Treatment Process	None	None
Ammonia	(NH_3-N) mg/L	4.9	USEPA 10. CFR 445.21	20	None
Alkalinity	mg/L as $CaCO_3$	20-600	F.A.C 62-302-500	332	Index*
BOD_5	mg/L as O_2	20	F.A.C 62-550	30	None
Calcium	mg/L as $CaCO_3$	50	Langelier Saturation Index/Ryznar Index	78.7	None (lower is better)
pH	Standard Units	6.5-8.5	EPA Secondary Drinking Water Standard	6.5-8.5	None (lower is better)
TDS	mg/L	27	USEPA 10. CFR 445.21	None	None (lower is better)

1.5 LEACHATE QUANTITIES

Another key factor in managing landfill leachate is understanding the quantity that is generated daily. The volume of leachate depends on the amount of rain that percolates through the landfill and the exposed surface area. Other factors that influence the volume of leachate include: surface runoff, groundwater intrusion, liquid waste in the landfill, irrigation, evapotranspiration, landfill depth, and refuse composition (Westlake and Phil, 1995), but the quantity of leachate is directly tied to the amount of precipitation and irrigation that the landfill receives. As a closed facility ages, waste decomposition slowly becomes the major driver of additional leachate over time, since the geomembrane protects against precipitation infiltration.

A survey was performed by Meeroff and Teegavarapu (2010) that polled 52 landfills in the state of Florida about their leachate generation rates. Facilities were divided into four different size classes based on their waste capacity as defined by USEPA (1999). The results of the survey from the 31 facilities that responded showed leachate volumes ranging from less than 100 to nearly 3,000 gpd/acre (refer to Table 7).

Table 7. Leachate generation rates for 31 Florida landfills (Meeroff and Teegavarapu 2010).

Class	Waste Capacity (MT/yr)	Range (gpd/acre)	Number of landfills
Small	<500,000	<100	14
Medium	500,000 – 5,000,000	100-300	9
Large	5,000,000 – 15,000,000	300-850	6
Super	>15,000	>850	2

The Hydrologic Evaluation of Landfill Performance (HELP) model is a computer program developed by the Waterways Experiment Station (WES), which is the headquarters for the U.S. Army Engineer Research and Development Center (ERDC) (USEPA, 2012). The HELP model is used to estimate the generation of leachate from landfills for comparison efforts in the planning and design of the landfill and leachate collection system. The HELP model gives a theoretical value in the South Florida area of 2,000 – 3,000 gpd/acre, which is the design value used for most landfills in the Southeast Florida region. However, most landfills do not have properly calibrated flow meters to record the actual leachate volumes from active cells, let alone the leachate generated by partially lined cells or older systems (Meeroff and Teegavarpu, 2010; Meeroff and McBarnette, 2011), so accurate generation values are not readily available.

Data from two landfills in south Florida, Monarch Hill and SWA Class 1 show that they produce between 600 to 1,000 gpd/acre. This amounts to 150,000 to 260,000 gpd or the same amount of water used by 1,000 to 1,600 people daily. According to Sam Levin, president of S2L Incorporated, typical leachate generation values in Florida vary from 1100 – 1200 gpd/acre for active areas and higher than that for sites accepting important quantities of biosolids. The closed, geomembrane-capped Southport Landfill in Osceola County generates about 4 gpd/acre, and has been closed for about 12 years. A closed, geomembrane-capped landfill facility is expected to dry out of leachate in about 10-30 years (Scott et al., 2005), but admittedly there is very little published data to support these values. The Dyer Park Landfill is a partially capped landfill in that it has a cover over the top flat surface but the side slopes are uncapped, so any irrigation or precipitation that falls on the slopes could penetrate into the cell and eventually become leachate. According to historical data, the quantity of leachate generated from the Dyer Park landfill comprises approximately 10-25% of the overall leachate flow for the SWA facility: 600,000 – 5,000,000 gallons per month. The eastern section of Palm Beach County has an average rainfall of 62 inches per year (Statom, Thyne, and McCray, 2004). Thus, over the 80-acre landfill area, the amount of leachate generated should average 200,000 gallons per month, but data provided by the Solid Waste Authority of Palm Beach County from 1989 to 2013 shows a historical average flow of 1.5 million gallons a month with a peak flow of 5 million gallons/month, seen in Figure 1, of which 150,000 gallons per month is attributed to the partially closed Dyer Park Landfill. To verify the leachate volume, in 2014, an annual rainfall of 61.3 inches of rain was recorded near the SWA facility (NOAA, 2015). Thus, over the 80-acre landfill site, the amount of leachate generated assuming that evaporation, top cap and 4:1 side slopes should reduce the rain entering the system to 1% of actual rainfall, should be 112,000 gallons per month or 47 gpd per acre. The 2014-15 SWA average monthly total leachate volume was 1,180,000 gallons. Dyer Park produced 10-25% of the total. The monthly range is 118,000 to 295,000 or 49 to 123 gpd per acre.

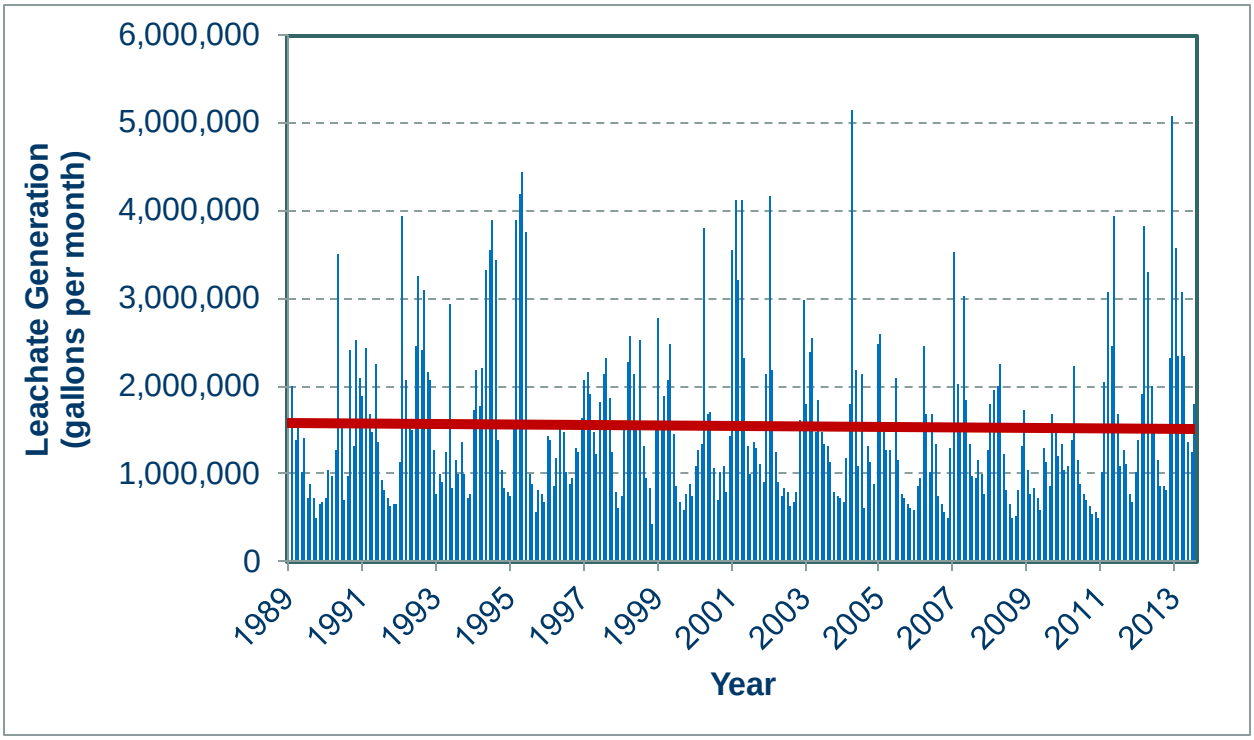

Figure 1. SWA 1989-2013 historical leachate quantities (Eyeington, 2013).

1.6 METHODS OF LEACHATE MANAGEMENT

As a consequence of collecting these concentrated volumes of leachate, containing synthetic organic compounds, heavy metals, and other constituents of concern as discussed earlier, the liquid waste must be eventually discharged back into the environment. A major limitation to the sustainable management of landfill leachate has been the lack of effective methods to guarantee safe long-term discharge back into the natural environment. This is further complicated by the extremely variable leachate quality and waste generation rates, along with the ever-changing regulatory environment, which has caused many conventional technologies to fail to meet this goal.

Currently viable leachate management options include: on-site treatment, municipal sewer discharge, deep well injection, hauling offsite, or a combination approach. In the case that deep wells cannot be permitted or hauling is not cost effective, municipal sewer discharge is favored. However, wastewater treatment plants are facing the possibility of having to meet discharge limits (for nutrients and emerging contaminants of concern) that exceed the boundaries of current technologies. Facilities that accept leachate may struggle to meet the proposed new limits (i.e. USEPA numerical nutrient criteria), and may stop accepting the material or impose excessively high surcharges. So it is conceivable that in the future, municipal sewer discharge will become a limited option. Given this scenario, landfill managers may soon be forced into on-site treatment to handle their leachate.

In previous work funded by the HCSHWM, 23 different engineering alternatives for long-term leachate management were evaluated (Meeroff and Teegavarapu, 2010). For on-site treatment to

work, some form of aerobic treatment would be expected to reduce leachate strength prior to discharge. However, biological systems are not well-suited for the removal of bio-toxics from water and are inefficient in dealing with wastes of varying quality, such as leachate. Thus post-treatment, using constructed wetlands, combined physicochemical treatment, or evaporation systems, would then be required. Unfortunately, technologies such as activated carbon and certain advanced treatment processes, such as ozone, do not adequately address inorganics, and membrane systems or air stripping merely transfer organics to another phase or create a side stream, like concentrate brine, that cannot be discharged readily. Furthermore, multiple barrier systems are complicated to operate, costly, and generally inefficient. For on-site treatment options, the most effective strategies involve technologies that can destroy different classes of harmful contaminants all at once, without producing adverse byproducts and residuals.

There are basically only a few major ways of treating or disposing of leachate. Treatment can be off-site transfer with or without pre-treatment or reused on-site with or without pre-treatment in the form of biodegradation, physicochemical treatment, or a combination approach. The current method used at Dyer Park is deep well injection, which is disposal without treatment.

One viable option for landfill managers is hauling off-site. Landfills will collect their leachate and send truckloads of the liquid waste to an ultimate disposal site; typically an off-site publicly-owned treatment works (POTW), where it is combined with domestic wastewater and processed along with the municipal sewage. This method does not address the ultimate disposal of leachate; it simply moves the leachate to another location off-site. The option presents a high transportation risk and can be a potentially expensive solution, depending upon the distance to the receiving site and the treatment performance of the facility accepting the material. If the travel distance is relatively short (<100 miles), the costs can be very competitive, and this can be a viable option. But if the site is located at distances greater than 100 miles, the costs can be potentially limiting. For example, Polk County, FL reported a three-year contract they signed in July 2009 for the disposal of their landfill leachate at $130 per thousand gallons (Blandford, 2011). Not all wastewater treatment plants will accept leachate due to the elevated concentrations of constituents found. In addition, leachate generally has low biodegradability and may contain heavy metals. So large volumes of leachate can upset the normal biological treatment processes at the POTW (Boyle and Ham, 1974; Booth et al., 1996), which may lead to expensive surcharge rates or even rejection. The costs associated with hauling can also vary depending on: the cost of fuel, the distance the leachate needs to travel, and if there may be a need to pre-treat the liquid waste prior to wastewater treatment plant acceptance. Besides the transportation risk and fuel cost volatility, the most problematic issue is if the contractor at the facility accepting the leachate suddenly decided that the material is not profitable to handle, treat, and dispose of safely, and terminated the agreement to accept the leachate. This will become particularly problematic if regulations governing wastewater disposal were to become more stringent with respect to ammonia-nitrogen, toxic trace metals, and/or inhibitory organic compounds with low biodegradability. The facility accepting the waste may find that leachate volumes are too high (e.g. >20% of the raw wastewater flow) compromising the treatment plant's ability to meet permitted discharge water quality levels (Çeçen and Çakıroglu, 2001). In this case, the treatment facility would likely consider no longer accepting the material. Furthermore, wastewater treatment plants are facing the possibility of having to meet discharge limits (for nutrients and emerging contaminants of concern) that exceed the performance capabilities of currently available technologies. Wastewater facilities that currently accept leachate may likely struggle to

meet the proposed new limits (i.e. USEPA numerical nutrient criteria), and may decide to stop accepting the material, or impose excessively high surcharges to discourage landfill leachate discharge to the sewer. With these pending regulations, municipal sewer discharge may become a limited option in the future. In this case, landfill managers must consider other viable options.

Leachate recirculation is another option for managing leachate. This process consists of reintroducing the leachate back into the landfill. The recirculating leachate accelerates the breakdown of organic materials within the landfill (Xing et al., 2012). This leads to increased methane production, which must be managed properly (Xing et al., 2012). The build-up of head pressure from the increased amount of leachate in the bottom of the landfill creates higher potential for the leachate to escape the landfill into the environment and towards the ground water and soil. Tropical climates make leachate recirculation particularly challenging due to high temperatures and elevated levels of evaporation, which lowers the moisture content of the solid waste thereby diminishing the biological activity. Bae et al. (1998) determined the effect of applying additional water, in order to maintain certain levels of moisture, on the methane production and stabilization of the landfill. Lab scale results demonstrated that supplementing the leachate with 85% more water kept elevated levels of methane production and lowered the time to reach stabilization (Sanphoti et al., 2006). Recirculation can improve moisture content and distribute nutrients and enzymes throughout the landfill. The COD of the leachate was lowered 89.5%, and methane production increased 30 to 50% initially, but it also lowered on the relative time scale of the landfill (Chugh et al., 1998). The implementation of a leachate recirculation system requires high capital and recurring maintenance costs. In addition, odor problems from leachate recirculation are common, typically from leachate exposed to the environment in collection ponds (Meeroff and McBarnette, 2011, Townsend, 1995). New River is the only landfill in the State of Florida operating as a bioreactor as press time. Polk County ceased its bioreactor operations due to sideslope seepage. Some cites recirculated leachate without operating as a true bioreactor. Recirculating leachate reduces COD in young and mature landfills. Mature landfills may even be used to treat young landfill leachate. However, recirculation rarely reduces all contaminants to discharge levels. Therefore, further treatment is needed before discharge.

If the appropriate aquifer conditions exist and permitting is available, another attractive disposal option for leachate is deep well injection. Essentially, this is the same as transferring the leachate off-site without treatment. In this option, the leachate is pumped deep into the ground below the aquifer and between confining layers to assure separation from the underground source of drinking water (USDW). The biggest concern with deep well injection is the risk of contamination of the potable water supplies (Groundwater Protection Council 2005). The exact geology thousands of feet underground can be challenging to establish with complete certainty. Even a minor fracture can cause a substantial problem as groundwater remediation is an incredibly difficult task at these depths. On July 7, 2000, the USEPA proposed revisions to the underground injection control (UIC) regulations that would restrict wastewater injection by existing Class I municipal disposal wells that have caused or may cause movement of contaminants into USDWs in specific areas of Florida (65 FR 42234) unless the owner meets certain additional requirements: 1) secondary wastewater treatment plus filtration and high level disinfection (so that primary health-based drinking water standards would not be violated) with a non-endangerment demonstration (basically the same requirements as for reclaimed water

irrigation systems) or 2) in-depth hydrogeological demonstration and added treatment, as necessary. The second option refers to 40CFR146.15(d), which states that to qualify for authorization the owner shall develop and implement a pretreatment program that is no less stringent than the requirements of Chapter 62-625, Florida Administrative Code, or have no significant industrial users as defined in that chapter. Furthermore, the owner must treat the injectate using secondary treatment in a manner that is no less stringent than the requirements of Florida Rule 62-600.420(1)(d), and using high-level disinfection in a manner that is no less stringent than the requirements of Florida Rule 62-600.440(5)(a)-(f). In this scenario, the specified treatment requirements then are designed to achieve an effluent after disinfection containing not more than 20 mg/L $CBOD_5$ and 20 mg/L TSS, or 90% removal of each of these pollutants from the wastewater influent, whichever is more stringent. The bottom line is that the proposed rule would require installation of additional wastewater treatment with high level disinfection for Class 1 injection wells. This means that injected water would need to meet at a minimum, secondary treatment and high-level disinfection as defined in the Florida regulations, with filtration required for total suspended solids (TSS) control prior to disinfection (such that the treated wastewater contains no more than 5.0 mg/L of TSS before the application of the disinfectant). The proposed rules would apply to: Brevard, Broward, Charlotte, Collier, Flagler, Glades, Hendry, Highlands, Hillsborough, Indian River, Lee, Manatee, Martin, Miami-Dade, Monroe, Okeechobee, Orange, Osceola, Palm Beach, Pinellas, St. Johns, St. Lucie, Sarasota, and Volusia Counties, which were targeted in the proposal because of the subsurface carbonate geology. Many of the large publically owned treatment works (POTWs) in those same counties dispose of treated wastewater effluent via deep injection wells. Therefore, if the leachate is sent to a POTW and it compromises the ability to meet the discharge limits set forth in the injection permit, the POTW may not wish to accept the leachate. This would cause problems for another important leachate management option of municipal sewer discharge, as stated earlier.

As the options begin to get limited, on-site pretreatment becomes more and more necessary. In that case, some form of multi-stage treatment process would be called for. Typically, some form of aerobic biological treatment would be required to reduce leachate organic strength prior to discharge. Biodegradation is performed by microorganisms, which degrade organic compounds under aerobic conditions and convert soluble BOD into particulate BOD, which can be readily removed via sedimentation. To cope with strong leachate with high COD, an anaerobic process may be used. However, anaerobic digestion will have long treatment times, although compared to aerobic systems, anaerobic processes use less electricity because aeration is not required (Berrueta and Castrillon, 1993). Both biological treatment processes (aerobic and anaerobic) operate best with a constant flow volume and stable influent concentrations. Leachate does not provide these optimal conditions for biological systems without additional processes for flow equalization and/or pretreatment. Biological systems also fail to remove bio-toxic constituents, which are found in sufficient concentrations in leachate to warrant concern. Thus, more post-treatment will be required, which may consist of constructed wetlands, combined physical/chemical/biological treatment, or evaporative systems (Booth et al., 1996).

Further on-site treatment options, such as physical and chemical treatment (e.g. flotation, coagulation/flocculation, adsorption, air stripping, membranes, and chemical oxidation) have critical limitation with respect to leachate treatment. Coagulation/flocculation is commonly used as a pre-treatment to remove non-biodegradable organic matter using aluminum sulfate

(Amokrane, Cornel, and Veron, 1997). The disadvantage is the large volumes of chemical sludge produced. Flocculation can also foul downstream filters or other processes in the treatment train, or require multiple filters to prevent clogging. Activated carbon adsorption can remove COD, halogens, and other toxic compounds but has difficulty dealing with heavy loads of organics and salts as would be expected in leachate. The use of air stripping merely transfers volatile constituents from liquid to gaseous phase, still releasing them into the environment, while ignoring the inorganic components. Options such as ozone and ultraviolet light deal with some forms of organics but do not degrade inorganics. Membrane systems like reverse osmosis (RO) produce two streams, one is a highly treated water (permeate) with 98% removal of COD (Renou et al. 2008), while the other (concentrate) is a highly concentrated brine containing a stronger concentration of constituents that have not been altered and still must be disposed of. Multiple barrier systems like RO are complicated to operate, costly, and only recover 80% of the liquid (Peters, 1998). Singh (2011) observed a 10% decrease in flux over 24 hours, which is evidence of rapid fouling.

Clearly, many of the existing treatment technologies and complicated multiple barrier approaches are not sufficient to manage landfill leachate; therefore, the most effective and sustainable strategies for the future would involve technologies that can destroy different classes of harmful contaminants all at once, without producing adverse byproducts and residuals. Chemical oxidation is widely studied (Wang, Smith, and El-Din, 2003) and is of growing interest with a focus on advanced oxidation processes (AOPs), which employ strong oxidants sometimes in concert with ultraviolet light. The process works best on mature, well-stabilized leachates (Renou et al., 2008) such as the type found at Dyer Park. From our previous work funded by the HCSHWM (Meeroff, Gasnier, and Tsai, 2006; Meeroff, Gasnier, and Tsai, 2008; Meeroff and Teegavarapu, 2010), our research team evaluated 23 different engineering alternatives for long-term leachate management. The results indicated that the most effective and sustainable strategies for the future would involve technologies that can destroy different classes of harmful contaminants all at once, without producing adverse byproducts and residuals. The top candidates suggested by this analysis were advanced oxidation processes.

1.7 ADVANCED OXIDATION PROCESSES

When selecting the most appropriate treatment scheme, it is desired to have a system that is a simple, single-stage process that produces no hazardous by-products or waste streams, but is still economical. Several advanced oxidation processes (AOPs) were considered. AOPs promote the creation of highly reactive oxidants such as hydroxyl radicals, which are chemical species that possess an unpaired electron, causing them to be very unstable. The unstable radicals attempt to stabilize themselves by rapidly reacting with surrounding constituents. The radicals will continue to react until stability is reached. Within milliseconds (Peyton and Glaze, 1988, cited by Fang et al., 2004), hydroxyl radicals are capable of achieving complete mineralization (i.e. degradation of complex organics to CO_2, H_2O, and mineral ions) of virtually all organic compounds (Feitz et al., 1999; Cho et al., 2002) rather than concentrate or transfer contaminants into a different phase. In this manner, pollutants that are only partially oxidized are decomposed into components that are potentially more readily biodegradable and less toxic to common microorganisms found in a wastewater treatment plant for instance (Schulte et al., 1995; de Morais and Zamora, 2005). When selecting what AOP process to use in treating the high

concentrations of constituents in the leachate, the process that has the most oxidation power relative to chlorine would be preferred, see Table 8.

Table 8. Relative oxidation power of selected oxidizing species (Munter et al., 2001).

Oxidation Species	Symbol	Relative Oxidation Power
Positively charged hole on titanium dioxide	(h^+)	2.35
Hydroxyl radical	($OH\cdot$)	2.05
Ozone	(O_3)	1.52
Hydrogen peroxide	(H_2O_2)	1.31
Permanganate	(MnO_4^-)	1.24
Hypochlorous acid	(HOCl)	1.10
Chlorine	(Cl_2)	1.00

The UV/titanium dioxide (UV/TiO_2) AOP has unmatched relative oxidation power. UV/TiO_2 performs photocatalytic oxidation in the presence of ultraviolet radiation and oxygen. Thus, the TiO_2 particles act like a catalyst and are therefore reusable without producing by-products or sludge. TiO_2 is a white semiconducting powder consisting of nanoparticles with an average size of 21-nm (Evonik Industries, 2008). The crystalline structure of TiO_2 is available in three forms: anatase, brookite, and rutile (Ohtani et al., 2010). A high quality form of TiO_2 which is commonly used, is the Degussa Aeroxide TiO_2 P-25 (Youngman, 2013).TiO_2 was rated as a Group 2B (possibly carcinogenic to humans) substance by the International Agency for Research on Cancer (IARC) in 2006 as an inhalation hazard because of its nature as a fine dust. The health limitations on TiO_2 are only expressed for inhalation, and there are none listed for ingestion. Although, adverse effects have been measured on fish (>1000 mg/L, 96 hr), daphnia (1000 mg/L, 48 hr), and bacteria (10,000 mg/L, 24 hr) (Evonik Industries, 2008), the material is extensively used in products such as paints and varnishes, floor coverings, roofing granules, sunscreens, cosmetics, printer inks, ceramics, plastics, paper coatings, pigments used in numerous foods, toothpastes, medicines, dielectric mirrors and tattoo pigments (US Department of Health and Human Services, 2011).

TiO_2 semiconducting particles generate strong oxidizing power when illuminated with UV light at wavelengths less than 400 nm. Irradiation of TiO_2 with photons of ultraviolet light energy produce areas of positive charge in the valence band of the semiconductor ("holes") and free electrons in the conductance band. When the "holes" and free electrons interact with water trapped in the pores of the catalyst, a mixture of indiscriminate oxidants are generated including hydroxyl radical ($HO^\bullet$) and superoxide radical ($O_2^{\bullet -}$). For photocatalysis to occur, electron "holes" must migrate to the surface of the TiO_2 crystal. The "holes" primarily react with hydroxide (OH^-) from water acting as electron donors to produce hydroxyl radicals (Rincon and Pulgarin 2005). The electrons primarily react with O_2(aq) (dissolved oxygen) in water acting as electron acceptors to yield the superoxide radical. Some of the electron-hole pairs, which do not participate in the redox reaction with water or oxygen, disappear as heat losses via the recombination of holes and electrons. Utilizing the combined oxidation power of holes and hydroxyl radicals generated in the valence band (VB), and electrons and superoxide radicals generated in the conduction band (CB), illuminated TiO_2 photocatalysts can decompose organic compounds by participating in a series of mineralization reactions (Rincon and Pulgarin 2005).

Chong et al. (2010) explained that the oxidative and reductive reactions from titanium dioxide are due to its unique characteristic of possessing a sole electron in its outer orbital. The reaction process begins when UV light energy photoexcites the lone outer shell electron, which creates an empty outer valence band.

Basically, the photocatalytic process is an array of multi-step reactions. The ability of TiO_2 photocatalyst to mineralize a wide range of pollutants is an attractive quality, but modeling the kinetics of such a complicated process is a challenging task. Sometimes, complex environmental processes allow only for empirical solutions because not all reactions or mechanisms are known. There may be lumped parameters, surrogates, indicators or just overly complex reaction pathways (Hemond and Fechner-Levy, 2000).

Recently, Meeroff and Youngman (2013) developed a falling pilot film reactor using the UV/TiO_2 photocatalytic oxidation technology. In preliminary pilot testing, the reactor achieved 34% COD removal, 57% color removal, 84% alkalinity removal, and 82% ammonia removal within 24 hours of treatment at a TiO_2 dose of 4–10 g/L. Although the process did not reduce the COD concentrations to below 800 mg/L, it demonstrated destruction of 1400 – 2400 mg/L of COD in just 24 hours. These long-term experiments led to the conclusion that first order reaction kinetics best fit the observed destruction of most water quality parameters. Therefore, it may be possible to meet the requirements for surface water discharge and to develop parameters for scale-up. Thus it may now be possible to eliminate impurities in water all at once using a single process, and if these processes work as well in the field (at pilot scale) as they do in the laboratory, providing a viable solution for landfill managers when they run out of options for safely managing their leachate. The questions that remain focus on the suitable intensity of the ultraviolet light radiation to apply and a simple method to determine the appropriate amount of photocatalyst to use for treatment due to the concentration dependence discovered in previous work (Meeroff and McBarnette, 2011; Meeroff and Youngman, 2013). In addition, refinements of the process still need to be worked out with respect to recovering the photocatalyst after a batch of treatment and determining the recovery number, which is related to the number of times the catalyst can be reused before it is spent. These improvements will allow operation at a much lower cost.

1.8 PHOTOCATALYST RECOVERY

Past research at FAU has shown that particulate TiO_2 can be recovered from leachate using centrifugation (Hamaguchi, 2008), reaching 80% TiO_2 recovery with centrifugation. However, the goal of that particular research was to demonstrate, not optimize, TiO_2 recovery from leachate after batch reaction. The biggest challenge with the separation technologies is obtaining $\geq$90% recovery of the TiO_2 in order for reuse to be economical (Meeroff and McBarnette, 2011). Li et al. (2009) found that the recovery of TiO_2 after its use in alkaline solution can be significantly impacted by the pH (Li et al., 2009), reporting that the highest recovery of TiO_2 in leachate was at a pH between 4 - 5 (98.8% recovery). In this case, the TiO_2 was coated with 5, 10, 15, 20-tetrakis (4-carboxyphenyl) porphyrin (TCPP), and the surface was examined for its ability to carry out oxygen photosensitization. Using x-ray photoelectron spectroscopy to measure the kinetic energy and the electrons which escape the top 0 – 10 nanometers (nm) of the

material being analyzed, it was determined that the best attraction between the TiO_2 and the TCPP occurred at a pH <5. It was also determined that the stability of TiO_2 was dependent on its zeta potential, and the higher its zeta potential, the more stable it was. It was also discovered that the TCCP and TiO_2 became a heterogeneous aggregate at a pH of 3.5 – 6, while below 3.5, they became heterogeneous colloids, making them very difficult to recover. When suspended in alkaline solution, the TiO_2 formed negatively charged colloids and began to precipitate from the alkaline solution, becoming unrecoverable.

The following paragraphs discuss the different TiO_2 recovery technologies available today to evaluate their effectiveness for this application. The technologies include: membrane filters, settling tanks, centrifuges, flocculation, diatomaceous earth, and dissolved-air flotation.

Filters with pore sizes of 20 µm, 10 µm, and 0.45µm were tested previously at FAU (Youngman, 2013). The 20 µm and 10 µm meshes only achieved a 17% recovery of the TiO_2, while the 0.45 µm filter achieved close to 100% recovery to the naked eye, meaning that it did not appear that any of the TiO_2 was passing through the filter, but the filter clogged very quickly, which would be an issue if employed in a full scale design (Meeroff and Lakner, 2014). Thiruvenkatachari et al. (2008) showed using coagulation, flocculation, sedimentation, and a 0.2 µm filter could be used to recover nearly 100% of the TiO_2 for circulation into a UV falling film reactor to treat leachate. However, it would be assumed that a separation process with this many unit processes would be very complex, time consuming, and FAU determined that filters can have clogging problems. Dey (2012) suggested the most effective, available options in separating the TiO_2 from treated industrial wastewater are centrifugation or sedimentation because they have been shown to be most effective in removal of suspended particles from similar applications. However, even if TiO_2 particles settle rapidly to the bottom of the sedimentation basin, they still may need to be separated using another technology such as a filter prior to reuse. Dey (2012) also mentioned the use of membrane filtration as being comparable to sedimentation and centrifugation.

A centrifuge is a technology that uses rotational energy in order to increase the gravitational force on the product being separated. A centrifuge spins the treated leachate with TiO_2 at very high rotations per minute (rpms) such that the TiO_2 sticks to the side walls of the centrifuge, and the treated leachate (centrate) would be discharged at the bottom of the centrifuge (Numeric Control, 2008). A centrifuge has been shown to effectively separate water and waste contaminants from waste oil (Numeric Control, 2008), and it is believed that it can separate TiO_2 from leachate. Hamaguchi (2008) showed that up to 80% of TiO_2 was recovered from leachate in previous research when centrifuged at 4,000 rpm for 25 minutes.

A lamella plate settler is a technology that is designed to remove particulate matter from liquids (in this application, the liquid is leachate). It uses a series of inclined lamella plates, which provide effective settling areas in smaller footprints. Figure 2 and Figure 3 show examples of the lamella settling tank design and the lamella plate media.

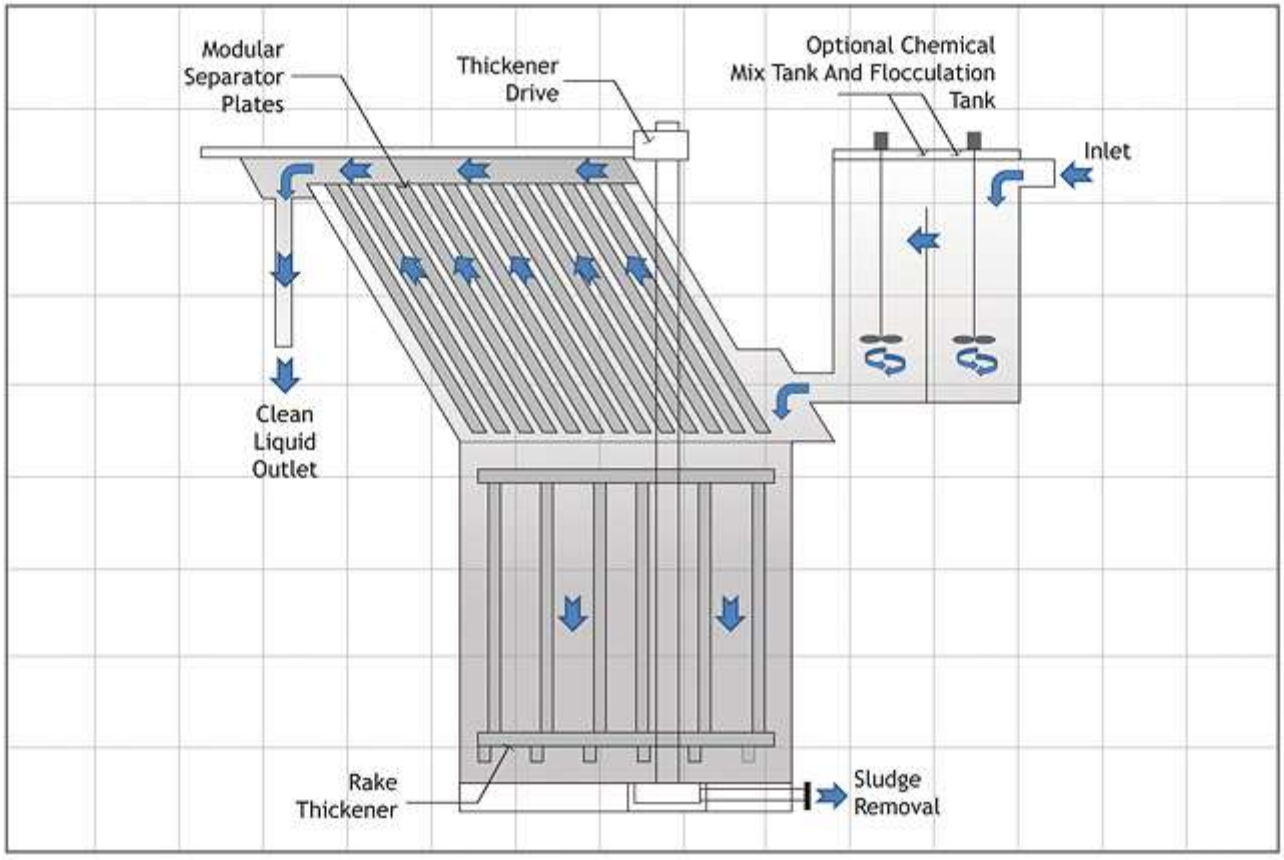

Figure 2. Schematic diagram of a lamella plate clarifier (http://www.terraenvironmental.com/Potable-Water-Treatment.html).

Figure 3. Lamella plate media example (http://www.gea-2h.co.uk/lamella-settlement/).

This technology will allow the treated leachate and TiO_2 to settle by gravity onto the inclined lamella plates or to the bottom of the clarification or thickening tank, where it will be directed into a hopper (McKean et al., 2010). The treated leachate would continue by overflowing over another weir for discharge. This is just a version of a standard settling tank with a much smaller

footprint. It operates the same way as a standard settling tank, except that it uses the inclined plates to assist the sedimentation process and improve solids capture. Typical sedimentation basins achieve 90% particle settling, while lamella tanks typically achieve up to 95% particle recovery (Parsons and Jefferson, 2006).

Filtration is a size exclusion unit process, in which water flows through a bed of granular media, and the suspended particles in the water (in this case leachate) are trapped in the pore spaces and removed. Common filter media used in standard filters are: sand, anthracite, and sometimes granular activated carbon (GAC) (Qasim, 2000), but typical filters would require backwash separation of the TiO_2 from the filter media itself, which would not be efficient. Therefore, the membrane filters may be a more efficient way to go. Membrane filters have smaller pore sizes (1.5 µm or smaller) than standard single, dual, or mixed media filters (0.40 mm) (Qasim, 2000). As a result, they can remove smaller particles, such as TiO_2 photocatalyst particles. Figure 4 shows an example of the pore size scales of membrane filters. Since TiO_2 is made up of very small nanoparticles (21 nm) (Evonik Industries, 2008), membrane filters would be needed in order to separate the photocatalyst particles from the treated leachate. Microfiltration membranes have shown to have relatively low operational costs ($0.09 – $0.14/1000 gallons of filtrate) (APHA, AWWA, and WEF, 2012), and their average lifespan, if maintained properly, can be 7 – 12 years (Pinnau, 2008). Reverse osmosis is the smallest pore size of filtration as seen in Figure 4, but can carry a high capital cost, particularly if the membrane material is damaged by the surface properties of TiO_2 or is irreversibly fouled by the corrosive properties of the leachate itself.

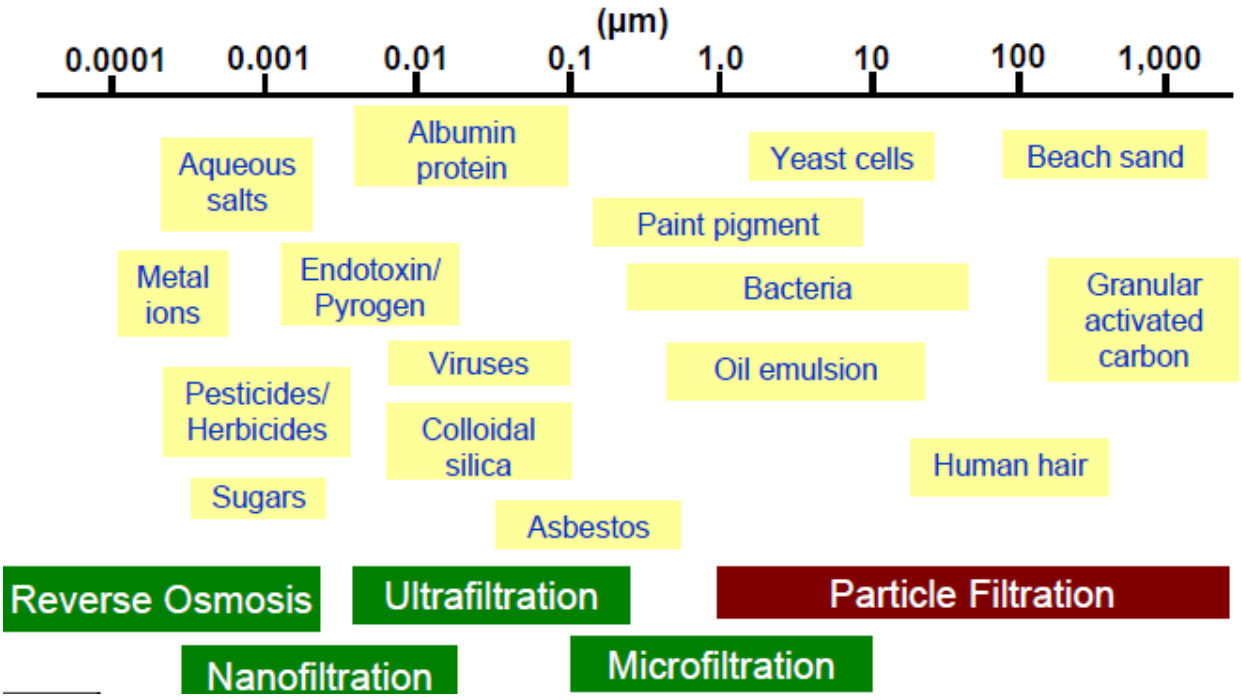

Figure 4. Typical filtration pore sizes (Pinnau, 2008).

Similar to filtration, diatomaceous earth has been shown to be effective at removing micron-sized particles from water (filtrate/backwash ratio of 99%). Diatomaceous earth is the fossilized

skeletal remains of single celled aquatic plants known as diatoms, which have the unique ability to extract silica from water to produce microporous exoskeletons. When the life cycle is completed, the organic matter decomposes, and the skeletal remains accumulate to form inorganic sedimentary deposits. The pores of these inorganic deposits can be smaller than 0.1 μm. There are about 200 operating plants with diatomaceous earth in North America today (2015), and the operating cost for this filtration process ranges between $0.08 – $0.12/1000 gallons of filtrate (Marsh, 2004). Farrah et al. (1991) reported 93% removal of viruses in some cases but only 42% in other cases with 10 liters of filtrate, but with 100 liters of filtrate, the virus removal was even lower at 28%. Also, the filter loading rates of diatomaceous earth range from 0.5 – 2 gpm/ft^2 (Bhardwaj and Mirliss, 2005). Lastly, the lifespan of most filters before needing to be replaced is about five years (Washington State Department of Health, 2003).

Another technology that is similar to sedimentation is dissolved air flotation. In this process, contaminants are removed by injecting air under pressure into a recycle stream of clarified (settled) dissolved air flotation effluent. That recycle stream is then combined and mixed with incoming wastewater in an internal contact chamber where the dissolved air comes out of solution in the form of micro-sized bubbles that attach to the contaminants and rise to the surface, forming a floating bed of material that is removed by a surface skimmer (ETS Environmental, 2012). With this technology, additional blowers would be necessary for the process, and blowers consume 70% of the energy in wastewater treatment plants (Atlas Copco, 2012). This cost makes this technology less attractive for practical use in wastewater treatment plants. It is also a concern that blowing air into the water will stimulate bacteria growth, which will increase the cost of post-disinfection.

With these available TiO_2 recovery technologies, an alternative analysis matrix was constructed to determine the most promising TiO_2 photocatalyst recovery technologies for performing bench scale laboratory tests. Four weighted criteria, based on their scale of importance, were established: performance or recovery efficiency measured by percent of contaminant/particle removal, design life, parameter flexibility, and commonality in wastewater treatment plants. Scores were assigned to each technology based on previous research and engineering judgment.

For recovery efficiency, the technologies were ranked based on their ability to recover particles with similar sizes and characteristics to TiO_2. The technologies that could recover the largest percentage, based on published research, received the highest score. This criterion was given the highest weight because the recovery of TiO_2 is the foundation for doing this research. For design life, the technologies were ranked based on how long (in years) they last before needing replacement or repair. The longer the design life, the higher the score. This criterion was given the second highest weight because this is a major operational and cost concern for wastewater treatment plants and operators. For control flexibility, the technologies were ranked upon how many variables could be changed in order to adjust for different operation concerns. The more flexible the operational parameters were, the higher the score it received. If a technology had many fixed parameters and could make many adjustments for different reasons, that technology received a lower score. This criterion was weighted third because design life of the treatment technology was considered more important in terms of judgment, and all of the technologies had some flexibility. For control complexity, the technologies were ranked upon how difficult they would be for operators to control. The more complex they are, the lower the score they would

receive. This criterion was weighted equally to the control flexibility because the two criteria relate to each other. For commonality in wastewater treatment plants, the technologies were researched on how often that technology has been or is currently used in treatment plants. Obviously, sedimentation tanks are the most common since primary and secondary clarifiers exist at nearly every wastewater treatment plant. Many of the other technologies are fairly standard too. It has been increasingly more common to find membranes at wastewater treatment plants due to indirect potable reuse (and the technology is very common at potable water treatment facilities that may be collocated with WWTPs). The rest of the technologies were ranked accordingly, based on research and can be seen in the matrix in Table 9.

Table 9. TiO_2 recovery technology alternative analysis matrix.

Selection Criteria	Weight	Diatomaceous Earth	Sedimentation, Flocculation, Membrane Filtration	Dissolved Air Flotation	Membrane Filtration	Sedimentation	Centrifugation
Particle Recovery	4	3 (12)	6 (24)	1 (4)	5 (20)	2 (8)	4 (16)
Design Life	3	2 (6)	1 (3)	5 (15)	3 (9)	6 (18)	4 (12)
Control Flexibility	2	1 (2)	3 (6)	5 (10)	4 (8)	2 (4)	6 (12)
Operation Complexity	2	3 (6)	1 (2)	2 (4)	4 (8)	6 (12)	5 (10)
Common in WWTPs	1	2 (2)	1 (1)	5 (5)	3 (3)	6 (6)	4 (4)
Total	**30 (72)**	**11 (28)**	**12 (36)**	**18 (38)**	**19 (48)**	**22 (48)**	**23 (54)**

As can be seen, the top three technologies based on their unweighted and weighted scores were the membrane filter, centrifuge, and sedimentation tank. Therefore, those technologies were investigated further in this study.

1.9 SUMMARY OF HISTORICAL FINDINGS

A summary of research performed using TiO_2 photocatalysis, focusing on COD removal is listed in Table 10.

Table 10. Summary of COD removal efficiencies of TiO_2 photocatalytic oxidation from published performance studies.

Water Type	TiO_2 Dose (g/L)	UV (W)	CODo (mg/L)	pH	Removal (%)	Time (min)	Reference
Grey water (recycled wash water)	2.0-5.0	nr (TQ 150z1)	3940	10.3	44	150	Sanchez et al., 2010
Simulated wastewater	1% Pt-TiO_2 immobilized on silica gel	88 W (1.8 mW/cm^2)	62	6.5	86	30	Suri et al., 1999
Simulated wastewater	0.3-1.0	8 W	10	n/a	82	120	Huang et al., 2008
Lagoon wastewater	2.0	Solar radiation	660	8.0	42	120	Araña et al., 2001
Industrial wastewater (petroleum refineries and chemical manufacturing)	0.6	6 × 18 W	3.2	6.0	62	60	Chen et al., 1997
Olive mill wastewater	1.0	Solar radiation (assumed 30 W/m^2)	6,600	2.8	26	1920	Gernjak et al., 2004
Simulated wastewater	4 plates immobilized	4 × 4 W	120 (TOC)	9.0	34	30	Nakamura et al., 2008
Olive mill wastewater	1.0	415 W	135	8.0	22 (diluted 1:100 + filtered)	1440	El Hajjouji et al., 2008
Industrial wastewater (textile dye wastewater)	0.5	400 W	404	3.0	40	240	Pekakis et al., 2006
Landfill leachate	5.0 (batch) immobilized	16 × 40 W 5.0 – 10.0 mW/cm^2	985	5.0	70	480	Bekbölet et al., 1996
Landfill leachate	3.0	8 W (21 W/cm^2)	1,673	8.7	30	720	Cho et al., 2004
Landfill leachate	1.0-2.0	150 W (0.5 mW/cm^2)	1,200	7.5	35-57	60	Poblete et al., 2012
Landfill leachate	TiO_2 coated sheet	120 W	26,000 – 30,000	5-7.6	76-92	150	Chemlal et al., 2013

Water Type	**TiO_2 Dose (g/L)**	**UV (W)**	**CODo (mg/L)**	**pH**	**Removal (%)**	**Time (min)**	**Reference**
Olive mill wastewater	3.0	7.6 W/m^2	20,000	6.8	36.3	1440	Baransi et al., 2012
Waste activated sludge	3.0	1.5 mW/cm^2	16,249	6.83	45	480	Liu et al., 2012
Landfill leachate	2.0	NA	2,440	8.24	60	4320	Jia et al., 2013
Simulated wastewater	3.2 g of TiO_2 coated on immobilized sheet	38 W/m^2	157,000	7.0	51.6	255	Yahiat et al., 2011
Paper mill wastewater	0.75	35-45 W/m^2	2,075	6.5	70.5	180	Ghaly et al., 2011
Industrial wastewater (distillery effluent)	0.2	Solar radiation	500	6	32	240	Vineetha et al., 2012
Landfill leachate	200 mg/L	Solar radiation	3270 to 4575	5	63%	1019 kJ/L	Rocha et al., 2011
Landfill leachate	2 to 10 g/L	15 W	2440	8.2	60%	4320	Jia et al., 2012
Swine and bovine manure	Immobilized with 1 g/L suspension	6-100 W UVA	Ammonia 100 ppm	7.1-8.7	55%	360	Altomare et al., 2012

A primary advantage of photocatalytic technologies over other advanced oxidation processes is that photons in the near-UV range can be used instead of the dangerous radiation of the UV-C region required for UV disinfection or oxidation. Consequently, energized processes can potentially make possible the use of free sunlight instead of expensive mercury lamps (Bolduc and Anderson 1997). To date, experiments conducted at FAU have used less than 0.5 mW/cm^2 of ultraviolet energy, which is one order of magnitude less than natural sunlight (5-7 mW/cm^2), measured at noon (Balasaaswathy et al. 2002). The technology is easy to operate because the process just requires sufficient contact time and does not rely on complex precipitation reactions, chemical addition, or biochemical processes. Another major advantage is the simultaneous removal of organics, metals, and pathogens without merely transferring the pollutant to another medium (i.e. air or sludge). Therefore, this technology may provide an efficient, environmentally-friendly, and sustainable approach to long-term leachate management as well as aquatic water quality protection. Potential applications extend beyond solid waste management and include indirect potable reuse, water recycling, aquifer recharge, advanced wastewater treatment, and even household or portable systems. These methods will allow landfill operators with little training to reliably manage leachate without spending too much time on the task.

1.10 OBJECTIVES

The main purpose of this research was to test UV/TiO_2 photocatalytic degradation of selected pollutants (COD, ammonia, alkalinity, etc.) in mature landfill leachate using a pilot scale reactor. The primary objective of this study was to determine an effective reactor configuration that meets the water quality goals of one or more of the following: 1) surface water discharge, 2) industrial reuse as cooling water or horticultural irrigation, or 3) on-site use as dilution water to reduce leachate clogging issues in pipes.

If UV/TiO_2 is to be used to treat landfill leachate, it must be combined with an effective TiO_2 separation/recovery process. Therefore, a secondary objective of this study was to show that a high percentage of TiO_2 can be recovered after chemical reactions with the leachate such that the photocatalyst can be reused for subsequent batch reactions. Thus, the goal will be: 1) to determine the bench scale TiO_2 recovery efficiency of centrifugation, sedimentation, and filtration; 2) to characterize the recovered TiO_2 particles; and 3) to develop preliminary scale-up parameters for design of recovery technologies, for economic analysis purposes.

2. METHODOLOGY

2.1 LEACHATE COLLECTION

Leachate for experimental testing was collected from the Dyer Park Landfill located in Palm Beach County, FL. The Dyer Park Landfill is operated by the Solid Waste Authority (SWA) of Palm Beach. The landfill is currently partially closed, no longer accepting waste, and is used as a recreational facility. The footprint of the landfill is approximately 80 acres producing 120,000 gallons per month on average in 2014-15. The leachate collection system is operated by SWA, and the facility collected un-milled municipal solid waste from 1984 to 1992 for disposal.

Samples were collected from the pump station located on the northwest corner of the landfill, designated by the star on Figure 5.

Figure 5. Dyer Park landfill sample collection point.

The first leachate samples were collected on May 30, 2014. Subsequent samples were collected on September 18, 2014, February 19, 2015, July 1, 2015, and August 21, 2015. The leachate was collected from the Dyer Park leachate pumping station (Figure 6). The samples were taken from a ¼-inch sampling port with a valve (Figure 7). The sampling port was purged for one minute before collection started (Figure 8). The leachate sample was collected in a five-gallon HDPE container (Figure 9). Typically, a total of 15 gallons was collected each day. Measurements of dissolved oxygen, pH, temperature, and conductivity were taken directly after collection using a YSI 550MPS, as described later. Samples were immediately placed in a cooler after collection to preserve the sample and limit its exposure to light. The samples were stored in a refrigerator at 4°C until treated in the laboratory.

Figure 6. Dyer Park sampling point pump station dry well.

Figure 7. Dyer Park sampling port at the pump station.

Figure 8. Purging the sample port prior to collection.

Figure 9. Filling 5-gallon sample containers.

For catalyst recovery tests, two plastic 10-gallon sample buckets from Home Depot were used to obtain the leachate samples on May 14, 2015. The buckets were put under the discharge point of a PVC pipe at the wet well for the deep injection well, which had leachate from Pump Station A running through it. One important note is that one leachate sample was taken in the morning, and one in the early afternoon. The sample in the morning was raw leachate, and the one in the early afternoon was leachate mixed with dilution water (shallow groundwater) at a ratio of approximately 1:1. Dilution was occurring as part of a preventative maintenance program to reduce scaling in the leachate collection system. This is why the leachate is weaker in terms of COD and ammonia compared to typical mature leachates. As a result, its TDS was much lower than that of the morning sample. Table 11 shows comparisons of the two leachate samples.

Table 11. Leachate sample characteristics for catalyst recovery leachate samples.

Leachate Sample	Leachate pH	Leachate DO (mg/L)	Leachate TDS (mg/L)
Morning	6.76	0.48	36,730
Afternoon	7.57	0.47	23,840

Only leachate from the morning was used in all of the experiments in the catalyst recovery section. For experimentation, the morning leachate sample was either used as it was (raw) or diluted in a (1:20) dilution mixing 50 mL of this leachate with 950 mL of deionized water. Doing this altered the TDS, the main parameter of interest, down to 2,000 mg/L, which was done because preliminary experiments indicated the organic color and TDS of raw leachate would have interfered with colorimetric tests.

2.2 PILOT SCALE REACTOR

The experiments for this pilot scale research were conducted using a: CE 584 Advanced Oxidation, which is part of the 2E – Energy and Environment product range. 2E is a sector owned by G.U.N.T. Gerätebau GmbH; a company based in Barsbuettel, Germany. The advanced oxidation unit is shown in **Error! Reference source not found.**. The reactor was operated in three configurations: 1) a falling film reactor, 2) a flow through reactor, and 3) a falling film with ElectroMagnetic Oxygen Hydrogen (EMOH) device in series. The reactor measures 1510 mm × 790 mm × 1990 mm and weighs approximately 330 lbs. The main components of the advanced oxidation unit are labeled in Figure 10.

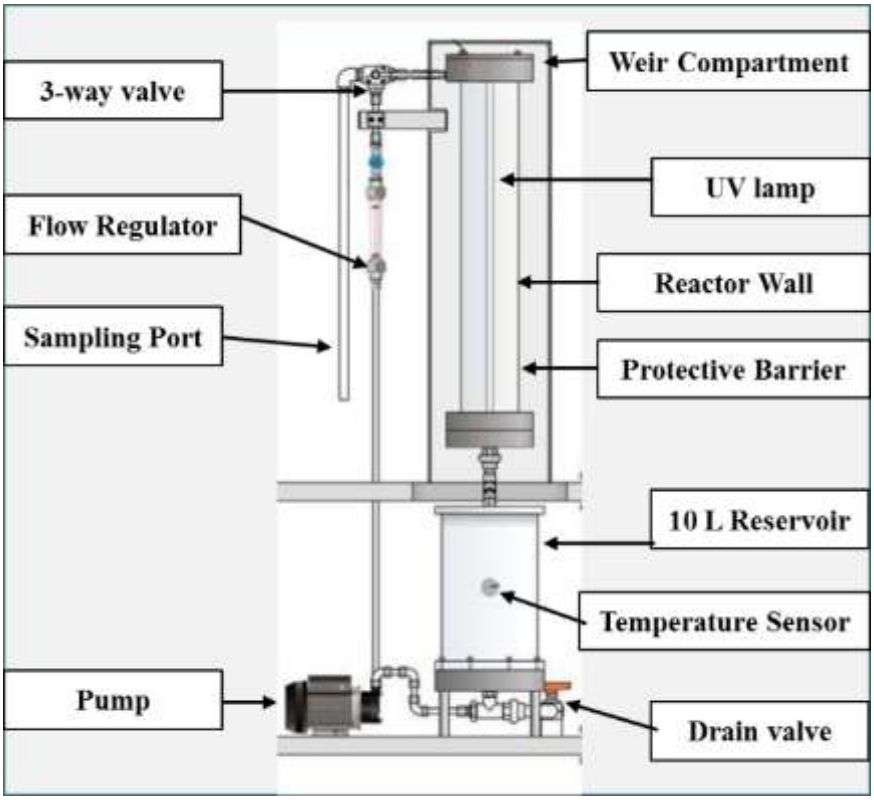

Figure 10. Main components for the pilot scale reactor.

The unit is equipped with a 10-L reservoir, temperature sensor (0-50°C), 260 Liter per hour (1.1-gpm) circulating centrifugal pump (at 29.5 feet of head), flow meter with regulating valve, sampling port with three-way valve, a weir compartment for distributing flow in the reaction

zone, a reaction zone with inner and outer lenses, a 150-W lamp mounted in the center, and a discharge pipe to the reservoir.

Two different light sources were also used for the research. The first was an Ace Glass Incorporated 450-W medium pressure (7825-35), quartz, mercury-vapor lamp, with a large spectrum radiance in the UV-A of 28-W, UV-B of 28.7-W and UV-C of 26.4-W (Figure 11).

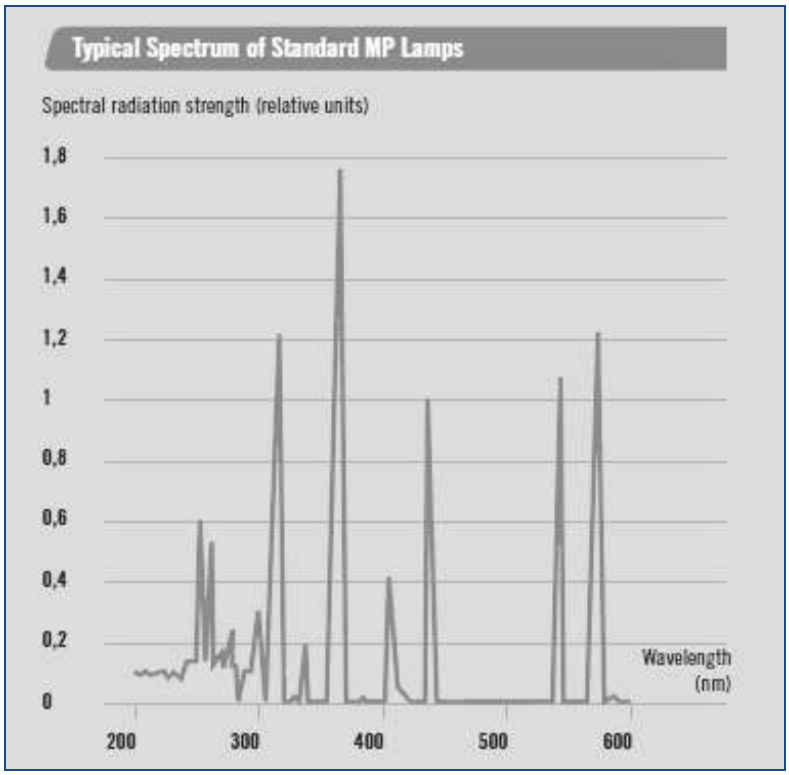

Figure 11. 450-W medium pressure (7825-35) wavelength spectrum (Provided by Ace Glass).

The second was a Heraeus Noblelight NNI 125/84 XL 150-W bulb, with irradiance at 254 nm of 0.35-mW/cm^2 and radiation flux at 254-nm of 38-W. The irradiation spectrum (Figure 12) shows that the lamp provides most of its intensity from 250 – 260 nm in the UV-C germicidal range. Inside the falling film reactor zone, there is an inner protective tube for the lamp. This tube is made of quartz glass (transmittance = 80-90%) with diameter 43-mm. The reactor wall is made of borosilicate glass with an outside diameter of 110-mm, and the glass tubing is protected with an external tube made of polymethyl methacrylate (PMMA XT) at 140-mm diameter. The borosilicate glass and the PMMA both block the transmittance of UV light at wavelengths less than 300-nm to protect the user.

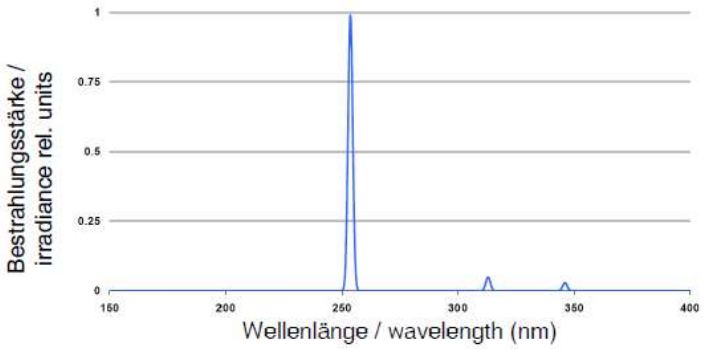

Figure 12. Irradiation spectrum for the Strahler NNI 125/84 XL low pressure UV lamp as provided by the manufacturer.

The UV-C light intensity was measured for both radiation sources using a Sper Scientific 850010 UVC light meter. The results are summarized in Table 12.

Table 12. Measured UV light intensity.

Light Source	UV-A&B	UV-C
150-W	0.518 mW/cm^2	7.21 mW/cm^2
450-W	56 mW/cm^2	0.06 mW/cm^2

2.2.1 Falling Film Reactor

The falling film reactor is how the pilot scale reactor was originally designed to operate, and the same configuration was used in previous experiments conducted by FAU (Meeroff and Youngman 2013). The process begins by adding 10 L of the desired liquid to the 14 L reservoir. The liquid flows out of the bottom of the reservoir and through the stainless steel piping to the circulating pump. Then the liquid is pumped up through the flow regulator, which allows a flow range of 30 – 320 Lph. Following the flow regulator, there is a three-way valve, which leads to either the sampling port or two flexible pipes to distribute the flow evenly between the two entrances to the weir compartment. The liquid builds up until it falls over the weir and cascades down in a thin falling film onto the cylindrical reactor wall, which surrounds the UV lamp. While the liquid runs down the reactor wall, it is exposed to ultraviolet light before collecting in the bottom of the reactor zone and draining back into the reservoir for recirculation. Underneath the reservoir is a drain valve to empty when testing is complete.

To operate as a falling film reactor (Figure 13), the leachate is added to the reservoir then the pump and aeration was is started. Aeration was done using Sweetwater SL22 linear air pump was utilized in conjunction with a large flask of deionized water (to saturate the air with moisture to limit evaporation) for all falling film experiments aeration was done in the reservoir. Once the leachate has started to circulate, the desired amount of TiO_2 is mixed in to the leachate. The method of introducing TiO_2 for experiments from June 6, 2014 to May 28, 2014 was to place the desired amount of TiO_2 into a 1000 mL plastic beaker, then a small amount of leachate from the discharge port is added to the beaker containing the TiO_2. A slurry is made and then added directly to the

reservoir. To ensure all the TiO_2 is added the beaker is rinsed three times with the discharge flow that is then put back into the reservoir. This method was chosen because TiO_2 is hydrophobic, does not mix well with water, and tends to float until the microbubbles around the nanoparticles dissipate. Once the TiO_2 is added, the UV source is activated, and the experiment time is started.

Figure 13. Falling film reactor.

For experiments from July 2, 2015 to September 17, 2015, a different method of introducing TiO_2 was used. The TiO_2 was weighed out in a 1000 mL plastic beaker and then small amounts were placed into a screen hoop with a 37-micron stainless steel mesh. This screen hoop was placed under the discharge stream where leachate passed through it, using this method ensured that no large clumps of TiO_2 would form (Figure 14). More TiO_2 was added until the entire weighed amount had been added to the reactor, and then the UV source was activated and the experiment time was started. All experiments were conducted for 8 hours unless otherwise noted.

Figure 14. Screen hoop with TiO_2.

A flow rate of 300 Lph is maintained by the flow regulator, and the temperature was monitored in the reservoir, during operation. Samples were collected from the discharge pipe of the reactor into a 120 mL sample jar. Samples were taken at 1-hour intervals for all tests from June 6, 2014

until August 10, 2014. After evaluating the results, it was determined that the amount of reduction in 1-hour was within the range of error for the dilutions used. Sampling was changed to a 2-hour increment for all tests except for the 48-hour test on September 17, 2015, where samples were taken at 2-hours for hours 0-8 then at hour 12 and hour 16. Thereafter, samples were taken at 8-hour intervals from 16 to 48 hours.

2.2.2 Flow Through Reactor

The flow through reactor is a modification of the falling film reactor design. A flow through reactor experimental run begins by adding 12 liters of the desired amount of leachate to the 14 L reservoir. The liquid flows out of the bottom of the reservoir and through the stainless steel piping to the circulating pump. Then it is pumped up through the flow regulator, which allows a flow range of 30 – 320 Lph. Following the flow regulator, there is a three-way valve, which leads to either the sampling port or two flexible pipes to the weir compartment. The liquid flows through the flexible pipes to the weir compartment, where it builds up until it cascades over the weir into the reactor and collects in the reactor zone surrounding the UV lamp in the middle. The leachate slowly drains through the reactor zone, where it is exposed to ultraviolet light before passing through the back pressure ball valve (which restricts the outflow) to discharge back into the reservoir for recirculation. Underneath the reservoir is a drain valve to remove the leachate from the unit after the experiment is complete.

To operate as a flow through reactor, the leachate is added to the reservoir, and then the pump is started. Once the leachate has started to circulate, the ball valve is partially closed (to restrict the outflow to 210 Lph), and then the reactor zone fills up with liquid. The desired amount of TiO_2 is then mixed in to the leachate. The TiO_2 is hydrophobic, so the method used to mix was to add a small amount of leachate from the discharge port to a beaker containing the TiO_2. A slurry was made and then added directly to the reservoir. To ensure all the TiO_2 was added, the beaker was rinsed three times with discharge liquid, which was then put back into the reservoir. Once the TiO_2 is added, the light is activated and the experiment time is started. All experiments were conducted for 8 hours unless otherwise noted. The flow through reactor can be seen in Figure 15.

Figure 15. Reactor configured as a flow through.

During the experiment on September 26, 2014, 20-mL of an anti-foam silicone emulsion by J.T. Baker was added at the start of the test to control foaming. It was added into the reservoir at the same time as the TiO_2 and almost instantaneous results were seen with the disappearance of foam in the reactor. Addition of antifoaming agents was discontinued after that one experiment because of positive interference with COD analysis.

Aeration was not used for June 12 and June 18, 2014 experiments. Aeration was used for the August 11 through September 26, 2014 experiments. For the aeration experiments, a Sweetwater SL22 linear air pump with outputting 2 cfm was used. Aeration was done directly in the reactor chamber with 8 aeration stones. Aeration was started once the reaction chamber started to fill with fluid.

2.2.3 Full Spectrum UV Reactor

The full spectrum UV reactor is a modification of the falling film reactor design. The main addition is the 450-W lamp was placed in the reservoir of the falling film reactor. The process begins by adding 10 L of the desired amount of leachate to the 14 L reservoir. The liquid flows out of the bottom of the reservoir and through the stainless steel piping to the circulating pump. Then it is pumped up through the flow regulator, which allows a flow range of 30 – 320 Lph. Following the flow regulator, there is a three-way valve, which leads to either the sampling port or two flexible pipes to the weir compartment. The liquid flows through the flexible pipes to the weir compartment, where it builds up until it cascades over the weir into the reactor. Then pass out the bottom of the reactor to the reservoir and around the 450-W lamp, then it is recirculated. Underneath the reservoir is a drain valve to remove the leachate from the unit after the experiment is complete. Figure 16 show the reactor configuration.

Figure 16. Full spectrum UV reactor.

To operate as a flow through reactor, the leachate is added to the reservoir, and then the pump is started. Once the leachate has started to circulating, the desired amount of TiO_2 is then mixed in to the leachate. The TiO_2 is hydrophobic, so the method used to mix was to add a small amount of leachate from the discharge port to a beaker containing the TiO_2. A slurry was made and then added directly to the reservoir. To ensure all the TiO_2 was added, the beaker was rinsed three times with discharge liquid, which was then put back into the reservoir. Once the TiO_2 is added, the light is activated and the experiment time is started. All experiments were conducted for 8 hours unless otherwise noted.

2.2.4 Photocatalytic Pilot Reactor Modifications/Improvements

The exposure of leachate to UV light creates an exchange of heat and radiation, causing the leachate to increase in temperature rapidly unless controlled. Tests in the pilot reactor prior to this research (Meeroff and Youngman, 2013) were limited to 4 hours because of the inability to cool the leachate to maintain a constant temperature for kinetics testing. The addition of a 50-foot long, 304-stainless steel cooling coil (Figure 17) in the reservoir attached to a VWR Recirculating Chiller 1150S and filled with 13 L of Dynalene HC-50 (hydro-coolant), enabled extended operation times while maintaining the selected temperature range for the leachate treatment.

Figure 17. Photograph of the 304 stainless steel cooling coil.

Cooling was further improved for experiments from July 22, 2015 onward with active cooling of the lamp. Temperatures inside the inner lens, with the lamp operating, reached 81.1°C. The inner lens was then radiating this heat into the reaction chamber while the liquid was cascading down the inner radius, causing the leachate to gain heat energy. To change from passive to active cooling of the lamp, a Sweetwater SL22 linear air pump, with 2 cfm flowrate was attached to a ¾ plastic hose submerged in an ice bath then routed to 8 separate pipette injection tips placed in passive cooling holes (Figure 18).

Figure 18. New active cooling of lamp.

The active cooling reduced the inner lens temperature to 41.6°C on average, this enabled the VWR Recirculating Chiller temperature to be raised from 8.0°C to 24.0°C and still maintain constant running temperatures of 25°C during any length of experiment.

A new stainless steel pump (Speck Pump Y-2951-W-MK) was also fitted to the reactor. This pump (Figure 19), in addition to being less susceptible to corrosion than the previous 260 Lph circulating centrifugal pump (Speck pump model Y-2951.0344 complete with 0.18kW, single-phase motor, 110V, 60Hz, 3600RPM, frame size 56, IP55, C-UL-US, flange turned 90°) has a magnetic coupled drive. This means that no drive shafts collect directly to the impeller, removing the likelihood of leaking from the bearing seals.

Figure 19. Speck stainless steel pump (Y-2951-W-MK).

To enable aeration during the flow through reactor configuration, a new reactor lid was created from scratch using a sheet of Starboard HDPE plastic. This new lid has openings so that aeration can be achieved directly in the reactor. The aeration provides mixing to maintain the photocatalytic particles in suspension within the reactor zone and also supplies oxygen for the oxidation process. (Figure 20).

Figure 20. Photograph of custom flow through reactor lid.

To create the flow through reactor from the falling film reactor, a simple 1-inch PVC ball valve was installed in the discharge line of the reactor, Figure 21. This allows the regulation of the

flow from the reactor increasing detention times and allowing us to create a flow through reactor zone.

Figure 21. Photograph of ball valve.

A Sweetwater SL22 linear air pump was utilized in conjunction with a large flask of deionized water (to saturate the air with moisture to limit evaporation) was used for aeration. Aeration is needed in the falling film reactor and flow through reactors to keep the TiO_2 in suspension and to ensure the proper dissolved oxygen level for advanced oxidation to occur. See Figure 22 for aeration system setup.

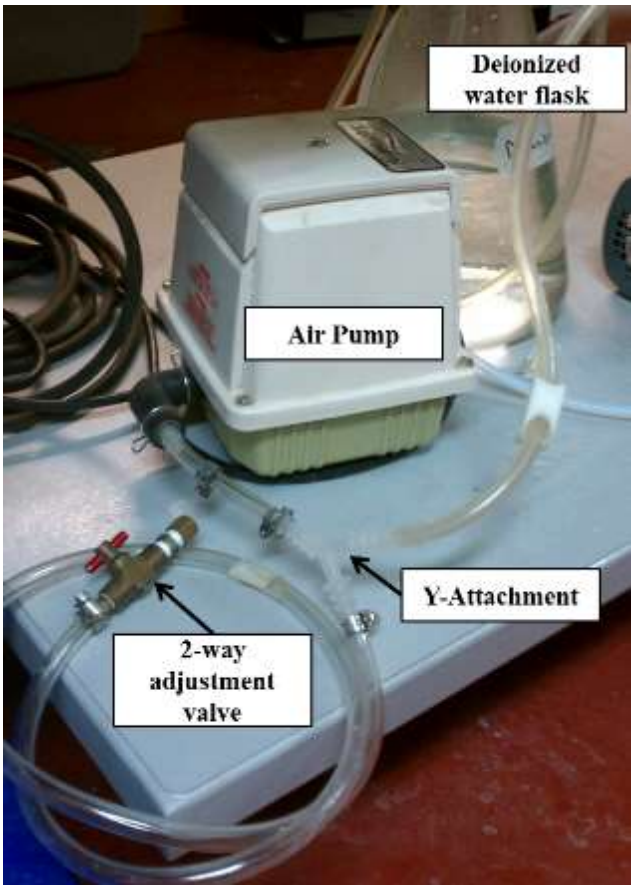

Figure 22. Photograph of aeration system.

2.2.5 EMOH Advanced Oxidation Process

In this research, an alternative advanced oxidation process was also tested (Electro-Magnetic Oxygen Hydrogen – EMOH). Initial proof of concept was conducted on a trailer based-unit, consisting of a 500-gallon mixing tank, 150-gpm Honda pump, a positive magnetic chamber, a negative magnetic chamber, bypass piping with control valves, and a critical orifice venturi (see Figure 23 for labeled components).

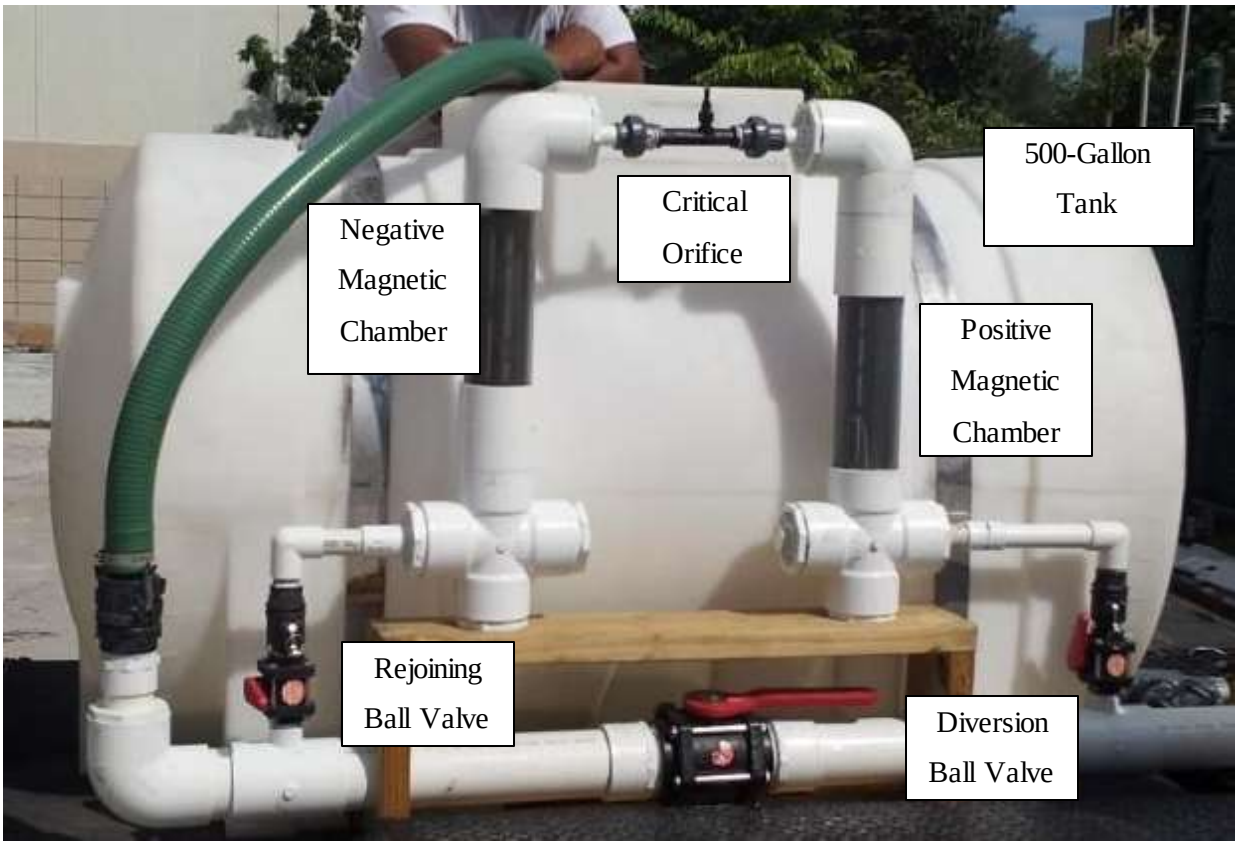

Figure 23. Alternative AOP EMOH device.

10-gallons of leachate collected from Dyer Park was poured into the 500-gallon tank and was diluted with 50-gallons of tap water. The pump was turned on, and once the flow was started, a 50 mL sample was taken. Then the rejoining ball valve and the diversion valves were opened fully causing the leachate to flow through the reaction chamber. Leachate flowed from the tank to the pump, and then the pump sent the leachate to the diversion valve. Only about 10% of the leachate was sent through the reactor, as controlled by the diversion ball valve. The rest (~90%) was diverted around the reaction zone. The leachate that was diverted passed through a positive magnetic field created by neodymium magnets and copper rods. Then the leachate was passed through a critical orifice venturi, where it became pressurized and was then ejected at a high velocity creating a vacuum where the dissolved oxygen came out of solution. This free oxygen created thousands of micro-bubbles with a relatively large combined surface area. This oxygen oxidized the COD, then the micro-bubbles and leachate traveled through the negative chamber and were reintroduced to the bypass stream of leachate where the micro-bubbles continued to oxidize COD. Samples were taken at 5 minute intervals from a sampling port near the discharge.

A second lab scale model was created for testing to be used in conjunction with the pilot scale photocatalytic reactor; this model is a bench top system, containing all of the same components of the trailer-based device, but on a smaller scale (Figure 24).

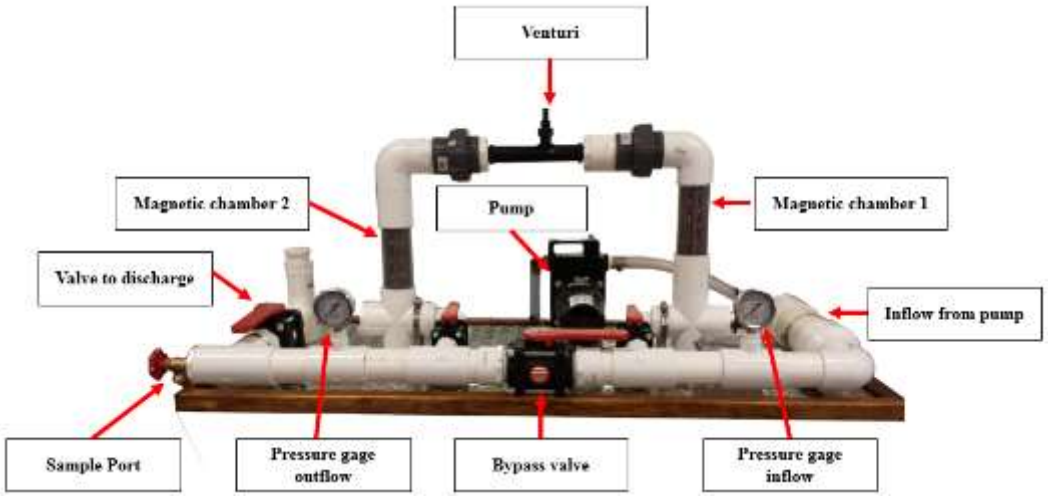

Figure 24. Lab scale EMOH device.

The theory of operation is the magnetic chambers where the liquid passes through are lined with rare earth magnets, and the magnetic fields interact with the electron orbits. By passing the liquid through these fields, the orbits spin and align with the field; they enter the next magnetic field and spin again. This tumbling encourages anions and cations to interact and causes some solids to dissolve. The venturi introduces micro-air bubbles that also interact with these ions, possibly inducing oxidation.

One combined reactor configuration employed in this study was a modification on the falling film reactor design (falling film + EMOH). The process begins by adding 12 liters of leachate to the 14 L reservoir. The flow path is described as follows (Figure 25): liquid flows out of the bottom of the falling film reservoir and through the drain valve into a ¾-inch plastic tube to a SRTO 5DT7 stainless steel pump with a capacity of 7 gpm. This pumps the water through a ¾-inch plastic tube into a 3 inch PVC expansion chamber. From the expansion chamber, the liquid enters 2 inch PVC pipe to a valve where the flow is diverted into the first magnetic chamber. After the chamber, the liquid enters a ½-inch venturi meter. The liquid then drops down through the second magnetic chamber and into a 2 inch PVC pipe and is pushed through a valve to a ¾-inch plastic pipe where the flow is split by a Y-connection to two flexible pipes to the weir compartment. The liquid builds up in the weir compartment until it over flows the weir and cascades down onto the cylindrical reactor wall, which surrounds the UV lamp. While the liquid runs down the reactor wall, it is exposed to ultraviolet radiation before collecting in the bottom of the tube and draining back into the reservoir, where the cycle is repeated. All experiments were conducted for 8 hours unless otherwise noted.

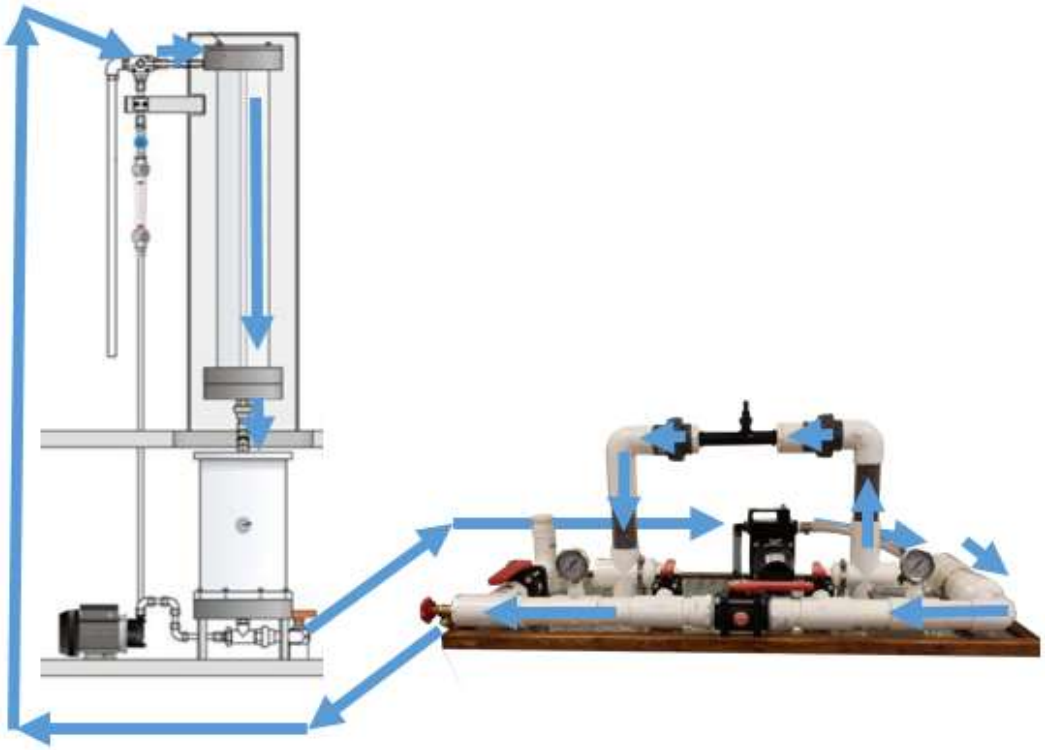

Figure 25. Falling film + EMOH reactor configuration flow path diagram.

2.3 EXPERIMENT PROCEDURE

To initiate the experiment, leachate was removed from the storage refrigerator and 10 L was measured out 2 L at a time using a 2000 mL plastic graduated cylinder (Figure 26). Once the leachate was added to the reservoir, the unit was powered up and the pump would begin circulating. At this point, a 50 mL sample was taken from the reservoir for testing as the initial concentration at t_o. Next the TiO_2 was added in slurry form, the dosing of the TiO_2 varied from 120 mg/L to 30 g/L. The TiO_2 was weighed on a Mettler-Toledo XS204 DeltaRange Analytical Balance in a 1000 mL HDPE beaker.

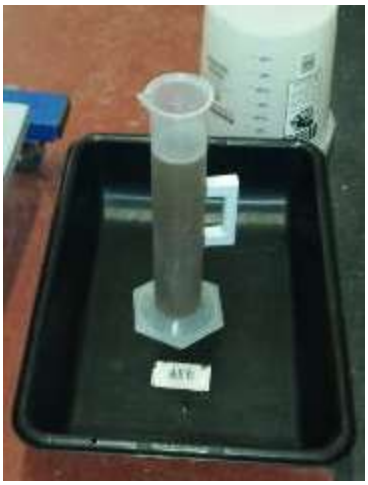

Figure 26. Measuring leachate in a 2000 mL graduated cylinder.

Once the TiO_2 was added, a digital timer was started, and the test began. For the initial runs, 50 mL samples were taken every hour. When the results of the test were examined, it was found that the change over a one hour period was within the range of error, so thereafter, samples were taken at 2 hour increments. Directly after the sample was collected, the temperature, dissolved oxygen content, and pH were taken. The remaining water quality tests were performed after the run was complete.

Once the sample was collected, the temperature and pH tests were conducted. The pH was taken with a Hach HQ40d Portable pH meter, which recorded pH and temperature. The pH temperature was then compared to the built in temperature probe on the G.U.N.T, the built in temperature probe was the primary value with the pH meter being quality control. Then the TiO_2 was removed from the sample. This was done in two ways, the first was using a VWR® Clinical 200 centrifuge (6000 rpm for 6 minutes). The contents of the centrifuge tubes were then poured back into the sample container, and the remainders of the tests were conducted. This method was used for tests conducted from June 6, 2014 to February 19, 2015. The second method used from February 20, 2015 to September 17, 2015 was filtering through a glass microfiber filter disk with a pore size of 1.5 µm. This method was very effective at removing the TiO_2.

2.4 CRYSTAL VIOLET TEST

The crystal violet experiment was used to verify the generation of hydroxide ions in the reaction mechanism indicating that the TiO_2 was working as intended. The crystal violet test was selected because the crystal violet will react with the hydroxide produced from the titanium dioxide and UV light. This neutralization is visually observed as the discoloration of the dye (i.e. the color will turn from violet to clear if the reaction happens). This test was performed in a photocatalytic chamber using the Ace Glass Incorporated 450-W medium pressure, quartz, mercury-vapor lamp. A glass petri dish containing 25 mL of deionized water with 10 g/L TiO_2 was prepared. Added to this was 5 mL of 1.0×10^{-4} M crystal violet. The lamp was turned on in the empty chamber and allowed to warmup for 15 minutes. Then the sample was placed in the chamber

uncovered at a distance of 4 inches from the light, and observations were taken at 1 minute intervals.

2.5 IMPROVING COD REMOVAL

To improve the COD removal process, different catalyst aids were tested in the photochemical chamber. The catalyst aids were selected to increase the efficiency of oxidants produced. Metals with low energy electron loss were believed to be ideal for this purpose, including: aluminum, zinc, steel wool, and combinations of these. A stock solution of 5 g/L of TiO_2 and leachate was made. Then 80 mL of the solution was added to quartz test tubes. Then different catalyst aids were added to eleven test tubes. The Ace Glass Incorporated 450-W medium pressure, quartz, mercury-vapor lamp was warmed up in the empty chamber for 15 minutes prior to initiating the experiment. Then the test tubes were added at a distance of 4 inches (Figure 27). The test was run for one hour, after which 2 mL samples were taken from each test tube and tested for COD removal efficiency.

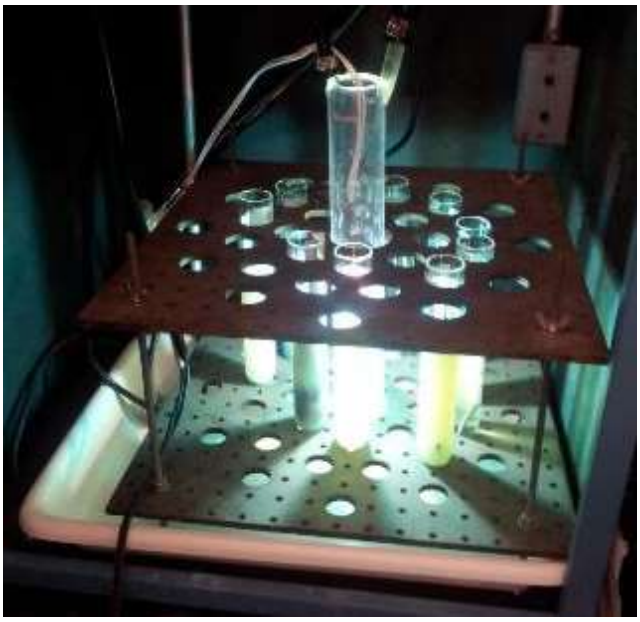

Figure 27. Photochemical chamber setup.

2.6 TiO_2 DOSING

A widely used, high quality TiO_2 product (Degussa Aeroxide TiO_2 P-25) was used as the photocatlyst for all testing. A breakdown of the composition in Aeroxide TiO_2 P-25 is shown in Table 13.

Table 13. Physical composition of Degussa Aeroxide TiO_2 P-25 (Evonik Industries, 2008).

Compound	Unit	Value
Titanium Dioxide	wt. %	≥ 99.5
Al_2O_3	wt. %	≤ 0.300
SiO_2	wt. %	≤ 0.200
Fe_2O_3	wt. %	≤ 0.010
HCl	wt. %	≤ 0.300
Sieve Residue	wt. %	≤ 0.050

The titanium dioxide in the Degussa Aeroxide TiO_2 P-25 is not a pure form of TiO_2. Ohtani et al. (2010) tested the crystalline composition of the Aeroxide P-25 and found that it contained a ratio of anatase, rutile and an amorphous phase of the two. They reported that the Degussa P-25 was 78% anatase, 14% rutile and 8% amorphous phase. Some notable chemical and physical properties of the two pure forms as well as the Aeroxide TiO_2 P-25 (used in this study) are listed in Table 14.

Table 14. Properties of anatase and rutile forms of titanium dioxide (Pelaez et al., 2012; Hong et al., 2005; Faure et al., 2010; Kosmulski et al., 2009; Evonik Industries 2008).

Property	Units	Anatase	Rutile	Aeroxide P-25
Molecular Weight	g/mol	79.88	79.88	79.88
Melting Point	°C	1825	1825	1850
Boiling Point	°C	2500-3000	2500-3000	n/a
Light Absorption	nm	<390	<415	<400
Density	g/cm^3	3.79	4.13	3.8
Crystal Structure	n/a	Tetragonal	Tetragonal	Tetragonal
Refractive Index	n/a	2.55	2.75	2.49
Dielectric Constant	n/a	31	114	78.5

Finding the proper dose of TiO_2 is vital to having the advanced oxidation process work correctly. The conventional method would be to have a balanced molar equation for the substance to remove. However, since leachate is a cocktail of different contaminants, to determine the exact value using stoichiometry is complicated. Likewise, titanium dioxide is not consumed during a reaction, it is just energized each pass through the reactor. When considering a basic molecule of an organic compound containing carbon, hydrogen, oxygen, and nitrogen to be oxidized to carbon dioxide, ammonia and water, the following chemical reaction is can be used:

Equation 1
$$C_nH_aO_bN_c + \left(n + \frac{a}{4} - \frac{b}{2} - \frac{3c}{4}\right)O_2 \rightarrow nCO_2 + \left(\frac{a}{2} - \frac{3c}{2}\right)H_2O + cNH_3$$

Assuming the average organic compound found in leachate is derived from a mixture of alkaloids, lipids, proteins and peptides, this theoretical molecule would contain six carbon atoms. From the chemical formula in Equation 1, then $n = 6$. Since the ratio is greater than 6:1 for protons from the TiO_2, then it would be expected that the theoretical TiO_2 dose should be 6 times

the COD value. It is important to note, that the theoretical dose may limit the distance that the UV light can travel in the bulk leachate solution. In other words, too much TiO_2 will cause only surface radiation, while too little TiO_2 will cause UV light to pass directly through the solution without activating the catalyst.

To determine the correct amount of TiO_2 to prevent only surface irradiation, dilutions of TiO_2 in deionized water were made from 0.0624 g/L to 30 g/L (Figure 28) and tested to determine the level of UV light scattering using a full absorption scan from 200 nm to 400 nm, the UV range. Surface irradiation occurs when the dosage of TiO_2 particles blocks UV light from penetrating the surface. Therefore shadowing the entire column of liquid behind the surface, this is of particular importance for the flow through reactor configuration. The cuvettes are 1-inch in diameter, which is slightly smaller than the inner diameter of the photocatalytic oxidation reactor. The peak absorbance was found to occur at 330-nm as shown in Figure 29.

Figure 28. Dilutions created for a standard Beer's Law curve.

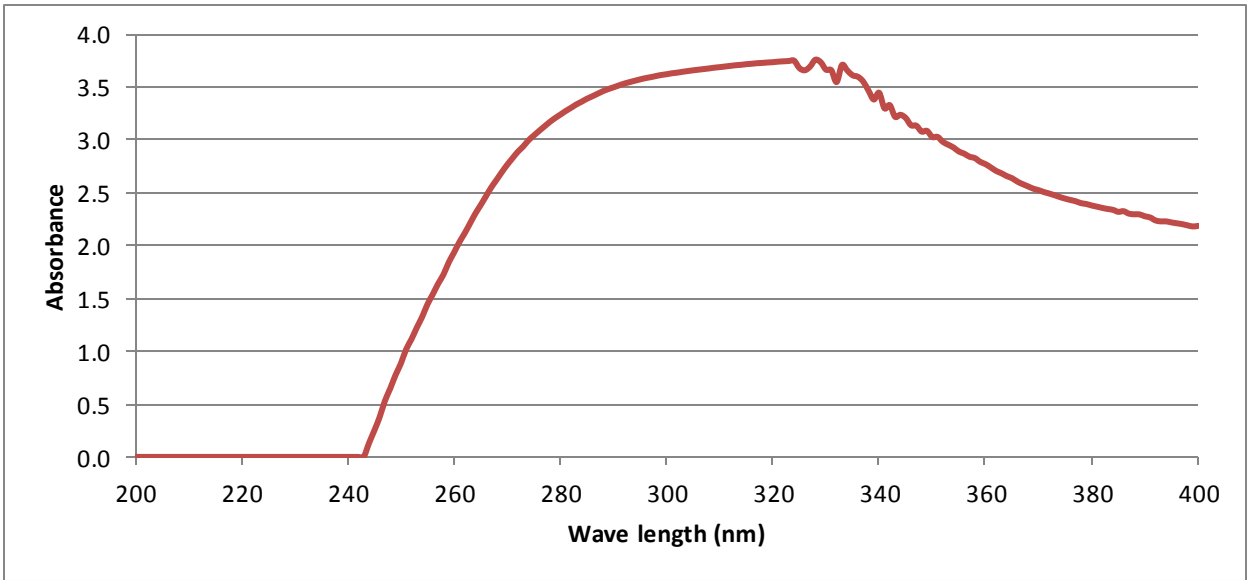

Figure 29. Full spectrum absorbance curve from 200-nm to 400-nm.

2.7 INTENSITY OF UV LIGHT

To measure the amount of UV light that the TiO2 is exposed to in the falling film and the flow through reactor configurations, the UV intensity was measured in three spectra, namely: 1) UV-A, 2) UV-B, and 3) UV-C ranges using a Fisher Scientific UV light meter 06-662-65 for UV-A and UV-B and a Sper Scientific 850010 UV-C light meter.

The lamps were allowed to warm up for 15-minutes to the correct operating temperature of 90°C. Then the measuring devices were placed 0.75-inches from the light, and a set of measurements was taken. This was repeated three times for each light source, and an average of the readings in units of mW/cm^2 was taken. To determine the light density in total watts produced by the entire lamp, Equation 2 was used for each experiment. In order to achieve universal units for light density in a recirculation system that could be applied on any scale, the unit of measure is joule per liter.

Equation 2.

$$Light\ Density\ \left(\frac{J}{L}\right) = \left\{\frac{\left(Exposure\ Area\ (cm^2) \times Measured\ Intesity\ \left(\frac{mW}{cm^2}\right)\right)}{1000\ \left(\frac{mW}{W}\right)}\right\} \times \left\{\{Exposure\ Time(sec) \times \frac{Recirculation\ Rate\ \left(\frac{L}{hr \cdot L}\right)}{Amount\ of\ leachate\ (L)} \times \frac{1}{3600\ (sec)}\right\} \times \left\{Length\ of\ Test\ (hr) \times 3600\ \left(\frac{sec}{hr}\right)\right\}$$

2.8 PRETREATMENT METHODS

In an effort to improve the TiO_2 photocatalytic removal process, pretreatment was used to reduce the initial calcium levels in the leachate. The raw leachate was tested for calcium hardness and initially contained 850 mg/L as $CaCO_3$. The first pre-treatment was adding 492 grams of TiO_2 to 16.4 liters of leachate; the mixture was stirred with a paddle mixer for 2.5 minutes. Then not allowing time for settling, the mixture was filtered immediately through a 5-micron cloth filter. It was hypothesized that none of the TiO_2 that had been coated with calcium would pass through the filter and only uncoated TiO_2 would. This mixture was then treated with no additional TiO_2 added in the falling film + EMOH device. The second pre-treatment conducted was mixing and settling with TiO_2 before photocatalytic reaction. The hypotheses was that the free calcium would bind to the excess TiO_2, and then new TiO_2 would be added in the photocatalytic stage such that minimal calcium would bind to the catalyst to inhibit the reaction. First, 2000 mL of leachate was poured into 7 different B-Ker square jars. Then 30 g of TiO_2 was weighed and placed into each jar. Then 4 at a time, the jars were placed in the Phipps & Bird compact jar tester and mixed for 5 minutes at 100 rpm. At the end of 5 minutes, the jars were removed and placed on a lab bench and allowed to settle for one hour (Figure 30).

Figure 30. TiO_2 pretreatment. Top: Mixing on jar tester. Middle: 1 minute into settling. Bottom: After one hour of settling.

The leachate was then decanted using the sample port on the jar (Figure 30); the sludge at the bottom of all the jars was poured into a single jar and allowed to settle to observe the type of settlement. With the pre-treatment complete, the liquid was treated with TiO_2 using the falling film + EMOH photocatalytic reactor procedures described in detail later.

2.9 ANALYTICAL METHODS FOR PARAMETERS OF INTEREST

The advanced oxidation unit was used to test the removal efficiency of the following constituents: COD, ammonia, and alkalinity. Experiments conducted from February 20, 2015 and thereafter also included removal efficiency of calcium hardness and total hardness. The experiment on September 17, 2015 included a BOD test to identify if COD was being converted to BOD. The standard operating procedures used for each of the tests are outlined in this section.

2.9.1 COD

For chemical oxygen demand (COD) testing the Reactor Digestion Method for the Hach DR5000 UV/Vis spectrophotometer was used with the High Range COD digestion vials (20 to 1,500 mg/L as O_2). The method relies on the reduction of the orange dichromate ion ($Cr_2O_7^{2-}$) to

the green chromic ion (Cr^{3+}), which is analyzed colorimetrically. Theoretically, since each dichromate ion accepts 6 electrons per molecule and each molecule of dioxygen accepts 4 electrons, the COD of 1 g of $Cr_2O_7^{2-}$ is equal to 1.5 g of molecular oxygen. The COD was tested prior to treatment and then after every subsequent 2-4 hours of treatment. All COD samples were centrifuged at 6000 rpm for 8 minutes prior to testing to separate out any photocatalytic and leachate particles that could interfere with the analysis. At least 2 duplicate samples were created for each COD test. Samples tested from June 6, 2014 to June 26, 2014 used a 1:5 dilution. Samples were diluted using 18.2MΩ-cm deionized water. Samples from August 11, 2014 onward were conducted without dilution to reduce the error range of the test. Once the leachate was pipetted into the COD vial, the 2.0-mL samples were inverted 20 times to mix and placed in a heating block at 150°C to digest for 2-hours.

Briefly, 2.0 mL samples were transferred to the Hach COD vials and inverted 20 times to mix before being placed in a heating block at 150°C to digest for 2 hours. Samples were removed from the heating block and inverted another 20 times before being allowed to cool for one hour in the dark. At this point, samples were wiped clean using a Kim-Wipe and analyzed using a Hach DR5000U UV-Vis spectrophotometer. The COD value in mg/L was recorded. A certified reference material (Total Organic Carbon Standard, 300 ppm prepared to EPA Method 415-1 Aqua Solutions, Deer Park, TX) was used to check the instrument calibration. This value varied from 0.1-26% error. The 26% error occurred on July 18, 2015. However, a duplicate measurement for that calibration check only had a 2% error, this suggests an analyst error during preparation. Removing this outlier, the average COD standard error was 3.7%. One calibration check standard was analyzed per batch of samples. It was discovered that high levels of copper that leached from the EMOH unit during the September 17, 2015 experiment had the same green color as the COD test, therefore skewing the results. A simple correction was introduced to drop the concentration of copper to below detectable levels by diluting the samples with a 1:2 ratio with deionized water. High levels of chloride in the samples can interfere in the COD test method. When elevated levels of chloride (>2,000 mg/L) are present in the sample, the chlorides can be quantitatively oxidized by the dichromate, consequently displaying erroneous levels of oxidizable organic compounds. Due to sample dilution, high levels of chlorides that would affect the COD test were not encountered.

2.9.2 Ammonia-Nitrogen

For ammonia-nitrogen, the EPA Method # 350.2 (Detection of Ammonia by Colorimetry), Nessler spectrophotometric method was used. An ammonia (Medium Range: 0.00 to 9.99 mg/L as NH_3-N) ion specific meter (Medium Range: 0.00 to 9.99 mg/L as NH3-N) from Hanna Instruments (Woonsocket, RI) was used for tests from June 5, 2014 until May 28, 2015. The dilution used for the medium range test was a 1:50 ratio using 18.2MΩ-cm deionized water. A Hanna Instruments High Range ammonia meter (HI96733, Range 0.0 to 50.0 mg/L) was obtained later, and all tests from July 2, 2015 onward were conducted with this meter. The higher detection range enabled a lower dilution of 1:10 to be used to reduce the magnitude of error due to high dilution. The methods for both the medium and high range tests are similar and explained as follows. The medium range test began by adding 10 mL of sample to a 10 mL cuvette. The outside of the cuvette was cleaned with a Kim-wipe to remove any fingerprints or dust and placed in the instrument to be zeroed out. Next, four drops of the first reagent (HI 93715A), which is a mineral stabilizer, and polyvinyl alcohol dispersing agent, were added to the cuvette,

and the solution was swirled. Then four drops of the second reagent (HI 93715B), which is Nessler's reagent were added (Figure 31), and the cuvette was swirled again.

Figure 31. Reagent addition to cuvette for ammonia testing.

The outside of the cuvette was cleaned once more before being placed back into the instrument. The recommended reaction time of 3.5 minutes was allowed to pass before the reading was taken. The instrument directly displayed the concentration in mg/L of ammonia-nitrogen (NH_3-N) on the liquid crystal display (Figure 32).

Figure 32. Sample reading from the HI 95715 Ammonia Medium Range ISM.

To convert the reading to mg/L of ammonia (NH_3), ammonia-nitrogen values can be multiplied by a factor of 1.216. Dilution was necessary to lower the concentrations of known interferences, such as organics, sulfides, color, chloramines, aldehydes, and hardness to below 1 g/L as $CaCO_3$. Due to the potency of the ammonia, a 20% dilution was used.

The high range test began by adding 0.1 mL of sample and 0.9 ml of 18.2MΩ-cm deionized water to a 10 mL cuvette, then 9.0 mL of the first reagent (HI 93733B-0) was pipetted in, the lid was closed, and contents were swirled to mix. The outside of the cuvette was cleaned with a Kim-wipe to remove any fingerprints or dust and placed in the instrument to be zeroed out. Next, four drops of the second reagent (HI 93733A-0), which is a mineral stabilizer, and polyvinyl alcohol dispersing agent were added to the cuvette, and the solution was swirled. The cuvette was placed into the instrument, and the read time button was depressed until the timer started for 3.5 minutes. Once the reaction time had lapsed, the value was recorded. A standard reference ammonia cuvette was used to check the ammonia meter before each test. The medium range ammonia meter had an error range from 0.83 to 2.0%. The high range ammonia meter had an error range less than 6.4%.

2.9.3 Alkalinity

For the total alkalinity measurements, SM 2320B method was used. A Hach digital titrator was loaded with a 1.600-N H_2SO_4 titrant cartridge for analyses from June 6, 2014 to July 10, 2015. For tests from July 18, 2015 to September 17, 2015, a 0.1600-N H_2SO_4 titrant cartridge was loaded. First the sample was diluted with deionized water (range: undiluted to 1:10), then phenolphthalein indicator was added to the sample. Titrant was added until the phenolphthalein

endpoint was reached (pink to clear), if necessary. The reading on the digital titrator was recorded as corresponding to the phenolphthalein alkalinity in mg/L as $CaCO_3$ by multiplying the dilution factor by the number of digits. No phenolphthalein alkalinity was measured during any of the experiments. Then the bromcresol green-methyl red indicator was added to the sample, and again titrant was added until the second endpoint was reached (blue-green to light pink). This is the bromcresol green methyl-red alkalinity. When the phenolphthalein alkalinity and bromcresol green methyl-red alkalinity values were added together, this corresponded to the total alkalinity value.

2.9.4 pH

For all experiments, pH was recorded during, prior, and at the end of every experiment using pH Indicator Strips (Whatman Inc., Clifton, NJ), a Hach SensIon 3 pH meter, a Hach MP-6 multiparameter unit, or a Hach HQ40d Portable pH, Conductivity, Dissolved Oxygen (DO), and ORP probes, with the latter being used for nearly all of the measurements reported. In the field, pH was measured with a YSI550 MPS. Probes were calibrated periodically with standard pH buffers (4, 7, and 10). Sensors were rinsed with deionized water and dried with kimwipes in between sample readings.

2.9.5 Dissolved Oxygen

Dissolved oxygen testing started June 6, 2014 for the pilot reactor. Dissolved oxygen needs to be known to insure that enough oxygen is available to react with the TiO_2 to remove metals. A Hach HQ40d Portable pH, Conductivity, Dissolved Oxygen (DO), and ORP meter with LDO101 probe (010105) was used to measure the dissolved oxygen content in the samples as soon as they were removed from the reactor. Dissolved oxygen tests were discontinued after the September 26, 2014 test because the samples remained completely saturated with oxygen during the entire duration of testing. In the field, DO was measured with a YSI550 MPS, calibrated with moist air. For BOD testing, a Hach HQ40d Portable pH, Conductivity, Dissolved Oxygen (DO), and ORP meter with Hach IntelliCAL BOD LDO probe was used, calibrated with moist air.

2.9.6 Temperature

The temperature was recorded prior to and during all experiments. The advanced oxidation pilot unit has a built-in temperature probe in the 14-L reservoir. The temperature was recorded from the digital output located on the control box of the unit. The temperature was recorded every 2 hours. The leachate temperature was also taken during the pH reading for QA/QC of the reservoir thermometer. For the falling film reactor the error between the two values ranged from 0.2 to 1.0%. For the flow through reactor, the error range was 5.8 to 30.0%. The large variation is because the reactor contained all the fluid and did not submerge the reservoir temperature probe completely. In the field, temperature was measured with a YSI556 MPS.

2.9.7 Calcium and Total Hardness

Calcium and total hardness were measured using the Hach digital titration method with EDTA (EPA Method 130.1). Two different dilutions were used for the testing: 1) a 1:10 dilution was used for high range calcium (typically the initial tests), and 2) when the values became lower, a 1:4 dilution was used. All dilutions were used in conjunction with a 0.08M EDTA cartridge. The desired amount of sample was placed in a clean 250 mL Erlenmeyer flask. Then 18.2MΩ-cm deionized water was added until the sample reached 100 mL. First, 2 mL of 8N Potassium

Hydroxide was added to the sample, the flask was swirled to mix the contents. Then one packet of Hach CalVer® reagent (94799) was added to the flask and swirled to make sure the contents of the package were completely dissolved. The Hach digital titrator (Model 16900) with the EDTA cartridge was introduced and titration started by adding titrant in known intervals. The flask was continuously swirled during the titration. When the color changed from red to blue, this indicated the ending point (sometimes this blue appears more as clear with a blue tint). The number of digits on the titrator were recorded at the endpoint. This indicated the calcium hardness, and then 1 mL of 5.25 M sulfuric acid was added to the flask. Additional drops were added until the color of the liquid changed from red to blue to red. This indicated that all of the magnesium hydroxide had dissolved into solution (on average another 2.5 mL were added for this reaction to happen). Once the solution reached the red color, 2 mL of Hach Hardness buffer solution was added and swirled. Next, the contents of one packet of Manver 2 hardness indicator (85199) was added to the flask and swirled into solution. The digital titrator was reintroduced without resetting the units to zero, and the titration was continued, with the color starting from red and ending at royal blue. The magnesium titration was done slowly, only adding a digit or two at a time and then allowing adequate swirling time for the reaction to happen before adding more units. When the titration was complete, the total digits of titrant added multiplied by the dilution factor and digit multiplier indicated the total hardness in mg/L as $CaCO_3$.

2.9.8 Biochemical Oxygen Demand (BOD_5)

For biochemical oxygen demand (BOD) testing, the standard 300 mL glass BOD bottles were used. Samples were collected from the raw leachate and from treated leachate after TiO_2 had settled to the bottom, and the liquid was decanted off the top. BOD to COD ratio from literature was estimated at 0.09 (Borglin et al., 2004). This value was used to estimate the appropriate dilutions for the BOD. Several dilutions were made to ensure even if the estimate was inaccurate that valid results could be obtained. Estimating the 5-day BOD to be 25-30 mg/L, the appropriate dilution to achieve a 5 day dissolved oxygen deficit of at least 2 mg/L was calculated to be 1:10, and the dilution to achieve a dissolved oxygen level of 1 mg/L on day 5 should be 10:1. Dilutions were prepared using 20 mL, 50 mL, 150 mL and 250 mL of sample in 300 mL (diluted with sterile dilution water). Additionally, seeded samples (1 mL each) of each dilution were prepared. The seed ensured that there were sufficient microorganisms in the sample to stimulate biodegradation. Seed was raw wastewater collected from Broward County North Regional wastewater treatment plant, retrieved on the morning of September 25, 2015.

BOD bottles were cleaned with a 10% bleach solution for 15 minutes, then rinsed with tap water and deionized water. The bottles were then sterilized in a Sanyo MLS 3751 autoclave (MLS-3751L-PA), running the water liquid sterilization program. Simultaneously a single 2000 mL bottle of deionized water (sterile dilution water) was sterilized. Once the bottles had cooled, they were labeled, and the correct amount of leachate sample was poured in to each of the 4 sets of dilutions. Samples tested were: raw leachate, raw leachate seeded, treated leachate, and treated leachate seeded. With the correct amount of leachate in each of the BOD bottles, a Hach BOD nutrient buffer pillow (1416066) was dispensed into each bottle. These pillows add trace elements, essential nutrients, and suppress nitrogen reactions. The bottle was then filled to the bottom of the neck with sterilized deionized water and/or sample (with or without seed), as necessary. A blank and a seeded blank were prepared with sterilized water and a nutrient pillow.

The dissolved oxygen was measured in each bottle using a Hach IntelliCAL BOD LDO probe. The probe was calibrated with the standard procedure prior to any readings. The BOD bottles were then topped with sterile water, the glass plug was placed in each bottle ensuring that no air bubbles were trapped in the bottle. The top of the bottles were then wrapped in foil to minimize evaporation of water. The bottles were placed in a dark Hach 205 BOD incubator (2616200) at 20.0°C for 5 days.

After 5 days, the BOD bottles were removed from the incubator, the dissolved oxygen probe was calibrated, and DO readings were taken on each bottle. The results were flagged if the blank dissolved oxygen deficit was more than 0.2 mg/L, the DO deficit was less than 2.0 mg/L, and the dissolved oxygen reading on day 5 was less than 1 mg/L. Ten of the 18 tests were valid or 44%. The remaining 56% were all flagged invalid because the final DO readings were below 1.0 mg/L. The large rejection rate was expected because a variety of dilutions were made to bracket the sample since the exact range was unknown.

2.9.9 Buffering Capacity

To measure buffering capacity, 100 mL of sample was placed in a 250 mL Erlenmeyer flask. The initial pH of the sample was recorded. Buffering capacity was measured as mL of 1.0 M HCl required to reduce the pH of 100 mL of sample by 1 pH unit, as measured with YSI550MPS pH probe. Refrigerated samples were taken out from the refrigerator and were allowed to reach room temperature for at least one hour before the tests were conducted.

2.10 STATISTICAL ANALYSIS METHODS

Statistics of the analytical data were used to compare the results. All data that was statistically analyzed was first checked for normality and for skew. Then the cumulative distribution factor was calculated, and the expected values were calculated. Finally, the z-values were obtained, and plots were made of z-values vs. actual values. The limited number of data points makes the statistical analysis of the data show a skew. T-tests were used to see if an effect was significant, but the skew makes much of this analysis weak.

2.11 CATALYST RECOVERY

An attempt to collect the used catalyst from the treated leachate for reuse was initially tried two different ways. The first preliminary trial was sedimentation of a sample of leachate that was taken from the reactor in a glass beaker. The beaker was then allowed to settle quiescently. Pictures were taken at 1-minute increments (Figure 33).

Figure 33. Sedimentation time lapse series over a 10-minute period.

The second preliminary trial was filtering with a 1-micron bag filter. The leachate was allowed to settle in a 5-gallon bucket. The dry filter bag was weighed. Then the filter bag was placed over a second 5-gallon bucket, and the leachate was poured through the filter.

Since it was determined that centrifuges, settling tanks, and filters were the most promising separation technologies for dealing with TiO_2 in leachate, laboratory tests with these three technologies were conducted. The Degussa Aeroxide TiO_2 P-25 product was used for all experiments in this thesis. In this section, each of the procedures used to conduct these tests is described in detail. Also, particle characterization tests were performed on the TiO_2 to investigate the TiO_2's behavior in the leachate.

2.11.1 Centrifuge Testing

Error! Reference source not found. shows a picture of the centrifuge used to conduct the preliminary tests. The centrifuge model number was the VWR International: Herstellungs Nr: 68105009 - Baujahr 2007 Clinical 200 centrifuge. This unit has a velocity range of 100 - 6,000 rpm. The centrifuge was operated by adjusting the time and velocity. One important parameter for operating the centrifuge was to ensure equal weight distribution in the centrifuge. This was achieved by weighing each 15 mL centrifuge tube with its liquid using a weighing scale that could go up to four decimal places. An even number of centrifuge tubes were split to where they were on opposite sides of the centrifuge rotor as shown in Figure 34.

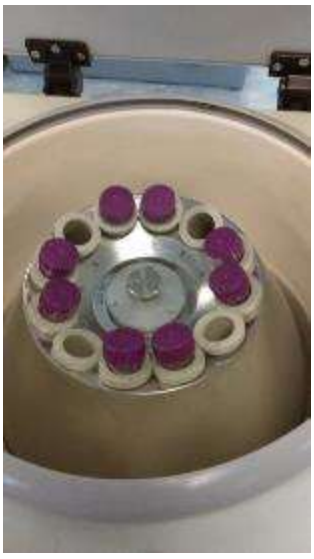

Figure 34. Photograph of the VWR International Clinical 200 Centrifuge.

The method for drying the TiO_2 samples was as follows. Aluminum/ceramic dishes were placed in a drying oven at 103°C for 24 hours. After 24 hours, the dishes were placed into a desiccator for one hour. Then the dishes were taken out with metal tongs and weighed to nearest 0.1 mg. After weighing them, they were placed back into the desiccator for another hour before taking them out and weighing them again to measure the weight convergence. If the difference between the initial dish weight and the second dish weight was $\leq 5\%$, then the dish weight was accepted. If the difference is $\geq 5\%$, then the procedure was repeated in intervals of one hour until the difference between the previous weight and the weight just obtained was $\leq 5\%$. If igniting is required, then the samples were placed into a Barnstead Thermolyne 1400 muffle furnace for 15 minutes at 550ºC after being dried and desiccated. After that time, the samples were removed and placed into the desiccator for at least one hour to return to room temperature before weighing, following the same procedure as mentioned previously for drying.

2.11.1.1 Preliminary Tests 1 – 19 with Raw Leachate

In the first 19 experiments, different centrifuge velocities and times were tested in order to determine the combination that generated the best results. The leachate and TiO_2 were mixed together at TiO_2 concentrations equal to 20 g/L, centrifuged, put into pre-weighed ceramic or aluminum dishes, and then were dried as described previously. After 12 experiments, the leachate and TiO_2 were also put into a muffle furnace in order to drive off organics in the leachate and TiO_2, as described previously. One note is that even though the amount (weight) of TiO_2 and the volume of leachate (mL) was varied, the TiO_2 concentration in the leachate was held constant (20 g/L). A summary of testing parameters is found in

Table 15.

Table 15. Summary of centrifuge parameters for tests 1 – 19.

Test #	Initial TiO_2 Mass (g)	Volume of Leachate (mL)	Centrifuge Time (min)	Centrifuge Velocity (rpm)	Igniting for 15 minutes at 550°C (Yes/No)	Dishes (ceramic/ aluminum)
1 – 3	2	Unknown	5	6,000	No	Ceramic
4 - 6	2	100	5, 10, 2	6,000	No	Aluminum
7 - 9	2	100	2	6,000, 4,000, 2,000	No	Ceramic
10 - 12	2	100	2	6,000, 4,000, 2,000	No	Ceramic
13 - 15	1	50	2	6,000, 4,000, 2,000	Yes	Aluminum
16 - 18	1	50	2	3,000, 2,000, 1,000	Yes	Ceramic
19	0.5	25	2	2,000	Yes	Aluminum

2.11.1.2 Effervescence Reaction

The effervescence reaction is the reaction of hydrochloric acid (HCl) and $CaCO_3$. When HCl (a strong acid) is added to a substance, and bubbles start forming, it may be very likely that $CaCO_3$ is present in the substance. In this reaction, CO_2 gas escapes from an aqueous solution. Equation 3 shows the balanced chemical equation for the effervescence reaction.

Equation 3. $\boldsymbol{CaCO_3(s) + 2HCl\,(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)}$

This equation shows that this reaction is not reversible, and that calcium chloride ($CaCl_2$), water, and carbon dioxide gas bubbles are the products of the reaction (Baxter and Hughes, 2001). It was suggested that $CaCO_3$ might be adsorbing to the TiO_2 during the reaction process. Therefore, HCl was added to the TiO_2, under a fume hood, to determine if $CaCO_3$ was indeed present in the TiO_2. First, a 1.0 M solution of HCl was created by diluting 11.65 mL of concentrated HCl using deionized water in a 250 mL volumetric flask. This was done using the law of conservation of mass shown in Equation 4, which comes from the logic of mass balance where inputs plus sources equal outputs minus sinks (Hemond and Fechner-Levy, 2000).

Equation 4. $\boldsymbol{M_1V_1 = M_2V_2}$

Therefore, the amount of 11.65 M (concentrated) HCl that needed to be added for the dilution could be calculated by solving for V_1.

$V_1 = (M_2V_2)/\,M_1 = (1M)(250mL)/11.65M = 21.5\,mL$

To make the dilution, first, a small amount of deionized water was added the 250 mL volumetric flask. Then the 21.5 mL of 11.65 M HCl was added to the water. Then, water was added to the

flask until it reached the 250 mL line. Last, the flask was capped and inverted several times in order to adequately mix the HCl and the water.

After dilution, using a pipet to transfer the 1M HCl, five milliliters of 1M HCl was added into each aluminum dish from test #19, which had recovered, used TiO_2 in it. Also, five milliliters of 1M HCl was added into three aluminum dishes with virgin TiO_2 in them. Figure 35 shows the three aluminum dishes with virgin TiO_2 and 1M HCl in them, and Figure 36shows the ten aluminum dishes from test #19 with recovered used TiO_2 and 1M HCl in them.

Figure 35. Virgin TiO_2 with 1M HCl.

Figure 36. Recovered TiO_2 from test #19 with 1M HCl.

There was no reaction that took place between the used or virgin TiO_2 using 1M HCl (no bubbles evolved). Therefore, it was recommended to use undiluted, concentrated HCl (11.65M HCl) on the used TiO_2. If there was no reaction between the used TiO_2 and the concentrated HCl, then it was unlikely that $CaCO_3$ was present in the leachate and therefore, the TiO_2. After drying the aluminum dishes with used TiO_2 with 1M HCl in them, 5 mL of concentrated HCl was added to each of the aluminum dishes to see if a reaction would take place. About ten seconds after adding the concentrated HCl, the TiO_2 started bubbling and giving off heat in the fume hood. This is evidence that $CaCO_3$ may have been present on the TiO_2 after it reacted with leachate, although a reaction with the aluminum in the dish cannot be ruled out. Figure 37 shows a picture of the TiO_2 after the reaction of $CaCO_3$ and HCl.

Figure 37. TiO_2 after its reaction with 11.65M HCl.

2.11.1.3 Preliminary Tests 20 – 31 with Diluted Leachate

Centrifuge tests 20 – 31 were performed on the same leachate used in tests 4 – 19, except this leachate was diluted (1:20). Therefore, 50 mL of the 37,000 mg/L TDS leachate was mixed with 950 mL of deionized water in a 1,000 mL volumetric flask. When the leachate was being diluted, its pH, dissolved oxygen (DO), and TDS concentrations were measured using a YSI 556 MPS for the raw leachate and the diluted leachate. The main parameter which was observed was the TDS. The diluted TDS was 2,097 mg/L which was within 4.85% of the target concentration (2,000 mg/L). As a result, this leachate was ready for centrifuge testing. This was the diluted leachate that was used for tests 20 – 25. The same dilution procedure was performed for tests 26 – 28 and 29 – 31. The only difference between the leachate for tests 20 – 25, 26 – 28, and 29 – 31 was that the pH was adjusted by adding concentrated hydrochloric acid to drop the pH or sodium hydroxide to raise the pH to see if changing the pH significantly changed the TiO_2 lost in centrifugation. Table 16 shows a summary of the initial pH, DO, and TDS concentrations of the diluted leachate samples as well as their pH ranges.

Table 16. Centrifuge tests 20 – 31 tested leachate qualities.

Centrifuge Test	Raw DO (mg/L)	Diluted DO (mg/L)	Raw TDS (mg/L)	Diluted TDS (mg/L)	Raw pH	Diluted pH	Tested pH
20 - 25	1.75	6.91	36,950	2,097	7.59	7.19	7.19
26 - 28	1.50	7.92	37,040	2,092	7.09	7.02	4.84
29 - 31	1.75	7.74	37,700	2,061	6.92	7.16	8.31

In centrifuge tests 20 – 25, the mass of TiO_2 and the volume of leachate were the same as what was tested in tests 16 – 18 (1g of TiO_2 and 50 mL of leachate). In these experiments, it was

desired to see if removing the igniting procedure used in tests 13 - 19 would improve TiO_2 recovery process. Also, the only dishes which were being weighed were the centrate (mixed TiO_2 and leachate) and leachate dishes because the amount of TiO_2 being lost in the centrate was measured as described in tests 16 – 19. The weights of the centrifuge tubes and aluminum dishes were carefully measured for these tests. Centrifuge tests 26 – 31 were performed in the exact same manner accept for testing at a different pH. Table 17 shows the centrifuge parameters which were tested for tests 20 – 31.

Table 17. Centrifuge tests 20 – 31 parameters.

Test #	Initial TiO_2 Mass (g)	Volume of Leachate (mL)	Centrifuge Time (min)	Centrifuge Velocity (rpm)	Igniting for 15 minutes	Dishes (ceramic/ aluminum)
20 - 31	1	50	2	2,000	No	Aluminum

When altering the pH of the leachate for tests 26 - 31, the buffering capacity of the leachate was measured. Buffering capacity is defined as the amount of solution needed to change a liquid solution's pH by one unit.

2.11.1.4 Centrifuge Tests 32 – 41 with Velocity Held Constant

These centrifuge tests were performed on diluted leachate (1:20), and these experiments were run at different centrifuge times at a constant velocity. The purpose of doing this was to verify that centrifuging for two minutes, which has been tested the most up to this point, produced optimal TiO_2 recovery results. Table 18 shows the different centrifuge parameters used in tests 32 – 41. Those time parameters were selected using results from tests 1 – 31, and ten minutes was selected to see if longer centrifuge times might actually be better than shorter times.

Table 18. Centrifuge test 32 – 41 parameters.

Test #	Initial TiO_2 Mass (g)	Volume of Leachate (mL)	Centrifuge Time (min)	Centrifuge Velocity (rpm)
40, 41	1	50	1	6,000
32, 36	1	50	2	6,000
33, 37	1	50	4	6,000
34, 38	1	50	6	6,000
35, 39	1	50	10	6,000

In the centrifuge tests themselves, several changes to the method used in tests 20 – 31 were made. First, the TiO_2 and leachate were mixed together in a capped glass jar by shaking and swirling the mixture rather than stirring it with a stirring rod and pouring it into a 100 mL graduated cylinder. Next, after the jar had been shaken before each 10 mL mixture had been transferred, the mixture was poured through a funnel into the centrifuge tubes to prevent mixture spilling. Third, only eight centrifuge tubes received 10 mL of either the mixed solution or leachate only. The purpose of doing this was to increase the accuracy of the amount of TiO_2 in the four centrifuge tubes, and by doing this, an even number of TiO_2 centrifuge tubes could be

arranged for proper balancing in the centrifuge rotor. Fourth, the centrifuge tubes, which had mixed TiO_2 and leachate in them, were allowed to settle until the TiO_2 interface heights were all at the same height (4 mL). This took about 15 minutes to achieve after the mixture had been transferred into the centrifuge tubes. Right before centrifuging, the tubes were shaken quickly to disperse the solids in them. They were then placed in the centrifuge according to their weights and then centrifuged. Lastly, a 5 mL pipetor was used to extract 5 mL of mixed solution or leachate only from the centrifuge tubes after centrifugation and place it into that tube's corresponding aluminum dish. The most important part of using the pipet was to make sure that the TiO_2 "pellet" in each TiO_2 tube was not disturbed when extracting the 5 mL sample. After every dish was filled with 5 mL of centrifuged sample, the dishes were put into an oven to dry for 24 hours at 101.5°C and then desiccated for 1 hour before weighing. Also, after weighing the dishes, they were put back into the desiccator for one hour. Then one dish from each test was randomly selected and weighed again to make sure there was less than 5% difference between that weight and that dish's previous weight. Pictures from test 32 can be seen in Figure 38 and Figure 39. The pictures show the TiO_2 process from centrifugation to being dried.

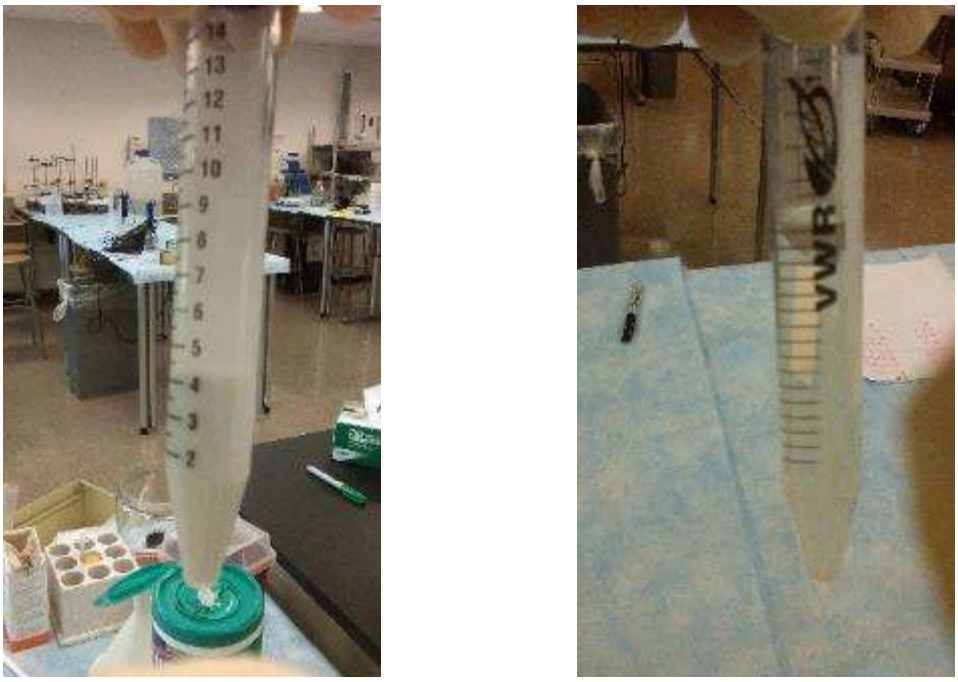

Figure 38. Settled TiO_2 in the leachate before centrifugation (left) and after centrifugation (right).

Figure 39. TiO_2 in the leachate before drying (left) and after drying (right).

2.11.1.5 Centrifuge Tests 42 – 49 with Time Held Constant

These centrifuge tests were performed using the same procedure as that of tests 32 – 41 accept for keeping the centrifuge time constant and changing the centrifuge velocities. By doing this, the optimal velocity with that centrifuge time could be obtained. That result could then be compared to the optimal centrifuge time and velocity obtained in tests 32 – 41 to determine which centrifuge time and velocity combination produced the most optimal TiO_2 recovery results. The parameters that were tested in tests 42 – 49 can be seen in Table 19. Those velocity parameters of 1,000, 2,000, and 6,000 rpm were selected using results from tests 1 – 31, and 3,000 was selected based on a recommended velocity by a manufacture of centrifuges (Numerical Controls, LLC).

Table 19. Centrifuge test 42 – 49 parameters.

Test #	Initial TiO_2 Mass (g)	Volume of Leachate (mL)	Centrifuge Time (min)	Centrifuge Velocity (rpm)
42, 46	1	50	2	1,000
43, 47	1	50	2	2,000
44, 48	1	50	2	3,000
45, 49	1	50	2	6,000

2.11.2 Sedimentation Testing

The second technology investigated was the settling tank. One way to compare the actual settling velocities with the theoretical value is to perform settling tests. In these tests, the height of the settling particles (in this case TiO_2) is measured over time. With these measurements, the effective particle settling velocities, Reynold's numbers, and drag coefficients can be calculated (Qasim, 2000).

The initial slope of the settling curve is analyzed for the initial Type 1 settling velocity. The effective particle diameter removed at this settling velocity is determined using Stokes Law or Newton's Law.

$$v_s = \frac{g d^2 (S_g - 1)}{18\, \upsilon}$$

Equation 5.

Where:
v_s = velocity of the settling particle (m/s)
g = acceleration due to gravity (m/s^2)
d = diameter of settling particle (m)
S_g = specific gravity of the particle
υ = kinematic viscosity of water at a certain temperature (m^2/s)

$$v_s = \sqrt{\left(\frac{4}{3}\right)\frac{dg(S_g - 1)}{C_d}})$$

Equation 6.

Where:
C_d = drag coefficient

$$C_d = \left(\frac{24\phi}{R_e}\right) + \left(\frac{3}{\sqrt{R_e}}\right) + 0.34$$

Equation 7.

Where:
ϕ = shape factor
R_e = Reynolds number

$$R_e = \frac{v_s d}{\upsilon}$$

Equation 8.

Before using a sedimentation tank, settling tests at different TiO_2 concentrations were performed in order to determine an appropriate tank size for design purposes. Experiments were conducted using 100 mL leachate with a TDS of about 37,000 mg/L, mixing the leachate with different TiO_2 concentrations for 90 seconds with a stirring rod, and measuring the settled TiO_2 interface height every 5 minutes for at least one hour; if the TiO_2 did not appear completely settled in one hour the interface height was recorded every additional hour until it appeared completely settled. Initial solids concentrations tested were 1 g, 3 g, 5 g, 7.5 g, and 10 g/100 mL.

When settling tests were performed, the points collected were plotted to form a settling curve. An example of a settling curve is shown in Figure 40. In general, a settling curve shows fast settling in the beginning (constant rate section), and then the curve flattens out after a certain amount of time.

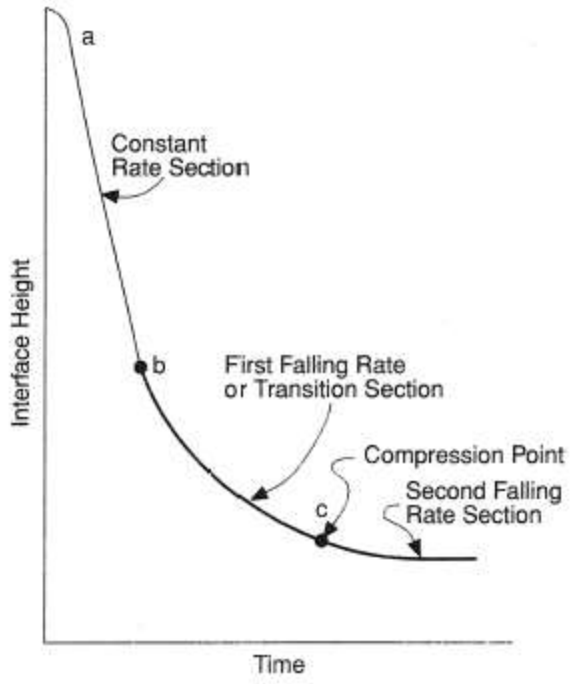

Figure 40. Settling curve example (http://www.thermopedia.com/content/1114/).

In order to find the time to reach a desired underflow concentration (t_u), the settling curve needed to be dissected. This was done using the Talmadge and Fitch method (Qasim, 1998). The steps for dissecting the curve are as follows:

1. Draw straight lines along the top and bottom parts of the curve until they intersect.
2. Draw a straight line from the intersection point until it hits part of the curved part of the settling curve.
3. Draw a tangent which touches the same point of the curve part of the settling curve as the previously drawn straight line.
4. Draw the H_u line at the appropriate location on the curve.
5. Draw a straight line down at the point where the tangent line and the H_u line intersect. This line is the t_u value.

An example of this can be seen by dissecting the example curve in **Error! Reference source not found.**.

.

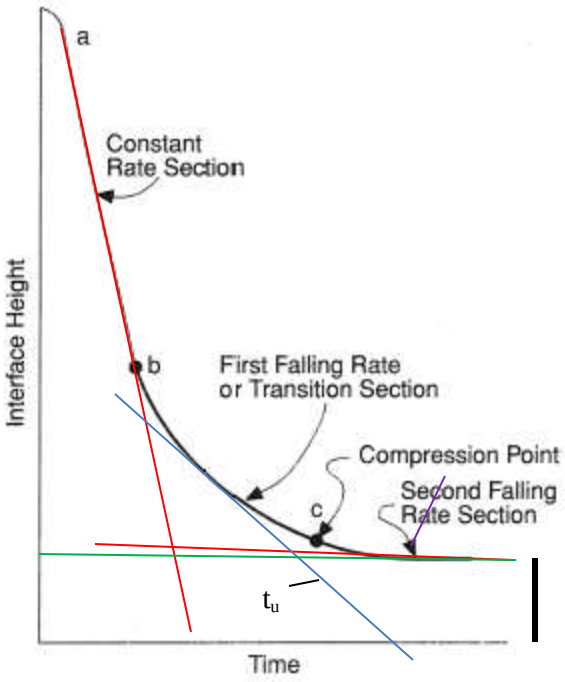

Figure 41. Settling curve dissected using Talmadge and Fitch method (http://www.thermopedia.com/content/1114/)

The area required for thickening (A_T) in m^2 is calculated as follows:

$$A_T = Qt_u/H_0$$

Equation 9.

Where:
Q = flow (m^3/s)
t_u = time to reach the desired underflow concentration (s)
H_u = height at the desired underflow concentration (m)
H_0 = tank height (m)

The clarification area requirement (A_C) in m^2 is calculated as follows:

$$A_C = Q_C/v$$

Equation 10.

Where:
Q_C = clarification flow: $Q_c = Q(H_0 - H_u)/H_0$
v = slope of the initial top portion of the settling curve: $v = (y_2 - y_1)/(x_2 - x_1)$

The following procedure was conducted for settling tests 1-5. First, TiO_2 was weighed out for each test in plastic 100 mL cups; the weight was measured up to four decimal places. The weights of TiO_2 for tests 1 – 5 were 1g, 2g, 5g, 4g, and 5g. One liter of 37,000 TDS leachate

was measured out in a 1L sample bottle, which was shaken for 60 seconds to completely disperse the contents, and then 100 mL of leachate was immediately poured into a 100 mL graduated cylinder. The 100 mL of leachate was then poured in with the TiO_2 and mixed for 90 seconds with a stirring rod to make sure the photocatalyst was well-mixed in the solution. The mixture was then poured back into the 100 mL graduated cylinder, and the cylinder was then capped and inverted several times in order to ensure that the TiO_2 interface height would start at the top of the liquid solution. After the last inversion, a stopwatch was started, and the time for the interface height to drop every 5 mL increment was recorded. Tests 1 – 3 were recorded until enough data points had been collected to form a settling curve. Tests 4 – 5 were recorded in the same manner (measuring the interface within 5 mL increments) except the settling time was recorded for one hour, 90 minutes, two hours, four hours, and six hours in order to help flatten out the settling curve. Table 20 shows the different TiO_2 concentrations tests in tests 1 – 5.

Table 20. Settling test 1 – 5 parameters.

Settling Test #	TiO_2 Concentration (g/100 mL)	Time Recorded (min)
1	1.0	20.50
2	2.0	27.25
3	5.0	30.50
4	4.0	480.00
5	5.0	480.00

Settling tests 6 – 17 were performed similarly. However, the length of recording time (number of minutes) was stopped when it had been determined that the TiO_2 interface height had reached its ultimate settling height (cm). This would help to produce more accurate calculations for the TiO_2 ultimate settling time (t_u). Table 21 shows the different TiO_2 concentrations in tests 6 – 17. One goal of these twelve tests was to look for trends in TiO_2 settling behavior based on TiO_2 concentration. The second goal was to determine an ultimate settling time (t_u), which would produce optimal TiO_2 recovery results through sedimentation. The ultimate settling time (t_u) could be used in the calculation of the sedimentation tank dimensions.

Table 21. Settling test 6 – 17 parameters.

Settling Test #	TiO_2 Concentration (g/100 mL)	Time Recorded (min)
6, 10, 14	3.0	60
7, 11, 15	5.0	120
8, 12, 16	7.5	120
9, 13, 17	10.0	180

A picture from tests 6 – 17 can be seen in Figure 42 which shows the TiO_2 settling height over time for the TiO_2 concentrations of 3, 5, 7.5, and 10 g/L.

Figure 42. Photograph of 3 g, 5 g, 7.5 g, and 10 g/100 L (left to right) during settling tests.

Another method for calculating tank dimensions was the solid flux method. However, that method involves knowing what the concentration of solids is at different times during settling, an underflow rate (the sludge withdrawal rate), and the mixed-liquor suspended solids concentrations a different times (Burton 2003). For a settling test, the underflow rate and mixed-liquor suspended solids concentrations could not be assumed and therefore not used. Therefore, this method could not be conducted, and the previous clarification and thickening areas method, which was previously calculated, was used in place of this.

2.11.3 Filter Testing

The filter TiO_2 recovery tests were performed in junction with the color change tests using TiO_2 and deionized water. The filters used had pore sizes of 1.5 µm (Whatman glass microfiber 934-AH 47 mm diameter circles) and 0.5 µm (Pall), and a magnetic porous plate with holes was underneath them to help pull the water and TiO_2 through the filters. This porous plate had a stopper underneath it to attach to a 500 mL filter flask for catching the filtered water, and it was magnetic so that a Büchner funnel could attach to it easily. A vacuum pump with a hose was attached to the filter flask for suction. Figure 43 shows a picture of this setup.

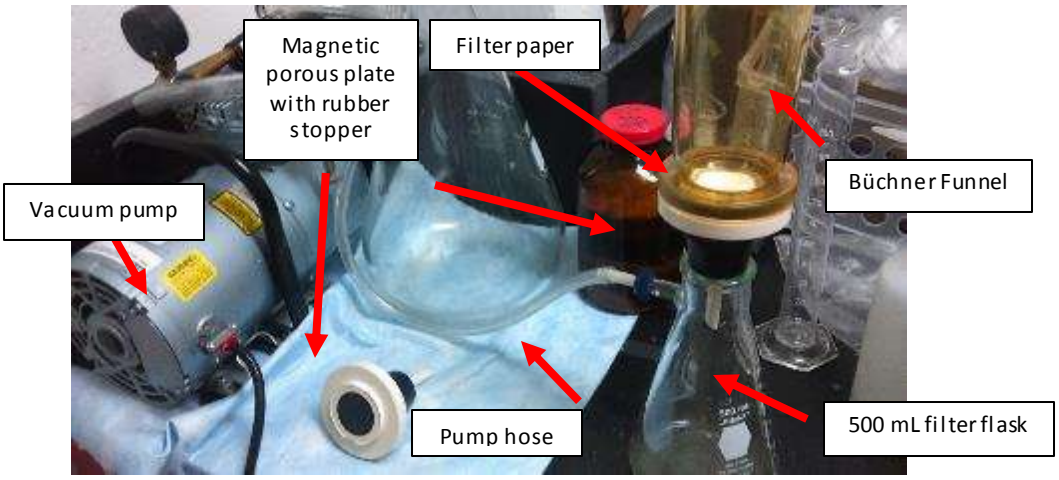

Figure 43. Photograph of filtration setup.

One important note is that it was required to run deionized water through these filters, put them in aluminum dishes, place them in the Barnstead Thermolyne 1400 muffle furnace for 15 minutes at 550˚C, and desiccate them for one hour before obtaining a pre-weight for each one before use.

First, the vacuum pump hose was connected to the 500 mL filter flask, and the magnetic porous plate was placed firmly on top of the flask. Then the prepared filter was placed on top of the porous plate, and the Büchner funnel was then placed on top of the porous plate; this helped to force the TiO_2 and water mixture loaded into the funnel to go through the filter. The initial sample volume was 10 mL. First, the vacuum pump was turned on to start vacuum filtration. The mixed TiO_2 and deionized water were first poured very slowly onto the first filter (1.5 µm filter). The mixture was poured gradually to attempt to model an actual filter loading rate in the field.

After all of the water had passed through the first filter (1.5 µm filter), the vacuum pump was turned off. The 1.5 µm filter was then taken off, and put back into its pre-weighed aluminum dishes. The 500 mL filter flask, which received the filtered water was put to the side, and a second 500 mL flask was attached to catch the filtered water, which was filtered through the smaller 0.5 µm filter. Lastly, the 0.5 µm filter and then Büchner funnel were then placed on top of the magnetic porous plate, the vacuum pump was turned back on, and the filtered water in the previous filter flask was loaded onto the new filter in the same manner as before (gradual loading). After that water had been filtered, the vacuum pump was turned off again, and the 0.5 µm filters were placed in their respective aluminum dishes. Table 22 shows the different TiO_2 concentrations that were filtered.

Table 22. Filter test concentrations.

Test #	TiO_2 Concentration (g/10 mL)
1 - 3	0.05 (5 g/L)
4 - 6	0.10 (10 g/L)
7 - 9	0.15 (15 g/L)
10 - 12	0.20 (20 g/L)

2.11.4 Color Change Tests with TiO_2 and Deionized Water

The color change tests were performed after centrifuge tests 20 – 31 were complete. The purpose of these tests were to see if TiO_2 that evaded recovery could be quantified by using an adapted version of the COD test which relies on a chromium color change caused by oxidation which is measured spectrophotometrically. These tests were initially performed using 0.5 g of TiO_2 in 50 mL of deionized water (10 g/L). These were done for samples that had been centrifuged, settled, and filtered. A 10 mL aliquot of the 50 mL total solution went into four separate centrifuge tubes. It was hypothesized that these tests would all produce apparent COD concentrations of zero mg/L, since the liquid was DI water and not leachate.

The general synopsis of the experimental procedure is as follows. First, the deionized water was mixed with the TiO_2 for 90 seconds. Next, the mixed solution was poured into a 100 mL graduated cylinder and shaken for ten seconds each time 10 mL of it was poured in order to create equally dispersed TiO_2 samples. Immediately after shaking, the solutions were poured into three centrifuge tubes: one which would allow the TiO_2 to settle to the bottom and the other two which would be centrifuged. What remained of the total solution (about 20 mL of mixed solution) was then poured through a vacuum-pump filtration apparatus, similar to **Error! Reference source not found.**, which used filter media composed of the Whatman 1.5 µm glass microfilter 934-AH 47 mm diameter circles and Pall 0.5 µm glass microfilter circles of the same diameter. The TiO_2 samples that were centrifuged were done so using parameters of six minutes at 6,000 rpm; these were the same parameters which were used for color change testing in the advanced oxidation process (Meeroff and Lakner, 2014). The TiO_2 that was allowed to settle was given a time between 30-40 minutes to allow for adequate settling. The filtered water was then transferred into an empty centrifuge tube.

After the four different samples were collected, they were added to ultra-low range (ULR) COD vials for analysis. An aliquot of 2 mL of sample from each centrifuge tube was transferred into each COD vial using a pipette. Also, 2 mL of deionized water was transferred into a ULR tube; this would be the blank sample to zero the Hach DR5000 UV/Vis spectrophotometer. All of the other samples (centrifuged, filtered, and settled) had deionized water and TiO_2 in them. The color change reading of the centrifuged, filtered, and settled waters would be a surrogate for how much TiO_2 evaded capture. Before the samples could be read by the spectrophotometer, they each had to be inverted twenty times and placed carefully into a Hach DRB 200 reactor block to be refluxed for 120 minutes at 150ºC. After reflux, the ULR vials each had to be inverted again twenty times and placed in a metal tube rack in a dark area so that they could cool to room temperature before being analyzed. This procedure followed the closed reflux colorimetric method for measuring COD (APHA, AWWA, and WEF, 2012). Again, it was hypothesized that

the color change readings of the different water samples would be zero, meaning there would be no color change in the deionized water due to the TiO_2.

For averaging purposes, three replicates of each sample (centrifuged, settled, and filtered) at four different TiO_2 concentrations (5 g/L, 10 g/L, 15 g/L, and 20 g/L) were analyzed. The purpose of doing these four different concentrations was to look for trends in TiO_2 concentration with color change. For accuracy purposes and for knowing exactly how much TiO_2 was in each sample, the TiO_2 was weighed out in a plastic weighing boat for each 10 mL sample, which was then transferred to either a centrifuge tube or filtered in a Whatman 1.5 µm and Pall 0.5 µm glass microfiber filter disk and then transferred to a centrifuge tube. Therefore, the weights of TiO_2 which were combined with 10 mL of deionized water were: 0.05 g, 0.10 g, 0.15 g, and 0.20 g for concentrations of 5 g/L, 10 g/L, 15 g/L, and 20 g/L, respectively. The same previous procedure for measuring color change in each sample was then carried out. Table 23 shows a summary of the variables tested in these experiments.

Table 23. Summary of color change parameters being tested.

Type of TiO_2 Separation	**TiO_2 Concentration (g/L)**
Centrifuge	5, 10, 15, 20
Sedimentation	5, 10, 15, 20
Filtration	5, 10, 15, 20

Figure 44 shows the color change measuring process in the COD vials before inverting them and after reflux.

Figure 44. Blank, settled, centrifuge, and filtered samples left to right before reflux (left) and settled, centrifuged, and filtered samples after reflux.

2.11.5 Particle Characterization

TiO_2 particle sizes and zeta potentials before and after its use in leachate was also studied. In this process, an electroacoustic effect occurs where sound waves are generated by an electronic field known as the electro-kinetic sonic amplitude (ESA) (O'brien, Cannon, and Rowlands, 1994). Zeta (ζ) potential is the potential difference between a dispersion medium and the stationary fluid layer which is attached to the suspended particle. It is caused by a net electrical charge confined in the region bounded by the slipping plane, and it depends on the location of that plane (Kirby, 2010). Figure 45 shows a diagram of these components in a suspended particle.

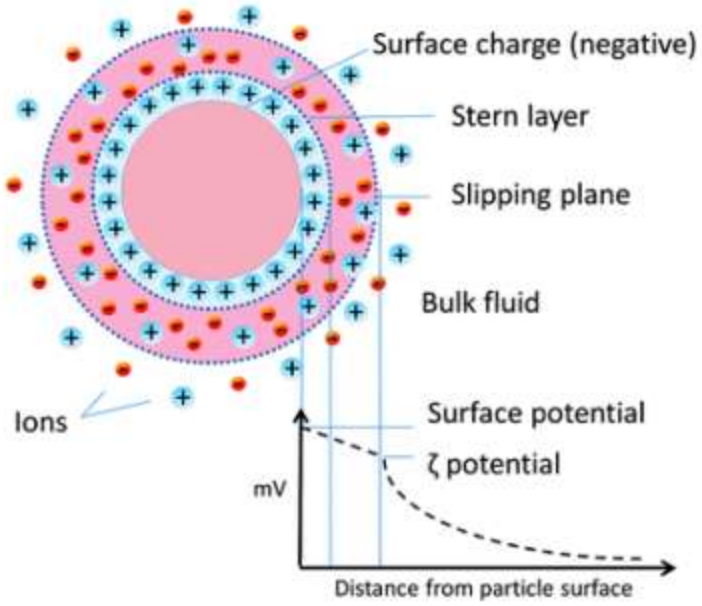

Figure 45. Zeta potential particle diagram (Liese and Hilterhaus, 2013).

Zeta potential is used to determine the charge of a particle. This charge helps to determine the stability of the particle indicated by its electrostatic repulsion between adjacent and similarly charged particles in that dispersion (Greenwood and Kendall, 1999). Table 24 shows the zeta potential particle stability range.

Table 24. Zeta potential stability range (Elango, Kannan, and Murugavel, 2015).

Zeta potential (mV)	Stability behavior of the colloid
from 0 to ±5	Rapid coagulation or flocculation
from ±10 to ±30	Incipient instability
from ±30 to ±40	Moderate stability
from ±40 to ±60	Good stability
more than ±61	Excellent stability

Particle size is determined by measuring the diameter. The average particle diameter of the Degussa P25 TiO_2 was reported to be on the order of 21 nm (Evonik Industries, 2008). Figure 46 shows the visible and non-visible particle size spectrum and the different techniques of visualization. Without a scanning electron microscope, measuring the diameter is a challenge. Therefore, a Malvern Zetasizer Nano Series: Nano-ZS90 unit was used to measure the particle size(s) in this study.

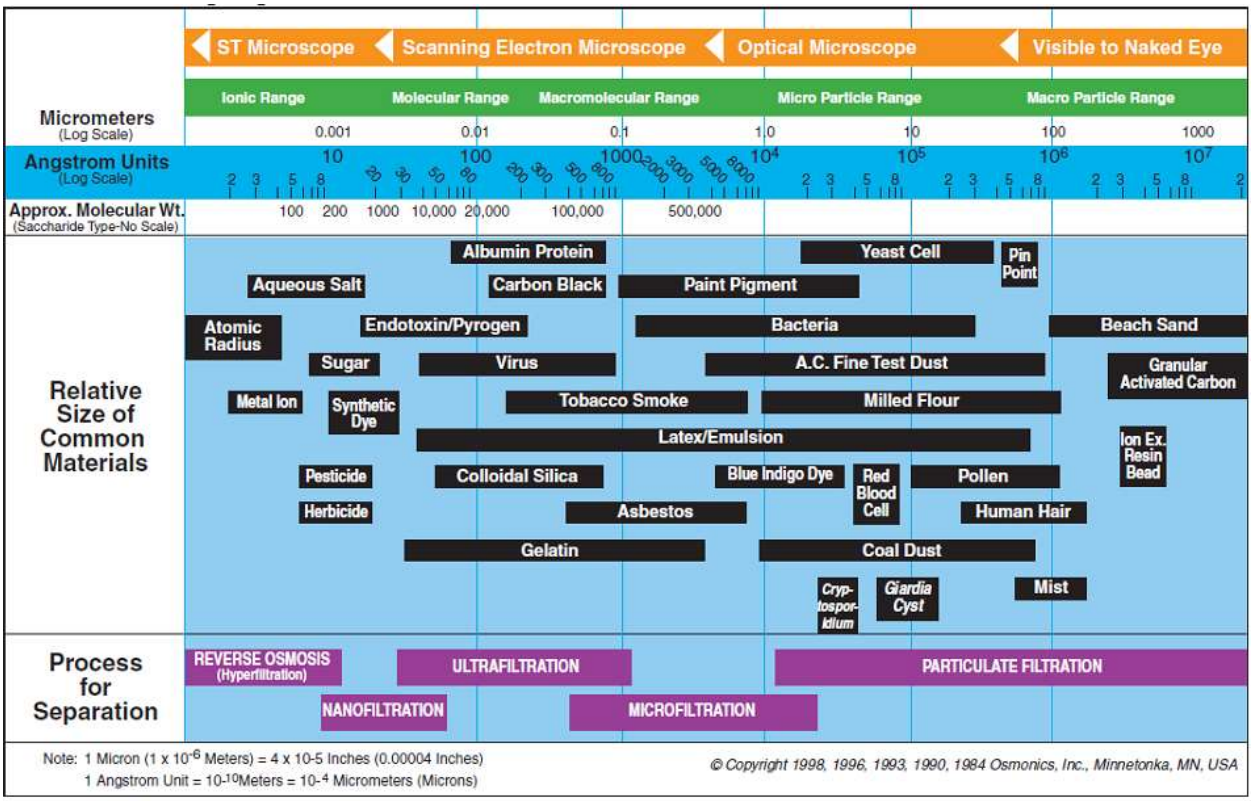

Figure 46. Particle size spectrum chart (Radcliffe and Zarnadze, 2004).

The particle sizes can be measured indirectly by suspending the nanoparticles in clear liquids in 4 mL fluorescent cuvettes, which allow the zetasizer unit to analyze the apparent diamter using laser light to determine an average particle size (Malvern, 2015). Research has shown that the zeta potential has a strong influence on particle sizes of different materials when suspended in fluid layers, such that the absolute zeta potential value increases with particle size (Ofir, Oren, and Adin, 2007). As shown in Table 24, as the absolute zeta potential increases, the particle stability improves. Therefore, it is expected to find a change in particle size and zeta potential of TiO_2 before and after it is used in leachate. It was hypothesized that the used TiO_2 would have particle sizes that were at least three times higher than that of the virgin TiO_2. It was also hypothesized that if the used TiO_2 had higher particle sizes than that of the virgin TiO_2, it would also have higher absolute zeta potential values, between ±30 to ±50 mV, which is classified as moderate to good stability. If that were the case, the virgin TiO_2 would have zeta potential ranges from 0 to ±30 mV which is considered to be unstable. By measuring particle size and zeta potential testing on the virgin and used TiO_2, future assumptions can be made about the TiO_2 particle interactions with other particles when in contact with leachate.

The behavior of colloids is highly dependent on the zeta potential of the colloid medium (Zeta-Meter Inc., 2012). When particles are free by themselves before they flocculate, they have higher zeta potentials. However, after flocculation, their zeta potential drops often from positive to negative. Part of this is because of Van der Waals attraction force which is demonstrated in Figure 47 (Zeta-Meter Inc., 2012).

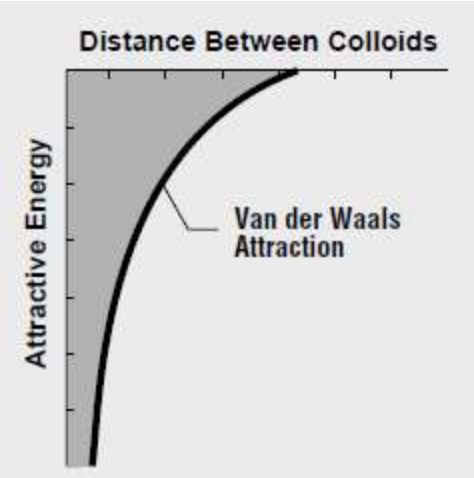

Figure 47. Van der Waals colloid attractiveness (Zeta-Meter Inc., 2012).

The particles may come to equilibrium in the same category that they started in (stable/unstable), but they may transition from positive to negative zeta potential in the process. Also, it is very common for particles to aggregate in the transition and finish with zeta potentials between 0 and -20 mV (Zeta-Meter Inc., 2012).

The particle sizes and zeta potentials of the TiO_2 particles before and after their use in leachate were measured from centrifuge tests 23 - 28. Three replicate samples of virgin TiO_2 were taken, and three replicate samples of used TiO_2 from each of those centrifuge tests were taken. Also, three replicate samples of the leachate itself from centrifuge tests 23 - 25 and 26 - 28 were taken to see if there were differences in the particle sizes and zeta potentials (n = 27 samples in total). This was accomplished using small TiO_2 samples from tests 23 - 28 or virgin TiO_2 and suspending them in fluorescent cuvettes. Samples were analyzed with a Malvern Zetasizer Nano Series: Nano-ZS90 particle size and zeta potential meter, which uses scattered light intensity to measure those two parameters (Malvern, 2015).

The virgin and used TiO_2 samples were suspended in different media in order to help make it easier to get clear distinctions between the virgin and used TiO_2. The virgin TiO_2 was suspended in deionized water, and the used TiO_2 was suspended in the same leachate sample that it was originally recovered from. The virgin TiO_2 could not be suspended in leachate because it would then become used TiO_2, and then no distinction could be made. Therefore, TiO_2 from centrifuge tests 23 - 25 was suspended in a leachate sample with a pH of 7.19, and tests 26 - 28 were suspended in a leachate sample with a pH of 4.84. Those were the same leachate samples that those TiO_2 particles were originally used on. Also, by doing this, it would make it easier to observe a distinction in particle size and zeta potential between leachate of different pH ranges.

First, the same concentrations that were used for TiO_2 recovery (20,000 mg/L) were used in measuring the particle sizes and zeta potentials of the TiO_2. Therefore, 0.2 g of TiO_2 for each used sample or virgin TiO_2 were mixed with 10 mL of leachate or deionized water, respectively (that would make the concentration of TiO_2 = 20,000 mg/L). Next, a 1 mL pipette was used to transfer the mixed TiO_2 and leachate sample to a fluorescent cuvette. If the sample was too concentrated (too turbid), then the sample was diluted with deionized water until it was clear enough to be read by the Nano-ZS90 unit. The dilution was performed by taking 500 µL of the turbid sample and then adding 1 mL of deionized water to it in a new fluorescent cuvette. Only the virgin TiO_2 samples and the test #28 samples were diluted due to their initial turbidity issues. It was often preferred to have a little more than 1 mL in the cuvette for zeta potential purposes. Last, the cuvette was put into the Nano-ZS90 meter for it to analyze the particle sizes and give an average particle size in the cuvette. If the particle size was beyond 10 µm, the Nano-ZS90 unit would not produce a particle size graph range, but it would provide an estimated average.

After the cuvette was read for particle size, the cuvette was taken out, and 1 mL of the sample was removed using a 1 mL needleless syringe. The 1 mL sample was then put into the 1 mL zeta potential cuvette and put back into the meter to be read for zeta potential. A photograph from the particle size and zeta potential tests can be seen in Figure 48.

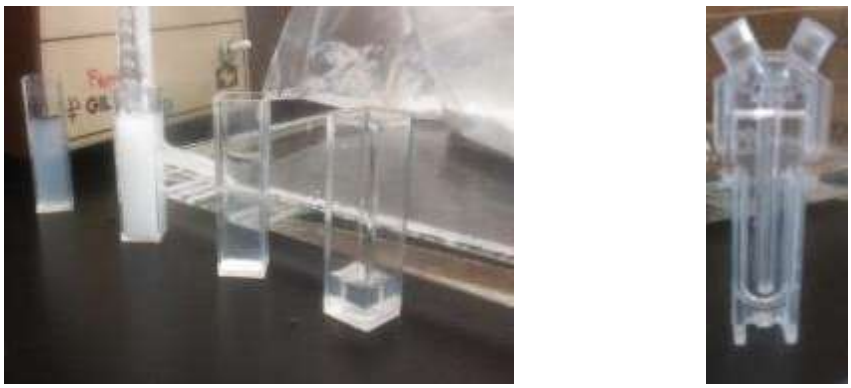

Figure 48. Fluorescent cuvettes containing diluted sample (left) and zeta potential cuvette (right)

Figure 49 (left) shows the TiO_2 particle size (nanometers) in the x-direction and light intensity (%) measured by the Nano-ZS90 unit to measure the particle sizes in the 1 mL sample in the y-direction. The screenshot in Figure 49 (left) clearly shows that the Nano-ZS90 unit produced a range for particle sizes from 200 – 1000 nm, in this case. Figure 49 (right) shows the TiO_2 zeta potential in millivolts in the x-direction, and the total number of measurements measured by the Nano-ZS90 unit to measure the zeta potential in the 1 mL sample in the y-direction. The screenshot in Figure 49 (right) shows that the range for zeta potential was 0 – 40 mV.

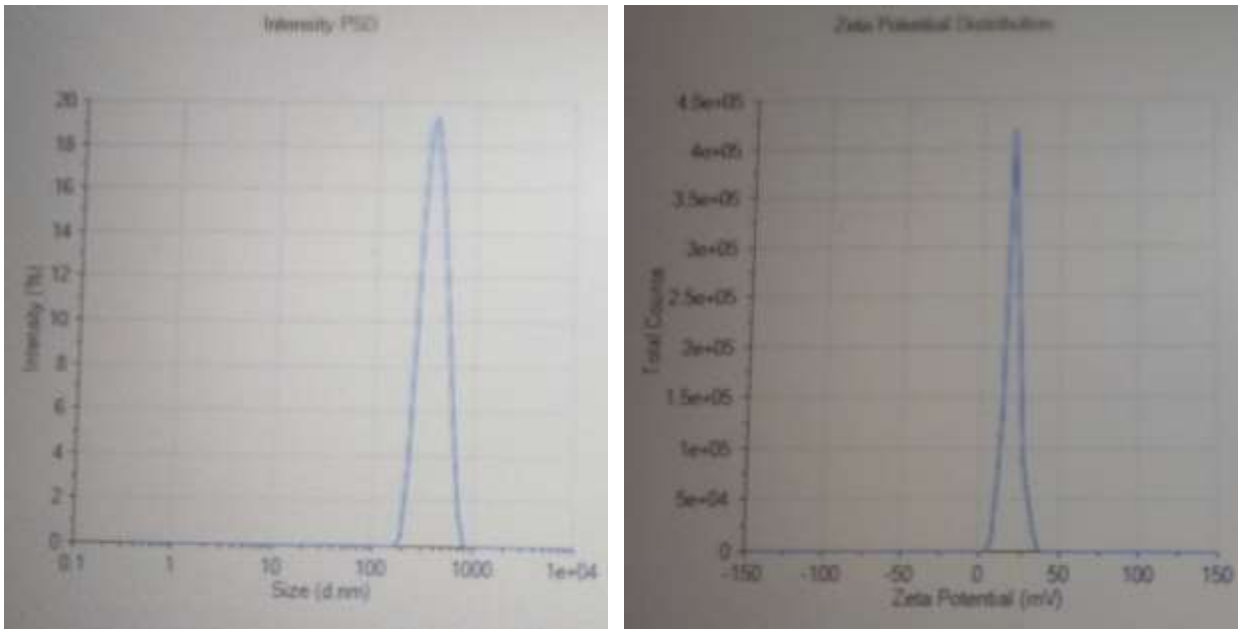

Figure 49. Virgin TiO_2 particle size graph (left) and virgin TiO_2 zeta potential graph (right)

Table 25 shows a summary of the parameters for all of the tests.

Table 25. Particle size and zeta potential test parameters.

Type of TiO_2/Leachate	**Dispersion Medium**	**Diluted (Yes/No)**
Virgin TiO_2	Deionized Water	Yes
Used TiO_2 from Centrifuge Test 23	Leachate pH = 7.19	No
Used TiO_2 from Centrifuge Test 24	Leachate pH = 7.19	No
Used TiO_2 from Centrifuge Test 25	Leachate pH = 7.19	No
Used TiO_2 from Centrifuge Test 26	Leachate pH = 4.84	No
Used TiO_2 from Centrifuge Test 27	Leachate pH = 4.84	No
Used TiO_2 from Centrifuge Test 28	Leachate pH = 4.84	Yes
Centrifuge Test 23 – 25 Leachate	Leachate pH = 7.19	No
Centrifuge Test 26 – 28 Leachate	Leachate pH = 4.84	No

3. RESULTS AND DISCUSSION

This chapter explains in detail the results obtained from the experimental procedures that were described in the methodology section.

3.1 BASELINE LEACHATE LEACHATE QUALITY CHARACTERIZATION

The research was conducted utilizing leachate that was collected during both the Florida wet and dry seasons. The amount of rain received within 30 days of collection directly affects the characteristics of the leachate. The leachate quality of raw samples collected is summarized in Table 26.

Table 26. Raw leachate samples from Dyer Park and rainfall data.

Date	**pH**	**COD** mg/L as O_2	**NH_3-N** mg/L	**Alkalinity** mg/L as $CaCO_3$	**Calcium** mg/L as $CaCO_3$	**Rainfall previous 30 days before sampling** inches
05/30/2014 (wet)	7.38	341	313	1550	Not recorded	2.80
09/18/2014 (wet)	7.17	441	193	1310	Not recorded	9.14
02/19/2015 (dry)	7.60	411	370	1290	850	2.05
07/10/2015 (wet)	7.71	331	276	1066	400	6.05
08/21/2015 (wet)	7.75	619	285	957	75	7.08

Higher alkalinity and calcium hardness values were recorded during the dry season, corresponding to the 1290 mg/L as $CaCO_3$ and 850 mg/L as $CaCO_3$. While in the wet season, the pH was higher (~7.75), but the alkalinity and the calcium were lower with 957 mg/L as $CaCO_3$ and 75 mg/L as $CaCO_3$, respectively. Both the highest and lowest ammonia reading occurred in the wet season but in different years.

3.2 CRYSTAL VIOLET TEST

This test was performed to confirm that the TiO_2 process was generating hydroxyl radicals. Crystal violet can be used to visualize a single proton replacement reaction, so it should show that hydroxyl radicals are being released and decomposing the crystal violet. A photograph of the petri dish taken before the test can be seen in Figure 50.

Figure 50. Petri dish with TiO_2 and crystal violet.

It was expected that the color would disappear in 20 minutes, and the first trial was conducted in the photochemical chamber to limit exposure of the analyst to UV radiation. Observations could only be done with the door of the cabinet open; therefore, to limit the amount of UV exposure to the operator, observations were taken at 5 minute intervals. However, upon the first observation at five minutes, it was discovered that the reaction had already taken place. A second trial was conducted with one minute interval observations, again at the first observation time of one minute, the reaction was complete. From these results, it was determined that hydroxides were being produced in large quantities, the reactions for TiO_2 were working, and the TiO_2 was favorable for degrading leachate.

3.3 IMPROVING COD REMOVAL

With the focus for the first part of the research being on methods for improving the removal of COD, additives that could potentially increase the removal efficiency were tested. It was hypothesized that the complete chain of the TiO_2 reaction may not be taking place. Not enough metals were present in the leachate to collect electrons, thus preventing the formation of hydroxyl radicals by the TiO_2 not releasing electrons. To test this hypothesis of preventing short circuiting, certain key metals were added to a stock solution of leachate collected on September 18, 2014 with 5 g/L of TiO_2. The results of this one hour exposure experiment are summarized in Table 27.

Table 27. Summary of results from using metal additives to stimulate COD removal.

Sample	COD Final	C/C_o
Leachate + TiO_2	258	0.83
Leachate + Zinc + TiO_2 solution	262	0.84
Leachate + UV	276	0.88
Leachate + Zinc + TiO_2 coated aluminum+ TiO_2 solution	276	0.88
Leachate + TiO_2 coated aluminum + TiO_2 solution	292	0.94
Raw Leachate	312	1.00
Leachate + TiO_2 coated aluminum	312	1.00
Leachate + Steel Wool + TiO_2 solution	315	1.01
Leachate + Steel Wool	317	1.02
Leachate + Steel Wool + TiO_2 coated aluminum + TiO_2 solution	319	1.02
Leachate + Zinc	340	1.09

From the results, it is clear that the TiO_2 without additional metals performs better in terms of COD process removal efficiency, and that there is no short circuiting happening in the process with fresh leachate. Both the zinc and the steel wool caused the COD to artificially rise. This is likely caused by the oxidative conversion of dissolved metal species, for example, Zn(0) → Zn(II) or Fe(0) → Fe(II), during the analysis. However, titanium dioxide with zinc achieves a similar COD removal of 84% to the titanium dioxide and UV, suggesting a possible synergistic effect. This experiment was conducted for only one hour, when most of the removal takes place in the small scale reactor experiments.

3.4 TiO_2 DOSING TEST

From previous research conducted at FAU using the G.U.N.T. falling film reactor (Meeroff and Youngman, 2013), the researchers recommended increasing the lamp power to increase efficiency. The falling film reactor is not easily modified for this type of change. The easiest way to increase the intensity is to change the lamp and power supply or move the liquid closer to the source of the energy. However, the upper weir of the falling film reactor and the glass wall that the liquid runs down are permanently fixed in placed at 55 mm from the light source. The liquid could be moved closer to the source without modifying the entire device by filling the reactor with liquid and in essence moving the liquid to a distance of 21.5 mm from the light source. This configuration is called the *flow through reactor*.

During testing, a question about how much light penetration is achieved came up. Since the flow through reactor light waves must travel 2 inches to reach the full bulk solution, the light absorbance of the TiO_2 at various concentrations was measured. In the falling film reactor, light penetration is not an issue because the solution falls in a thin sheet. Twelve 1-inch cuvettes were prepared with different dilutions to scan at 330 nm, which was the maximum observed absorbance wavelength for TiO_2 particles in aqueous solution. The results are plotted in Figure 51.

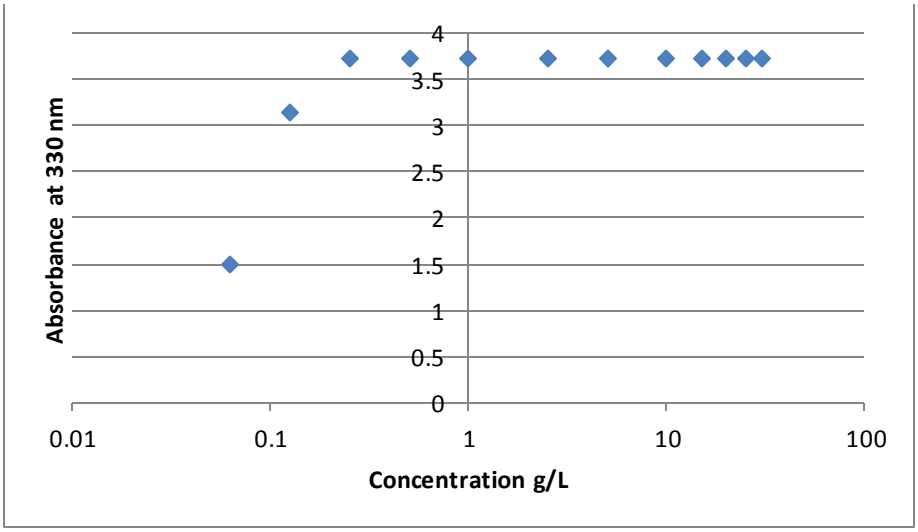

Figure 51. Absorbance curve of TiO_2 dosing.

Figure 51 shows that the maximum absorbance measurable within the range of the spectrometer, is between 125 mg/L and 250 mg/L for 25 mm of light penetration. If this is true and the flow through reactor has 55 mm thickness, then this ensures that most of the UV energy will be dissipated within the reactor. Altomare and Selli (2013) found that 100 mg/L TiO_2 was sufficient to block UV radiation in aqueous ammonia suspensions, which corresponds to the absorbance data reported here. This study used concentrations of catalyst that were several orders of magnitude larger, but this does not necessarily mean that UV was blocked at higher doses because it is not possible to determine the localized catalyst concentration at the falling film surface.

3.5 INTENSITY OF UV LIGHT

Calculations for energy that the TiO_2 was exposed to per liter were made for both the falling film and the flow through reactor. The energy available for titanium dioxide to absorb in conjunction with exposure time should be directly related to efficiency. The results can be seen in Table 28 and Table 29. The results show that the leachate in the flow through reactor receives 200 times more light energy per liter in an eight hour test when compared to the falling film reactor. However, this increase in light energy did not translate to greater COD removal with 25% increase in the 150-W and a 9% decrease in the 450-W. The results were similar for ammonia removal with a 10% increase in 150-W and 24% increase for the 450-W.

Table 28. Falling film UV light intensity for 8 hour testing

Light	Arc Length (cm)	Area (cm^2)	Measured UV (mW/cm^2)	Total Power (W)	Total Volume (L)	Falling Time (s)	Exposure Time (s)	Recirculation Rate (L/hr)	Passes per L per hr	Exposure Time (s/hr)	Energy Input (W/L)	Energy Intensity (W-hr/L)
450W UVA&B	27.94	439	56.00	24.56	9.3	0.41	0.14	320	34	4.75	0.03	0.26
450W UVC	27.94	439	0.06	0.03	9.3	0.41	0.14	320	34	4.75	0.01	0.01
150W UVA&B	79.30	1245	0.50	0.62	10.0	0.41	0.39	320	32	12.54	0.01	0.02
150W UVC	79.30	1245	7.21	8.98	10.0	0.41	0.39	320	32	12.54	0.03	0.25

Table 29. Flow through UV light intensity for 8 hour testing.

Light	Arc Length (cm)	Area (cm^2)	Measured UV (mW/cm^2)	Total Power (W)	Total Volume (L)	Retention Time (s)	Fraction of Exposure	Recirculation Rate (L/hr)	Exposure per Liter (L^{-1})	Energy Input (W/L)	Energy Intensity (W-hr/L)
450W UVA&B	27.94	439	56.00	24.56	8.6	0.03	0.34	24	34	6.63	53.08
450W UVC	27.94	439	0.06	0.03	8.6	0.03	0.34	24	34	0.01	0.06
150W UVA&B	79.30	1245	0.50	0.62	9.1	0.03	0.96	23	32	0.45	3.61
150W UVC	79.30	1245	7.21	8.98	9.1	0.03	0.96	23	32	6.50	52.02

The light intensity of each lamp was measured with the inner quartz tube in place. The quartz allows 80 to 90% of the UV light to pass in the 220 to 400 nm range. The 150-W lamp had an average measured irradiance of 7.21 mW/cm^2 in the UV-C range, and 0.50 mW/cm^2 in the UV-A&B range. The 450-W lamp had an average measured irradiance of 0.06 mW/cm^2 in the UV-C range and 56.00 mW/cm^2 in the UV-A&B range. With this information, the light intensity for each experiment was calculated, and results can be seen in Table 30. As a reference, Meeroff and McBarnette (2011) achieved 100% mineralization of COD in simulated leachate with an initial COD average of 1000 mg/L. The light density for those experiments averaged approximately 33,600 J/L in the UV-A&B range.

Table 30. Light intensity measurements for each experiment.

Test	TiO_2 (g/L)	Lamp Used (W)	Reactor Used	Light Intensity UV-C (J/L)	Light Intensity UV-A&B (J/L)
06/05/2014	5	150	Falling Film	900	62
06/12/2014	5	450	Falling Film	1	933
06/18/2014	5	450	Flow Through	205	191,000
06/26/2014	5	150	Flow Through	187,200	12,980
08/11/2014	10	450	Flow Through Aerated	225	210,600
08/28/2014	5	150	Flow Through Aerated	185,200	12,840
09/26/2014	0.2	150	Flow Through Aerated	142,000	9,849
02/20/2015	15	150 & 450	Full Spectrum UV	1,076	164,300
04/03/2015	30	150 & 450	Full Spectrum UV	1,078	164,300
05/28/2015	20	150	Lime Softened Falling Film	1,007	70
07/02/2015	10	150	Falling Film	1,125	78
07/09/2015	0	150	Falling Film + EMOH	675	47
07/10/2015	10	150	Falling Film	750	52
07/18/2015	2-8	150	Falling Film + EMOH	1068	74
07/22/2015	30	150	TiO_2 Filtering Falling Film + EMOH	984	68
07/29/2015	3-15	150	TiO_2 Settling Falling Film + EMOH	937	65
09/17/2015	8-12	150	Falling Film + EMOH	4,500	312

When the ratio of removal of all the constituents to light intensity was compared, there was no direct relationship found. This is not to say that light density does not have an effect, but none was found in this research.

3.5.1 COD Removal Using the 150-W Lamp Compared to the 450-W Lamp

Six different experiments were conducted to determine the effects of using lamps with different wattages. The lamps tested produce wattage in different spectrums, such that it was hypothesized that the different UV regimes could affect the rate of removal. A summary of the results can be seen in Table 31.

Table 31. COD removal comparison for 150-W and 450-W.

Experiment	TiO_2 g/L	Type of Reactor	Lamp (W)	Avg. Temp. (°C)	Avg. pH	COD mg/L as O_2 C_o	COD mg/L as O_2 C_f	Treatment Goal Met*	COD % Removal
06/5/2014	5	Falling Film	150	9.6	8.0	341	300	RC,DW	12
06/12/2014	5	Falling Film	450	19.7	8.5	341	255	RC,DW	25
06/18/2014	5	Flow Through	450	27.5	9.0	255	235	RC,DW	8
06/26/2014	5	Flow Through	150	13.1	8.6	300	225	RC,DW	25
08/11/2014	10	Flow Through Aerated	450	23.0	8.6	239	197	RC,DW	18
8/28/2014	5	Flow Through Aerated	150	18.8	8.7	268	245	RC,DW	9

***SD=Surface Discharge, RW=Reclaimed Water, DW=Dilution Water**

The COD removal difference in the falling film experiments showed double the removal with the 450-W lamp. When comparing these results to the flow through experiments, the exact opposite is true; the 150-W lamp had higher removal. An unpaired T-test was used to identify if any of the results were statistically significant within the limits of the experiments. The COD removal of the two different types of lamps was compared using a simple T-test. The two-tailed P value equals 0.8225, which in general indicates no difference that is statistically significant between the two lamps. The COD removal of the two different types of reactors was also compared with the T-test. For the falling film compared to the flow through results, the two-tailed P value equals 0.8690, which in general indicates no difference that is statistically significant between the reactors. Even with the much higher amount of light density. The falling film reactor was also compared to the flow through reactor with aeration, the two-tailed P value equals 0.5918, which in general indicates no difference that is statistically significant between the reactors with or without aeration.

With these results, no statistically significant difference could be shown for COD removal between the different lamps or the different types of reactors. It was observed in the flow through reactor configuration that the 450-W lamp produces more heat. This heat may have resulted in more calcium carbonate scale forming faster on the inner protective lens of the reactor. The scale could have contributed to the 17% and 9% lower removal rates when compared to the 150-W lamp experiments.

3.5.2 Ammonia Removal Using the 150-W Lamp Compared to the 450-W Lamp

The same six experiments were also compared for the removal of ammonia. The results can be seen in Table 32.

Table 32. Ammonia removal comparison for 150-W and 450-W.

Experiment	TiO_2 g/L	Type of Reactor	Lamp (W)	Avg. Temp. (°C)	Avg. pH	NH_3-N mg/L C_o	NH_3-N mg/L C_f	Treatment Goal Met *	NH_3-N % Removal
06/05/2014	5	Falling Film	150	9.6	8	313	116	DW	63
06/12/2014	5	Falling Film	450	19.7	8.5	313	243	DW	23
06/18/2014	5	Flow Through	450	27.5	9	243	133	DW	45
06/26/2014	5	Flow Through	150	13.1	8.6	232	193	DW	17
08/11/2014	10	Flow Through Aerated	450	23.0	8.6	100	75	DW	25
08/28/2014	5	Flow Through Aerated	150	18.8	8.7	135	119	DW	12

***SD=Surface Discharge, RW=Reclaimed Water, DW=Dilution Water**

In the falling film test, the 150-W lamp had 40% better removal, while in the flow through reactor, the 450-W lamp had 31% and 13% in the two experiments. However, ammonia removal can be affected by temperature and pH. Comparing the temperature of the four flow through experiments, it can be seen that the 450-W lamp had +14 degree and a +4 degree difference in average temperature when compared to the 150-W lamp. This temperature difference could be the explanation for the different removal rates. The ammonia removal of the two different types of lamps was compared using a simple T-test. The two-tailed P value equals 0.9859, which in general indicates no difference that is statistically significant between the two lamps. The T-test also showed with the 95% confidence level that there was no difference in falling film to flow through with aeration, as well.

These experiments demonstrate that the 450-W lamp shows better COD removal in the falling film reactor by 13% over the 150-W lamp. However, T-tests found no evidence of statistically significant differences between lamps. The 150-W lamp had the best ammonia removal, with 40% better removal than the 450-W lamp. In comparing all of the experiments, the 450-W lamp had an increase in average removal of 25%; however, this may be attributed to the higher temperatures of the 450-W lamp experiments. From these findings, the 150-W lamp and the falling film reactor were determined to be the most efficient pairing of technologies due to lower power output and electrical costs compared to gains in treatment performance. Both lamps created excessive scaling on the reactor's lens. This physically blocks UV radiation from reaching the target bulk solution and greatly diminishes the amount of UV light that the TiO_2 receives in the reactor. The primary cause of the scaling is the heat radiating from the lamp that then increases the temperature of the lens. Any liquid or mist that comes in contact with the lens

readily evaporates leaving the solids behind. An improvement of actively cooling the lamp decreases the scaling, enabling light to pass more easily through lens, but minor scaling was still observed in long term exposures.

3.6 FALLING FILM REACTOR CONFIGURATION WITH 150-W LAMP

The 150-W lamp with falling film reactor configuration was also used exclusively by Meeroff and Youngman (2013) for all experiments conducted. Those previous experiments used young leachate, maximum removal for these 24-hour tests were: COD 34%, ammonia 82% and alkalinity 84%, conducted in six 4-hour segments (Meeroff and Youngman 2013). Experiments during this current block of research in this study were conducted for 8 hours, except July 2 2015, which ran for 7 hours. Different doses for TiO_2 were used to define the optimum ratio of TiO_2 to COD. Three different experiments were conducted, and the results will be discussed in this section.

3.3.1 COD Removal Using the 150-W Lamp with Falling Film Reactor Configuration

The average COD removal for all of the 150-W lamp experiments is 16%. In experiments with TiO_2 dosage ranging from 0.2 g/L to 10 g/L, no statistical difference was found in the COD removal rates. Foaming of the leachate created overflow issues, causing aeration to be suspended to reduce the foam. Once the foaming subsided, the aeration was then resumed. This creates and uneven aeration process, which is difficult to reproduce for each experiment. To prevent foam, an anti-foaming agent was added to the September 26, 2014 experiment. This did stop the foaming, but an unexpected consequence was that anti-foaming agent caused the COD to nearly double from 294 mg/L to 441 mg/L. Anti-foaming agent was never used again. Instead foaming of the leachate was controlled by varying the amount of aeration provided. A summary of the results can be seen in Table 33.

Table 33. COD Removal Using the 150-W Lamp with Falling Film Reactor Configuration.

Experiment	TiO_2 g/L	Type of Reactor	Lamp (W)	Avg. Temp. (°C)	Avg. pH	COD mg/L as O_2 C_o	COD mg/L as O_2 C_f	Treatment Goal Met *	COD % Removal
09/26/2014	0.2	Flow Through	150	18.5	8.3	441	388	RC,DW	12
07/02/2015	10	Falling Film	150	21.9	8.5	203	170	RC,DW	16
07/10/2015	10	Falling Film	150	27.2	8.5	331	278	RC,DW	16

***SD=Surface Discharge, RW=Reclaimed Water, DW=Dilution Water**

3.3.2 Ammonia Removal Using the 150-W Lamp with Falling Film Reactor Configuration

Ammonia removal also had no statistical difference with the TiO_2 dosage. The two 10 g/L TiO_2 only had a 2% difference, showing consistent results. While the 0.2 g/L dosage had 4% less removal compared to the higher dosage (10 g/L), indicating that higher TiO_2 dosage may improve removal. A summary of the results is shown in Table 34.

Table 34. Ammonia Removal Using the 150-W Lamp with Falling Film Reactor Configuration.

Experiment	TiO_2 g/L	Type of Test	Lamp (W)	Avg. Temp. (°C)	Avg. pH	NH_3-N mg/L C_o	NH_3-N Mg/L C_f	Treatment Goal Met *	NH_3-N % Removal
09/26/2014	0.2	Flow Through	150	18.5	8.3	194	174	DW	10
07/02/2015	10	Falling Film	150	21.9	8.5	153	131	DW	14
07/10/2015	10	Falling Film	150	27.2	8.5	276	232	DW	16

***SD=Surface Discharge, RW=Reclaimed Water, DW=Dilution Water**

From these results, no correlation was found for the dose of TiO_2 and removal for COD. However, a small difference was seen in the TiO_2 dose and ammonia removal, suggesting that the higher the dose, the more removal achieved.

3.7 FULL SPECTRUM UV LIGHT EFFECT

Two experiments were performed using both the 150-W lamp and the 450-W lamp, in combination. The 150-W lamp was located in the falling film reactor, while the 450-W was located in the reservoir. No aeration was used during these experiments. All experiments were run for 8 hours. It was hypothesized that using the combined lights would increase removal, decreasing treatment time. The difference in removal between these two experiments was 348%, the addition of acetic acid (0.837 M) contributed to the large difference by increasing the COD in the reactor while lowing the pH. A single application of 80 mL of acid was added at the 3 hour and 45 minute mark. When the acid was added, the pH initially dropped from 8.43 to 7.31. However, within 45 minutes, the pH had risen back to 8.04, and at the 6-hour mark, the pH was back up to 8.23. This is further evidence that the TiO_2 photocatalytic reaction produces hydroxide ions, shown by the change in the pH. Reviewing why COD increased with acid addition, the chemical formula for acetic acid highlights the problem. Acetic acid (CH_3COOH) contains two carbon atoms. By adding 80 mL of 0.837M acetic acid, a total of 0.06696 mol were added. The theoretical acid oxygen demand would be 4285 mg as O_2; this can be directly related to COD measurements. By adding, the 411 mg COD as O_2 before acid addition and the 4285 mg of O_2 the total theoretical COD would be 4696 mg as O_2. If this is compared to the ending COD of 1362 mg as O_2 this would be a 71% removal. With no aeration, this would be the best removal seen in all of the tests. Further review of COD shows a 1% reduction until the acid addition. An organic acid should never be added to any solution that is attempting to reduce COD. The February 20, 2015 COD data should not be used for other comparisons because of the pH adjustment.

Not having aeration in this experiment decreased the ammonia removal. Altomare and Selli (2013) found that the concentration of dissolved oxygen in the reactor medium is directly related to the photocatalytic oxidation of ammonia to nitrate. The two experiments show essentially no ammonia removal (<7%). This should be expected with the average pH (8.1) and temperature ranges (18.4 – 21.4°C). The 2% difference in removal also indicates that the dose of TiO_2 has little if any effect on the ammonia removal, in contrast to the 150-W lamp falling film

experiments. This suggests that aeration is the contributing factor in the removal of ammonia via conversion to nitrate. This corroborates the finding that no gaseous ammonia emissions were detected using an ammonia gas sensor during testing.

3.8 EMOH ADVANCED OXIDATION PROCESS TESTING RESULTS

In an effort to increase the removal efficiency of the process, the EMOH device was tested. It was hypothesized that magnetically aligned molecules and smaller bubbles may increase the overall process removal efficiency. The first experiment was conducted to determine if any effects without the photocatalytic reaction were measurable. This trial was conducted on October 1, 2014 with the trailer-based system operated by the inventors, Craig Jones and Ted Batkin. The experiment was run for 20 minutes with samples taken at 5 minute intervals. Since the leachate was diluted, no treatment goals will be shown in this section. The test showed impressive results as seen in Table 35.

Table 35. EMOH advanced oxidation process test results, trailer scale (October 1, 2014).

Sample	DO (mg/L)	TDS (g/L)	pH	Total Alkalinity (mg/L as $CaCO_3$)	Cond. (mS/cm)	COD mg/L as O_2	COD % Removal
Diluted Leachate Sample Time 0	5.25	0.437	7.99	230	0.673	281	--
Diluted Leachate Sample Time 5	5.63	0.376	8.02	230	0.579	103	63
Diluted Leachate Sample Time 10	5.97	0.587	7.63	210	0.903	91	67
Diluted Leachate Sample Time 15	6.12	0.669	7.71	330	1.029	79	71
Diluted Leachate Sample Time 20	5.53	0.677	7.75	360	1.026	83	70

The trailer EMOH showed 70% COD removal within 20 minutes of treatment. The COD is thought to have been reduced by the micro-bubbles of oxygen gas interacting with the leachate. The magnetic chambers did not remove any calcium; however, there is some suggestion that the crystal structure of the calcium may be re-arranged, and the structure of the calcium may change from calcite to aragonite (Coey and Cass, 2000). The aragonite calcium has a long linear shape increasing surface area. Aragonite crystals stay in solution better preventing them from coating the TiO_2. This test was conducted with diluted leachate containing tap water because of the volume required for the centrifugal pump.

In March 2015, FAU took delivery of a lab scale EMOH device with a ¾-inch venturi. A test was conducted with Dyer Park leachate on May 1, 2015. The system was configured to recirculate with 16.2 liters of leachate. The EMOH was run for 30 minutes, and the results of this test can be seen in Table 36.

Table 36. EMOH advanced oxidation process test results, bench scale (May 1, 2015).

Elasped Time (Minutes)	Temp. (°C)	DO (mg/L)	pH	Total Alkalinity (mg/L as $CaCO_3$)	Calcium mg/L as $CaCO_3$	NH_3-N mg/L	COD mg/L as O_2	COD % Removal
0	18.5	7.53	7.53	1360	590	268	427	--
1	18.5	9.41	7.77	1250	530	265	403	5
3	18.5	9.43	7.92	1250	590	256	470	-10
5	18.5	9.41	8.00	1350	450	326	401	6
10	20.3	9.06	8.15	1240	420	267	404	5
15	21.9	8.82	8.28	1270	500	302	402	5
30	21.9	8.82	8.54	1080	440	294	403	5

The results from this experiment show a degradation of COD, but nowhere near the same extent as the full scale October 1, 2014 EMOH trailer-based experiment. At FAU, aeration of similar leachate showed an increase of pH by one unit within one hour, the EMOH accomplished this in a half an hour. The bench scale results also differed from the trailer-based EMOH in that the pH increased from 7.53 to 8.54, in contrast to the October 1, 2014 experiment, when pH fell from 7.99 to 7.75. The ammonia also increased with the EMOH, which is the opposite that should have happened with the increase in pH. The results from the May 1, 2015 test were not as expected. Ted Batkin, one of the inventors, suggested changing the pump and size of the venturi. These modifications were made, and the EMOH was connected directly to the photocatalytic reactor in series for further tests.

3.9 FALLING FILM + EMOH COMBINED TREATMENT

Since the trailer-based EMOH system was observed to function with promising results, pilot scale testing with the EMOH and photocatalytic process was hypothesized to improve the overall process removal efficiency for COD and ammonia. All experiments were conducted with the ½-inch venturi installed. The experiment on July 9, 2015 was run for 6 hours. The experiment on July 18, 2015 ran for 9.5 hours.

The EMOH introduces aeration directly before the photocatalytic reaction chamber possibly enhancing COD removal. An experiment (07/09/2015) was conducted with UV/EMOH. This experiment contained no TiO_2, but did utilize the EMOH and UV lamp. The average COD removal was 20% for all non-EMOH experiments containing TiO_2. Both of the EMOH experiments performed better than this value, including UV/EMOH, which had 22% removal of COD. The second experiment with 5 g/L of TiO_2 performed even better with 43% removal. A summary of the removal can be seen in Table 37.

Table 37. COD removal using EMOH and UV/TiO_2

Experiment	TiO_2 g/L	Type of Reactor	Lamp (W)	Avg. Temp. (°C)	Avg. pH	COD mg/L as O_2 C_o	COD mg/L as O_2 C_f	Treatment Goal Met *	COD % Removal
07/09/2015	0	UV/EMOH	150	22.8	7.8	424	331	RW,DW	22
07/18/2015	5	Falling Film + EMOH	150	25.2	8.5	305	175	RW,DW	43

***SD=Surface Discharge, RW=Reclaimed Water, DW=Dilution Water**

The average ammonia removal is 32% for all non-EMOH experiments. The falling film with 150-W lamp alone showed 35% removal; this can be attributed to the new aeration method using the EMOH. The July 18, 2015 experiment with the combined treatment had 47% ammonia removal, surpassing most other experiments. This higher removal is due to the availability of oxygen micro-bubble to the TiO_2 in the UV reaction chamber. A summary of removal can be seen in Table 38.

Table 38. Ammonia removal using EMOH and UV/TiO_2

Experiment	TiO_2 g/L	Type of Reactor	Lamp (W)	Avg. Temp. (°C)	Avg. pH	NH_3-N mg/L C_o	NH_3-N mg/L C_f	Treatment Goal Met *	NH_3-N % Removal
07/09/2015	0	UV/EMOH	150	22.8	7.8	423	276	DW	35
07/18/2015	5	Falling Film + EMOH	150	25.2	8.5	317	167	DW	47

***SD=Surface Discharge, RW=Reclaimed Water, DW=Dilution Water**

The removal rates increased for all of the constituents tested by a percentage that is statistically different. These results show that the 5 g/L TiO_2 dose with EMOH + UV/TiO_2 came close to meeting all three treatment goals. From this finding, more experiments should be conducted with the EMOH to improve or optimize removal efficiency.

3.10 48-HOUR EXPERIMENT

With none of the 8-hour tests able to meet all three treatment goals, a 48-hour test was conducted to determine if longer treatment exposure time would yield better removal efficiency results. It was hypothesized that more UV light exposure and longer aeration times could improve removal. A single continuous 48-hour experiment was performed from September 17-19, 2015. The leachate pump and UV lamp were run for the entire test. To improve removal, pure oxygen was used instead of air for aeration, flowing at 1 cfm. Table 39 shows the results of the experiment.

Table 39. Summary of 48-hour experimental results.

Experiment	TiO_2 g/L	Type of Reactor	Lamp (W)	Avg. Temp. (°C)	Avg. pH	C_o	C_f	Treatment Goal Met *	% Removal
COD mg/L as O_2	8-12.6	Falling Film + EMOH	150	26.8	8.56	619	330	RW,DW	47
Ammonia mg/L as NH_3-N	8-12.6	Falling Film + EMOH	150	26.8	8.56	285	93	DW	68
Alkalinity mg/L as $CaCO_3$	8-12.6	Falling Film + EMOH	150	26.8	8.56	957	321	SD,RW,DW	66
Calcium as $CaCO_3$ mg/L	8-12.6	Falling Film + EMOH	150	26.8	8.56	75	0.8	SD,RW,DW	99

***SD=Surface Discharge, RW=Reclaimed Water, DW=Dilution Water**

The results of this experiment showed that increasing the UV exposure 6-fold only increased removal of COD by 4% over the July 18, 2015 (8-hour) experiment with COD removal of 44%. An increase in ammonia removal was seen improving by 21% when compared to the July 18, 2015 removal of 47%. The additional ammonia removal is likely due to the additional aeration time plus the use of pure oxygen instead of air. Carneiro, Moulijn, and Mul (2010) reported that TiO_2 can become deactivated by surface coating slowing down the reaction rate. To prevent any deactivation, additional dosages of TiO_2 were added during the 48-hour experiment. The initial dose was 8 g/L. A second dose was added after the 8-hour sample, making the dose 8.6 g/L of TiO_2. At the 24-hour sample, it was noted that most of the TiO_2 was out of solution collecting on the walls of reservoir. An additional fresh input of TiO_2 was added after the 24-hour sample making it 10.9 g/L of TiO_2. After the 32-hour sample, an additional dose of TiO_2 was added making the total dose 12.6 g/L of TiO_2. COD removal from 0 to 16 hours was 41%. From hour 16 to hour 48 COD removal was only 6%. The additional dosage did not improve process removal efficiency. It is possible that the initial removal mechanism is related to flocculation of the TiO_2 particles enmeshing COD.

3.11 BOD DECAY

To determine if the COD was only partially reduced, a BOD test was conducted on the 48-hour experiment run from September 17-19, 2015. It is hypothesized that if the BOD increased during the experiment, then the COD was converted to BOD and instead of complete mineralization, a partial reaction took place in which recalcitrant COD was converted to more readily biodegradable BOD. Both seeded and unseeded samples were analyzed. A summary for raw and treated leachate DO and BOD_5 values can be seen in Table 40.

Table 40. Leachate BOD_5 results.

Sample	Raw Leachate				Treated Leachate			
	Leachate Quantity mL	Initial DO_0 as O_2 mg/L	Final DO_5 as O_2 mg/L	BOD_5	Leachate Quantity mL	Initial DO_0 as O_2 mg/L	Final DO_5 as O_2 mg/L	BOD_5
Blank	0	9.24	9.05	Na	0	9.24	9.05	Na
Seeded Blank	0	9.22	8.51	Na	0	9.22	8.51	Na
B20	20	9.00	6.85	32.28	20	9.03	6.70	34.89
B50	50	8.44	3.10	32.05	50	9.13	4.43	28.18
B20 Seeded	20	Na	Na	Na	20	9.03	5.72	36.35
B50 Seeded	50	8.84	1.72	32.04	50	9.05	2.65	28.43

Na = not applicable

From these tests, there was no evidence that high levels of ammonia (237 mg/L) in the leachate affected the microorganisms in the BOD test. An unpaired T-test was run on these two data sets, and no statistical difference was found. The results suggest that COD is being completely mineralized.

3.12 PRETREATMENT RESULTS

To determine if the surface of the TiO_2 was being coated during the experiments and if the initial removals were just from flocculation, pretreatment was performed using TiO_2. It was hypothesized that calcium was the most likely to plate out on the TiO_2 surface. Following pretreatment, the leachate was then treated in the falling film UV/TiO_2 + EMOH reactor. Two pretreatment experiments were conducted. One used TiO_2 and filtering (July 22, 2015), and the second used TiO_2 and settling (July 29, 2015).

The pretreatment was not intended to remove COD, and the June 22, 2015 experiments had no major effect on COD removal efficiency; however, the July 29, 2015 experiment removed 42 percent of COD. The starting concentrations in each experiment were the same, because the same raw leachate sample was used. No ammonia removal was hypothesized to happen with pretreatment, and no effect was observed. A summary of results can be seen in Table 41.

Table 41. COD and ammonia removal results with pretreatment.

Experiment	TiO_2 g/L	Pretreatment	pH	COD mg/L as O_2 C_o	COD mg/L as O_2 C_f	COD % Removal	NH_3-N mg/L C_o	NH_3-N mg/L C_f	NH_3-N % Removal
07/22/2015	30	TiO_2 and filter	7.71	366	362	1	316	253	20
07/29/2015	30	TiO_2 and settling	7.71	366	209	43	316	265	16

Slightly larger removal by the filtered leachate may have been related to more surface area exposure to air. The filter spread the leachate out over an area of 113 in^2 compared to if it fell 10

inches through air. This additional aeration could explain the 4% difference in ammonia removal. The 42% removal of COD was unexpected. It is hypothesized that the effect of the nanoparticles settling through the liquid and flocculating together enmeshed COD. Ohtani et al. (2010) found that TiO_2 nanoparticles change appreciably when wet, presumably due to the aggregation of the particles. Figure 52 show the appreciable difference in particle size from freshly mixed TiO_2 (left), which appears like milky colloids compared to TiO_2 that has been settled for 15 minutes (right), which appears like agglomerated flocs. The size of the settled particles in addition to the large voids between particles would allow both large surface area and enmeshment of COD.

Figure 52. Unsettled TiO_2 (left) and settled TiO_2 (right).

3.12.1 COD Removal with Photocatalytic Process after Pretreatment

The reason for pretreatment was to improve the removal process in the photocatalytic stage. To further increase removal, the 07/22/2015 and 07/29/2015 experiments also utilized continuous dosing. Continuous dosing is when fresh, unused TiO_2 is added after each sample is taken, this was done to see if the removal seen in the first 2-hour segment could be reproduced at a later time. The time was also extended for these experiments in an attempt to meet the treatment goal. The July 22, 2015 experiment was run for 10.5 hour, while the July 20, 2015 experiment was run for 10 hours. A summary of the photocatalytic removal of COD results can be seen in Table 42.

Table 42. COD removal with falling film UV/TiO_2 + EMOH with 150-W lamp after pretreatment and overall process efficiency.

Experiment	TiO_2 g/L	Avg. Temp. (°C)	Avg. pH	COD mg/L as O_2 C_o	COD mg/L as O_2 C_0	COD mg/L as O_2 C_f	COD % Removal by Treatment	COD % Overall Removal	Treatment Goal Met *
07/22/2015 Filter Pretreatment	2-8	24.0	8.6	366	362	238	34	35	RW,DW
07/29/2015 Settling Pretreatment	3-14	26.3	8.5	366	209	149	35	63	RW,DW

***SD=Surface Discharge, RW=Reclaimed Water, DW=Dilution Water**

The settled and filtered leachate removed large particles creating a higher surface area to volume ratio, it also improved the leachate quality making UV light penetrate further into the leachate. This effect did not yield better COD removal as hypothesized. The 34% and 35% COD removal was lower than expected. If the hypothesis was true, and TiO_2 was being deactivated, then pretreatment should have removed the plating agent. The removal should have been greater than the July 18, 2015 experiment with 43% removal. With less initial calcium, the COD removal was lower. Neither full treatment achieved removal to reach surface discharge, but promise is shown with the July 29, 2015 only 24 mg/L from the goal.

3.12.2 Ammonia Removal with Photocatalytic Process after Pretreatment

The ammonia removal after pre-treatment was near the same as the July 18, 2015 with 48% removal. The results of the ammonia removal by the photocatalytic treatment can be seen in Table 43. As expected, the two experiments show no improvement with pretreatment because removing calcium should not influence ammonia removal, which is governed by aeration and pH.

Table 43. Ammonia removal with falling film UV/TiO_2 + EMOH with 150-W lamp after pretreatment and overall process efficiency.

Experiment	TiO_2 g/L	Avg. Temp. (°C)	Avg. pH	NH_3-N mg/L as O_2 C_o	NH_3-N mg/L as O_2 C_0	NH_3-N mg/L as O_2 C_f	NH_3-N % Removal by Treatment	NH_3-N % Overall Removal	Treatment Goal Met*
07/22/2015 Filter Pretreatment	2-8	24.0	8.6	316	253	151	40	52	DW
07/29/2015 Settling Pretreatment	3-14	26.3	8.5	316	265	149	44	53	DW

***SD=Surface Discharge, RW=Reclaimed Water, DW=Dilution Water**

With pretreatment, the overall ammonia removal was better than the July 18, 2015 experiment with 47% removal. However, the total photocatalytic treatment time used in these experiments was longer, and this has a direct effect on ammonia removal, causing the increase. Combined treatment did eliminate 98% of calcium and 73% of alkalinity with settling pretreatment.

Just as important was the finding that after the 16-hour mark in the 48-hour long-term test, the calcium levels had dropped by 91% to 7 mg/L as $CaCO_3$. If calcium was believed to be plating onto the TiO_2 surface at the start, all the additional TiO_2 added after 16 hours should not have any plated calcium because there is no more free calcium. This would have provided evidence that the initial removal is by absorption onto the TiO_2 particles if the COD and ammonia removals improved after the 16-hour mark, but they did not.

3.13 REACTION KINETICS

The complete set of safe discharge goals has not been met by any of the conditions described thus far. However, Meeroff and Youngman (2013) determined that all the reactions with TiO_2 in a photocatalytic reaction can be modeled as first order. Two experiments were selected to establish the first order removal rate (k). They are the July 29, 2015 experiment that had the highest process removal efficiency and the 48-hour experiment, which was the longest test.

The July 29, 2015 experiment consisted of pre-treatment with TiO_2 settling and photocatalytic treatment in the falling film + EMOH reactor. The TiO_2 was continuously added with dosage ranging from 3-14 g/L. Aeration was provided with a pump at a rate of 2 cfm. This experiment used the 150-W lamp and had an average leachate temperature of 26.3°C and an average pH of 8.54. The treatment removal for the July 29, 2015 and treatment goals met are summarized in Table 44.

Table 44. July 29, 2015 experiment removal and treatment goals met summary.

Experiment	TiO_2 g/L	Type of Reactor	C_o	C_f	% Removal	Surface Discharge Goal Met	Reclaimed Water Goal Met	Dilution Water Goal Met
COD mg/L as O_2	3-14	Falling Film + EMOH	366	137	63	No	Yes	Yes
Ammonia (as NH_3-N) mg/L	3-14	Falling Film + EMOH	316	149	53	No	No	Yes
Alkalinity mg/L as $CaCO_3$	3-14	Falling Film + EMOH	1762	470	73	Yes	No	Yes
Cal. as $CaCO_3$ mg/L	3-14	Falling Film + EMOH	479	10	98	Yes	Yes	Yes

The 48-hour experiment was conducted using the falling film + EMOH reactor with the 150-W lamp. The TiO_2 was continuously dosed over the test and ranged from 8.0-12.6 g/L. Pure oxygen was used for aeration with a flow rate of 1 cfm. The temperature of the leachate during treatment averaged 26.8°C with an average pH of 8.56. The treatment removal for the 48-hour experiment and treatment goals met are summarized in Table 45.

Table 45. Summary of 48-hour experiment removal and treatment goals met.

Experiment	TiO_2 g/L	Type of Reactor	C_o	C_f	% Removal	Surface Discharge Goal Met	Reclaimed Water Goal Met	Dilution Water Goal Met
COD mg/L as O_2	8-12.6	Falling Film + EMOH	619	330	47	No	Yes	Yes
Ammonia (as NH_3-N) mg/L	8-12.6	Falling Film + EMOH	285	93	68	No	No	Yes
Alkalinity mg/L as $CaCO_3$	8-12.6	Falling Film + EMOH	957	321	66	Yes	Yes	Yes
Cal. as $CaCO_3$ mg/L	8-12.6	Falling Film + EMOH	75	0.8	99	Yes	Yes	Yes

Since the rate of removal varied, 5 rate constants (k) were calculated for each constituent. Figure 53 shows the definitions of each individual k value.

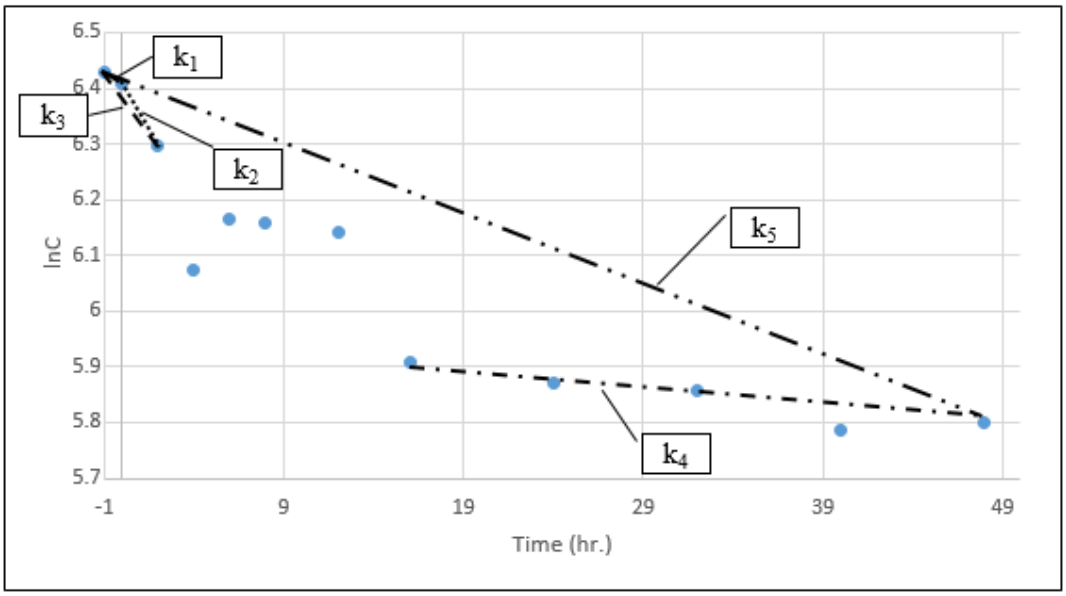

Figure 53. Example of COD removal rate (k) locations for 48-hour experiment.

The point at -1 on the x-axis represents the initial raw leachate, while the point at time zero represents leachate after the initial dose of TiO_2 was added. The k_1 value will represent the removal from pretreatment for the July 29, 2015 experiment and the initial removal after adding TiO_2 in the 48-hour experiment. The k_2 value will represent the initial removal rate by the photocatalytic treatment. The k_3 value represents the total removal rate of TiO_2 addition and initial photocatalytic treatment. The k_4 value will represent the long-term removal rate by the photocatalytic process. Finally, k_5 will represent the total removal first order reaction rate. All k values are in units of hr^{-1}.

3.13.1 COD Reaction Kinetics

First order reaction rates were found by plotting the natural log of the measured value versus time and finding the slope. The resulting slope is the removal rate k. Summary of the removal rate for COD can be seen in Table 46.

Table 46. Summary of k values in units of (hr^{-1}) found for COD removal.

Experiment	COD k_1	COD k_2	COD k_3	COD k_4	COD k_5
July 29, 2015	-0.5603	-0.0719	-0.2115	-0.0376	-0.0776
48 Hour	-0.0202	-0.0554	-0.0453	-0.0038	-0.0124

The slowest reaction rate for both sets of data was k_4. However, the difference was a full magnitude difference. This difference is because the length of each experiment was different. The reaction rates were highest in both experiments for the k_3 value. This high reaction rate indicates that a majority of the removal take place in the first few hours, suggesting that multiple short reactions could be the most effective treatment process.

Using the slowest reaction rate, the July 29 experiment's k_4 model suggests that the average COD should be removed in 41.1 hours. The 48-hour experiment k_4 suggest the total time of removal to be 410 hours. A full summary of expected treatment times for the average COD value of leachate with the 5 different found k values for each test can be seen in Table 47.

Table 47. Predicted treatment times of average COD with estimated k values.

Experiment	Avg. COD C_o mg/L as O_2	Treatment Goal Time (hr) Surface Discharge
July 29, 2015 COD k_1	475	2.7
July 29, 2015 COD k_2	475	21.7
July 29, 2015 COD k_3	475	34.4
July 29, 2015 COD k_4	475	41.1
July 29, 2015 COD k_5	475	20.1
48 Hour COD k_1	475	77.2
48 Hour COD k_2	475	28.1
48 Hour COD k_3	475	34.4
48 Hour COD k_4	475	410
48 Hour COD k_5	475	125

Comparing these results to the reaction rate reported by Meeroff and McBarnette (2011) found the intial k_3 to be -0.0459/hr. Compared to the 48-hour experiment with a k_3 of -0.0453/hr, this indicates the reaction rate is consistent over multiple sets of research. However, the k_5 values between studies vary by a factor of 10 (-0.1067/hr compared to the 48-hour experiment having a k_5 = -0.0124/hr). This overall difference increases treatment time. The major differences in the studies were the type of reactor, the lamp used, the temperature of the leachate and the use of acid. Comparing these results to Meeroff and Youngman (2013), found that with 4 g/L of TiO_2 the reation rate was -0.0102 hr^{-1} and for 16 g/L of TiO_2 the reaction rate was 0.0127 hr^{-1}. Meeroff and Youngman (2013) were using the same reactor type and lamp as this research. This reaction rate matches well with the 48 hour experiment of -0.0124 hr^{-1}.

3.13.2 Ammonia Reaction Kinetics

Ammonia removal is linked to the amount of aeration that is received by the leachate. This can clearly be seen in the reaction time since the July 29, 2015 experiment received twice as much aeration as the 48-hour experiment. Table 48 is a summary of the 5 different first order reaction rates.

Table 48. Summary of k values in units of (hr^{-1}) found for ammonia removal.

Experiment	NH_3-N k_1	NH_3-N k_2	NH_3-N k_3	NH_3-N k_4	NH_3-N k_5
July 29, 2015	-0.176	-0.0076	-0.0557	-0.0803	-0.0689
48 Hour	0	-0.0053	-0.0038	-0.0211	-0.0230

The ammonia reaction rate for the July 29, 2015 experiment has a high initial rate and then constant removal rate indicated by k_4 and k_5. Pre-treatment in the July 29, 2015 experiment had the highest k, suggesting that a sequenced batch process could reduce ammonia more efficiently. The 48-hour experiment removed 68% of the total ammonia down to 93 mg/L as NH_3-N; however, to achieve surface discharge the ammonia must be 4.9 mg/L as NH_3-N. The predicted ammonia removal times vary from 24 to 1124 hours. For the 48-hour experiment, there was no initial drop in ammonia so k_1 could not be determined. Table 49 is a summary of the predicted removal times for both experiments. Note that no additional treatment is required to meet the ammonia conditions for the dilution water application.

Table 49. Predicted treatment times for ammonia removal.

Experiment	Avg. C_o NH_3-N mg/L	Treatment Goal Time (hr) Surface Discharge	Treatment Goal Time (hr) Reclaimed Water
July 29, 2015 COD k_1	351	24	16
July 29, 2015 COD k_2	351	562	377
July 29, 2015 COD k_3	351	77	51
July 29, 2015 COD k_4	351	53	36
July 29, 2015 COD k_5	351	62	124
48 Hour COD k_1	351	Na	Na
48 Hour COD k_2	351	806	540
48 Hour COD k_3	351	1124	753
48 Hour COD k_4	351	202	135
48 Hour COD k_5	351	185	124

Na = no removal calculated

The overall treatment times vary from 62 to 185 hours. The 48-hour experiment treatment time for surface discharge of 185 hours would be the limiting factor. Meaning this is the longest treatment time of all reactions, so it determines the length of the treatment process.

3.14 RECOMMENDED REACTOR DESIGN

This study evaluated several different reactor configurations, different lamps, different aeration regimes, and different pretreatment approaches. The configuration that had the highest process removal efficacy was the UV/TiO_2 falling film + EMOH using the 150-W lamp with settling pretreatment. The falling film enables a wide area of leachate to be exposed to UV radiation without the potential of overdosing with TiO_2. The EMOH device should be configured to operate before the leachate enters the reaction chamber. The flow pattern through the EMOH should have a pressure difference of 10 psi from inflow to outflow, with approximately 75% of the total flow passing through the EMOH device. The air intake on the EMOH's venturi should be connected to the Sweetwater SL22 linear air pump with airflow of 2 cfm. The 150-W lamp should be actively cooled by pumping 2 cfm or more of chilled air through the inner lens past the lamp. Large air holes in the top and bottom of the lamp cavity should be made to allow for greater cooling load. If sufficient cooling is provided to the lamp itself, then the leachate can be stored in the reservoir at ambient temperature without an active chiller.

3.15 CATALYST RECOVERY

By visual inspection, the flocculation test took 9 minutes for all of the TiO_2 to settle. This corresponds to a settling rate of 2.5 mm/min. Decanting the water from the top caused a small current, and the TiO_2 needed additional time to re-settle before further decanting could take place. The test with the 1-micron filter bag resulted in the TiO_2 flowing right through it. This was expected because the TiO_2 has an average size of 20 nm, which is 98% smaller than 1 micron. This test was not successful, but filtration with tighter pore sizes could be used as a finishing step to photocatalytic treatment, subject to inorganic fouling from calcium carbonate scale. Additional tests were conducted to evaluate the efficiency of different options for catalyst recover.

3.16 CENTRIFUGATION TESTING

The purpose of the preliminary centrifuge experiments (tests 1 – 31) was to establish the range of testing for the key variables, which included: mass of TiO_2 (g), volume of leachate (mL), centrifuge time (minutes), centrifuge velocity (rpm), and type of weighing dish used (ceramic or aluminum). The results of these tests were used to determine the range of parameters for further testing. A summary of the variables for these experiments is presented in Table 50.

Table 50. Summary of variables for preliminary centrifuge tests 1 – 31.

Test #	Initial TiO_2 Mass (g)	Volume of Leachate (mL)	Centrifuge Time (min)	Centrifuge Velocity (rpm)	Ignition for 15 minutes	Dishes (ceramic/ aluminum)	(1/20) dilution (Yes/No)
1 – 3	2	Not recorded	5	6,000	No	Ceramic	No
4 - 6	2	100	5, 10, 2	6,000	No	Aluminum	No
7 - 9	2	100	2	2,000, 4,000, 6,000	No	Ceramic	No
10 - 12	2	100	2	2,000, 4,000, 6,000	No	Ceramic	No
13 - 15	1	50	2	2,000, 4,000, 6,000	Yes	Aluminum	No
16 - 18	1	50	2	1,000, 2,000, 3,000	Yes	Ceramic	No
19	0.5	25	2	2,000	Yes	Aluminum	No
20 - 31	1	50	2	2,000	No	Aluminum	Yes

Preliminary tests showed that centrifuge times of 2 minutes at 2,000 rpm achieved the highest TiO_2 recoveries. Secondly, aluminum dishes produced more accurate recovery results than ceramic dishes. The variability of leachate composition particularly with respect to TSS was causing invalid test results in more than one sample; therefore, the leachate itself had to be centrifuged, and its dry weight accounted for by subtracting out from the TiO_2 weight in order to obtain a more accurate and realistic weight of TiO_2 recovered. Igniting the aluminum dishes after drying them confounded the results; therefore the ignition step was eliminated after test 19. Finally, it was determined that centrifuging leachate at different pH values had negligible effects on TiO_2 recovery.

The next set of centrifuge experiments consisted of tests 32 – 49. These experiments all used raw composite leachate diluted 1:20. These results were all valid, close to 100% recovery and exhibited low standard deviations. Table 51 shows all of the parameters for these tests. As can be seen, tests 32 – 41 held the centrifuge velocity constant and varied the time, and tests 42 – 49 held the time constant but varied the velocity.

Table 51. Centrifuge test 32 – 49 parameters.

Test #	Initial TiO_2 Mass (g)	Leachate Volume (mL)	Centrifuge Time (min)	Centrifuge Velocity (rpm)
32 – 41	1	50	1, 2, 4, 6, 10	6,000
42 – 49	1	50	2	1,000, 2,000, 3,000, 6,000

3.16.1 Centrifuge Time

As shown previously, tests 32 – 41 were performed at a constant velocity of 6,000 rpm, and the centrifuge time at this velocity was varied. The results of tests 32 – 41 can be seen in Table 52. By doing this, the optimal centrifugation time could be identified as the time produced the highest TiO_2 recovery results, and any time below or above that time produced lower recovery results.

Table 52. Centrifuge test 32 – 41 TiO_2 recovery results at 6,000 rpm.

Centrifuge Time (min)	Centrifuge Velocity (rpm)	Average TiO_2 Recovery (%)	Standard Deviation (%)	Test #
1	6000	99.62	0.04	40, 41
2	6000	99.86	0.07	32, 36
4	6000	99.82	0.08	33, 37
6	6000	99.81	0.03	34, 38
10	6000	99.76	0.08	35, 39

As can be seen from **Error! Reference source not found.** and Figure 54, the optimum centrifugation time occurs between 1 and 4 minutes.

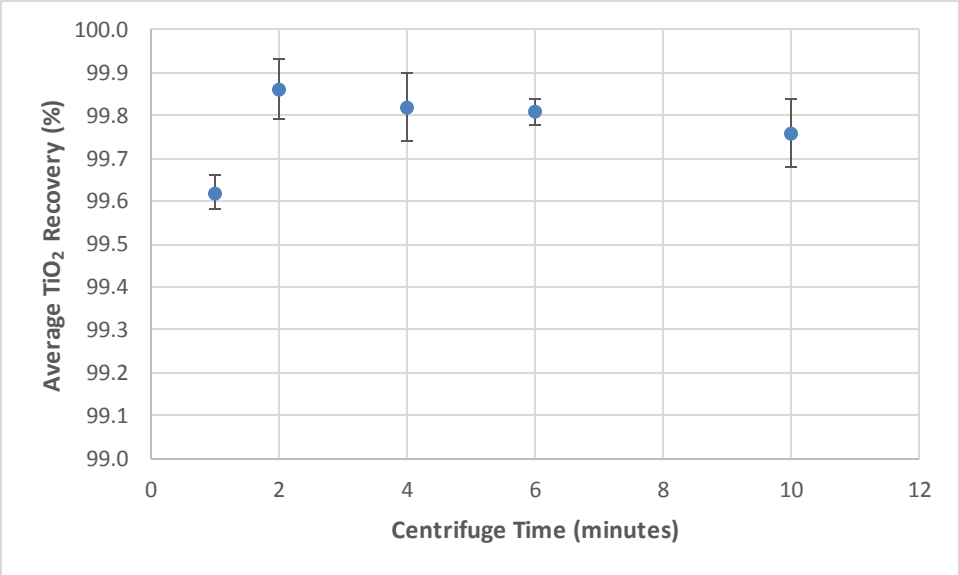

Figure 54. Centrifuge test 32 – 41 TiO_2 recovery results at 6,000 rpm.

3.16.1 Centrifuge Velocity

Tests 42 – 49 were performed at a constant centrifugation time of 2 minutes (based on previous optimization testing), and the centrifuge velocity was varied from 1000 to 6000 rpm. The results

of tests 42 – 49 can be seen in Table 53. By doing this, the optimal centrifugation velocity could be identified as the value that produced the highest TiO_2 recovery results, and any value below or above that produced lower recovery results.

Table 53. Centrifuge test 40 – 49 TiO_2 recovery results at 2 minutes.

Centrifuge Time (min)	Centrifuge Velocity (rpm)	Average TiO_2 Recovery (%)	Standard Deviation (%)	Test #
2	1000	99.32	0.03	42, 46
2	2000	99.85	0.03	43, 47
2	3000	99.54	0.06	44, 48
2	6000	99.53	0.03	45, 49

As can be seen from Table 53, the centrifuge velocity of 2,000 rpm produced the best TiO_2 recovery results in terms of minimizing the mass lost. Figure 55 shows that the optimum lies between 1000 – 3000 rpm.

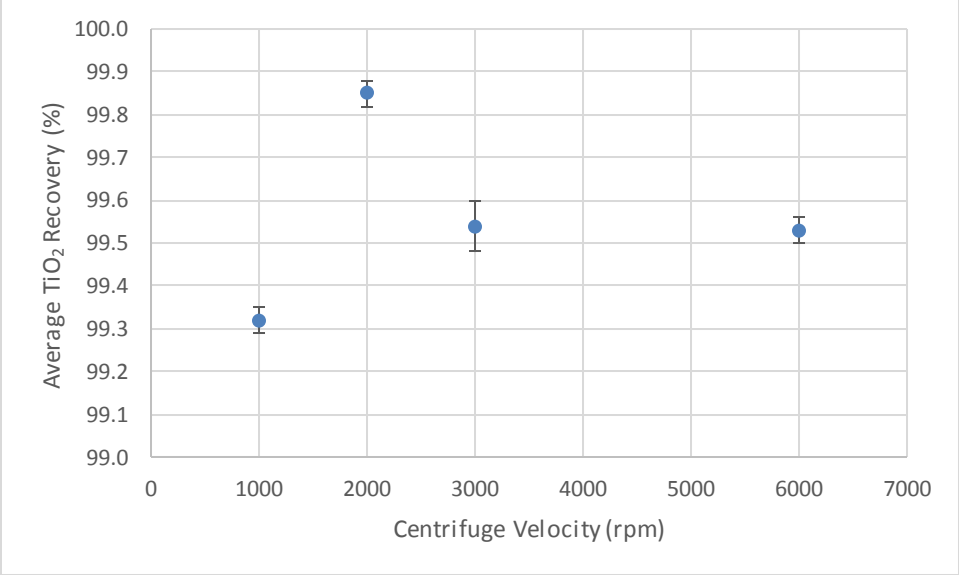

Figure 55. Centrifuge test 42 – 49 TiO_2 recovery results at 2 minutes.

The results of all centrifuge tests at these conditions are very close to one another, only varying from 99.32% to 99.86%. Clearly, from the data shown, there is no advantage in removal efficiency to increase rotor velocity to reduce recovery time. Therefore, it is recommended to centrifuge at 2000 rpm for 2 minutes for maximum recovery. Going lower than that time and velocity will recovery but only by a small margin but will reduce operational costs for centrifugation. Based on these results, a conservative estimate of 99.5% TiO_2 recovery efficiency for centrifugation was used for subsequent economic calculations. It is important to

note that these tests were conducted with 1 gram of TiO_2, and scale up tests should be conducted to confirm the optimal time and velocity conditions for field implementation.

3.17 SEDIMENTATION TESTING

Preliminary settling tests consisted of tests 1 – 5. The variables for these tests were the starting TiO_2 dose (1 – 5 g/100 mL) and the settling time range (20 – 480 minutes). The results of tests 1 – 5 all showed that longer settling times (30 minutes > t > 480 minutes) were required to accurately determine settling characteristics. Figure 56 shows an example graph from test 4 (4 g/100 mL), which explains how the time to reach the desired underflow concentration was computed.

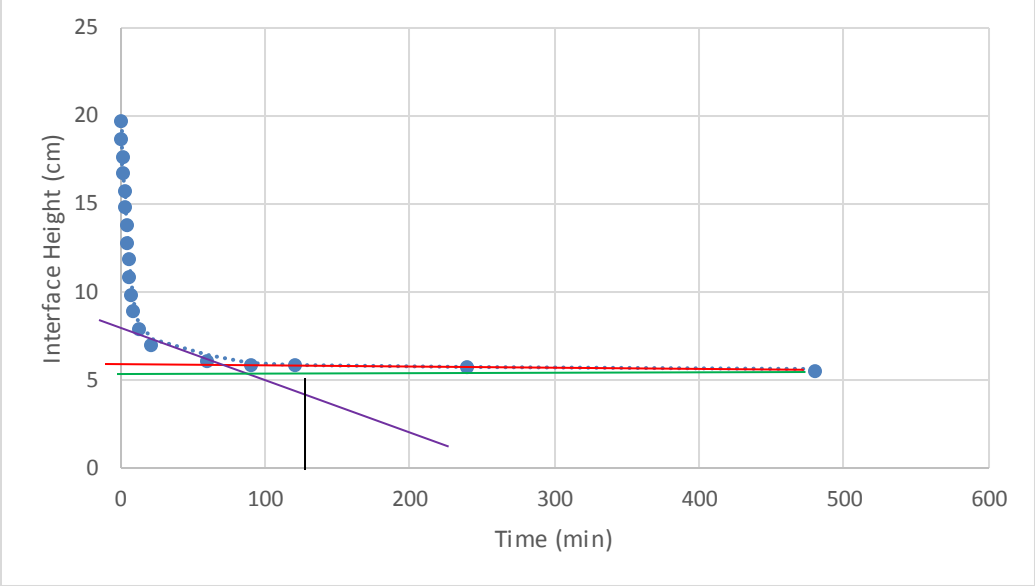

Figure 56. 4g/100 mL settling curve.

This procedure was repeated for four different TiO_2 doses (3 g, 5 g, 7.5 g, and 10 g/100 mL) measured in triplicate, with type one settling slope calculated, as shown in Figure 57. As the TiO_2 dose increased, the ultimate settling times (minutes) also increased.

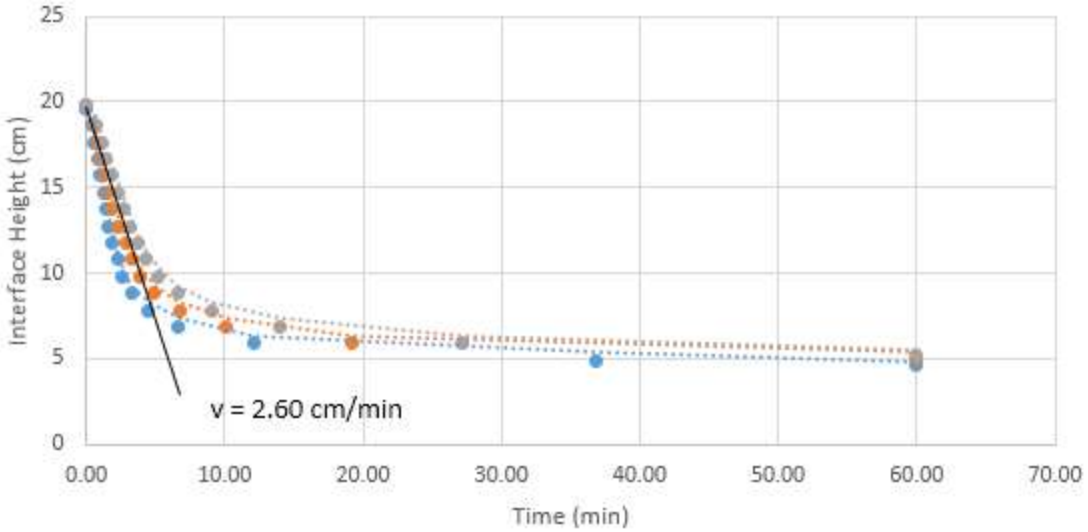

Figure 57. 3g/100 mL combined settling curves.

The results of those tests are summarized in Table 54.

Table 54. Summary of TiO_2 settling times at different doses.

TiO_2 Doses (g/100 mL)	t_u (min)	t_u (min)	t_u (min)	Average (min)	SD (min)	95% Confidence Interval
3	15	16	18	16.3	1.5	16.3 min ± 1.76 min
5	33	53	48	44.7	10.4	44.7 min ± 10.4 min
7.5	74	59	77	70.0	9.6	70.0 min ± 9.64 min
10	83	135	120	113	26.8	113 min ± 26.8 min

Plotting the results and trends of this data, the strength of the trend can be seen by the correlation coefficient value, and the standard deviation error bars show the range of the data for each TiO_2 dose. The charts for ultimate settling time can be seen in Figure 58, and the data for settling time follows a linear trend increasing with dose ($R^2 = 0.8819$).

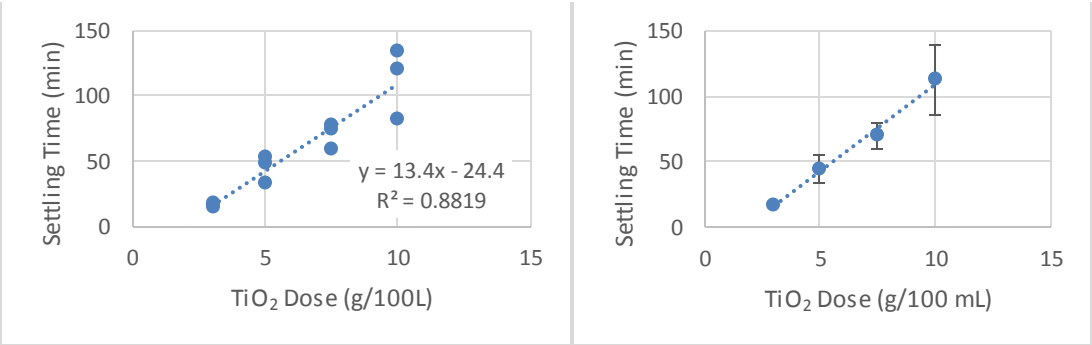

Figure 58. TiO_2 ultimate settling time trends (all samples on the left and averages with error bars plotted on the right).

The settling times do eventually level out when the TiO_2 dose reaches a level of about 13 – 15 g/100 mL because the amount of volume taken up by the mass of the TiO_2 particles is taken up the entire graduated cylinder. In that case, a deeper settling unit would be required for TiO_2 doses outside this range.

3.17.1 Settling Velocity

In each settling test, the initial settling velocity was determined from the straight line portion of the settling curve corresponding to the discrete Type 1 settling velocities for each TiO_2 dose. A summary of these results in shown in Table 55. What can be seen is that as TiO_2 dose increases, the slower its Type 1 settling velocity (cm/min) and the longer its time duration for Type 1 settling is. After that time, the settling transitioned to hindered settling.

Table 55. Summary of type 1 discrete settling velocity results.

TiO_2 Dose (g/100 mL)	Type 1 Settling Velocity (cm/min)
3	2.60
5	0.65
7.5	0.21
10	0.10

Using the observed initial settling velocity, the effective particle diameter was calculated using Stoke's Law and Newton's Law. The supplier of the TiO_2 reported that the individual TiO_2 particles are 21 nm in diameter and have a density of 4 g/cm^3 giving them a specific gravity (S_g) of 4.0 (Evonik Industries, 2008). When applying Stoke's Law, the calculation at 20˚C is shown as:

$$v_s = \frac{\left(\frac{9.81m}{s^2}\right)(21\times10^{-9}m)^2(4-1)}{18\,(1.002\times10^{-3}\frac{m^2}{s})} = 7.18\times10^{-10}\ m/s\ (4.31\times10^{-6}cm/min)$$

From that settling velocity, the Reynold's number (N_{Re}) could be calculated as follows:

$$N_{Re} = \frac{v_s d}{\upsilon} = \frac{7.18\times10^{-10}m/s\times21\times10^{-9}m}{1.004\times10^{-6}\frac{m^2}{s}} = 1.5\times10^{-11} < 1$$

Since the Reynold's number is less than 1, laminar flow is indicated. However, since the Stoke's Law theoretical settling velocity does not model closely with actual measurements (0.1 – 2.6 cm/min), Newton's Law for settling velocity was investigated for applicability. First, the drag coefficient (C_d) could be calculated assuming a shape factor of 0.85, as follows:

$$C_d = \left(\frac{24\phi}{N_{Re}}\right) + \left(\frac{3}{\sqrt{N_{Re}}}\right) + 0.34$$

$$C_d = \frac{24\phi}{N_{Re}} + \frac{3}{\sqrt{N_{Re}}} + 0.34 = \frac{24 \times 0.85}{1.5 \times 10^{-11}} + \frac{3}{\sqrt{1.5 \times 10^{-11}}} + 0.34 = 1.36 \times 10^{12}$$

When using Newton's Law, the first iteration of the theoretical settling velocity can be calculated as:

$$v_s = \sqrt{\left(\frac{4}{3}\right)\frac{21 \times 10^{-9} m \times 9.8 m/s^2 \times (4-1)}{1.36 \times 10^{12}}}) = 7.79 \times 10^{-10} m/s$$

After eight iterations, the particle settling velocity (v_s) converged to 8.45×10^{-10} m/s, which was even higher than that calculated by Stoke's Law. For both Stoke's Law and Newton's Law, using the particle size provided by the manufacturer of the TiO_2 (Evonik Industries, 2008) for settling calculations does not reflect the observed results of the settling behavior of TiO_2 in leachate. This is attributed to formation of TiO_2 flocs and compaction of the TiO_2 bed as they settled to the bottom of the 100 mL graduated cylinder. Even though Stoke's Law was not reflective of the actual TiO_2 settling behavior, there is not a current method used to calculate settling velocity for flocculent settling, only discrete settling (Qasim, 2000). Therefore, Stoke's Law was used to back-calculate the effective particle diameter of the TiO_2 flocs in leachate. Therefore, based on the settling tests, the slowest settling velocity was for 10 g/100 mL was measured as 0.10 cm/min (1.67×10^{-5} m/s). This settling velocity was then plugged back into Stoke's Law in order to find an effective average diameter of the TiO_2 settling particles as follows:

$$d = \sqrt{\frac{v_s 18 \upsilon}{g(S_g - 1)}} = \sqrt{\frac{(1.67 \times 10^{-5}\ m/s)(18)(1.004 \times 10^{-6} m^2/s)}{(9.81\ m/s^2)(4-1)}} = 3.2 \times 10^{-6} m = 3.2 \mu m$$

Using this calculated effective particle diameter, the effective Reynold's number could be calculated as follows:

$$N_{Re} = \frac{(1.67 \times 10^{-6} m/s) \times (3.202 \times 10^{-6} m)}{1.004 \times 10^{-6} m^2/s} = 5.33 \times 10^{-6} < 1$$

This Reynold's number still showed laminar settling. Using the fastest settling velocity from the settling tests obtained with 3 g/100 mL (4.33×10^{-4} m/s), the diameter of the particle would be 1.63×10^{-5} m (16.3 µm), which would generate a Reynold's number of 7.03×10^{-3}, which is also laminar. Table 56 shows a summary of the comparisons of these calculations.

Table 56. Summary of theoretical settling characteristics.

Particle Description	Effective Particle Diameter (m)	Stoke's Law Settling Velocity (m/s)	Reynold's Number
Evonik	2.10×10^{-8}	7.79×10^{-10}	1.50×10^{-11}
10 g/100 mL	3.20×10^{-6}	1.67×10^{-5}	5.33×10^{-6}
3 g/100 mL	1.63×10^{-5}	4.33×10^{-4}	7.03×10^{-3}

This wide range of results shows there is uncertainty about the true settling behavior of TiO_2 particles since the experimental results are very different from the theoretical settling behavior. Witherana et al. (2012) noted that polydisperse spherical alumina (Al_2O_3) nanoparticles with particle sizes from 10 – 100 nm (similar to the size range of TiO_2 - 21 nm) had similar settling behavior to what was observed in the TiO_2 settling tests. By measuring the Al_2O_3 suspension height over time, the average settling velocity was 1.8 cm/min (the average settling velocity from the TiO_2 tests was 1.2 cm/min). Using that settling velocity, the effective particle diameter was back-calculated using Stoke's Law to be 1.13×10^{-5} m (Witharana et al., 2012). The calculated effective particle diameter of the TiO_2 using the same method was $2.10 - 5.04\times10^{-6}$ m, which is one order of magnitude smaller but within the correct range based on the alumina particle size distribution. Youngman (2013) measured the settling behavior of TiO_2 in leachate at a TiO_2 dose of 10 g/100 mL. The calculated effective particle diameter of the TiO_2 was 3.38×10^{-6} m, which also falls within the range calculated here. However, there was no mention in any of these reports about what the actual shape factor of Al_2O_3 or TiO_2 was, and no literature reviews on this subject were found, which adds to the error difference.

3.17.2 Calculation of Settling Tank Dimensions

The thickening and clarification areas were calculated using the Talmadge and Fitch method, and the slope of the initial straight portion of the settling curve (Qasim, 1998) was computed. The flow (Q) of leachate being used was 10 liters (L) per day as that is the flow of leachate currently being treated via photocatalytic oxidation in the process described in this report.

The following shows a sample calculation for test #6 (3 g/100 mL):

$$A = \frac{10L}{day} \times 15\,\text{min} \times \frac{1}{19.6\ cm} \times \frac{1m^3}{1000L} \times \frac{1day}{1440\ min} \times \frac{100cm}{1m} = 5.3 \times 10^{-4}\ m^2$$

$$A_T = 5.3 \times 10^{-4}\ m^2 \times \left(3.28\frac{ft}{m}\right)^2 = 0.0057\ ft^2$$

$$Q_c = \frac{10L}{day} \times \frac{19.6\ cm - 4.704\ cm}{19.6\ cm} \times \frac{1m^3}{1000L} = 0.0076\frac{m^3}{day}$$

$$v_1 = \frac{18.62\ cm - 19.6\ cm}{0.42\ min - 0\ min} = -2.35\ cm/\text{min} \Longrightarrow absolute\ value = 2.35\ cm/min$$

$$v_2 = \frac{17.64\ cm - 18.62\ cm}{0.64\ min - 0.42\ min} = -4.9\ cm/\text{min} \Longrightarrow absolute\ value = 4.9\ cm/min$$

$$v_2 = \frac{16.66\ cm - 17.64\ cm}{0.80\ min - 0.64\ min} = -5.35\ cm/\text{min} \Longrightarrow absolute\ value = 5.35\ cm/min$$

$$v_{avg} = \frac{(2.35 + 4.9 + 5.35)cm}{\min * 3} = 4.2\ cm/min$$

$$A_C = 0.0076 \frac{m^3}{day} \times \frac{1min}{4.2\ cm} \times \frac{1day}{1440\ min} \times \frac{100cm}{1m} \times \left(\frac{3.28ft}{m}\right)^2 = 1.26 \times 10^{-4}\ ft^2$$

Based on these results with the thickening area controlling the design, the dimensions for a square tank settling chamber for test #6 would be 1 inch × 1 inch × 1 inch, which is extremely small. The same procedure was followed for calculating the thickening areas for tests 7 – 17 (Table 57).

Table 57. Settling test tank dimensions.

Settling Test Concentration (g/100 mL)	Thickening Length, Width, Depth (inches)
3	1, 1, 1
5	1.5, 2, 2
7.5	2, 2, 2.5
10	2.5, 3, 3

For a pilot test of 10 L/day, the average settling time (t_u) using the 10 g/100 mL concentration results was 113 minutes. This was used to calculate the dimensions for a pilot scale sedimentation tank. The design flow was assumed to be 112,000 gallons per month, but leachate would only be treated via UV/TiO_2 once per week. Therefore, a tank volume of 30,000 gallons of leachate and TiO_2 would be sufficient for this case. Also, in the tank itself, there are about 4% additional solids. Therefore, this information was used to calculate the amount of tank volume needed to accommodate those additional solids. Using the highest average settling time (t_u = 113 minutes) from settling tests 6 – 17 and design flow of 112,000 gal/month assuming a tank depth of 5 ft (152.4 cm) for sludge storage, the settling area is calculated as follows:

$$A_T = Q_u \times \frac{t_u}{H_o} : \left(\frac{gal}{day}\right)(t_u)\left(\frac{1\ day}{1{,}440\ min}\right)\left(\frac{1\ ft^3}{7.48\ gal}\right)\left(\frac{1}{H_0}\right)\left(100\frac{cm}{m}\right)\left(\frac{1m}{3.28\ ft}\right)$$

$$+ 4\%\ of\ previous\ area\ (ft^2)$$

$$A_T = \frac{30{,}000\ gallons}{day} \times \frac{1\ day}{1{,}440\ min} \times 113\ min \times \frac{1\ ft^3}{7.48\ gal} \times \frac{1}{152.4\ cm} \times 100\frac{cm}{m} \times \frac{1m}{3.28\ ft}$$

$$= 63\ ft^2 + (0.04 \times 63\ ft^2) = \mathbf{65.5\ ft^2}$$

The tank dimensions of a practical tank can be calculated by assuming a length to width ratio for the tank dimensions. The actual tank dimensions will be using a length to width (L/W) ratio of 2:1 (Qasim, 2000) which would make the actual length to be 6 ft, and the corresponding width would be 11 ft. This would make the actual tank area to be 66 ft^2 which is higher than the required 65.5 ft^2, and the solids loading rate is calculated as follows:

$$Solids\ Loading\ Rate\ \left(\frac{gpm}{ft^2}\right) = \left(\frac{gal}{month}\right)\left(\frac{1\ month}{30\ days}\right)\left(\frac{1\ day}{1{,}440\ min}\right)\left(\frac{1}{Area}\right)$$

$$SLR = \frac{30{,}000\ gal}{day} \times \frac{1\ day}{1{,}440\ min} \times \frac{1}{512\ ft^2} = \ 0.32 \frac{gpm}{ft^2}$$

Literature was reviewed to estimate a reasonable expected TiO_2 removal efficiency for a lamella clarifier. According to Parsons (2006), lamella plate clarifiers usually remove about 90 – 95% of turbidity, which is higher than the average 90% removal by most sedimentation basins (Parsons, 2006). With a lamella clarifier, the lamella plates act like baffles by slowing the water down when it hits them. As a result, the plates reduce the distance for a particle to enter the sludge zone of the tank (Qasim, 2000). Therefore, a conservative estimate of 92.5% TiO_2 recovery efficiency for a lamella clarifier was used for economic calculations. No commercially available lamella plate clarifiers with the design dimensions noted earlier were obtained for laboratory testing of TiO_2 recovery efficiency.

3.18 FILTRATION TESTING

Filter recovery tests were used to determine how much initial TiO_2 was retained using first 1.5 µm and then subsequently 0.5 µm filters at different TiO_2 doses (5 g/L, 10 g/L, 15 g/L, and 20 g/L). Table 58 shows the combined filtration recovery results of the filters at different doses, and Figure 59 shows the average results plotted in a bar graph with the standard deviations set as the error bar dimensions.

Table 58. Summary of filtered TiO_2 recovery results.

TiO_2 Dose (g/L)	TiO_2 Recovered (%)			Average TiO_2 Recovered (%)	SD (%)
	Trial 1	Trial 2	Trial 3		
5	100.4%	99.6%	95.9%	98.6%	2.41%
10	98.5%	97.0%	96.8%	97.4%	0.91%
15	98.3%	97.7%	96.3%	97.4%	1.03%
20	98.0%	95.8%	95.1%	96.3%	1.51%

As can be seen in Table 58, as the TiO_2 dose increases, the recovery decreases. Plotting the results and trends of this data, the strength of the trends can be seen by correlation coefficient value, and the standard deviation error bars show the range of the average data for each TiO_2 dose (Figure 59). It was curious to note, that less than 1% additional recovery occurred with the 0.5 µm filter. Thus, even though the TiO_2 particles are smaller than the pore size, nearly all of the recovery was recorded with the 1.5 µm filters.

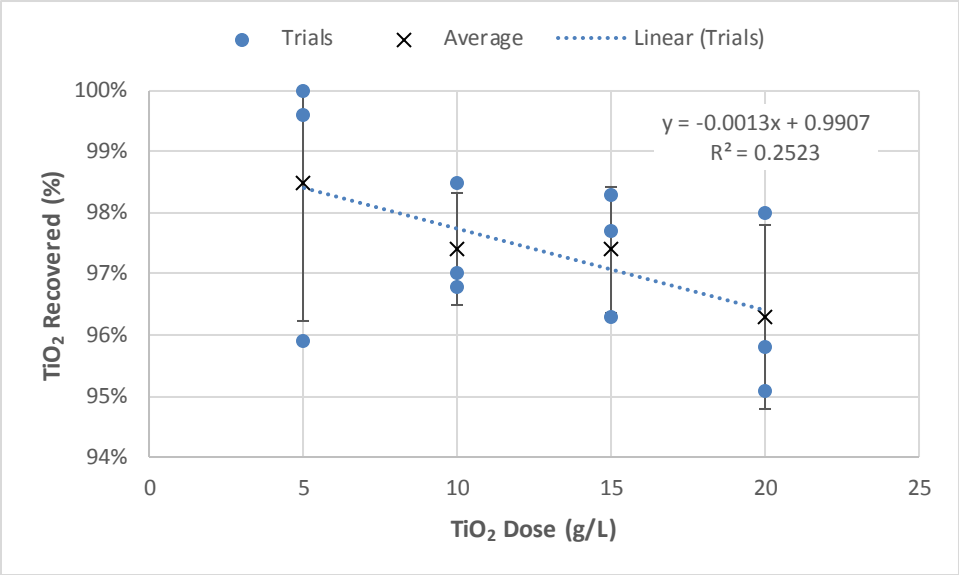

Figure 59. Filtered TiO_2 recovery results with varying doses.

As shown in Figure 59, the individual points on the trend line show weak correlation based on the low correlation coefficient value (0.2523). However, the data appear to show decreasing TiO_2 recovery efficiency with an increase in dosage, and this is expected because there is more mass that can break through or more probability of smaller sized particles being in the matrix. Since the TiO_2 dosage used for UV/TiO_2 pilot plant experiments was 20 g/L, the same dosage was used to select the expected recover efficiency of filtration for the economic analysis. Therefore, with a TiO_2 dosage of 20g/L, the average filter efficiency was 96.3%.

3.19 PARTICLE CHARACTERIZATION EXPERIMENTS

In order to check to see if TiO_2 particles were generating false positives in the COD analysis by oxidizing the chromium in the COD vials inducing a colorimetric change, which was detected by the spectrophotometer in units of mg/L as O_2 (oxygen), or by simply blocking light from passing due to suspended particles in the matrix, an experiment was devised. The variables being controlled for this experiment were the varying TiO_2 dose in deionized water (5 g/L, 10 g/L, 15 g/L, and 20 g/L) and the different types of separation processes applied (centrifugation, sedimentation, or filtration). This experiment also performed as alternative function to determine how much TiO_2 was being lost via sedimentation, filtration, and centrifugation, if the oxidation reaction was fooling the spectrophotometer. It was hypothesized that if the losses are truly minute, then the COD technique would measure 0 mg/L COD when exposed to centrate, supernatant, or filtrate of TiO_2 in deionized water. No results for settled water could be obtained because the TiO_2 did not settle in the deionized water as well as it did in the leachate. Therefore, the TiO_2 caused a color change that was beyond the detection range of the instrument. Figure 60 shows that the filtered sample appears to have a strong correlation meaning that fine TiO_2 particles have made their way passed the filter, but the centrifugation samples show no such concentration dependence, meaning that no fine particles made it to the centrate. This trend for filtration (Figure 60 left) indicated that the TiO_2 is either oxidizing the chromium or the nanoparticles are scattering the light in the spectrophotometer to produce false positives. In either

case, the data indicates that a small, but appreciable amount of TiO_2 is escaping capture by filtration, sufficiently to interfere with the COD analysis and most likely causing unaccounted for oxidation. Centrifuged samples show no such concentration dependence and are expected to have little to no effect on the COD analysis.

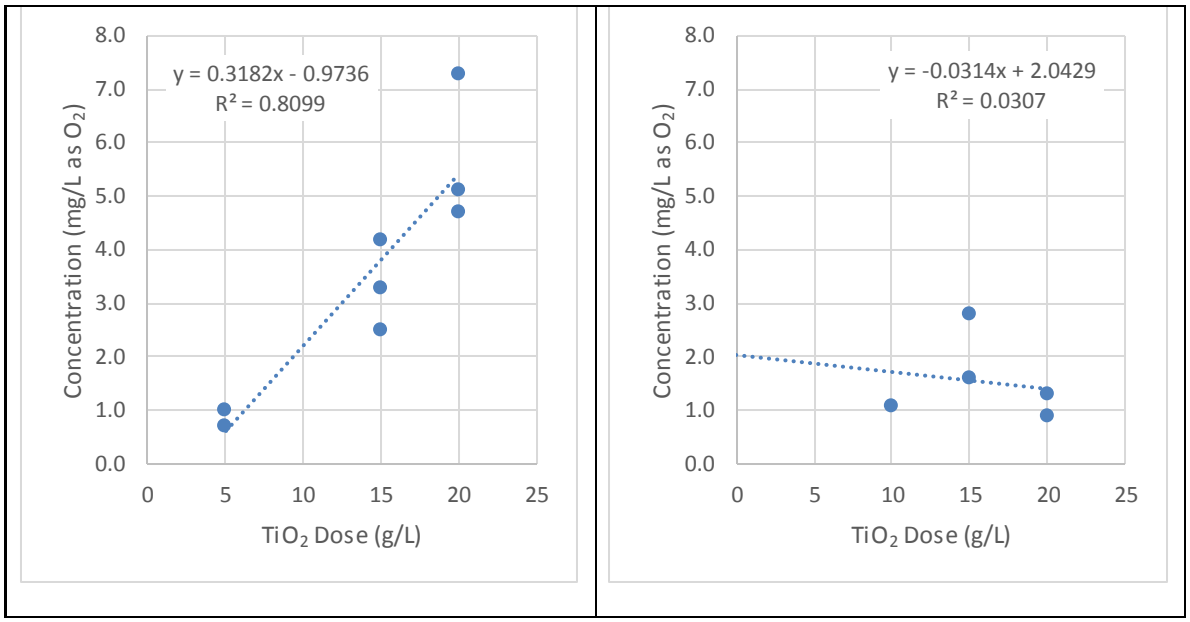

Figure 60. TiO_2 color change during COD analysis (left: filter results and right: centrifuge results).

The next test of particle characterization was to measure if the particle sizes and zeta potentials of the TiO_2 changed after interaction with leachate. It was hypothesized that the used TiO_2 particle sizes would be at least three times greater than that of the virgin TiO_2, due to metals such as calcium plating on the surface, and the used TiO_2 absolute zeta potential values would be between 30 – 60 mV, while the virgin TiO_2 absolute zeta potential values would be between 0 – 30 mV. Table 59 shows the results for the average particle sizes for both the virgin and used TiO_2 as well as the leachate samples themselves, which were read by the Nano-ZS90 unit.

Table 59. Summary of TiO_2 particle size results in nanometers.

Sample	TiO_2	Trial 1	Trial 2	Trial 3	Average	Standard Deviation
Virgin	20 g/L (DI water)	643	368	435	482	144
Test 24	20 g/L (Leachate)	3428	1966	2239	2544	777
Test 25	20 g/L (Leachate)	1930	2782	2804	2505	498
Test 28	20 g/L (Leachate)	2098	2092	1871	2020	129
Test 23-25	0 mg/L (Leachate)	1151	1015	765	977	196
Test 26-28	0 mg/L (Leachate)	1621	655	604	960	573

The used TiO_2 and leachate from centrifuge tests 24, 25, and 28 had higher particle sizes (2.0 – 2.5 μm) compared to that of the virgin TiO_2 (0.48 μm), even though the reported size is 21 nm. However, previous settling tests estimated the effective TiO_2 particle size to vary between 3 – 16 μm using Stoke's Law, although the instrument detection limit maxes out at 10 μm. The measured effective TiO_2 particle size in leachate is 5 times larger than in deionized water, indicating that something is either interfering with the analysis, or constituents in the leachate matrix such as calcium are binding to the photocatalyst surface or the large amount of ions and counter-ions are artificially swelling the particle size distribution.

The average measured particle size for leachate alone was larger than that of the virgin TiO_2 (969 vs. 482 nm, respectively). This result is expected because a liquid with a TDS of 2,000 mg/L would have larger particles than that of a pure nanopowder suspended in a deionized water with a TDS of zero mg/L. Also, based on previous settling experiments, the TiO_2 did not settle very well in deionized water, but it settled well in leachate. Therefore, it can be assumed that the TiO_2 had heavier particles attached to it in the leachate, which caused rapid agglomeration and aided settling. These larger agglomerations would then attract counter-ions and increase the effective particle size diameter more than expected. The question is does this larger structure maintain the same photocatalytic efficiency as the virgin TiO_2? One way to find out would be to physically inspect the surface through scanning electron microscopy.

The average measured particle size from the Malvern Zetasizer Nano Series: Nano-ZS90 was 2.4 microns. This value was used in Stoke's Law to estimate the particle settling velocity (9.05×10^{-5} m/s; $N_{Re} = 2.12\times10^{-4}$). TiO_2's manufacturing company (Evonik Industries, 2008) reported a particle diameter 2 – 3 orders of magnitude smaller than its effective size in aqueous solution. Therefore, the settling parameters of all four of the different particle diameter sizes are summarized in Table 60. This data supports the observation the particles are aggregating when exposed and/or leachate. This is very important information, which may be useful for finding a true shape factor (Φ) value.

Table 60. Summary of the settling behavior.

Particle Description	Particle Diameter (m)	Settling Velocity (m/s)	Reynold's Number
Evonik	2.10×10^{-8}	7.79×10^{-10}	1.50×10^{-11}
10g/100 mL	3.20×10^{-6}	1.67×10^{-5}	5.33×10^{-6}
3g/100 mL	1.63×10^{-5}	4.33×10^{-4}	7.03×10^{-3}
Nano ZS90	2.36×10^{-6}	9.05×10^{-5}	2.12×10^{-4}

In terms of zeta potential, Table 61 summarizes the results in this study.

Table 61. Summary of TiO_2 zeta potential results in millivolts.

Sample	TiO_2 Concentration	Trial 1	Trial 2	Trial 3	Average	Standard Deviation
Virgin	20 g/L (DI water)	+21.1	+22.2	+19.7	+21.0	+1.25
Test 24	20 g/L (Leachate)	-20.1	-21.0	-21.5	-20.9	-0.71
Test 25	20 g/L (Leachate)	-20.4	-20.3	-19.8	-20.2	-0.32
Test 28	20 g/L (Leachate)	-12.6	-10.7	-12.3	-11.9	-1.02
Test 23-25	0 mg/L (Leachate)	-17.8	-17.7	-19.6	-18.4	-1.07
Test 26-28	0 mg/L (Leachate)	-16.4	-18.2	-19.5	-18.0	-1.56

The virgin TiO_2 in deionized water had zeta potentials measured to be in the positive direction (+21.0), but due to its high stability (Li et al., 2009), the measured value was expected to greater than +30 mV. The used TiO_2 in leachate (-17.6 mV) and pure leachate (-18.2 mV) had zeta potentials in the negative direction. Particles can often transition from positive to negative when they are introduced into a liquid medium (Zeta-Meter Inc., 2012). It is common for particles to aggregate during the transition from positive to negative zeta potential and finish with zeta potentials between 0 to -20 mV. Thus, the used TiO_2 zeta potential results clearly support the agglomeration evidence in the particle size data. However, the absolute values of zeta potential for all of the samples measured were relatively close to each other, and they were all in the absolute range from 10 – 26 mV. Based on this information, the TiO_2 and leachate samples themselves would be classified as "incipient instability" ($\pm$10 - $\pm$30 mV). Since the TiO_2 and leachate is in that category, that may explain why the used TiO_2 particle size increased by about five times compared to that of the virgin TiO_2. The inorganic leachate particles (such as calcium carbonate) want to attach themselves to the initially unstable TiO_2 particles, which helps to stabilize them. However, part of the reason why the zeta potential is not above 30 mV (stable) is because the TiO_2 started out as positively unstable and the leachate being used has been diluted significantly. This dilution factor along with initial unstable TiO_2 may have caused the zeta potential to level out just before 30 mV. This can be verified by combining TiO_2 with undiluted leachate.

4. CONCLUSION

4.1 SUMMARY

The objective of this research was to test several UV/TiO_2 photocatalytic oxidation reactor configurations for the successful degradation of selected pollutants (COD and ammonia) in mature landfill leachate using a pilot scale reactor. The definition of an effective reactor configuration and UV lamp for this study is one that meets the water quality goals of one or more of the following criteria: 1) surface water discharge, 2) industrial reuse as cooling water or irrigation, or 3) on-site use as dilution water to reduce leachate-clogging issues in pipes. Several different reactor configurations were tested, and every one of them achieved removal of the parameters of interest. However, the leachate pretreated with 30 g/L of TiO_2 and then settled and followed by the falling film UV/TiO_2 + EMOH reactor achieved the best overall process removal efficiency in an 8 hour test with 62% of COD removed and 50% of ammonia removed.

The effect of UV spectrum and light density was tested to improve efficiency. The results were that the 150-W lamp, producing light in the UV-C spectrum, with a focus of energy at 254 nm was comparable in treatment performance with respect to COD removal to the 450-W lamp operating in the UV-A&B spectrum. The 150-W lamp achieved a maximum ammonia removal of 63% compared to 30% average for the 450-W.

This research included methods to improve the removal rate, while the addition of different metals to increase the rate of removal proved to be ineffective. The pretreatment of leachate before the photocatalytic process was shown to increase removal. Pretreatment with TiO_2 removed 41% of alkalinity and 77% of calcium, while simultaneously leading to 42% COD removal and 16% ammonia removal. Testing further showed that additional removal was achieved with the photocatalytic process after pretreatment. With more efficient treatment, discharge to the environment and reclaimed water treatment goals can be achieved. The treated leachate with a Langelier saturation index of -0.59 and a Ryznar index of 9.66 is corrosive; therefore, it would be less advantageous for potential cooling tower reuse application, depending on materials. However, corrosive water is beneficial if added in dosed amounts because evaporation causes the water in the cooling tower to become hard and to scale. The corrosive water would help to remove scale and prevent deposits, improving efficiency. The discharge water would dissolve $CaCO_3$, a possible component of leachate pipe clogging.

To determine if the COD was being converted to more readily biodegradable organics, a BOD_5 test was conducted on the 48-hour experiment. Theoretically, the COD should be converted in complete mineralization to CO_2 and H_2O. This conversion would be expected to have several step-wise stages of decomposition, particularly when dealing with complex organics typically found in leachate. If one of those stages converts COD to more biodegradable BOD, the effluent could be treated biologically. The BOD_5 test showed with a 95% level of confidence that COD is not converted to BOD in the 48-hour experiment. The notion of using treated leachate to unclog pipes in an incinerator ash-accepting landfill is fairly novel, but demonstration testing is underway at the SWA Class I landfill in Palm Beach County. Other sources of dilution water for this purpose are limited. For instance, potable water is very expensive and groundwater sources have a monthly flowrate restriction which cannot be exceeded, so additional sources of dilution

water were needed. Of course, treated leachate is less effective than potable water or even native groundwater when used in flushing or jet cleaning of leachate collection system pipes serving a conventional landfill.

After treatment, it was necessary to: 1) determine the bench scale TiO_2 recovery efficiency of centrifugation, sedimentation, and filtration; 2) characterize the recovered TiO_2 particles; and 3) develop preliminary scale-up parameters for design of each of the recovery technologies for economic analysis purposes. Centrifugation and membrane filtration with pore size of 1.5 μm achieved recovery efficiencies of 92.5 – 99.5%, which was not affected by pH. Particle characterization studies revealed that TiO_2 agglomerates rapidly in leachate and has an effective diameter that is 100x larger than the photocatalyst particle itself, and the zeta potential is around -20 mV, which is incipiently unstable. Using the COD test as a proxy to analyze for fine photocatalyst particles that escaped recovery, it was shown that centrifugation had no detectable fines break through compared to detectable amounts with filtration.

Estimating the rate of removal to achieve treatment for discharge was found for the best removal experiment conducted on July 29, 2015. The reaction rates were also found for the 48-hour experiment. The overall reactions rates for COD were -0.0776/hr and -0.0124/hr, respectively. The estimated treatment time on the average Dyer Park leachate to reach surface discharge goals using the conditions from the 48-hour experiment was 125 hours for COD with a first order reaction rate. The ammonia removal rate for the 48-hour experiment was found to be -0.023/hr. The estimated first order treatment time for average Dyer Park leachate is 185 hours for ammonia. The discovery of a higher initial reaction rate for the first 3 hours led to a new proposed treatment method as follows: one hour of pretreatment with TiO_2 and settling, followed by 2 hours of falling film + EMOH treatment and repeating in series until the target removal is achieved. The proposed sequential batch reactor could reduce the treatment time of ammonia to 78 hours, compared to the current 185 hours. The ammonia was the limiting parameter in experiments conducted in this study; however, Meeroff and Youngman (2013), found that the limiting parameter was COD. The kinetics for COD and ammonia removal from this configuration suggests that the use of a sequential batch reactor would improve efficiency, while reducing treatment times for COD from 125 hours to just 9 hours. In previous work (Meeroff and Youngman, 2013), a treatment time of 24 hours for removal of COD from high strength leachate was found to be cost-competitive with alternative technologies.

4.2 PRELIMINARY COST ANALYSIS – ADVANCED OXIDATION

Solid waste management professionals are likely to be hesitant to invest capital resources for treating leachate from closed sites that are not generating revenue, particularly when the quantity of leachate will continue to diminish over time. However, previous work (Meeroff and Youngman, 2013) has demonstrated promise of this photocatalytic technology for dealing with the same pollutants in high-strength leachates from active landfills. Therefore, any on-site treatment option for mixed or combined leachate has to be cost effective for it to be adopted. Based on the photocatalytic oxidation kinetic reaction rate, the cost was calculated for treating the Dyer Park leachate to meet the surface discharge goal. This treatment would be limited by the ammonia removal taking 185 hours. The generation rates are based on the average volume for Dyer Park of 117,000 gallons a month. However, the treatment was designed for a maximum volume of 500,000 gallons a month. Electrical costs were based on the number of lamps and pumps. The ratio of reservoir sized to number of lamps was decreased by 100, expecting the

increase in scale to allow for an increase in the falling film reactor size. Two different costs were calculated, Table 62 is the cost of treatment using the photocatalytic process for 185 hours with 10 g/L of TiO_2 in the reactor. The capital cost was spread out over 20 years at a 6% interest rate for treating an average of 1.8 million gallons per year over the life of the unit. The cost to treat leachate with this method is $280 per 1000 gallons. As a comparison point, according to Sam Levin, president of S2L Incorporated, typical leachate management costs in Florida average about $100/1000 gallons. The range is from $3/1000 gallons at Brevard County, where leachate is pumped to a POTW, to $30/1000 gallons at Seminole County, which sends its leachate via tanker to one of two POTWs, to $110/1000 gallons in Volusia County for on-site SBR at their Tomoka Farms Road site, to $130/1000 at Lake County, with ash landfills and Polk County, which hauls its leachate to disposal.

Table 62. Preliminary cost analysis for UV/TiO_2 (10 mg/L) + EMOH and reuse of photocatalytic particles.

Capital costs	**Units**	**Unit Cost**	**Total Cost**
TiO_2 chemical costs	504	$1,390	$700,560
150,000 Gallon Tank	2	$225,000	$450,000
UV lamps/ballast/lens	504	$2,000	$1,008,000
Pumps/blowers/plumbing/etc.	2	$50,000	$100,000
Total capital cost			$2,258,560
Annualized (6%, 20 years)			**$194,172**
O&M costs			
Electric ($0.12/kW-hr)	12	$8,000	$96,000
Employees	12	$16,000	$192,000
Maintenance			$23,614
Total O&M			$311,615
Total annual costs			**$505,787**
Cost per 1000 gallons (1.8 million gallons)			**$280.99**

The second scenario is for pretreatment with settling of 30 g/L of TiO_2, then treatment with 10 g/L of TiO_2. The breakdown of cost can be seen in

Table 63, the continuous replacement of TiO_2 greatly increase the cost of treatment. The cost to treat 1000 gallons would be $24,320, this is directly related to the cost of TiO_2, 1000 gallons is 3800 liters and the dose is 40 g/L means that 152 kg of TiO_2 is needed. The current cost of nano-TiO_2 in bulk is $139/kg, the cost just for TiO_2 is $18,916.

Table 63. Preliminary cost analysis for UV/TiO_2 (10 mg/L) + EMOH with settling pretreatment (30 g/L) and reuse of photocatalytic particles with replacement every two years.

Capital costs	Units	Unit Cost	Total Cost
150,000 Gallon Tank	2	$225,000	$450,000
UV lamps/ballast/lens	504	$2,000	$1,008,000
Pumps/blowers/plumbing/etc.	2	$50,000	$100,000
Total capital cost			$1,558,000
Annualized (6%, 20 years)			**$133,943**
O&M costs			
Electric ($0.12/kW-hr)	12	$8,000	$96,000
Employees	12	$16,000	$192,000
Maintenance + Chemical costs			$2,802,240
Total O&M			$3,090,240
Total annual costs			**$3,224,183**
Cost per 1000 gallons (1.8 million gallons)			**$1,791.21**

Comparing these costs to the current cost to dispose of leachate via the sewer system in Broward County, Florida. An industrial user is allowed to discharge the first 12 million gallons free of fees, but for more volume, a charge of $11.08 per 1000 gallons is assigned. An additional fee is assessed for exceeding the COD and NH_3-N (COD > 800 mg/L and NH_3-N > 25 mg/L) standards, Meeroff and McBarnette, (2011) reported this fee to be $3.65 per 1000 gallons for both constituents. If Dyer Park was subjected to the Broward County regulations, it would not produce enough volume to exceed the 12 million gallons per year threshold. If it is further assumed that Dyer Park only exceeds the ammonia limit, the fine would be half, the total cost of disposal would then be $1.83 per 1000 gallons. This cost is very low; on the other hand, the Polk County (Florida) landfill had a leachate hauling/disposal cost of $130 per 1000 gallons. It is important to note that all of these preliminary estimates assume a 185 hour treatment time. However, sequencing batch reactor process has the potential to reduce the treatment time to less than 10 hours, which would reduce the capital cost significantly, which shows with skillful engineering, and a greater understand of optimization of advanced oxidation process could be an alternative for some landfill locations.

4.3 PRELIMINARY COST ANALYSIS – TiO_2 RECOVERY

Using the results of bench scale tests conducted with centrifugation, sedimentation, and filtration procedures and conditions, a preliminary cost analysis was conducted to compare the three different unit processes tested for this application in terms of TiO_2 recovery efficiency, capital cost, and operational cost. Therefore, by using the percent recoveries and reuse efficiencies of the TiO_2 for the centrifuge, sedimentation, and filtration devices, the actual cost of TiO_2 could be calculated for each technology. Both the capital cost of the equipment and operating costs for each TiO_2 removal technology were performed.

Using the same leachate flow of 112,000 gallons per month, which became 30,000 gallons per day in one week, 2 centrifuges from Numerical Controls, LLC would be required for a 2 minute, 2,000 rpm run. Also, it was assumed that the total time for the centrifuge to get up to that

velocity and slow down again to zero, drain the treated leachate from the centrifuge, remove the recovered TiO_2 from the centrifuge, and bring in new treated leachate would take three minutes. Therefore, the total time in-between runs of treated leachate would be five minutes. The preliminary cost analysis is presented in Table 64.

Table 64. Preliminary cost analysis TiO_2 recovery using centrifugation.

Capital costs	**Units**	**Unit Cost**	**Total Cost**
Centrifuge	2	$14,800	$29,600
Pumps/blowers/plumbing/etc.	2	$50,000	$100,000
Total capital cost			$129,600
Annualized (6%, 20 years)			**$11,299**
O&M costs			
Electric ($0.12/kW-hr)			$77
Maintenance (+10%)			$12,960
Replacement TiO2 @ 99.5% recovery			$1,458
Total O&M			$14,495
Total annual costs			**$25,794**
Cost per 1000 gallons (1.8 million gallons)			**$14.33**

For the sedimentation option, a lamella plate settler is assumed at 6 ft × 11 ft × 5 ft. Typical first costs for lamella clarifiers vary between $750 - $2,500 per cubic meter of water that is treated (Cheremisinoff, 2002). In order to be conservative, $2,500 per cubic meter of tank was chosen as the cost. This number was then brought to today's cost. Looking at the interest rates between 2003 to today, the average interest rate was 2% (Trading Economics, 2015). Therefore, assuming 2% interest in 1.02^{14}, which is 1.32 (Blank and Tarquin, 2005), the 2016 cost would be $3300/m^3$. Also, the screw pumps were estimated to cost $2,000 per pump (5 m^3/hr; 1.2 Mpa, 3 kW unit with 50 mm inlet diameter). The preliminary cost analysis is presented in Table 65.

Table 65. Preliminary cost analysis TiO_2 recovery using sedimentation.

Capital costs	**Units**	**Unit Cost**	**Total Cost**
Lamella tanks	2	$30,837	$61,674
Screw pump	4	$2,000	$8,000
Total capital cost			**$69,674**
Annualized (6%, 20 years)			**$6,075**
O&M costs			
Electric ($0.12/kW-hr)			$694
Maintenance (+10%)			$6,967
Replacement TiO_2 @ 92.5% recovery			$17,730
Total O&M			$25,391
Total annual costs			**$31,466**
Cost per 1000 gallons (1.8 million gallons)			**$17.48**

For the microfiltration option with a pore size of 0.5 μm, the calculated efficiency was 96.3% membrane filter.

Table 66. Preliminary cost analysis TiO_2 recovery using filtration.

Capital costs	Units	Unit Cost	Total Cost
Membrane filters	2	$116,424	$232,848
Total capital cost			**$232,848**
Annualized (6%, 20 years)			**$20,301**
O&M costs			
Electric ($0.12/kW-hr) + Maintenance (+10%)			$23,285
Replacement TiO_2 @ 96.3% recovery			$8,896
Total O&M			$32,181
Total annual costs			**$52,482**
Cost per 1000 gallons (1.8 million gallons)			**$29.16**

Besides the TiO_2 operational cost, the microfilter membrane cost was broken down into capital costs, other operational costs, and the maintenance cost, which was calculated in the operational costs. The capital cost of the 0.5 µm filters were estimated using Figure 61. Using the 0.1 MGD point on the graph and assuming high flux to be conservative, the capital cost was about $3/gpd of filtrate in 2003. For 2016, using 2% interest (1.02^{13}), which is 1.29, the capital cost for the 0.5 µm filters would be $3.88/gpd in 2016. With 30,000 gpd for leachate, the capital cost would be $116,425 in 2016.

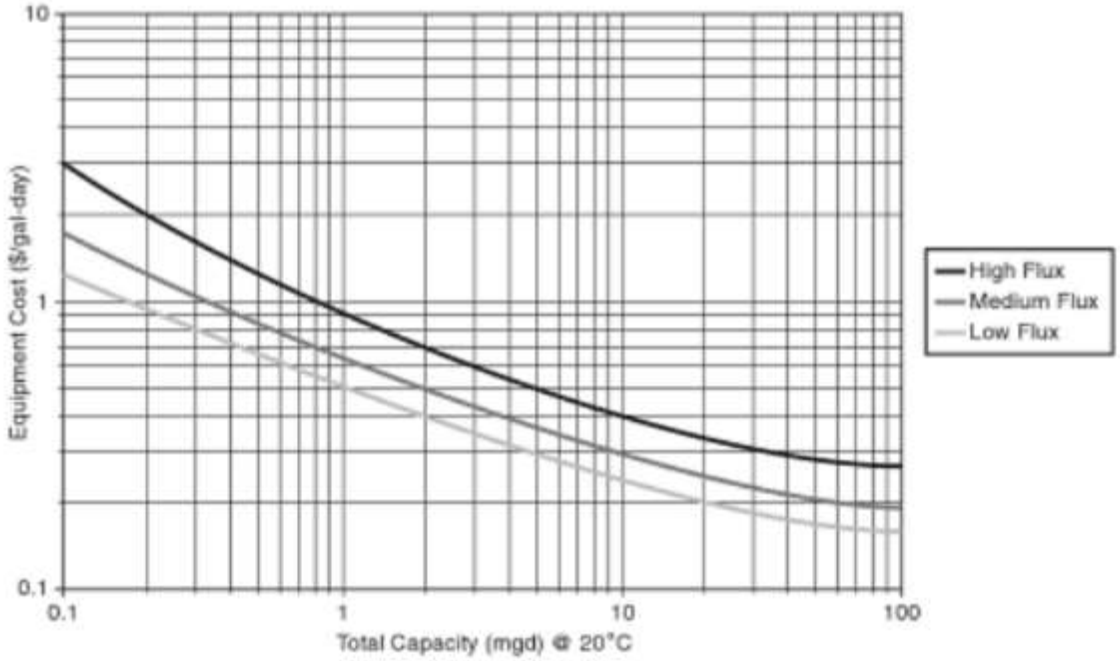

Figure 61. Microfiltration 2003 capital cost (AWWA, 2005).

Based on these preliminary estimates, it can be seen that the centrifuge had the lowest cost of the three technologies. In fact, for a technology to be deemed appropriate to use in a wastewater treatment plant setting, it would need to be lower than $10 - $15/1,000 gallons (Youngman, 2013), and centrifugation is the only one in that range ($14.33/1000 gallons). Of course, the TiO_2 cost had a big impact on the final cost, so it is important to establish the recovery number for the

photocatalyst, so that the material will last longer with less replacement. Also, these estimates assume no quantities of scale pricing on the photocatalyst.

4.4 RECOMMENDATIONS

- An 11% COD removal was seen when TiO_2 was added. Then the reaction rate changed indicating that a sequencing batch reactor could be more effective. An experiment where leachate is treated for two hours should be performed. Then the TiO_2 should be removed, and fresh TiO_2 added, prior to treatment for two hours. This should be done in a series of treatments to see if this reaction is repeatable and for how long, in preparation for sequencing batch reactor experiments.
- Pretreatment should to be tested much more rigorously to learn clues about the mechanism of removal, determined by experimentation.
- Aeration in the reservoir should be discontinued. An ultrasonic mixer should be used to reduce clumping of TiO_2 and reduce foaming. Aeration is needed before solution enters the reactor, which can be achieved using the EMOH device.
- With active lamp cooling, the scaling on the inner and outer lamp noticeably decreased. With this change, the 450-W lamp should be tested since the flow through tests may have been greatly influenced by rapid scaling from overheating.
- Studies should be conducted to evaluate the particle size after treatment using scanning electron microscopy. This will determine if calcium or other substances are adhering to the nanoparticles and interfering with the reaction, pre- and post-treatment.
- Studies need to be conducted on the EMOH device to determine if all the effects are just because the venturi is introducing air or if the magnetic fields are having any measureable effect.
- More research needs to be done on how to improve the particle sizes and zeta potentials of the TiO_2 particles because the results show they have incipient instability. The TiO_2 particles probably need to have at least moderate stability (± 30 - ± 40 mV) in order for their interaction with leachate to improve. This may require polymer addition or coagulation aids.
- It is critical to make sure that the TiO_2 reusable after its first several runs in leachate. The UV/TiO_2 photocatalytic process can only be economically viable if the particles are catalytic and can be recovered at a high efficiency. Results have shown that pollutants such as $CaCO_3$ may attach themselves to the TiO_2 during its interaction in leachate, possibly inhibiting performance, sort of like a fouling mechanism. The number of times that the catalyst can be used for a new batch of treatment is called the turnover number. This value must be determined for the process to work effectively and for preliminary cost estimates to be meaningful.
- Only limited settling tests were conducted in this study. It is recommended to perform TiO_2 recovery tests with a bench scale lamella plate settler. If recovery efficiency test results for the lamella plate settler are comparable to those of the centrifuge (99.5% recovery), lamella plate settlers may be more cost effective compared to the centrifuge with its larger energy requirements.

5. REFERENCES

Abu Amr, S. S., and Aziz, H. A. "New treatment of stabilized leachate by ozone/Fenton in the advanced oxidation process." *Waste Management*. 32(9): 1693–1698. (2012)

Adlan, M.N., Palaniandy, P., Aziz, H.A. "Optimization of coagulation and dissolved air flotation (DAF) treatment of semi-aerobic landfill leachate using response surface methodology (RSM)." *Desalination*. 277(1–3): 74–82. (2011)

Åkesson, M. and Nilsson, P. "Seasonal Changes of Leachate Production and Quality from Test Cells." *Journal of Environmental Engineering*. 123(9): 892–900. (1997)

Altomare, M, and Selli, E. "Effects of metal nanoparticles deposition on the photocatalytic oxidation of ammonia in TiO_2 aqueous suspensions." *Catalysis Today*. 209: 127-133. (2013)

Al-Yaqout A.F., Hamoda, M.F., and Zafar, M. "Characteristics of wastes, leachate, and gas at landfills operated in arid climate." *Practice Periodical of Hazardous, Toxic, and Radioactive Waste Management*. 9(2): 97-102. (2005)

American Water Works Association. Microfiltration and Ultrafiltration Membranes for Drinking Water: Manual of Water Supply Practices, M53, First Edition. American Water Works Association (AWWA). Denver, CO. (2005)

Amokrane, A., Comel, C., and Veron, J. "Landfill leachates pretreatment by coagulation-flocculation." *Water Research*. 31(11): 2775–2780. (1997)

Anglada, Á., Urtiaga, A., Ortiz, I., Mantzavinos, D., and Diamadopoulos, E. "Treatment of municipal landfill leachate by catalytic wet air oxidation: Assessment of the role of operating parameters by factorial design." *Waste Management*. 31(8): 1833-1840. (2011)

APHA, AWWA, WEF. Standard Methods for the Examination of Water and Wastewater. American Public Health Association (APHA), American Water Works Association (AWWA), and Water Environment Federation (WEF). 22nd edition. (2012)

Araña, J., Rendón, E.T., Rodrıguez, J.D., Melián, J.H., Dıaz, O.G. and Peña, J.P. "Highly concentrated phenolic wastewater treatment by the Photo-Fenton reaction, mechanism study by FTIR-ATR." *Chemosphere*. 44(5): 1017-1023. (2001)

Atlas Copco. "Energy Consumption in Wastewater Plants." http://www.efficiencyblowers.com/efficiencyblowersus/energy/water/. Accessed November, 2015.

Aziz, H.A., Ling, T.J., Haque, A.A.M., Umar, M., Adlan, M.N. "Leachate treatment by swim-bed bio fringe technology." *Desalination*. 276(1–3): 278–286. (2011)

Bae, J.H., Cho, K.W., Lee, S.J., Bum, B.S. and Yoon, B.H. "Effects of leachate recycle and anaerobic digester sludge recycle on the methane production from solid wastes." *Water Science and Technology*. 38(2): 159-168. (1998)

Balasaraswathy, P., Kumar, U., Srinivas, C.R. and Nair, S. "UVA and UVB in sunlight, optimal utilization of UV rays in sunlight for phototherapy." *Indian Journal of Dermatology, Venereology, and Leprology*. 68(4): 198-201. (2002)

Baransi, K., Dubowski, Y., and Sabbah, I. "Synergetic effect between photocatalytic degradation and adsorption processes on the removal of phenolic compounds from olive mill wastewater." *Water Research.* 46(3): 789–798. (2012)

Bashir, M.J.K., Aziz, H.A., Yusoff, M.S., Aziz, S.Q., Mohajeri, S. "Stabilized sanitary landfill leachate treatment using anionic resin: Treatment optimization by response surface methodology." *Journal of Hazardous Materials.* 182(1–3): 115–122. (2010)

Baun, A, Hartmann, N.B., Grieger, K. and Kusk, K. "Ecotoxicity of engineered nanoparticles to aquatic invertebrates: a brief review and recommendations for future toxicity testing." *Ecotoxicology.* 17(5): 387-395. (2008)

Baxter, E.D. and Hughes, P.S. Beer: Quality, Safety and Nutritional Aspects. Royal Society of Chemistry: Cambridge, UK. (2001)

Bekbölet, M., Linder, M., Weichgrebe, D., and Bahnemann, D.W. "Photocatalytic detoxification with the thin film fixed bed reactor (TFFBR): Clean up of highly polluted landfill effluents using a novel TiO_2 photocatalyst." *Solar Energy*. 56(5): 455–469. (1996)

Bernard, C., Colin, J. R., and Le Dû-Delepierre, A. "Estimation of the hazard of landfills through toxicity testing of leachates: 2. Comparison of physico-chemical characteristics of landfill leachates with their toxicity determined with a battery of tests" *Chemosphere*. 35(11): 2783–2796. (1997)

Berrueta, J. and Castrillón, L. "Anaerobic treatment of leachates in UASB reactors." *Journal of Chemical Technology and Biotechnology*. 54(1), 33-37. (1992)

Bhardwaj, V. and Mirliss, M.J. "Diatomaceous Earth Filtration for Drinking Water." Water Encyclopedia. 1: 174-177. (2005)

Bila, D.M., Montalvão, A.F., Silva, A.C., and Dezotti, M. "Ozonation of a landfill leachate: Evaluation of toxicity removal and biodegradability improvement." *Journal of Hazardous Materials*. 117(2–3): 235–242. (2005)

Black, C., Ziemkiewicz, P. and Skousen, J., "Adding alkalinity to water by limestone leach beds." *Green Lands, 29*(7): 49 – 54. 1999

Blandford, L.K. "St. Lucie's new way of getting rid of leachate costs less, is environmentally friendly." *TCPalm News.* <http://www.tcpalm.com/news/2011/oct/18/st-lucies-new-way-of-getting-rid-of-leachate-is> (Nov. 18, 2012). (2011)

Blank, L. and Targuin, A. "Compound Interest Factor Tables." In Engineering Economy, 6th ed. McGraw-Hill: New York, NY. (2005)

Bolduc, L. and Anderson, W.A. "Enhancement of the biodegradability of model wastewater containing recalcitrant or inhibitory chemical compounds by photocatalytic pre-oxidation." *Biodegradation*. 8(4): 237-249. (1997)

Booth, S.D.J., Urfer, D., Pereira, G., and Cober, K.J. "Assessing the impact of a landfill leachate on a Canadian wastewater treatment plant." *Water Environment Research*. 68(7): 1179–1186. (1996)

Borglin, S.E., Hazen, T.C., Oldenburg, C.M. and Zawislanski, P.T. "Comparison of aerobic and anaerobic biotreatment of municipal solid waste." *Journal of the Air & Waste Management Association*. 54(7): 815-822. (2004)

Bouhezila, F., Hariti, M., Lounici, H., and Mameri, N. "Treatment of the OUED SMAR town landfill leachate by an electrochemical reactor." *Desalination*. 280(1–3): 347–353. (2011)

Boyle, W.C. and Ham, R.K. "Biological Treatability of Landfill Leachate," *Journal of the Water Pollution Control Federation*. 46(5): 860–872. (1974)

Calli, B., Mertoglu, B., and Inanc, B. "Landfill leachate management in Istanbul: Applications and alternatives." *Chemosphere*. 59(6): 819–829. (2005)

Carneiro, J.T., Moulijn, J.A. and Mul, G. "Photocatalytic oxidation of cyclohexane by titanium dioxide: Catalyst deactivation and regeneration." *Journal of Catalysis*. 273(2): 199-210. (2010)

Çeçen, F. and Çakıroglu, D. "Impact of landfill leachate on the co-treatment of domestic wastewater." *Biotechnology Letters*. 23(10): 821–826. (2001)

Cheibub, A. F., Campos, J. C., and Da Fonseca, F. V. "Removal of COD from a stabilized landfill leachate by physicochemical and advanced oxidative process." *Journal of Environmental Science and Health, Part A*. 49(14): 1718-1726. (2014)

Chemlal, R., Abdi, N., Drouiche, N., Lounici, H., Pauss, A., and Mameri, N. "Rehabilitation of Oued Smar landfill into a recreation park: Treatment of the contaminated waters." *Ecological Engineering*. 51: 244–248. (2013)

Chen, J., Rulkens, W.H., and Bruning, H. "Photochemical Elimination of Phenols and COD in Industrial Wastewaters." *Water Science and Technology*. 35(4): 231–238. (1997)

Cheremisinoff, N.P. Handbook of Water and Wastewater Treatment Technologies. Butterworth-Heineman: Woburn, MA. (2002)

Cho, S.P., Hong, S.C., and Hong, S.I. "Photocatalytic degradation of the landfill leachate containing refractory matters and nitrogen compounds." *Applied Catalysis B: Environmental*. 39(2): 125–133. (2002)

Cho, S.P., Hong, S.C., and Hong, S.I. "Study of the end point of photocatalytic degradation of landfill leachate containing refractory matter." *Chemical Engineering Journal*. 98(3): 245–253. (2004)

Chong, M.N., Jin, B., Chow, C.W.K., and Saint, C. "Recent developments in photocatalytic water treatment technology: A review." *Water Research*. 44(10): 2997–3027. (2010)

Chugh, S., Clarke, W., Pullammanappallil, P. and Rudolph, V. "Effect of recirculated leachate volume on MSW degradation." *Waste Management & Research*. 16(6): 564-573. (1998)

Coey, J M, and Cass, S. "Magnetic water treatment." *Journal of Magnetism and Magnetic Materials*. 209(1): 71-74. (2000)

Commonwealth of Australia. "Ammonia (total): Overview." <http://www.npi.gov.au/substances/ammonia/index.html> (September 13, 2012). (2010)

de Morais, J. L., and Zamora, P. P. "Use of advanced oxidation processes to improve the biodegradability of mature landfill leachates." *Journal of Hazardous Materials*. 123(1 – 3): 181 – 186. (2005)

Deng, Y., and Ezyske, C. M. "Sulfate radical-advanced oxidation process (SR-AOP) for simultaneous removal of refractory organic contaminants and ammonia in landfill leachate." *Water Research*. 45(18): 6189–6194. (2011)

Dey, T. Nanotechnology for Water Purification. BrownWalker Press, Boca Raton, FL (2012)

Eddy, F.B. "Ammonia in estuaries and effects on fish." *Journal of Fish Biology*. 67(6): 1495–1513. (2005)

El Hajjouji, H. Barje, F., Pinellie, E., Bailly, J.R., Richard, C., Winterton, P., Revel, J.C., and Hafidi, M. "Photochemical UV/TiO_2 treatment of olive mill wastewater (OMW)." *Bioresource Technology*. 99(15): 7264–7269. (2008)

Elango, T., Kannan, A. and Murugavel, K.K. "Performance study on single basin single slope solar still with different water nanofluids." *Desalination*. 360: 45-51. (2015)

ETS Environmental. "Dissolved Air Flotation." Environmental Treatment Systems (ETS), Environmental Inc. Accessed November, 2015. http://www.etsenvironmental.com/products-and-services/dissolved-air-flotation. (2012)

Evonik Industries. "Aeroxide TiO2 P 25." *Safety Data Sheet*. EC 1907/2006, 08 28, (2008)

Eyeington, M. Solid Waste Authority of Palm Beach County, West Palm Beach, FL, personal communication, 2013.

Fang, J.M., Fowler, P.A., Sayers, C. and Williams, P.A. "The chemical modification of a range of starches under aqueous reaction conditions." *Carbohydrate Polymers*. 55(3): 283-289. (2004)

Farrah, S.R., Preston, D.R., Toranzos, G.A., Girard, M., Erdos, G.A. and Vasuhdivan, V. "Use of modified diatomaceous earth for removal and recovery of viruses in water." *Applied and environmental microbiology*. 57(9): 2502-2506. (1991)

Faure, B., Lindeløv, J.S., Wahlberg, M., Adkins, N., Jackson, P. and Bergström, L. "Spray drying of TiO_2 nanoparticles into redispersible granules." *Powder Technology*. 203(2): 384-388. (2010)

FDEP. "*Solid Waste Management in Florida 2002-2003*." Florida Department of Environmental Protection (FDEP). http://www.dep.state.fl.us/ (April 19, 2007). (2007)

Feitz, A., Alpin, R., and Waite, D. "Advanced oxidation processes and potential applications." *Water: Official Journal of the Australian Water and Wastewater Association*. 26(1): 34–35. (1999)

Fernandes, A., Pacheco, M. J., Ciríaco, L., and Lopes, A. "Review on the electrochemical processes for the treatment of sanitary landfill leachates: present and future." *Applied Catalysis B: Environmental*. 176-177: 183-200. (2015)

Frost R.C. *EU practice in setting wastewater emission limit values*. http://wgw.org.ua/materials.php. Accessed August 2, 2015. (2009)

Geenens, D., Bixio, B., and Thoeye, C. "Combined ozone-activated sludge treatment of landfill leachate." *Water Science and Technology*. 44(2–3): 359–365. (2000)

Gernjak, W., Maldonado, M.I., Malato, S., Caceres, J., Krutzler, T., Glaser, A., and Bauer, R. "Pilot-plant treatment of olive mill wastewater (OMW) by solar TiO_2 photocatalysis and solar photo-Fenton." *Solar Energy*. 77(5): 567–572. (2004)

Ghaly, M.Y., Jamil, T.S., El-Seesy, I.E., Souaya, E.R., and Nasr, R.A. "Treatment of highly polluted paper mill wastewater by solar photocatalytic oxidation with synthesized nano TiO_2." *Chemical Engineering Journal*. 168(1): 446–454. (2011)

Greenwood, R. and Kendall, K. "Selection of suitable dispersants for aqueous suspensions of zirconia and titania powders using acoustophoresis." *Journal of the European Ceramic Society*. 19(4): 479-488. (1999)

Gonze, E., Commenges, N., Gonthier, Y., and Bernis, A. "High Frequency Ultrasound as a Pre- or a Post-Oxidation for Paper Mill Wastewaters and Landfill Leachate Treatment." *Chemical Engineering Journal*. 92(1–3): 215–225. (2003)

Groundwater Protection Council. "Injections wells: An Introduction to their use, operation, and regulation." http://www.gwpc.org (July 17, 2007). (2005)

Hamaguchi, H. "Investigation of Options for Long-Term Leachate Management." 2008, Page 17.

He, X. S., Xi, B. D., Gao, R. T., Zhang, H., Dang, Q. L., Li, D., and Huang, C. H. "Insight into the composition and degradation potential of dissolved organic matter with different hydrophobicity in landfill leachates." *Chemosphere*. 144: 75-80. (2016)

Hemond, H.F. and Fechner-Levy, E.J. Chemical Fate and Transport in the Environment. Academic Press, San Diego, CA. (2000)

Hickman, L. American Alchemy – The History of Solid Waste Management in the United States, ForesterPress, Santa Barbara, CA. (2003)

Hong, X., Wang, Z., Cai, W., Lu, F., Zhang, J., Yang, Y., Ma, N. and Liu, Y. "Visible-light-activated nanoparticle photocatalyst of iodine-doped titanium dioxide." *Chemistry of Materials*. 17(6): 1548-1552. (2005)

Huang, X., Leal, M., and Li, Q. "Degradation of natural organic matter by TiO_2 photocatalytic oxidation and its effect on fouling of low-pressure membranes." *Water Research*. 42(4–5): 1142–1150. (2008).

Iaconi, C. D., Pagano, M., Ramadori, R., and Lopez, A. "Nitrogen recovery from a stabilized municipal landfill leachate." *Bioresource Technology*. 101(6): 1732–1736. (2010)

Imai, A., Onuma, K., Inamori, Y., and Sudo, R. "Effects of pre-ozonation in refractory leachate treatment by the biological activated carbon fluidized bed process." *Environmental Technology*. 19(2), 213–221. (1998)

Ince, N.H. "Light-enhanced chemical oxidation for tertiary treatment of municipal landfill leachate," *Water Environment Research*. 70(6): 1161–1169. (1998)

Jia, C., Wang, Y., Zhang, C., and Qin, Q. "UV-TiO_2 Photocatalytic Degradation of Landfill Leachate." *Water Air Soil Pollution*. 217(1–4): 375–385. (2011)

Jia, C., Zhu, J., and Qin, Q. "Variation Characteristics of Different Fractions of Dissolved Organic Matter in Landfill Leachate during UV-TiO_2 Photocatalytic Degradation." Report for the 2013 Third International Conference on Intelligent System Design and Engineering Applications. (2013)

Kim, D., Ryu, H., Kim, M., Kim, J., and Lee, S. "Enhancing struvite precipitation potential for ammonia nitrogen removal in municipal landfill leachate." *Journal of Hazardous Materials*. 146(1–2): 81–85. (2007)

Kim, Y.-K. and Huh, I.-R. "Enhancing biological treatability of landfill leachate by chemical oxidation." *Environmental Engineering Science*. 14(1): 73–79. (1997)

Kirby, B.J. Micro-and Nanoscale Fluid Mechanics: Transport in Microfluidic Devices. Cambridge University Press: New York, NY. (2010)

Kjeldsen, P., Barlaz, M.A., Rooker, A.P., Baun, A., Ledin, A., and Christensen, T.H. "Present and longterm composition of MSW landfill leachate: A review." *Critical Reviews in Environmental Science and Technology*. 32(4), 297–336. (2002)

Kosmulski, M., Próchniak, P. and Rosenholm, J.B. "Electrokinetic study of adsorption of ionic surfactants on titania from organic solvents." *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 348(1): 298-300. (2009)

Kurniawan, T.A. and Lo, W.H. "Removal of refractory compounds from stabilized landfill leachate using an integrated H_2O_2 oxidation and granular activated carbon (GAC) adsorption treatment," *Water Research*. 43(16): 4079–4091. (2009)

Lee, A.H., Nikraz, H. and Hung, Y.T. "Influence of waste age on landfill leachate quality." *International Journal of Environmental Science and Development*. 1(4), 347-350. (2010)

Li, H., Zhoua, S., Sun, Y., Feng, P., Li, J. "Advanced treatment of landfill leachate by a new combination process in a full-scale plant." *Journal of Hazardous Materials*. 172(1): 408–415. (2009)

Li, W., Gandra, N., Ellis, E.D., Courtney, S., Li, S., Butler, E. and Gao, R. "pH-responsive, TiO2-Attached Porphyrin for Singlet Oxygen Production in an Aqueous Solution." *Applied Materials and Interfaces*. 1(8): 1778-1784. (2009).

Liese, A. and Hilterhaus, L. "Evaluation of immobilized enzymes for industrial applications." *Chemical Society Reviews*. 42(15): 6236-6249. (2013)

Lin, S.H. and Chang, C.C. "Treatment of landfill leachate by combined electro-Fenton oxidation and sequencing batch reactor method." *Water Research*. 34(17): 4243-4249. (2000)

Liu, C., Yang, Y., Wang, Q., Kim, M., Zhu, Q., Li, D., and Zhang, Z. "Photocatalytic degradation of waste activated sludge using a circulating bed photocatalytic reactor for improving biohydrogen production." *Bioresource Technology*. 125: 30-36. (2012)

Mahmud, K., Hossain, Md. D., and Shams, S. "Different treatment strategies for highly polluted landfill leachate in developing countries." *Waste Management*. 32(11): 2096–2105. (2011)

Malvern. "Zetasizer Nano ZS." http://www.malvern.com/en/products/product-range/zetasizer-range/zetasizer-nano-range/zetasizer-nano-zs/ Accessed October, 2015. (2015)

Marsh, J.H. "Water filtration using diatomaceous earth." *WaterWorld*. 20(6). (2004).

McKean, T., Bourke, B., Mitchell, W., Caplygin, L. and McKeown, R. "Novel application of a lamella clarifier for improved primary treatment of domestic wastewater." In *73rd Annual Victorian Water Industry Engineers and Operators Conference, Exhibition Centre–Bendigo*. (2010)

Meeroff, D.E. and Lakner, J. "Safe Discharge of Landfill Leachate to the Environment." Final Report for the William W. "Bill" Hinkley Center for Solid and Hazardous Waste Management, Gainesville, FL. Report #1332027-A. (2014)

Meeroff, D.E. and McBarnette, A. "*Energized Processes for Onsite Treatment of Leachate*," Final Report for the William W. "Bill" Hinkley Center for Solid and Hazardous Waste Management, Gainesville, FL. Report # 0932015. (2011)

Meeroff, D.E. and Teegavarapu, R. "*Interactive Decision Support Tool For Leachate Management*," Final Report for the William W. "Bill" Hinkley Center for Solid and Hazardous Waste Management, Gainesville, FL. Report # 0832028. (2010)

Meeroff, D.E. and Youngman, F. "*Onsite Treatment of Leachate Using Energized Processes*," Final Report for the William W. "Bill" Hinkley Center for Solid and Hazardous Waste Management, Gainesville, FL. Report # 1132023. (2014)

Meeroff, D.E., Gasnier, F., and Tsai, C.T. (2006). "*Investigation of Energized Options for Leachate Management: Photochemical: Iron-Mediated Aeration Treatment of Landfill Leachate*." Final Report Year 1 for the William W. "Bill" Hinkley Center for Solid and Hazardous Waste Management, Gainesville, FL.

Meeroff, D.E., Gasnier, F., and Tsai, C.T. (2008). "*Investigation of Energized Options for Leachate Management: Year Two Tests of Advanced Oxidation Processes for Treatment of Landfill Leachate*." Final Report Year 2 for the William W. "Bill" Hinkley Center for Solid and Hazardous Waste Management, Gainesville, FL.

Metcalf and Eddy. Wastewater Engineering, Treatment and Reuse. 4th ed., eds. Tchobanoglous, G., Burton, F.L., and Stensel, H.D., McGraw-Hill Companies, New York. (2003)

Mohajeri, S., Aziz, H.A., Isa, M.H., Zaheda, M.A., and Adlan, M.N. "Statistical optimization of process parameters for landfill leachate treatment using electro-Fenton technique." *Journal of Hazardous Materials.* 176(1–3): 749–758. (2010)

Mohammad, A.W., Hilal, N. and Pei, L.Y. "Treatment of landfill leachate wastewater by nanofiltration membrane." *International Journal of Green Energy.* 1(2): 251–263. (2004)

Moraes, P.B., and Bertazzoli, R. "Electrode gradation of landfill leachate in a flow electrochemical reactor." *Chemosphere.* 58(1): 41 – 46. (2005)

Munter, R., Preis, S., Kallas, J., Trapido, M., and Veressinina, Y. "Advanced Oxidation Processes (AOPs): Water Treatment Technology for the Twenty-first Century." *Kemia. Kemi.*, 28(5): 354–362. (2001)

Nakamura, Y., Kobayashi, F., Daidai, M., and Kurosumi, A. "Purification of seawater contaminated with undegradable aromatic ring compounds using ozonolysis followed by titanium dioxide treatment." *Marine Pollution Bulletin.* 57(1–5): 53–58. (2008)

NOAA. 2014 South Florida Weather Year in Review. National Oceanic and Atmospheric Administration (NOAA). Miami, FL (2015)

O'brien, R.W., Cannon, D.W. and Rowlands, W.N. "Electroacoustic determination of particle size and zeta potential." *Journal of Colloid and Interface Science*. 173(2): 406-418. (1995)

Ofir, E., Oren, Y. and Adin, A. "Electroflocculation: the effect of zeta-potential on particle size." *Desalination*. 204(1): 33-38. (2007)

O'Leary and Walsh "*Decision Maker's Guide to Solid Waste Management, Volume II, (EPA 530-R-95-023)*", http://www.epa.gov, accessed April 7, 2006. (1995)

Ohtani, B., Prieto-Mahaney, O.O., Li, D. and Abe, R. "What is Degussa (Evonik) P25? Crystalline composition analysis, reconstruction from isolated pure particles and photocatalytic activity test." *Journal of Photochemistry and Photobiology A: Chemistry*. 216(2-3): 179-182. (2010)

Oweis, I.S. and Kehra, R.P. Geotechnology of Waste Management, 2nd Ed. PWS Publishing Company, Boston, MA. (1998).

Parsons, S.A. and Jefferson, B. Introduction to Potable Water Treatment Processes. Blackwell publishing: London, UK. (2006)

Pekakis, P.A., Xekoukoulotakis, N.P., and Mantzavinos, D. "Treatment of textile dyehouse wastewater by TiO_2 photocatalysis." *Water Research*. 40(6): 1276–1286. (2006)

Pelaez, M., Nolan, N.T., Pillai, S.C., Seery, M.K., Falaras, P., Kontos, A.G., Dunlop, P.S., Hamilton, J.W., Byrne, J.A., O'shea, K. and Entezari, M.H. "A review on the visible light active titanium dioxide photocatalysts for environmental applications." *Applied Catalysis B: Environmental*. 125: 331-349. (2012)

Pescod, M B. Wastewater Treatment and Use in Agriculture. United Nations, 1992.

Peters, T. A. "Purification of landfill leachate with reverse osmosis and nanofiltration." *Desalination*, 119(1): 289-293. (1998)

Peyton, G.R. and Glaze, W.H. "Destruction of Pollutants in Water with Ozone in Combination with Ultraviolet Radiation. 3. Photolysis of Aqueous Ozone." *Environmental Science and Technology*. 22(7): 761–767. (1988)

Pinnau, I. "Membranes for water treatment: Properties and characterization." http://web.stanford.edu/group/ees/rows/presentations/Pinnau.pdf Accessed October, 2015. Presented at Advanced Membrane Technologies, Stanford University, May 7, 2008. (2008)

Poblete, R., Prieto-Rodríguez, L., Oller, I., Maldonado, M.I., Malato, S., Otal, E., Vilches, L.F., Fernández-Pereira, C. "Solar photocatalytic treatment of landfill leachate using a solid mineral by-product as a catalyst." *Chemosphere*. 88(9): 1090–1096. (2012)

Qasim, S.R. and Chiang, W. Sanitary Landfill Leachate – Generation, Control and Treatment. CRC Press, Boca Raton, FL. (1994)

Qasim, S.R. Wastewater Treatment Plants: Planning, Design, and Operation. CRC Press: Boca Raton, FL. (1998)

Qasim, S.R. Water Works Engineering: Planning, Design, and Operation, Pearson Education, Upper Saddle River, NJ. (2000)

Radcliff, R.and Zarnadze, A. Application of Membrane Technology to the Production of Drinking Water. Water Conditioning & Purification International, 48-51. (2004)

Reinhart, D.R. and Grosh, C.J. "*Analysis of Florida MSW landfill leachate quality*." Florida Center for Solid and Hazardous Management, Report #97-3. (1998)

Reinhart, D.R. and Townsend, T. Landfill Bioreactor Design & Operation, Lewis Publishers, Boca Raton, FL. (1998)

Renou, S., Givaudan, J. G., Poulain, S., Dirassouyan, F., and Moulin, P. "Landfill leachate treatment: review and opportunity." *Journal of Hazardous Materials*, 150(3), 468-493. (2008)

Rincon, A.-G. and Pulgarin, C. "Use of Coaxial Photocatalytic Reactor (CAPHORE) in the TiO_2 photo-assisted treatment of mixed *E.coli* and *Bacillus* sp. and bacterial community present in the wastewater." *Catalysis Today*. 101(3–4): 331–344. (2005)

Rocha, E.M.R., Vilar, V.J.P., Fonseca, A., Saraiva, I., and Boaventura, R.A.R. "Landfill leachate treatment by solar-driven AOPs." *Solar Energy*. 85(1): 46–56. (2011)

Salem, Z., Hamouri, K., Djemaa, R., and Allia, K. "Evaluation of landfill leachate pollution and treatment." *Desalination*. 220(1–3): 108–114. (2008)

Sanchez, M., Rivero, M.J., and Ortiz, I. "Photocatalytic oxidation of grey water over titanium dioxide suspensions." *Desalination*, 262(1–3). 141–146. (2010)

Sanphoti, N., Towprayoon, S., Chaiprasert, P., and Nopharatana, A. "The effects of leachate recirculation with supplemental water addition on methane production and waste decomposition in a simulated tropical landfill." *Journal of Environmental Management*. 81(1): 27–35. (2006)

Sari, H., Yetilmezsoy, K., Ilhan, F., Yazici, S., Kurt, U. and Apaydin, O. "Fuzzy-logic modeling of Fenton's strong chemical oxidation process treating three types of landfill leachates." *Environmental Science and Pollution Research*. 20(6), 4235-4253. (2013)

Schulte, P., Bayer, A., Kuhn, F., Luy, T., and Volkmer, M. "H_2O_2/O_3, H_2O_2/UV and H_2O_2/Fe^{2+} processes for the oxidation of hazardous wastes." *Ozone: Science & Engineering*. 17(2): 119–134. (1995)

Scott, J., Beydoun, D., Amal, R., Low, G. and Cattle, J. "Landfill management, leachate generation, and leach testing of solid wastes in Australia and overseas." *Critical Reviews in Environmental Science and Technology*, 35(3): 239-332. (2005)

Silva, A.C., M. Dezotti, and G.L. Sant'Anna Jr. "Treatment and detoxification of a sanitary landfill leachate." *Chemosphere*. 55(2): 207 – 214. (2004)

Singh, S. K. Stablized Landfil Leache Treatment using Physico-Chemical Treatment Processes: Coagulation, Anion Exchange, Ozonation, Membraine Filtration, and Adsorption. Dissertation, Gainsville, FL: University of Florida. (2011)

Solid Waste Authority of Palm Beach County. http://www.swa.org (accessed on several dates). (2006)

Statom, R.A., Thyne, G.D., and McCray, J.E. "Temporal changes in leachate chemistry of a municipal solid waste landfill cell in Florida, USA." *Environmental Geology*. 45(7): 982 – 991. (2004)

Steensen, M. "Chemical oxidation for the treatment of leachate - Process comparison and results from full-scale plants." *Water Science and Technology*. 35(4): 249–256. (1997)

Suri, R.P.S., Crittenden, J.C., and Hand, D.W. "Removal and destruction of organic compounds in water using adsorption, steam regeneration, and photocatalytic oxidation processes." *Journal of Environmental Engineering*. 125(10): 897–905. (1999)

Tammemagi, H.Y. The Waste Crisis - Landfills, Incinerators, and the Search for a Sustainable Future, Oxford, New York. (1999)

Tamrat, M., Costa, C., Márquez, M.C. "Biological treatment of leachate from solid wastes: Kinetic study and simulation." *Biochemical Engineering Journal.* 66: 46– 51. (2012)

Tatsi, A.A., Zouboulis, I, Matis, K.A., and Samaras, P. "Coagulation–flocculation pretreatment of sanitary landfill leachates." *Chemosphere*. 53(7): 737–744. (2003)

Tchobanoglous, G. and Kreith, F. Handbook of Solid Waste Management, 2nd Ed. McGraw-Hill Handbooks, New York. (2002)

Tchobanoglous, G., Theisen, H., and Vigil, S. Integrated Solid Waste Management: Engineering Principles and Management Issues. McGraw-Hill Companies, New York. (1993)

Thiruvenkatachari, R., Vigneswaran, S., and Moon, I.S. "A review on UV/TiO_2 photocatalytic oxidation process." *Korean Journal of Chemical Engineering*. 25(1). 64–72. (2008)

Trading Economics. "United States Fed Funds Rate." http://www.tradingeconomics.com/united-states/interest-rate. Accessed November, 2015. (2015)

Townsend, T G. Leachate Recycle at Solid Waste Landfills using Horizontal Injection. Dissertation, University of Florida, Gainesville, FL (1995)

US Department of Health and Human Services. Occupational Exposure to Titanium Dioxide. *Current Intelligence Bulletin* 63: April 2011. (2011)

USEPA. "Ambient Water Quality Criteria for Ammonia - 1984 *EPA* 440/5-85-O1U.S." U.S. Environmental Protection Agency (USEPA). (1985)

USEPA. "Managing Nonhazardous Solid Waste." U.S. Environmental Protection Agency (USEPA) (<http://www.epa.gov/osw/inforesources/pubs/orientat/rom2.pdf> (Dec. 14, 2012). (2012a)

USEPA. "National Recommended Water Quality Criteria." U.S. Environmental Protection Agency (USEPA). <http://water.epa.gov/scitech/swguidance/standards/criteria/current/index.cfm#cmc> (Sept. 13, 2012). (2012b)

USEPA. "U.S. Methane Emissions 1990 – 2020: Inventories, Projections, and Opportunities for Reductions. Chapter 2: Landfills." U.S. Environmental Protection Agency (USEPA). (1999)

Vilar, V. J.P., Rocha, E. M.R., Mota, F. S., Fonseca, A., Saraiva, I., and Boaventura, R.A.R. "Treatment of a sanitary landfill leachate using combined solar photo-Fenton and biological immobilized biomass reactor at a pilot scale." *Water Research.* 45(8): 2647–2658. (2011)

Vineetha, M.N., Matheswaran, M., and Sheeba, K.N. "Photocatalytic colour and COD removal in the distillery effluent by solar radiation." *Solar Energy*. 91: 368–373. (2012)

Wang, F., Smith, D.W. and El-Din, M.G. "Application of advanced oxidation methods for landfill leachate treatment-A review." *Journal of Environmental Engineering and Science,* 2(6): 413-427. (2003)

Ward, M.L., Bitton, G., Townsend, T. and Booth, M. "Determining Toxicity of Leachates from Florida Municipal Solid Waste Landfills Using a Battery of Tests Approach." *Environmental Toxicology*. 17(3): 258–266. (2002)

Washington State Department of Health. Guidance Document: Slow Sand Filtration and Diatomaceous Earth Filtration for Small Water Systems. Washington State Department of Health Environmental Health Programs Division of Drinking Water. http://www.doh.wa.gov/portals/1/Documents/pubs/331-204.pdf (2003)

Westlake, K. and Phil, M. Landfill Waste Pollution and Control. Albion Publishing, Chichester, West Sussex, England. (1995)

WHO. Guidelines for Drinking-Water Quality: Recommendations. World Health Organization (WHO), 2004.

Wichitsathian, B., Sindhuja, S., Visvanathan, C. and Ahn, K.H. "Landfill leachate treatment by yeast and bacteria based membrane bioreactors." *Journal of environmental science and health. Part A*. 39(9): 2391 – 2404. (2004)

Witharana, S., Hodges, C., Xu, D., Lai, X. and Ding, Y. "Aggregation and settling in aqueous polydisperse alumina nanoparticle suspensions." *Journal of Nanoparticle Research*. 14(5): 1-11. (2012)

Wu, J.J., Wu, C.-C., Ma, H.-W., and Chang, C.-C. "Treatment of landfill leachate by ozone-based advanced oxidation processes." *Chemosphere*. 54(7): 997–1003. (2004)

Xing, W., Lu, W., Zhao, Y., Deng, W., and Christensen, T. H. "Environmental impact assessment of leachate recirculation in landfill of municipal solid waste by comparing with evaporation and discharge (EASEWASTE)." *Waste Management*. 33(2): 382–389. (2012)

Yahiat, S., Fourcade, F., Brosillon, S., and Amrane, A. "Photocatalysis as a pre-treatment prior to a biological degradation of cyproconazole." *Desalination*. 281: 61–67. (2011)

Youcai, Z., Hua, L., Jun, W. and Guowei, G. "Treatment of Leachate by Aged-Refuse-Based Biofilter." *Journal of Environmental Engineering*. 128(7): 662–668. (2002)

Youngman, F. Optimization of TiO_2 photocatalyst in an advanced oxidation process for the treatment of landfill leachate. Masters thesis. Florida Atlantic University (2013)

Zeta-Meter, Inc. "Zeta potential: a complete course in 5 minutes," (2012).

Zhao, X., Qu, J., Liu, H., Wang, C., Xiao, S., Liu, R., Liu, P., Lan, H., and Hu, C. "Photoelectrochemical treatment of landfill leachate in a continuous flow reactor." *Bioresource Technology*. 101(3): 865–869. (2010)