
**ONSITE TREATMENT OF LEACHATE
USING ENERGIZED PROCESSES**

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LIST OF ABBREVIATIONS, ACRONYMS & UNITS OF MEASUREMENT

AOP: *Advanced Oxidation Process*
APO: *Aerated Photochemical Oxidation*
BDL: *Below Detection Limits*
BMP: *Best Management Practice*
BOD₅: *Biological Oxygen Demand in mg/L*
BTEX: *Benzene, Toluene, Ethylbenzene, and Total Xylenes*
C&D: *Construction and Demolition Waste*
CB: *Conduction Band*
CCA: *Copper, Chromium, and Arsenic*
CFR: *Code of Federal Regulations*
C₀: *initial concentration in mg/L or M*
COD: *Chemical Oxygen Demand in mg/L*
DC: *Direct Current*
DO: *Dissolved Oxygen in mg/L as O₂*
DSS: *Decision Support System*
DST: *Decision Support Tool*
ED: *Electrodialysis*
EDCs: *Endocrine Disrupting Compounds*
EDTA: *Ethylenediamine Tetraacetic Acid*
EP: *Energized Process*
FAC: *Florida Administrative Code*
FDEP: *Florida Department of Environmental Protection*
FGDL: *Florida Geographical Data Library*
Flux: *in units of gpd/ft²*
FTIR: *Fourier Transform Infrared Spectroscopy*
GAC: *Granular Activated Carbon*
GUI: *Graphical User Interface*
HCSHWM: *Hinkley Center for Solid and Hazardous Waste Management*
HRT: *Hydraulic Retention Time*
IACUC: *Institutional Animal Care and Use Committee*
IMA: *Iron Mediated Aeration*
KHP: *Potassium Hydrogen Phthalate or Potassium Acid Phthalate*
Leachate Production: *in units of gallons per day per acre*
MAP: *Magnesium Ammonium Phosphate*
MBR: *Membrane Bio-Reactor*
MF: *Microfiltration*
MGD: *Million Gallons per Day*
MIEX: *Magnetic Ion Exchange*
MINCF: *Minimum Confidence Factor*
MSW: *Municipal Solid Waste*
MWCO: *Molecular Weight Cut-Off*
n/a: *not available*
NF: *Nanofiltration*

nm: *wavelength in nanometers*
nr: *not recorded*
OCUCLUS: *FDEP Division of Waste Management Document Management System*
PAC: *Powdered Activated Carbon*
pBOD₅: *Particulate Biological Oxygen Demand in mg/L*
pCOD: *Particulate Chemical Oxygen Demand in mg/L*
pH: *-log[H⁺] in standard units*
PIMA: *Photochemical Iron-Mediated Aeration*
POTWs: *Publicly Owned Treatment Works*
Q: *flowrate in m³/s*
RCRA: *Resource Conservation and Recovery Act*
Redox: *Oxidation-reduction reaction*
RO: *Reverse Osmosis*
SBR: *Sequencing Batch Reactor*
SC: *Specific Conductivity in S/m*
SWANA: *Solid Waste Association of North America*
t_{1/2}: *Half-life in minutes*
TAG: *Technical Advisory Group*
TCLP: *Toxicity Characteristic Leaching Procedure Test*
TDS: *Total Dissolved Solids in mg/L*
TKN: *Total Kjeldahl Nitrogen in mg/L as N*
TN: *Total Nitrogen in mg/L as N*
TSS: *Total Suspended Solids in mg/L*
UF: *Ultrafiltration*
UIC: *Underground Injection Control*
US: *Ultrasound*
USEPA: *United States Environmental Protection Agency*
UV: *Ultraviolet*
VB: *Valence Band*
VOCs: *Volatile Organic Compounds*
W: *Watts*
ZVI: *Zero-Valent Iron*
λ: *Wavelength*

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FINAL REPORT

09/01/2011 – 08/31/2013

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USING ENERGIZED PROCESSES

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KEY WORDS: Landfills, leachate, advanced oxidation, wastewater, solid waste management, COD, BOD, ammonia, lead, conductivity, TDS, advanced oxidation, titanium dioxide, iron-mediated aeration, sustainability

ABSTRACT (1 page only)

With new, more stringent regulations for wastewater disposal in Florida's horizon, the ability to safely discharge leachate will become increasingly difficult. Florida's future rules include among others: severe numerical nutrient criteria as well as reuse water quality requirements for deepwell injection. To remain at the leading edge of environmentally responsible solid waste management, new technologies are needed to effectively treat leachate on site in the future. Florida Atlantic University has been pioneering advanced oxidation methods for leachate management that can mineralize COD, remove heavy metals, disinfect pathogens, reduce ammonia levels, decrease color, and effectively detoxify leachate so that it can be safely discharged to a wastewater treatment plant. Photocatalytic oxidation is an advanced oxidation process (AOP) which has shown ability to reduce toxicity of an array of leachate constituents including organics, inorganics and heavy metals. The purpose of this manuscript is to scale up the batch scale study of UV/TiO₂ photocatalysis of leachate utilizing a pilot scale falling film reactor. In this research, the use of UV/TiO₂ for the removal of chemical oxygen demand (COD), ammonia, alkalinity and color was studied in order to optimize catalyst dosage, determine pH effects and reaction kinetics and develop preliminary cost estimates. This research will address a major technological need for sustainable, economical options for routine leachate treatment and safe discharge to the environment.

EXECUTIVE SUMMARY

09/01/2011 – 08/31/2013

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USING ENERGIZED PROCESSES

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OBJECTIVES

The objective of the proposed research is to pilot test a UV/TiO₂ photocatalytic treatment process for the removal of parameters of interest including COD, ammonia, alkalinity, and color in landfill leachate using a pilot scale falling film reactor. The main focus was to validate previous laboratory scale performance. For the pilot tests, reactors were designed to collect performance data with respect to process flow rates, air injection, mixing conditions, exposure time, degradation rates, catalyst dose, pretreatment requirements, and operational conditions. It is hypothesized that the degradation rate of the contaminants will follow overall first-order reaction kinetics. The primary objective of this study is to determine an optimum dosage of catalyst using a falling film reactor without the use of any pretreatment or chemical addition methods. This report tackles the major technological need for addressing the safe disposal of leachate by bringing sustainable, economical options for routine leachate management into the hands of the end users in the solid waste management industry.

RATIONALE

A major limitation to landfill leachate management has been the lack of effective methods for safe long-term discharge back into the natural environment. The extremely variable water quality and generation rates, along with the ever-changing regulatory environment, often complicate conventional treatment technologies and disposal planning. As the options begin to get limited, on-site pretreatment becomes more and more necessary. Typically, some form of aerobic treatment would be required to reduce leachate strength prior to discharge. However, biological systems are not well-suited for

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 physical/chemical/biological treatment, or evaporative systems, is generally required. Unfortunately, activated carbon and certain advanced treatment processes, such as ozone or ultraviolet light, do not adequately address inorganics, and membrane systems or air stripping merely transfer organics to another phase. Furthermore, multiple barrier systems are complicated to operate, costly, and generally inefficient. Unfortunately, most current processes cannot adequately address inorganics and organics simultaneously. 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.

If advanced oxidation processes work as well in the field (at pilot scale) as they do in the laboratory, then we may have an answer to the leachate management issue because advanced oxidation processes are: 1) designed to use the power of sunlight, which is free and requires no additional energy input, 2) easy to operate because they just require sufficient contact time and do not rely on complex precipitation reactions or biochemical processes, 3) not subject to biological upsets because they are physico-chemical processes that create broad spectrum oxidants to remove aqueous contaminants, and 4) designed to avoid merely transferring the pollutant to another medium (i.e. air or sludge).

This research will address a major technological need for sustainable, economical options for routine leachate treatment and safe discharge to the environment by investigating photochemical oxidation using TiO_2 currently being developed at FAU for solid waste management applications. This innovative process works by using ultraviolet light (energy from sunlight) to activate the surface of a semi-conductor (i.e. titanium dioxide) to produce highly reactive substances (i.e. hydroxyl radicals) derived from water. These reactive radicals rapidly destroy man-made organic chemicals, breaking them down into carbon dioxide, water, and innocuous salts. In addition, it has been discovered recently by a UM-FAU partnership (funded by HCSHWM) that these processes can also remove heavy metals and reduce nitrogen-containing constituents. Thus it may now be possible to eliminate impurities in water all at once using a single process.

Florida's solid waste industry needs to have tools ready for managing leachate in the near future if the current methods become restricted. Right now, only a few landfills are exploring on-site treatment technologies. With the great variation in site characteristics, waste composition, leachate volumes, and constituents of concern, there is a lack of performance data needed to design on-site systems for landfill leachate treatment. This proposal tackles the major technological need for addressing this gap in bringing sustainable, economical options for routine leachate management using advanced oxidation technologies into the hands of the end users in the solid waste management industry.

METHODOLOGY

The study used a modified falling film advanced oxidation reactor with TiO₂ photocatalytic particles to test the removal efficiency of COD, ammonia, color, and alkalinity in real leachate. Long term tests were performed using real leachate provided by the Monarch Hill landfill facility in Pompano Beach, FL. Addition of 4 g/L to 40 g/L of TiO₂ was investigated in longterm trials from 24-40 hours to determine removal efficiency of the contaminants of concern and determine the reaction kinetics for scale-up. The desired amount of catalyst was to be determined from the various experiments at different TiO₂ doses. For longterm testing, the system was operated with a temperature control unit to limit the effects of rising temperature over time. Catalyst recovery methods were evaluated using bag filtration, centrifugation, and sedimentation.

MAJOR FINDINGS

Previous batch scale studies achieved 100% mineralization of COD, 79% removal of copper and 50% degradation of ammonia in simulated leachate using 4 g/L TiO₂ (3.88 TiO₂:COD). This catalyst dose became the starting point for the pilot studies presented in this document. TiO₂ dosages were tested from 4 – 40 g/L (0.64 – 5.73 TiO₂:COD). No pH control was implemented and thus ranged from 7.5 – 9.3 throughout the duration of all experiments. The mean pH for all experiments ranged from 8.72 – 8.89, which had no observable effect on the removal efficiencies for any of the parameters. Maximum COD mineralization (34%) was carried out at catalyst doses of 25 and 40 g/L after 24 hours of treatment. Ammonia reached maximum removal (82%) with 4 g/L TiO₂ after 24 hours of treatment. The highest alkalinity destruction in 24 hours was 84%, occurring with a catalyst dosage of 10 g/L. Maximum color removal in 24 hours was 57% with a catalyst dose of 40 g/L.

To find the desired amount of catalyst, it was necessary to balance the removal percentages of COD versus ammonia, color, and alkalinity. It was found that catalyst dosages above 10 g/L reduced ammonia removal by 32 – 38% and alkalinity removal by 9 – 12% below their respective maximum values. For COD, catalyst doses less than 25 g/L exhibited only 8 – 12% less removal than the maximum. Since large increases in catalyst provided minimal increases in COD mineralization and great decreases in ammonia and alkalinity degradation, optimization of the catalyst resulted in a preferred dose range of 4 – 10 g/L TiO₂. In this optimum range at 24 hours, 22 – 26% of COD, 72 – 82% of ammonia, 81 – 84% of alkalinity, and 26 – 30% of color was removed from the leachate. The parameters that incurred the most exceedance fees for the Monarch Hill landfill were COD and ammonia, which in the optimum range degrade to the target levels in 160 – 200 hours and 55 – 75 hours of treatment, respectively.

The kinetics studies within this manuscript evaluated the overall reaction order, which is defined by the slowest reaction in the matrix (the rate-limiting step). The results determined that the photocatalytic degradation of COD followed overall pseudo-first order behavior closer than zero or second order. We recommend modeling the removal of

all parameters as a first order reaction. Using the optimum range of catalyst (4 – 10 g/L) the decay rates of COD ranged from -0.0102 to -0.0127 hr⁻¹. Based on the data and literature, ammonia and alkalinity were recommended to also be modeled as overall first order reactions at ambient pH levels. The optimum range of catalyst gave decay rates for ammonia ranging from -0.058 to -0.073 hr⁻¹ and alkalinity ranging from -0.078 to -0.079 hr⁻¹. From the data analysis and literature review, it was suggested to model color removal as an overall zero order reaction. Under the optimum range of TiO₂ (4 – 10 g/L) color was degraded at -13.7 to -8.82 PCU/hr. At these rates and these conditions, the goal of meeting the Broward County sewer use limitations is not met in less than 24 hours of treatment for the raw composite leachate sampled at Monarch Hill landfill.

Attempts to recover the used catalyst after 8 hours of treatment using nylon monofilament filter bags were unsuccessful. The average primary size of Aeroxide P25 TiO₂ nanoparticles is reported to be 21 nm. It was expected that this size would increase due to adsorption of organics and other compounds. The 5-micron bag did not catch many catalyst particles as the filtered leachate clearly still contained a large amount of TiO₂ and leachate TSS (141.3 % recovery). Thus, the bag filter system was determined to be an inefficient method of catalyst recovery. Instead, a sedimentation trap or centrifugation is recommended.

**ONSITE TREATMENT OF LEACHATE
USING ENERGIZED PROCESSES**

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1. INTRODUCTION

The most widely used form of waste disposal in the United States is the sanitary landfill (USEPA 2012). Landfill regulations have been enacted by the United States Environmental Protection Agency (USEPA) to prevent the spread of leachate contaminants into the groundwater and soil underneath landfills (Qasim and Chiang 1994). Leachate is created when liquid, mostly rain water, percolates through the waste inside the landfill, picking up contaminants along the way. A significant issue associated with leachate is its high variability. Leachate quantities are directly related to the amount of rain water received by the landfill and the number of open acres being filled. The quality varies according to the waste that the water passes through along the way to the bottom of the landfill liner and collection system. Every landfill's leachate is different and a single landfill's leachate can vary at different points of time. Because of the potential toxicity of the contaminants in municipal solid waste, leachate will pollute the groundwater and soil underneath and downstream of the landfill if the leachate is not properly managed. USEPA regulations require landfills to implement a leachate collection system to prevent the leachate from being released into the environment: "New Municipal Waste Solid Landfill (MSWLF) units and lateral expansions shall be constructed with a composite liner and a leachate collection system that is designed and constructed to maintain less than a 30-cm depth of leachate over the liner" (40 CFR 258.40). In the absence of a leachate collection system, the leachate that is released to the environment becomes difficult and/or too expensive to manage because of the widely varying nature of the contaminants (Westlake and Phil 1995).

1.1 LEACHATE WATER QUALITY

Several excellent 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 values for selected constituents are summarized in Table 1.

Table 1. Typical leachate water quality data from young and mature landfills (Tchobanoglous, Theisen, and Vigil 1993; Metcalf and Eddy 2003)

Constituent	Units	Young	Mature
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^-) with heavy metals (arsenic, cadmium, chromium, cobalt, copper, lead, mercury, nickel and zinc), in the microgram per liter range; iii) 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 among others.

It is difficult to define a typical landfill leachate because each landfill produces varying compositions of leachate at different times. A review of leachate water quality from 125 sources reported in the literature is summarized in Table 2. 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 water quality that can be found.

Table 2. Summary of extreme values for the composition of leachate developed through review of technical literature

Parameter	Units	Concentration	
		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), de Morais and Zamora (2005), Deng and Ezyske (2011), Geenens et al. (2000), Gonze et al. (2003), 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 et al. (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), Tammemagi (1999), Tatsi et al. (2003), Tchobanoglous and Kreith (2002), 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), Tamrat et al. (2012), 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).

The USEPA (40 CFR 445.21) requires that the effluent from a non-hazardous waste sanitary landfill does not exceed the limitations summarized in Table 3. The USEPA defines the effluent limitations in 40 CFR 122.2 as “any restriction imposed on the quantities, discharge rates and concentrations of pollutants which are discharged into waters of the United States.” When discharging sanitary landfill leachate, meeting these limitations can be challenging. The amount of contaminants in leachate can far exceed these effluent limitations.

Table 3: USEPA Effluent limitations for non-hazardous waste landfill (40 CFR 445.21)

Regulated Parameter	Units	Maximum Daily	Maximum Monthly Average
BOD	mg/L	140	56
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	0.120	0.071
<i>p</i> -Cresol	mg/L	0.025	0.014
Phenol	mg/L	0.026	0.015
Zinc	mg/L	0.200	0.11
pH	pH units	6 – 9	6 – 9

This work focuses on the primary pollutants that have been specified in the Broward County, FL effluent limitations (Table 4). The leachate used in this study was collected from Monarch Hill Landfill (Pompano Beach, FL) and their specific pollutants of concern result in fines based upon exceeding the regulated effluent limitations, specifically COD, BOD₅, suspended solids, total Kjeldahl nitrogen, ammonia, phosphorus, and oil and grease. Of those listed, COD and ammonia are of the greatest concern for the landfill managers.

COD is a measure of the total quantity of oxygen required to chemically oxidize organic and inorganic matter in water or wastewater (EPA 2012). COD is typically reported as an amount of oxygen in mg/L and COD was chosen as a primary parameter over biochemical oxygen demand (BOD) due to first-hand reported local issues with municipal solid waste disposal sites; Monarch Hill landfill operators reported exceedance fees incurred on account of elevated COD levels. COD is generally higher than BOD because COD includes the oxidation of recalcitrant materials which typically would not be microbiologically degraded. A high concentration of COD present in water causes a decrease in dissolved oxygen (DO) levels, which can be fatal to aquatic life. The federal government currently has set limitations for BOD (see Table 3), but not for COD. 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 (see Table 6).

Table 4: Broward County sewer use limitations surcharge levels (Sewer Use Ordinance, Broward County Code Chapter 34 Article VI, Ordinance No. 2001-43)

Parameter	Units	High strength wastewater surcharge can apply if concentrations are:
BOD ₅	mg/L	Greater than 400
COD	mg/L	Greater than 800
TSS	mg/L	Greater than 400
TKN	mg/L	Greater than 30 and not exceeding 100
NH ₃ -N	mg/L	Greater than 25 and not exceeding 70
Total P	mg/L	Greater than 5 and not exceeding 20
O&G (Oil and Grease)	mg/L	Greater than 100 and not exceeding 500

Ammonia (NH₃) is an inorganic form of nitrogen that is created naturally in the environment, especially during the anaerobic degradation of many organic compounds (EPA 2012). Ammonia is a colorless gas, which is easily dissolved in water and is used as such in many household cleaners (NYSDOH 2004), although when aqueous ammonia is exposed to open air, it rapidly turns into a gas, which produces a strong odor (Commonwealth of Australia 2010). The concentration of aqueous ammonia is higher in waters with increased temperatures and/or pH (EPA 1985). Concentrations of ammonia at levels of 0.03 mg/L have been found to be toxic to aquatic life, and the LC₅₀ (Lethal Concentration which is fatal to 50% of the subjects) for freshwater fish occurs at 0.068 – 2.00 mg/L as NH₃-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 levels naturally found in groundwater and surface water are usually less than 0.2 mg/L, although anaerobic groundwaters 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. The concentrations found in leachate, which were shown in Table 2 (up to 13,000 mg/L as NH₃-N) far exceed these levels, which is one reason that ammonia must be regulated. Broward County sewer use limitations stipulate high strength wastewater surcharges if the NH₃-N is above 25 mg/L as NH₃-N, and they do not permit concentrations above 70 mg/L as NH₃-N (refer to Table 4).

1.2 LEACHATE WATER QUANTITIES

Another challenge to the management of leachate is the variable quantities of this material generated by landfills. The volume of leachate produced depends on the amount of rain that percolates through the landfill and the exposed surface area. Other factors which influence the volume of leachate include: surface runoff, groundwater intrusion, liquid waste in landfill, irrigation, evapotranspiration, landfill depth and refuse

composition (Westlake and Phil 1995). A survey was performed by Florida Atlantic University (Meeroff and Teegavarapu 2010) polling 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: small (500,000 MT/yr), medium (5,000,000 MT/yr), large (15,000,000 MT/yr), and super (> 15,000,000 MT/yr) (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 5).

Table 5: Leachate generation rates for 31 Florida landfills (Meeroff and McBarnett 2011)

Class	Range (gpd/acre)	Number of landfills
Small	<100	14
Medium	100-300	9
Large	300-850	6
Super	>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 and leachate is also generated in partially lined cells or older systems (Meeroff and McBarnette 2011), so accurate generation values are not readily available.

1.3 STRATEGIES FOR LEACHATE MANAGEMENT

As a consequence of collecting these concentrated volumes of leachate, containing synthetic organic compounds and heavy metals, 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 water quality and waste generation rates, along with the ever-changing regulatory environment, which has caused many conventional technologies to fail in this goal.

There are a number of methods currently utilized in leachate management from physical to chemical to biological processes. A review of the currently available treatment

processes can provide a basis for the most appropriate leachate management strategies for the future. One attractive option for landfill managers is hauling. 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). 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). Another issue is that not all wastewater treatment plants will accept leachate due to the extremely high concentrations found. In addition, large volumes of leachate can upset the normal biological treatment processes at the plant (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 (Çeçen and Çakıroglu 2001) compromising the treatment plant's ability to meet permitted discharge water quality levels. In this case, the treatment facility would likely consider no longer accepting the material.

Leachate recirculation is another option for managing leachate. This process consists of reintroducing the landfill 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 to prevent elevated photochemical ozone formation (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 circulation difficult due to high temperatures and elevated levels of evaporation, which lowers the moisture content of the solid waste thereby diminishing the biological activity. One study determined the effect of applying additional water in order to maintain certain levels of moisture, on the methane production and stabilization of the landfill. It was found that supplementing the leachate

with water kept elevated levels of methane production and lower time periods of landfill stabilization (Sanphoti et al. 2006). The implementation of a leachate recirculation system requires high capital and recurring maintenance costs. Also, odor problems from leachate recirculation are common (McBarnette 2011).

Evaporation is another practice used in managing landfill leachate. The primary objective of the evaporation/distillation process is to produce a high quality condensate that can be disposed of more easily than raw leachate. Evaporation rates change with seasonal variations in temperature and other conditions, making evaporation difficult in areas where excessive humidity and/or rain or excessive cold temperatures are common. The high levels of humidity in Florida diminish evaporation rates and make the evaporation of leachate an inefficient method of leachate management. It is possible to control the evaporation rate by utilizing thermal treatment, but this requires additional equipment and energy to generate the heat necessary (Birchler et al. 1994; Zhao et al. 2012).

Another attractive disposal option for leachate is deep well injection, if the appropriate aquifer conditions exist and permitting is available. In this option, the leachate is pumped deep into the ground below the aquifer and between confining layers to assure separation from the groundwater supply. The biggest concern with deep well injection is the risk of contamination of the drinking water supply (Groundwater Protection Council 2005). The exact geology thousands of feet underground can be difficult 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 United States Environmental Protection Agency (EPA) 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 underground sources of drinking water (USDWs) in specific areas of Florida (65 FR 42234) unless the owner met certain additional requirements: 1) advanced wastewater treatment (AWT) and high level disinfection (so that primary health-based drinking water standards would not be violated) with a non-endangerment demonstration or 2) in-depth hydrogeological demonstration and advanced 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). The specified treatment requirements then are designed to achieve an effluent after disinfection containing not more than 20 mg/L CBOD₅ 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 requires installation of advanced wastewater treatment with high level disinfection by 2015 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). Existing (installed before December 22, 2005) Class I municipal disposal wells that have caused or may cause fluid movement into USDWs in specific counties and under certain geologic conditions in Florida are limited 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. These counties were targeted in the proposal because they have the unique geologic conditions that are predominated by carbonate rocks. Class 1 industrial disposal wells are designed with additional levels of protection, and it is unclear whether industrial disposal wells have suffered the same issues as municipal disposal wells. The basic regulations for industrial wells are not substantially different than municipal wells, but an additional layer of protection is designed and built into industrial wells. The only differences include seismic studies for structural integrity, an additional area of review of 2 miles compared to 0.25 miles, modeling studies to show the waste will remain in the injection zone for 10,000 years, automatic alarms and shutdown devices, year internal mechanical integrity testing, and additional monitoring and reporting requirements. They are built with a tubing and packer system that places the injection tube inside a liquid filled annulus. This allows for better monitoring of performance.

The unique problems associated with deep well injection are not limited to the solid waste manager owning an onsite well. Many of the large publically-owned treatment works (POTWs) in those same counties dispose of treated wastewater effluent via deep wells. Therefore, if the leachate 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 the options begin to get limited, on-site pretreatment becomes more and more necessary. Typically, some form of aerobic treatment would be required to reduce leachate strength prior to discharge. However, biological systems are not well-suited for 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 physical/chemical/biological treatment, or evaporative systems, is generally required (Booth et al. 1996). Unfortunately, activated carbon and certain advanced treatment processes, such as ozone or ultraviolet light, do not adequately address inorganics, and

membrane systems or air stripping merely transfer organics to another phase. Furthermore, multiple barrier systems are complicated to operate, costly, and generally inefficient. Unfortunately, most current processes cannot adequately address inorganics and organics simultaneously. 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.

So the question is: “Can we develop systems to treat landfill leachate at the source, cost effectively?”

If energized processes work as well in the field (at pilot scale) as they do in the laboratory, then the answer is “**yes,**” because energized processes are: 1) designed to use the power of sunlight, which is free and requires no additional energy input, 2) easy to operate because they just require sufficient contact time and do not rely on complex precipitation reactions or biochemical processes, 3) not subject to biological upsets because they are physico-chemical processes that create broad spectrum oxidants to remove aqueous contaminants, and 4) designed to avoid merely transferring the pollutant to another medium (i.e. air or sludge).

This research will address a major technological need for sustainable, economical options for routine leachate treatment and safe discharge to the environment by investigating energized processes, such as photochemical oxidation (which includes photochemical iron-mediated aeration, TiO_2 , and UV/peroxide). Two of these emerging technologies are currently being developed at FAU. These include: photochemical iron-mediated aeration (PIMA) and magnetic-photocatalytic oxidation. These new and innovative processes work by using ultraviolet light (energy from sunlight) to activate the surface of a semiconductor (i.e. titanium dioxide or metallic iron) to produce highly reactive substances derived from water. These reactive radicals rapidly destroy man-made organic chemicals, breaking them down into carbon dioxide, water, and innocuous salts. In addition, it has been discovered recently by a UM-FAU partnership (funded by HCSHWM) that these processes can also remove heavy metals and reduce nitrogen-containing constituents. Thus it may now be possible to eliminate impurities in water all at once using a single process.

1.4 ADVANCED OXIDATION TECHNOLOGIES

Advanced oxidation processes were defined by Glaze et al. (1987) as “near ambient temperature and pressure water treatment processes, which involve the generation of hydroxyl radicals in sufficient quantity to effect water purification.” An AOP can utilize ozone (O_3), hydrogen peroxide (H_2O_2), or other agents to oxidize the pollutants through the production of the hydroxyl radical (OH^\bullet), which is a powerful and indiscriminate oxidant. The hydroxyl radical has a relative oxidation power of 2.05 compared to 1.00 for chlorine. Table 6 summarizes the relative oxidation power of the species used in most AOPs. Within milliseconds (Peyton and Glaze 1988, cited by Fang et al. 2005), 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 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).

Table 6. Relative oxidation power of selected oxidizing species (Munter et al. 2001)

Oxidation Species		Relative Oxidation Power
Positively charged hole on titanium dioxide	(h^+)	2.35
Hydroxyl radical	(OH^\bullet)	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

Many different advanced oxidation processes exist. Some of these include a combination of ultraviolet light (UV), hydrogen peroxide (H_2O_2), and/or O_3 . AOPs can be accelerated by using catalysts such as iron species and/or TiO_2 . A partial list of commonly used AOPs is shown in Table 7.

Table 7: Partial List of Advanced Oxidation Processes (Andreozzi et al. 1999, Meeroff et al. 2008, Zhang et al. 2012)

Process	Type of Reaction
H_2O_2/Fe^{2+}	Fenton reaction
H_2O_2/Fe^{3+}	Fenton-like reaction
$H_2O_2/Fe^{2+/3+}/UV$	Photo assisted Fenton
H_2O_2/Fe^{3+} -oxalate/UV	Photo assisted Fenton w/ferrioxalate
$H_2O_2/Fe^{2+}/I$ (electric current)	Fered-Fenton method
$Mn^{2+}/O_3/Oxalic\ acid$	Manganese/Ozone/Oxalic acid
O_3/ H_2O_2	Ozone/Hydrogen Peroxide
H_2O_2/GAC	Hydrogen Peroxide/Granular Activated Carbon
O_3/UV	Ozone/Ultraviolet Light
H_2O_2/UV	Hydrogen Peroxide/Ultraviolet Light
Fe^{2+}/O_2	Iron Mediated Aeration (IMA)
$Fe^{2+}/O_2/UV$	Photochemical Iron Mediated Aeration (PIMA)
$TiO_2/UV/O_2$	Photocatalysis

Advanced oxidation processes can occur both with and without the addition of energy. If used as a pre-treatment step before a biological treatment, AOPs can reduce the detention time required for subsequent biological treatment (Kabra et al. 2004; Bila et al. 2005). Initial filtration or sedimentation is still often required as a pre-treatment step to remove solids that would interfere with the action of UV. One important drawback of AOPs is the high demand for electrical energy (e.g. ozone corona discharge generators, UV lamps, ultrasound, etc.), which increases cost (Lopez et al. 2004). Also, for complete mineralization of pollutants to occur, high oxidant doses may be required. Silva et al. (2004) needed 3.0 g/L of ozone to attain significant toxicity decrease. Furthermore, some intermediate oxidation byproducts generated by incomplete mineralization can increase the toxicity of leachate during treatment.

In the following discussion, the use of various advanced oxidation methods is reviewed with respect to COD, ammonia, and heavy metal removal efficiency.

1.4.1 COD Removal

AOPs have shown excellent results in the removal of COD from many types of wastewaters. A study done by Dincer et al. (2008), utilizing a continuously stirred batch reactor, compared the COD removal efficiencies of Fenton, photo Fenton and UV/ H_2O_2 processes in oil recovery industry wastewater. This high strength wastewater had an initial COD concentration of 21,000 mg/L. The Fenton oxidation process delivered 86%

removal of COD in one hour. The photo Fenton oxidation of the same wastewater exhibited 81% removal of COD. The UV/H₂O₂ had the lowest removal efficiency (39%) of the 3 processes, but nonetheless, removal was still recorded.

Mandal et al. (2010) attempted to optimize the Fenton process parameters (temperature, pH, FeSO₄ concentration and H₂O₂ concentration) for treatment of industrial wastewater. At FeSO₄ and H₂O₂ concentrations of 6 mg/L and 277.7 mg/L, respectively, 95% removal of the COD was achieved using a continuously stirred batch reactor. A study by Liu et al. (2012) showed the results of COD removal from waste activated sludge (WAS) using TiO₂ photocatalytic degradation. At the optimal catalyst value of 3 g/L the maximum COD degradation was 45% using a sloping trough circulating bed photocatalytic reactor (STCBPR). A schematic of the reactor is shown in Figure 1.

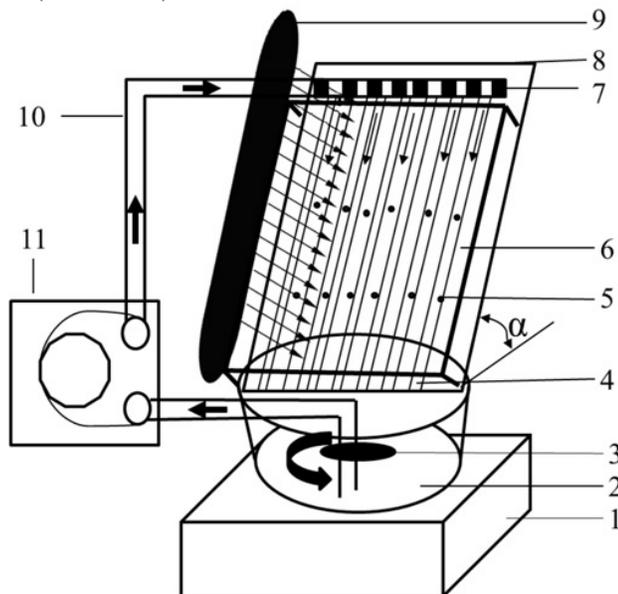


Figure 1. Schematic of sloping trough circulating bed reactor (Liu et. al 2012)

The addition of electrical current to the Fenton process increases the production of hydroxyl radicals and is called the Fered-Fenton method. Zhang et al. (2012) used this method to investigate its effects on the removal of COD from landfill leachate. The reactions were carried out in 0.8 L electrolytic Plexiglas batch reactors. The maximum COD removal efficiency achieved was 66.4% using concentrations of 0.438 mol/L and 0.037 mol/L of H₂O₂ and Fe²⁺, respectively.

Another study on the comparison of AOPs for COD degradation was performed by Naumczyk et al. (2012). The reactions were all carried out in 2-L batch reactors for 360 minutes. The raw leachate with an initial COD of 5000 – 6000 mg/L was subjected to 30 minutes of sedimentation prior to testing. They compared the COD removal efficiency of

the modified Fenton, modified photo-Fenton, H_2O_2/UV and O_3/H_2O_2 , which exhibited COD destruction at levels of 87.5, 89.9, 91.0 and 92.7%, respectively (Naumczyk et al. 2012). Investigation of the COD removal from wastewater reveals evidence that advanced oxidation processes can be efficient in their removal of refractory organics. Even though excellent COD removal was achieved, none of these studies reported any removal of ammonia in a leachate matrix simultaneously.

1.4.2 Ammonia Removal

Ammonia can also be removed from landfill leachate by means of advanced oxidation processes. Deng and Ezyske (2011) achieved 100% ammonia removal and 79% COD removal when testing the treatment of landfill leachate using a sulfate radical advanced oxidation process (SR-AOP). They tested multiple doses of persulfate and found that increased dose resulted in significantly higher levels of ammonia and COD degradation. When the persulfate concentration was increased from the minimum ($S_2O_8^{2-}:12COD_0 = 0.1$) to the maximum tested dose ($S_2O_8^{2-}:12COD_0 = 2.0$), the ammonia and COD removal increased from 23 – 100% and 39 – 91%, respectively, at the optimal temperature (50°C).

Abu Amr and Aziz (2012) performed comparative tests on the effectiveness of advanced oxidation using ozone, Fenton, Fenton followed by ozone, and the combination of Fenton and ozone simultaneously. The study reported removal rates for ammonia, COD and color ranging from 0 – 12%, 15 – 65%, and 27 – 98% removal, the least effective being ozone by itself and the most effective being Fenton and ozone together. Higher ammonia removal was achieved by Zhao et al. (2010) utilizing photoelectrochemical (PEC) oxidation, which combines the processes of electrolysis and photocatalysis. They tested landfill leachate in a 6.5-L capacity continuous flow reactor. Under the optimum conditions, the PEC process removed 94.5% of the ammonia, 74.1% of the COD and 41.6% of the TOC from the landfill leachate.

Sonolysis is another advanced oxidation process. In this case, ultrasound is utilized to generate hydroxyl radicals. Wenjun et al. (2012) tested the efficiency of combining sonolysis with H_2O_2 . The effect of various pH levels, ultrasonic power, and hydrogen peroxide concentrations were compared. At the optimum conditions, pH = 11, 1/1 minute intermittent ultrasonic application and 2% H_2O_2 , the ammonia reduction reached 90.4%. At the same conditions removal for COD, hydrazine and urea reached 68%, 60% and 25%, respectively.

1.4.3 Heavy Metal Removal

Dutta et al. (2004) studied arsenic removal from wastewater utilizing photocatalytic reactions with titanium dioxide. The removal efficiencies were tested at a pH range from

3 – 9 in a continuously stirred batch reactor. The study was based on two reactions: first, the oxidation of As(III) to As(V) and then the adsorption of As(V) onto the TiO₂. The tests were run until an adsorption equilibrium was established (2 – 3 hours) with 0.05 g/L TiO₂. It was found that adsorption of As(V) is much higher at pH 4.

Advanced oxidation processes also have been demonstrated to remove Cr(VI) from wastewater. Kebir et al. (2011) combined the process of photocatalysis with adsorption to remove Cr(VI) from water samples in a continuously stirred batch reactor. The advanced oxidation was found to reduce the Cr(VI) to the less harmful form, Cr(III) under optimum conditions (pH = 2, temperature = 25°C, and CuAl₂O₄/TiO₂ = 1/1), 58% of the Cr(VI) was removed from the waters in 2 hours using the coupled treatment processes.

Multiple heavy metals can be removed from wastewater using combined treatment processes. Vedrenne et al. (2012) showed this in their study on the treatment of landfill leachate by combining coagulation/flocculation with a photo-Fenton process. Arsenic, lead and mercury removal were all tested in the leachate samples. The combined treatment process achieved 85% removal of Pb, 47% removal of As and 9.1% removal of Hg. Although the mercury removal is low, it still demonstrates the promise of multiple contaminant removal of advanced oxidation processes.

Meeroff et al. (2012) performed batch scale studies of the removal of COD, ammonia, color and lead from simulated and actual landfill leachate utilizing AOPs. The first process evaluated was photochemical iron-mediated aeration (PIMA). The testing of the synthetic leachate achieved 45 – 60% removal of COD with starting concentrations ranging from 1000 – 10,900 mg/L. However, the removal of COD from the real leachate only reached 10% degradation. This was attributed to the high initial color (>500 PCU) interference of the real leachate. The lead concentrations in the simulated leachate were reduced below detectable limits within 16 hours. However, they found that removal of ammonia for the PIMA process was dependent on pH level and the ability for ammonia to escape the reactor. Once the proper adjustments were made, ammonia removal went from 2% to 29% in a 150-minute test. The PIMA process also demonstrated 88 – 98% removal of color in the real leachate. The second process tested was TiO₂ photocatalysis, which showed higher removal efficiencies for both COD and ammonia. The COD degradation in the simulated leachate reached levels of 94 – 99% removal, while the real leachate exhibited 55 – 86% removal. The photocatalysis showed 23 – 51% removal of ammonia in synthetic leachate and 71% ammonia eradication in the real leachate. The TiO₂ photocatalytic process exhibited >90% color removal in real leachate. Their study shows that these two advanced oxidation processes have the ability to destroy multiple constituents of landfill leachate in one treatment process at laboratory scale. The photocatalytic process showed the more promising results, which formed the basis of this study.

1.4.4 TiO₂ Photocatalytic Oxidation

The focus of this study is photocatalytic oxidation utilizing TiO₂/UV/O₂. The photocatalysis principle is based on the excitation of a metal semiconductor by photons to produce an electron-hole pair. This pair has a very powerful oxidation potential and should be able to oxidize almost any chemical. Titanium dioxide first became a popular photocatalyst of interest in 1972 when Fujishima and Honda discovered the photoelectrochemical reaction of TiO₂ combined with the power of UV light (Teh and Mohamed 2011). The process is thought to generate oxidants by the combined action of ultraviolet radiation and the titanium catalyst. Konaka et al. (1999) showed that the irradiation of the titanium dioxide generates both singlet oxygen and super oxide anion. Following this, Sturini et al. (2001) demonstrated the reaction pathways for photocatalyzed degradation of organics and their derivatives.

Titanium dioxide (TiO₂) is the naturally occurring oxide of titanium and is among the most widely used metal oxides in the industry for photocatalytic applications. Titanium dioxide is a noncombustible, white, crystalline powder. It is soluble in hydrochloric acid, alcohol, and nitric acid, as well as hot concentrated sulfuric acid, alkali or hydrogen fluoride (Department of Health and Human Services 2011). TiO₂ (CAS#13463-67-7) is purchased as a dry powder, and has a mild dust inhalation hazard (time weighted average inhalation exposure level threshold is 10 mg/m³). Its particle density is 3.8 g/cm³ and is insoluble in water. According to the material safety data sheet, TiO₂ is relatively benign with respect to ecotoxicity. In 2011, 1.47 million metric tons of TiO₂ pigment was produced in the United States and 6.55 million metric tons worldwide (USGS 2012). TiO₂ was rated as a Group 2B (possibly carcinogenic to humans) substance by the International Agency for Research on Cancer (IARC) in 2006. The health limitations on TiO₂ are only expressed for inhalation, there are none listed for ingestion (DHHS 2011). Furthermore, no adverse effects have been measured to fish, daphnia, or bacteria in ecotoxicological studies. The material is extensively used in products such as paints and varnishes, floor coverings, roofing granules, sunscreens and cosmetics, printer inks, ceramics, plastics, paper coatings, pigments used in numerous foods, toothpastes, medicines, dielectric mirrors and tattoo pigments (Department of Health and Human Services 2011). The cost of a 22 lb bag of titanium dioxide (Figure 2) is around \$600.

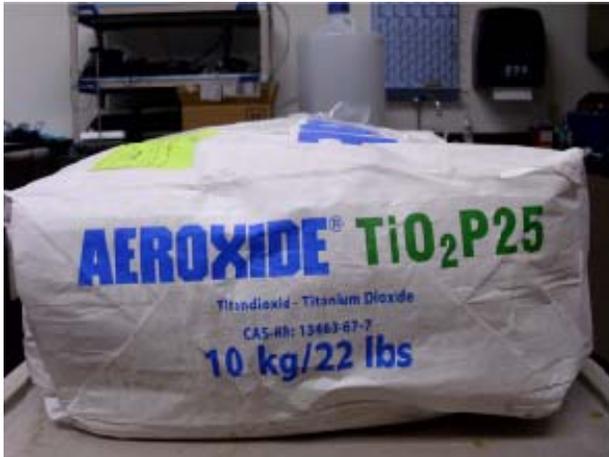


Figure 2. Photograph of 22 lb bag of titanium dioxide P25 photocatalyst.

TiO₂ particles generate strong oxidizing power when illuminated with UV light at wavelengths less than 400 nm. Irradiation of TiO₂ with photons of light energy produce areas of positive charge in the valence band of the semiconductor (“holes”) and free electrons in the conduction 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•) and superoxide radical (O₂•⁻). For photocatalysis to occur, electron “holes” must migrate to the surface of the TiO₂ 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 TiO₂ photocatalysts can decompose organic compounds by participating in a series of mineralization reactions (Rincon and Pulgarin 2005).

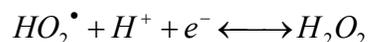
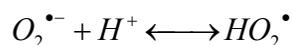
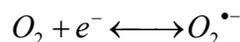
Chong et al. (2010) explained that the oxidative and reductive reactions from titanium dioxide are due to its unique characteristic of possessing a lone electron in its outer orbital. The reaction process begins when UV light energy photoexcites that lone outer shell electron, which creates an empty outer valence band. The reaction process steps are shown in Table 8.

Table 8: Chain of oxidative-reductive reactions that occur at the UV activated TiO₂ surface (Chong et al. 2010)

Step	Process	Formula
1	Photoexcitation	$TiO_2 + h\nu \rightarrow e^- + h^+$
2	Charge-carrier trapping of e^-	$e^-_{CB} \rightarrow e^-_{TR}$
3	Charge-carrier trapping of h^+	$h^+_{VB} \rightarrow h^+_{TR}$
4	Electron-hole recombination	$e^-_{TR} + h^+_{VB} (h^+_{TR}) \rightarrow e + \text{heat}$
5	Photoexcited e^- scavenging	$(O_2)_{ads} + e^- \rightarrow O_2^{\bullet-}$
6	Oxidation of hydroxyls	$OH^- + h^+ \rightarrow OH^\bullet$
7	Photodegradation by OH^\bullet	$R-H + OH^\bullet \rightarrow R^\bullet + H_2O$
8	Direct photoholes	$R + h^+ \rightarrow R^{\bullet+} \rightarrow \text{Intermediate(s)/Final Products}$
9	Protonation of superoxides	$O_2^{\bullet-} + OH^\bullet \rightarrow HOO^\bullet$
10	Co-scavenging of e^-	$HOO^\bullet + e^- \rightarrow HO_2^-$
11	Formation of H_2O_2	$HO_2^- + H^+ \rightarrow H_2O_2$

CB = conduction band, VB = valence band, TR = surface trapped

According to Munter et al. (2001), the presence of dissolved oxygen is necessary for this reaction to take place. It prevents the recombination of the electron-hole pair, while producing H_2O_2 in the process:



The hydrogen peroxide is then free to combine with dissolved ferrous iron for a Fenton reaction or to break down into hydroxyl radicals for secondary oxidations.

Another important precursor to these set of reactions is the absolute necessity of water molecules, without which, hydroxyl radicals could not be created. The formation of not only hydroxyl radicals, but also the superoxide anions ($O_2^{\bullet-}$) contributes to the formation of hydrogen peroxide. The combination of these two strong oxidants generates a series of mineralization reactions geared toward the destruction of organic contaminants. Chong et al. (2010) simply represented the overall photocatalysis reaction with the following equation:



The organic compounds are mineralized to carbon dioxide and water, given enough irradiation time. A basic visual representation of the photocatalytic mechanism can be

seen in Figure 3, which demonstrates the process that occurs when light energy irradiates TiO₂ particles. The illumination ejects electrons from the valence band resulting in a positively charged area with “holes” (h⁺). These holes primarily react with water molecules to generate hydroxyl radicals, thus creating the dominant destructive component of the photocatalytic process. The free electrons jump to the conduction band where they can react with oxygen molecules in the water to form superoxide radical anions.

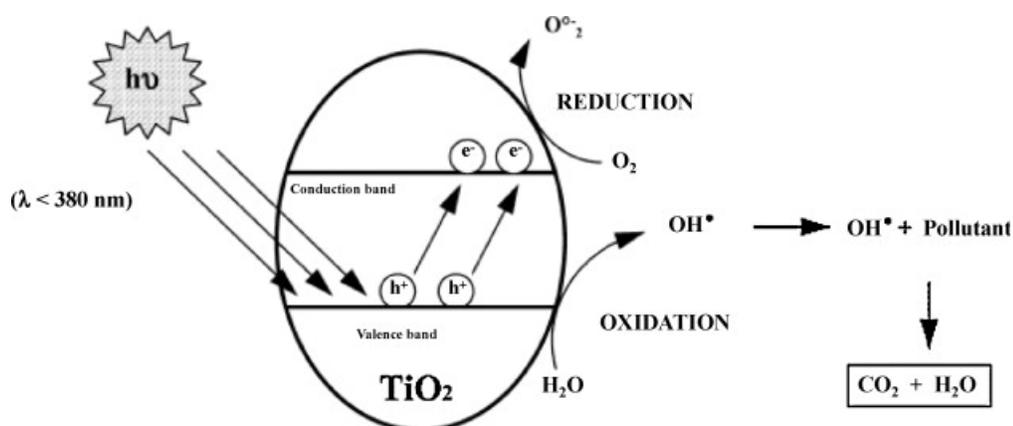
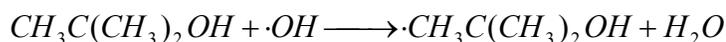


Figure 3: Generalized process of photocatalytic oxidation (Ghaly et al. 2011)

As explained earlier, the photocatalytic process is an array of multi-step reactions (Table 8). The ability of TiO₂ photocatalyst to mineralize such a wide range of pollutants is an attractive quality, but modeling the kinetics of such a complicated process is a difficult 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). This is why few reviews are found focusing on the kinetics studies of photocatalytic systems.

Due to the complexity of the reaction mechanism, most kinetics evaluations in photocatalytic studies focus on the overall kinetics of the degradation of a certain pollutant. The photocatalytic breakdown of any particular pollutant takes place in a system of reactions (Valencia et al. 2011). Some reactions in the overall mechanism may occur simultaneously and at different rates. The kinetics can only be modeled to the overall combination of these processes, even though some of the elementary steps in the reaction may compete with each other to inhibit the photodecomposition. The TiO₂ photocatalyst simply plays a role in initiating the array of reactions; TiO₂ is not in itself a reactant, no matter the overall reaction order that is observed (Helali et al. 2013). Also, in the case of COD, multiple hydroxyl radical reactions are required to mineralize organic

material depending on the complexity of the molecule. The initial hydroxyl radical reaction for the destruction of a relatively simple *t*-butanol molecule is as follows:



The initial reaction of one molecule of *t*-butanol with one molecule of hydroxyl radical produces an organic radical, which still registers as COD. After a number of hydroxyl radical attacks, among other reactions, the organic compound eventually will degrade to CO₂ and H₂O.



When kinetics are monitored for the destruction of COD, only the final mineralization is measured (Wang and Xu 2012). So, for the purpose of this study, all the kinetics implications within are referring to the overall reaction kinetics, since the true reaction processes are too complex, too numerous, and too unknown to model with any degree of accuracy or certainty.

1.4.4.1. TiO₂ Photocatalysis Treatment Performance Studies

As explained earlier, the generation of mixed radicals in the photocatalytic process makes it possible to decompose an array of contaminants. There are many different process configurations that have been tested in the literature. These include continuously stirred batch reactors, continuous flow batch reactors, thin film fixed bed reactors, falling film reactors, sloping trough circulating bed photocatalytic reactors and recirculating parabola cylindrical concentrator solar photoreactors. Some variations adjust the pH, or add hydrogen peroxide, ozone, or oxygen. A literature review of photocatalytic alternatives for detoxification and treatment of leachate revealed that several researchers have investigated a wide range of other photocatalytic techniques such as: fluidized bed photocatalysis (Kanki et al. 2005; Kostedt and Mazyck 2006; Mazyck et al. 2004), photocatalytic detoxification with thin film fixed bed reactors (Bekbölet et al. 1996), fixed film spinning discs (Yatmaz et al. 2001), fixed film slurry reactors (Toor et al. 2006), plug flow fixed film reactors (Grzechulska and Morawski 2003), and a process similar to the one investigated here, which utilizes fine particles suspended in solution in a batch-type treatment process (Cho et al. 2002).

The simultaneous photocatalytic degradation of COD, dissolved organic carbon (DOC) and color in landfill leachate was demonstrated by Jia et al. (2013). They designed a continuous flow batch reactor which ran at 1.5 L/min, and all experiments were run for

72 hours, sampled at 6-hour intervals. Multiple catalyst dosages were tested from 0.0 – 4.0 g/L, with 2.0 g/L being the optimal value for COD removal and 3.0 g/L for color removal. At a pH of 4.0 and TiO₂ concentration of 2.0 g/L, 60% of the COD was mineralized, 72% of the DOC was eliminated and 97% of the color was removed. Vineetha et al. (2012) used TiO₂ photocatalysis to treat highly concentrated effluent with a continuously stirred batch reactor. They reported a removal of 32% of COD and 84% of color from the wastewater at a catalyst dosage of 0.2 g/L and pH 6. To accelerate the hydroxyl radical production, H₂O₂ (0.3 M) was added to the mix.

Specific organic oxygenates were targeted using photocatalytic oxidation with TiO₂ in a falling film reactor, similar to the system pilot tested in this study. The TiO₂/UV/O₂ process was compared to photocatalytic ozonation (TiO₂/UV/O₃) for the removal of Methyl Tertiary Butyl Ether (MTBE), Ethyl Tert-Butyl Ether (ETBE), Tertiary Amyl Ethyl Ether (TAAE) and Tert-Butyl Alcohol (TBA). The experiment used a flow rate of 0.1 L/min and a UV intensity of 1.0 mW/cm² at a pH of 6-7. The photocatalytic ozonation outperformed the photocatalytic oxidation by removing nearly all contaminants from the solutions within 20 minutes. The TiO₂/UV/O₂ process managed to remove 100% of ETBE and TAAE, 88% of MTBE and 82% of TBA within 50 minutes of treatment (Mehrjouei et al. 2012). However, these tests were not conducted with landfill leachates and organic oxygenates are relatively rare in the landfill leachate matrix.

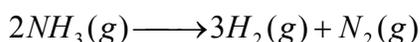
Chemlal (2013) treated landfill leachate using TiO₂ photocatalysis with a 3-L Thin Film Fixed Bed Reactor (TFBR), in which the catalyst is fixed onto a sheet that is illuminated, and the contaminated water passes over it. During the testing, the glass reactor plate was illuminated by three UV-C 15W lamps for 30 – 54 hours. For the leachate containing initial concentrations of 26,000 – 30,000 mg/L COD, pH variations influenced the COD removal from 76 – 92%, with the optimal pH value being 5 (Chemlal 2013).

Another application of photocatalytic oxidation is for mineralizing the organic toxins produced by cyanobacteria. Shephard et al. (2002) utilized a falling film reactor with a fixed sheet impregnated with TiO₂. A total of twelve 15W UV lamps were used to create a 204.5 W/m² UV intensity. The tests were run for 20 minutes. The microcystin degradation was 77–84% in 20 minutes, when spiked in natural lake water. The additional natural organic material and inorganic ions from the lake water, competed for photoactivation reaction sites with the contaminants of concern, compared to removal rates in distilled water controls (87% in 8-10 minutes).

Hapeshi et al. (2010) studied the photocatalytic degradation of the antibiotic ofloxacin and the β-blocker atenolol. They tested six commercially available TiO₂ products. At a 30-minute irradiation time, the Degussa P25 outperformed the other five catalysts by removing 85% of the ofloxacin and 67% of the atenolol. After 240 minutes of UV

illumination, both the Degussa P25 and Hombikat UV 100 destroyed nearly 100% of the ofloxacin (Hapeshi et al. 2010).

Photocatalytic processes for destruction of organics via the hydroxyl radical oxidation pathway are well known; however, recently the destruction of certain nitrogen-containing organic pollutants through a reductive pathway has been reported (Schmelling et al. 1996). TiO₂ photolysis can also be used as a means to degrade ammonia from wastewater. The photocatalytic process can be used to provide the energy necessary for the conversion of ammonia to hydrogen gas and nitrogen gas, as follows:



The equation shows that 2 moles of ammonia can be converted to 3 moles of hydrogen gas and 1 mole of nitrogen gas. Kominami et al. (2012) tested the formation of H₂ from the photocatalytic destruction of NH₃. After 30 hours of irradiation, elevated levels of H₂ (160 μmol) were detected when compared to the initial 107 μmol of NH₃. This 3:2 molar ratio satisfies the above equation and is an indication of stoichiometric conversion of ammonia (Kominami et al. 2012). Utilizing a 1.1-L batch scale photo-reactor and 0.1 g/L TiO₂, 56% ammonia removal was observed (C₀ = 1,250 mg/L NH₃). The study had tested the photocatalytic degradation of ammonia in manure as well and found that although some pretreatment was necessary, 88% of the ammonia was removed. It was also noted that the photocatalysis of the manure samples removed the odor as well (Altomare et al. 2012).

With regards to certain heavy metals and metallic oxyanions, TiO₂ photocatalysis has also demonstrated some success. Since TiO₂ is a metal oxide with a high sorption capacity, it can adsorb various arsenic species, namely As(V) and As(III). Jegadeesan et al. (2010) tested TiO₂ sorption capacities for arsenic in batch solutions, at a pH range of 3 – 11 for 72 hours. They observed TiO₂ sorption capacities for As(III) and As(V) to range from 146 – 392 μg/m² and 46 – 201 μg/m², respectively. The TiO₂ photocatalytic process also oxidizes the more toxic As(V) to As(III) (Jegadeesan et al. 2010). The ability to remove lead (Pb) from wastewater using TiO₂ photocatalytic oxidation was discussed earlier (Meeroff et al. 2012). In addition, Vohra and Davis (2000) measured nearly 70% removal of lead at circumneutral pH after 50–70 minutes of treatment, which indicated that adsorption of intermediate complexes containing organically bound inorganics by TiO₂ particles can occur. The removal of Cr(IV) was also recently studied by Wang et al. (2013) utilizing TiO₂ photosensitized reduction. An amorphous TiO₂ was prepared and compared to the efficiency of Degussa P25 TiO₂. The amorphous TiO₂ outperformed the Degussa P25 in the removal of Cr(IV), showing removal efficiencies of 53.5% compared to 42.1% (Wang et al. 2013). The photocatalytic reduction of copper and selenium was studied by Aman et al. (2011) while testing the efficiencies of various photocatalysts:

TiO₂, TiSi and TiZr. Under visible light, the TiZr outperformed the Degussa P25 TiO₂ by removing 87% and 75% of Se and Cu, respectively, compared to TiO₂'s respective removal of 26% and 22% for Se and Cu. However, under UV light, the Degussa P25 outperformed the synthesized TiZr by removing 91% and 82% Se and Cu, respectively, compared to TiZn's respective removal of 87% and 77% (Aman et al. 2011). Hilmi et al. (1999) used glass plates coated with immobilized TiO₂ to remove mercury, lead, copper, and cadmium from aqueous solutions containing individual metals and mixtures. In those tests, individual metals at concentrations of 1.0 to 5.2 mg/L were reduced to undetectable levels in less than one hour of treatment. Bekbölet et al. (1996) performed experiments with leachate but were not very successful using a thin film fixed bed reactor. They achieved only 3% TOC reduction with 5 g/L Degussa P25, but at pH < 3-5, they increased removal to 4%. They found that when inorganic salts were present, degradation was inhibited and recommended that at high concentration levels, dilution with recirculation of treated wastewater would be beneficial compared to a single pass system.

The effect of pH in this process has not been fully investigated yet, but when protonated, the photocatalyst forms the hydroperoxyl radical, which may also bind to absorbed substrates and may undergo hydrogenation by intermediates thus leading to irreversible oxidation. Several researchers report success with acidic waste streams (pH < 4.5) (Bekbölet et al. 1996; Cho, Hong, and Hong 2002; Toor et al. 2006). In a case study of the end point of photocatalytic degradation of landfill leachate containing refractory matter (Cho, Hong, and Hong 2002), 52% COD removal and 79% TOC removal was found after 5 hours, and 56% COD removal and 88% TOC removal after 10 hours, with an initial pH of 3.1. On the other hand, with initial pH of 6.5-7.0, TiO₂ photocatalytic processes have also been demonstrated to achieve 99% removal efficiency of phenol in 160 minutes with irradiation of 254 nm (Ilisz et al. 2002). Pantelis et. al (2006) found that textile effluent degradation was enhanced under acidic conditions (i.e. pH = 3) and in the presence of hydrogen peroxide. The TiO₂ suspensions were capable of decolorizing the effluent completely, as well as reducing the COD from 40-90% in just after 4 hours of treatment, depending on the operating conditions. The extent of photocatalytic degradation was also found to increase with increasing TiO₂ concentration up to 0.5 g/L, above which degradation remained fairly constant, reaching a plateau.

Toor et al. (2006) reported a concentration-dependence in their experiments, which suggests that if the surface per unit volume ratio can be increased, then the process can possibly achieve higher removal efficiencies. This means that the particle size must decrease. Cho and co-workers tested Degussa P25 TiO₂ particles with a diameter of 20 nm (2002). The trend has been towards developing smaller particle sizes in the nanometer range. This can be done by carefully controlling the calcination temperature. The tradeoff is that the particles have lower purity but can be much smaller in diameter by decreasing

particle agglomeration, which occurs readily at higher temperatures. Since suspended TiO₂ catalysts enjoy free contact with UV irradiation in an aqueous photoreactor, they would be expected to achieve higher levels of efficiency compared to immobilized TiO₂ catalysts. However, the separation and reuse of suspended catalyst powders from treated water often limits this application in practice, particularly as the diameter of the photocatalyst decreases. To retrieve the used photocatalyst (i.e. Degussa P25), two primary options have been used by investigators: 1) vacuum filtration with a 0.2 μm nitrocellulose membrane filter (or similar) type of setup, or 2) centrifugation of the treated liquid at very high speeds to separate the particles. If vacuum filtration is used, once recovered on the filter, according to Kostedt (personal communication July 2007), it is possible to dry the catalyst at 105°C and re-use the catalyst. In the field, this could be accomplished using exhaust heat from waste-to-energy plants.

In the applications research community, there is a general consensus that Degussa P-25 TiO₂ gives better degradation efficiency compared to other forms, such as anatase, rutile, and brookite (Reeves et al. 1992; Yamazaki et al. 2001; Thiruvengkatachari et al. 2008). The effect of particle size on the photocatalytic activity is generally related to surface area (anatase=10m²/g, rutile=20m²/g, Degussa P25=50m²/g). Generally, smaller particle sizes mean larger surface areas and higher expected photoactivities. This can be explained in terms of an increase in the number of photoactive sites per square meter, as well as greater number of adsorption sites on the catalyst surface.

Cho, Hong, and Hong (2002) also investigated photocatalytic degradation of landfill leachate. In these tests, suspended Degussa P25 (70% anatase) was used (diameter = 20 nm). Photodegradation of refractory and nitrogen-containing substances was favored under acidic conditions (pH_{optimal} = 4.0). Degradation increased with photocatalyst concentration until 8000 mg/L. Photocatalyst particles in these experiments were removed after treatment using 3000 rpm centrifuge for 20 minutes and washed with deionized water and dried for 24 hours at 103°C and by filtration with a GF/C filter. The same researchers (Cho, Hong, and Hong 2004) continued this work and reported 52% COD removal and 79% TOC removal after 5 hours at pH = 4.0 with a photocatalyst dose of 3.0 g/L in a continuously stirred aerated quartz tube reactor at λ = 254 nm. Under these conditions, 20% of the TOC was found to adsorb onto the photocatalyst particles after just one hour of treatment. And the pH was found to increase from 4.5 to 5.3 in the same period of time. Doubling the reaction time to 10 hours increased removal only slightly to 56% for COD and 88% for TOC.

When UV/TiO₂ was used for treatment of leachate with BOD₅/COD <0.05, 80% removal of COD was achieved (Deng and Englehardt 2007). Deep color in wastewaters such as landfill leachate can significantly impede the transmission of light (including UV) through the solution, so photo-efficiency is reduced and fewer radicals are produced.

However, the process may only be able to oxidize the color, if it is organic in origin. In summary, the application of photocatalytic technology has been shown to be successful in removal of organics, inorganics, nitrogen-containing compounds, and even pathogen indicators. A summary of published research focusing on COD removal using photocatalysis is listed in Table 9. However, to our knowledge, the process has not been demonstrated at field scale for treatment of highly variable, high strength wastewaters, such as those characteristic of landfill leachate.

Table 9. Summary of COD removal performance tests conducted with photocatalytic oxidation technologies.

Water Type	TiO ₂ Dose (g/L)	UV (W)	COD ₀ (mg/L)	pH	Removal (%)	Time (min)	Reference
Grey 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. 2002
Industrial wastewater	0.6	6 x 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
Industrial wastewater	4 plates immobilized	4 x 4 W	120 (TOC)	9.0	34	30	Nakamura et al. 2008
Industrial wastewater	1.0	415 W	135	8.0	22 (diluted 1:100 + filtered)	1440	El Hajjouji et al. 2008
Industrial wastewater	0.5	400 W	404	3.0	40	240	Pekakis et al. 2006
Landfill leachate	5.0 (batch) immobilized	16 x 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
Industrial wastewater	3.0	7.6 W/m ²	20,000	6.8	36.3	1440	Baransi et al. 2012

Water Type	TiO ₂ Dose (g/L)	UV (W)	COD ₀ (mg/L)	pH	Removal (%)	Time (min)	Reference
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	0.2	Solar radiation	500	6	32	240	Vineetha et al. 2012

Cho et al. (2004 Cho, S.P., Hong, S.C., Hong, S.I.) investigated the photocatalytic degradation of landfill leachate using TiO₂ and Fe(III). They used a solid by-product obtained from the titanium dioxide production industry as their photocatalyst. This material contained 68–70% TiO₂ and the rest was Fe(III). They ran the process under UV radiation at a maximum emission wavelength of 365 nm for catalyst loadings of 1 and 2 g/L. Under these conditions, they obtained an additional TOC removal of 24–25% (Cho et. al 2003). In trying different techniques to improve the process efficiency, Nakamura et al. (2008) pioneered the use of O₃ and TiO₂ photocatalysis. They showed that treatment of aromatic ring compounds: 2,4-dichlorophenoxy acetic acid (2,4-D), 2,4,5-trichlorophenoxy acetic acid (2,4,5-T), and bisphenol A, was an effective method for decreasing the TOC in artificial seawater. After 50 hours of reaction time, they reduced the concentrations by a factor of 3-5 (Nakamura et. al 2008).

El Hajjouji et al. (2008) investigated a similar process at laboratory scale for treating olive mill wastewater effluent. COD, UV₃₃₀, and phenols all showed decreases which, after 24 hours of treatment, reached 22%, 57% and 94%, respectively. The differences between these three values indicated the persistence of colorless, non-phenolic compounds (El Hajjouji et. al 2008). Merabet et al. (2009) investigated the photocatalytic degradation of indole using a recirculating reactor. The effects of various factors such as initial concentration, catalyst-loading, pH, agitation and flow rate on the photodegradation rate were examined. At an optimal pH of about 6–7, the effect of catalyst loading shows an optimal value of 1 g/L at an initial concentration of 10-40 mg/L indole. They also found out that the increase of recirculation rate led to a decrease of degradation rate due to the reduction of the residence time. In addition, the agitation speed was found to only have a slight influence on the indole degradation by improving the mass transfer step (Merabet et al. 2009).

Further research with advanced oxidation of TiO_2 needs to be conducted on landfill leachate at pilot or full scale to provide the missing data that will allow more widespread adoption of this promising technology. The treatments described in Table 9 are currently not sufficient to reach the level of purification needed to fully reduce the negative impact of landfill leachate on the environment. From current research, in order for photocatalysis with titanium dioxide to be effective, a neutral pH is required. Sodium bicarbonate can be used to help neutralize acidic or basic leachates. However, bicarbonate may also have photo-sensitizing properties. As you can see in Figure 4, alkalinity is needed to initiate the reaction for COD removal. When no alkalinity is present there is essentially no removal of COD in simulated leachate. However when 4333 mg/L as CaCO_3 is added, nearly 100 percent of the COD is removed.

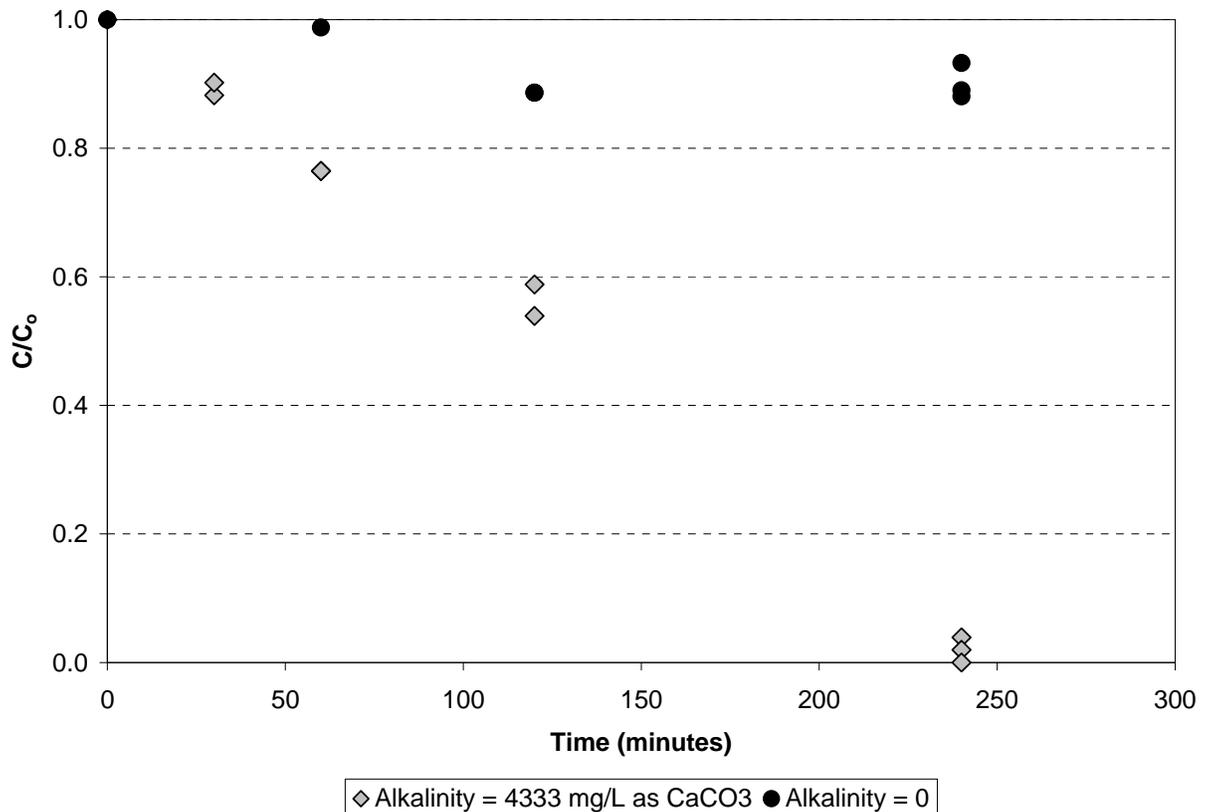


Figure 4. Removal of COD from simulated leachate with and without alkalinity.

1.4.4.2. pH Effects

The degradation kinetics for photocatalytic processes are affected by pH (Ghaly et al. 2011, Chong et al. 2010, Nemoto et al. 2007). More specifically, the process removal efficiency is reported to improve with decreasing pH. The surface charge plays a role in the adsorption and desorption processes between the contaminant molecule and the catalyst. The point of zero charge for TiO₂ is between pH = 5.6 – 6.4 (Chemlal et al. 2013). Below that range results in a positive charge on the catalyst surface, and above that range results in a negative surface charge. The pH can also change the structure of a target pollutant, thereby affecting its interaction with the catalyst. For example, at low pH conditions, higher COD degradation is reported, while a high pH increases the destruction of ammonia (Chemlal 2013). Rocha et al. (2011) studied this phenomenon by comparing the photocatalytic degradation of leachate with and without pH adjustment. The study found that reducing the landfill leachate to a pH of 4 gave 10 times the degradation of DOC compared to the samples that were not adjusted. Hapeshi et al. (2010) also tested the effect of pH on TiO₂ photodegradation from pH = 3 – 10. The results showed that an increase in pH led to a decrease in the degradation kinetics for atenolol (an organic beta blocker used to treat hypertension). At pH values of 3, 6 and 10 the first order degradation rate constant decreased from 1.49 to 1.24 to 0.95 min⁻¹, respectively. Nemoto et al. (2007) studied the pH effect on the photodecomposition of ammonia and found only minimal destruction at pH values below 9 and maximum pollutant breakdown at pH 11. Helali et al. (2013) reported that the photocatalytic decay of methylamine, like ammonia, proved to be more efficient at higher pH values (pH = 11.7). Meeroff et al. also reported similar findings (2012).

1.4.4.3. Catalyst Poisoning

One serious drawback of TiO₂ is the possible deactivation of the catalyst due to adsorption of partially oxidized intermediates on the catalyst surface, thus changing the effective shape of the TiO₂ particle itself (Carneiro et al. 2010). Gandhi et al. (2012) tested the regeneration of spent Degussa P25 from the photocatalytic degradation of phthalic acid by using three notably prominent regeneration techniques: washing with methanol, thermal treatment, and treating with hydrogen peroxide. The spent TiO₂ was collected and the samples were regenerated using the three different methods and subsequently reused. Within 40 minutes, the new TiO₂ degraded >99% of the phthalic acid. The spent catalyst was used again in a second cycle which resulted in 49% removal of the contaminant. The second cycle using regenerated TiO₂ via the wash method, thermal treatment, and H₂O₂ treatment showed 55%, 87%, and 99% degradation,

respectively. The third cycle showed lower degradation for the wash method and thermal treatment, while the H₂O₂ treatment exhibited similar removal to fresh leachate. The change in the degradation rate constants from the different regeneration methods and their cycles can be seen in Table 10. The full regeneration of the catalyst was achieved by treating the spent TiO₂ with a 30% hydrogen peroxide solution (10-mL per gram of catalyst) for a one hour period. This shows that the life of the catalyst can be extended through multiple uses by chemical desorption or surface oxidation pathways.

Table 10: Rate constant comparison of fresh and regenerated catalysts for the photocatalytic oxidation of phthalic acid (Gandhi et al. 2012)

Catalyst	Rate Constant (min ⁻¹)	
	2 nd Cycle	3 rd Cycle
Fresh catalyst	0.104	
Regenerated catalyst using wash method	0.021	0.014
Regenerated catalyst using thermal treatment	0.048	0.044
Regenerated catalyst using H ₂ O ₂ treatment	0.103	0.099

The reuse of TiO₂ catalyst not only depends on the regeneration, but also on the recovery efficiency. Suryaman and Hasegawa (2010) studied the reuse of recovered TiO₂ in the treatment of various chlorophenols in water. The recovery method involved simple sedimentation of the catalyst after each run was performed. They discovered that using tap water instead of deionized water led to higher coagulation of TiO₂ particles which delivered greater catalyst settling for reuse, but resulted in lower degradation efficiency of the catalyst. The additional electrolytes in the tap water neutralized charged species on the catalyst surface and diminished repulsion. The study showed that the settled catalyst particles were used at least 3 times before any drop in efficiency was noted. Another study confirmed the theory of pollutant adsorption being the primary inhibitor of TiO₂, but also found that an increase in alkalinity also plays an inhibitory role. The carbonates, just like the NOM, act as competing OH[•] scavengers. Also, the excess alkalinity in the water led to the formation of large TiO₂ aggregates, which would lower efficiency due to surface area to volume ratio changes but also improve sedimentation recovery due to larger effective particle diameter. The destruction of metaldehyde using UV/TiO₂ dropped from 93% to 45% in the presence of alkalinity, even though the presence of organics in the matrix had no effect on the degradation rate (Autin et al. 2013). However, this is contradicted by Meeroff and McBarnette (2011), which found that complete mineralization of KHP in laboratory tests required alkalinity to initiate the process.

1.4.4.4. Process Modifications

Recent studies focus on the combination of processes to enhance contaminant degradation. Selvam et al. (2007) combined the Fenton reaction with TiO₂ photocatalysis, utilizing a UV/ferrioxalate/H₂O₂/TiO₂ process. Within 10 minutes of reaction 93% decolorization and 60.0% degradation of reactive orange 4 was observed. The TiO₂ photocatalysis alone resulted in 22% decolorization and 9.7% degradation and the solo ferrioxalate process exhibited 9.7% and 2.8%, respectively (Selvam et al. 2007). Potassium persulfate (K₂S₂O₈), which promotes the production of sulfate radicals, can potentially increase the concentration of oxidants in the matrix. Hazime et al. (2013) tested this additive on the removal of imazalil. Without the potassium persulfate the photocatalytic process took 21 minutes to degrade 90% of the contaminant. The addition of K₂S₂O₈ brought the reaction time down 5 minutes for 90% pollutant destruction. The process of photocatalysis in the presence of TiO₂ was studied by Ghaly et al. (2011). The study focused on the removal of COD in highly polluted paper mill wastewater. A catalyst loading experiment was performed with samples ranging from 0.25 to 1.5 g/L with a resulting optimum catalyst load of 0.75 g/L. Using the optimum amount of catalyst, the effects of pH were tested in four samples at a range of 3 – 10 pH units. The final series of tests dealt with the investigation of additional hydrogen peroxide concentration. The experiments were conducted with four samples, utilizing the optimum TiO₂ value (0.75 g/L), pH of 6.5 and the addition of varying volumes of hydrogen peroxide: from 1 – 4 ml/L. The concentration of hydrogen peroxide addition resulted in COD removal efficiencies ranging from 62.0% - 77.9%, with 2 ml/L being the optimum amount. One final note in this experiment was that the reaction was deemed to obey pseudo-first-order kinetics. The results of the testing are shown in Table 11.

Table 11: Summary of experimental data in treatment of paper mill wastewater with photocatalytic oxidation(Ghaly et al. 2011)

Catalyst loading (g/L)	pH	Solar radiation	H ₂ O ₂ (ml/L)	k ₀ (min ⁻¹)	φ180(%)
0	6.5	+	0	0.0003	4.70
0.75	6.5	-	0	0.0007	12.0
0.75	6.5	+	0	0.0066	70.5
0.25	6.5	+	0	0.0036	46.3
0.50	6.5	+	0	0.0043	55.1
1.00	6.5	+	0	0.0060	67.3
1.25	6.5	+	0	0.0049	57.5
1.50	6.5	+	0	0.0038	48.4
0.75	3.0	+	0	0.0032	43.1
0.75	5.0	+	0	0.0039	50.6
0.75	8.0	+	0	0.0068	72.1

Catalyst loading (g/L)	pH	Solar radiation	H ₂ O ₂ (ml/L)	k ₀ (min ⁻¹)	φ180(%)
0.75	10	+	0	0.0076	74.7
0.75	6.5	+	1	0.0073	73.9
0.75	6.5	+	2	0.0087	77.9
0.75	6.5	+	3	0.0065	68.0
0.75	6.5	+	4	0.0053	62.0

k₀ is the pseudo-first-order reaction rate constants in min⁻¹

φ180 is the efficiencies of %COD removals within 180-minute reaction time

+ means with or in the presence of

- means without

Chemical additives show some promise for the enhancement of photocatalytic oxidation process removal efficiency, but further research needs to be performed on the basic TiO₂ process before enhancements should be made. Again, one of the most attractive features of the TiO₂ photocatalyst is its potential economic efficiency.

1.5 PROBLEM STATEMENT

Current and proposed leachate management options have been discussed extensively (Meeroff and Teegavarapu 2010). From biological to physical-chemical processes to advanced oxidation and energized processes, it seems that each technology has its limitations due to the complexity of the leachate composition and the variability in volumes generated. Regardless of the disposal option, the nature of the leachate waste stream is such that some form of biological treatment is more than likely required. However, biological treatment is not suitable for removal of bio-toxics from water. Thus polishing steps, such as activated carbon adsorption, membrane processing, air stripping, or chemical addition may be necessary. Multiple barrier approaches are complicated to operate, costly, and generally inefficient. Unfortunately, activated carbon and certain advanced treatment processes (i.e. O₃) do not adequately address inorganics, while membrane systems or air stripping merely transfer organics to another phase. Catalytic and photochemical processes may be needed to address these concerns.

More and more offsite wastewater treatment facilities are indicating that they will not accept leachate from sanitary landfills because of the high concentrations of ammonia or COD or other site-specific contaminants (such as boron or arsenic, for instance). Leachate, with high levels of certain biotoxic constituents, will upset the biological wastewater treatment process, particularly in smaller facilities. These facilities are setting fees at such high rates to discourage the discharge of leachate, and since the price of fuel is already high, the alternative of leachate hauling is also becoming less attractive.

Furthermore, if regulations to require advanced treatment of wastewater discharged to deep injection wells get promulgated, this option may require pretreatment to become cost-competitive. Therefore, reliable low cost, low-tech processes are needed for on-site treatment of landfill leachate. This proposal addresses those needs.

1.6 OBJECTIVES

The main purpose of this study is to test UV/TiO₂ photocatalytic degradation of selected pollutants (COD, ammonia, alkalinity, and color) in landfill leachate using a pilot scale falling film reactor. It is hypothesized that the degradation rate of the contaminants will follow overall (pseudo) first-order reaction kinetics. The primary objective of this study is to determine an optimum dosage of catalyst using a falling film reactor without the use of any pretreatment or chemical addition methods. For the pilot tests, the reactor was designed to collect performance data with respect to process flow rates, air injection, mixing conditions, exposure time, degradation rates, catalyst dose, pretreatment requirements, and operational conditions. The secondary objective is to determine the collection efficiency of filter bags used to recover the catalyst once the leachate has been through the treatment process. This report tackles the major technological need for addressing the safe disposal of leachate by bringing sustainable, economical options for routine leachate management into the hands of the end users in the solid waste management industry.

2. METHODOLOGY

2.1 INFORMATION COMPILATION

FAU conducted an extensive literature review of government publications, empirical studies, textbooks, industry reports, journal articles, current legislation, and government/association web sites, information gathered from site visits/interviews, and the technical literature. For this task, input from the Technical Advisory Group (TAG) was solicited to make sure that the latest information on the industry-wide state-of-the-art was included. The ongoing literature review focuses on viable leachate treatment methods, including the TiO₂ photocatalysis process. The review began with FAU graduate students: Courtney Skinner, Adriana Toro, François Gasnier, and Tammy Martin in 2005. A visiting researcher from the Indian Institute of Technology in Bombay, Mr. Swapnil Jain, continued the work by conducting an exhaustive search of the photocatalytic literature up to 2007 with the aid of the FAU S.E. Wimberley Library Information Services Department. Mr. Swapnil Jain prepared an annotated bibliography, which was refined by two other visiting scholars, one from Japan, Ms. Hatsuko Hamaguchi, and the other from Stanford University, Mr. Joseph Vasquez in 2007-2008. From 2009, Mr. Richard Reichenbach, Mr. Anthony Ruffini, and Mr. André McBarnette updated the existing annotated bibliography focusing on technological innovations of the past three calendar years including Dr. Hala Sfeir's work on a statewide survey of leachate management options that was presented at the SWANA Conference in July 2007. Mr. McBarnette's worked covered up to 2010. Mr. Frank Youngman updated the literature review from 2010 up to and including 2012.

The main focus of this targeted literature review was to identify precedents using photocatalytic oxidation and other advanced oxidation technologies for wastewater treatment applications. Precedents for advanced oxidation pilot testing using energized processes such as UV/peroxide, PIMA, photo-Fenton, and TiO₂ for water treatment applications were targeted. Specific questions to be addressed were: 1) advanced oxidation process efficacy and degradation rates for various pollutants, 2) appropriate UV intensity range using UV fluence determination methods if possible, 3) appropriate reactor conditions to maximize the efficiency of the process (i.e. pH, temperature, alkalinity, catalyst reconditioning requirements, catalyst poisoning, pollutant interactions, surfactants, impurities, etc.), 4) appropriate range of catalyst dose (in grams or m²), 5) appropriate hydraulic retention times or reaction/exposure times for certain pollutants, and 6) appropriate mixing regime.

2.2 BASELINE LEACHATE WATER QUALITY CHARACTERIZATION

As part of other research projects in the recent past, the PI has been approached by Orange County, St. Lucie County, the Solid Waste Authority of Palm Beach County, Waste Management Central Disposal Sanitary Landfill, and Miami-Dade County for possible locations to conduct the pilot testing. In addition, the Waste Management Okeechobee facility has also been suggested. FAU, with contributions from the TAG, determined that the best possible location for the pilot testing would be the Waste Management Monarch Hill (formerly Central Disposal) Sanitary Landfill (see Figure 5) because of its close proximity to the FAU Boca Raton campus.



Figure 5. Aerial view of Monarch Hill Landfill

A certified lab conducted testing of a composite leachate sample from the Central Disposal Sanitary Landfill in Broward County, FL on October 28, 2009. Only the parameters that were detected are listed in Table 12.

Table 12. Historical leachate water quality data for the Monarch Hill (formerly Central Disposal) Sanitary Landfill in Broward County, FL (Source: Test America Analytical 2010).

Parameter	2009	Flag	2010	Flag	Reporting Limit	Units	Above Reporting Limit
Antimony	46		31		15	µg/L	Yes
Arsenic	650		500		25	µg/L	Yes
Barium	380		440		10	µg/L	Yes
Beryllium	0.90	B	ND		5.0	µg/L	No
Chromium	350		370		10	µg/L	Yes
Cobalt	20		21		10	µg/L	No
Copper	5.4	B	2.4	I	15	µg/L	No
Iron	1800		2200		100	µg/L	Yes
Mercury	0.12	B	0.27		0.20	µg/L	No
Nickel	67		68		40	µg/L	Yes
Selenium	10	B	12	I	15	µg/L	No
Sodium	n/a		7300	V	1.0	mg/L	Yes
Thallium	0.10	B	ND		5.0	µg/L	No
Tin	32	B	ND		100	µg/L	No
Vanadium	88		99		10	µg/L	Yes
Zinc	20		49		20	µg/L	Yes
1-4 dichlorobenzene	21	J	ND		160	µg/L	No
2-butanone	2100		860		120	µg/L	Yes
2-methylnapthalene	60	J	ND		160	µg/L	No
2-methylphenol	130	J	200	I	400	µg/L	No
3-methylphenol and 4-methylphenol	2500		12000		400	µg/L	Yes
4-methyl-2-pentanone	78	J	170		75	µg/L	Yes
Acenaphthene	48	J	ND		400	µg/L	No
Acetone	4300		1900		200	µg/L	Yes
Acetophenone	ND		180	I	940	µg/L	No
Aldrin	0.093	COL	ND		0.050	µg/L	No
Benzene	13	J	9.3	I	20	µg/L	No
Bis (2-ethylhexyl) phthalate	110	J, B	ND		400	µg/L	No
Carbon disulfide	20	J	5.3	I	40	µg/L	No
Dibenzofuran	35	J	ND		160	µg/L	No
Ethylbenzene	28		18		15	µg/L	Yes
Fluorene	29	J	ND		160	µg/L	No
Gamma chlordanes	0.022	J	ND		0.050	µg/L	No
Gamma-Lindane	0.089	COL	0.064	V	0.050	µg/L	No
Naphthalene	130	J	ND		160	µg/L	No
Phenanthrene	24	J	ND		160	µg/L	No
Phenol	1500		1600		400	µg/L	Yes
Toluene	52		36		20	µg/L	Yes

Parameter	2009	Flag	2010	Flag	Reporting Limit	Units	Above Reporting Limit
Xylenes	55		40		40	µg/L	Yes
Alkalinity	5600		9400	V	5.0	mg/L as CaCO ₃	Yes
Ammonia	1600		2300	V	20	mg/L as N	Yes
BOD ₅			930		500	mg/L	Yes
Chloride	7000	Q	13000		600	mg/L	Yes
COD			3800		800	mg/L	Yes
Conductivity	31920		33900		n/a	µmho/cm	n/a
Cyanide	0.020	B, G	0.025		0.050	mg/L	No
pH	7.29		7.48		n/a	pH units	n/a
Sulfide	22	G	2.7		1.0	mg/L	Yes
TDS	15000	Q	25000		100	mg/L	Yes
Turbidity	35.1		25.1		n/a	NTU	n/a

Flags:

B = method blank contamination

J = estimated result; result is less than the limit of quantitation

COL = more than 40% relative percent difference between primary and confirmation result, the lower value is reported

Q = elevated reporting limit due to high analyte levels

G = elevated reporting limit due to matrix interference

I = reported value is in between method detection limit and practical quantitation limit

V = analyte was detected in both the sample and the method blank

ND = analyzed for but not detected

A chemical analysis report by Test America on October 9, 2010 summarized that the water quality of landfill leachate varies considerably. Samples from different cells of the landfill were analyzed by a National Environmental Laboratory Accreditation Certified (NELAC) laboratory; however, as shown in Table 13, the leachate from different cells with different waste composition had fluctuating leachate water quality values. Cells 1 and 2 represent two different sites located at this landfill. The type of waste, the type of liner, the type of cover, the amount of rainfall, and the age of the landfill and thus the degree of solid waste stabilization clearly has a significant effect on the composition of leachate.

Table 13: Composition of Landfill Leachate from different cells at the Central Disposal Sanitary Landfill in Broward County, FL (Source: Test America Analytical 2010).

Constituent	Unit	Values	
		Cell 1	Cell 2
Barium	µg/L	440	250
Cadmium	µg/L	450	350
Cobalt	µg/L	21	35
Copper	µg/L	2.4	17
Lead	µg/L	2.6	2.9
Ammonia	mg/L as N	2300	1500
COD	mg/L	3800	4500
Alkalinity	mg/L as CaCO ₃	9400	6600
TDS	mg/L	25,000	11,000
BOD	mg/L	930	430

The Monarch Hill landfill in Pompano Beach, FL currently pumps its leachate directly to the Broward County Regional Wastewater Treatment Facility located about one mile south of the facility. When comparing the typical values of the Monarch Hill leachate to the Broward County sewer discharge limits, it can be seen that additional surcharges (which are applied when the limits have been exceeded) are incurred (see Table 14).

Table 14: Monarch Hill leachate concentration versus Broward County sewer use limitations

Parameter	Units	Broward County Discharge Limitation	Typical Monarch Hill leachate
COD	mg/L	800	5,700
NH ₃ -N	mg/L	25 – 70	1,600
BOD ₅	mg/L	400	700
Copper	µg/L	2.0	2.6
Lead	µg/L	0.8	2.9

Table 14 shows that the concentrations of both the COD and ammonia greatly exceed the sewer use limitations, resulting in fines being assessed. The typical leachate from Monarch Hill also exceeds the limit for lead and copper. BOD and COD are generally treated through an activated sludge process and less commonly through ozonation, ion exchange, coagulation/flocculation and adsorption (Qasim et al. 2000). Ammonia is

typically removed from wastewater by means of air stripping, ion exchange, breakpoint chlorination, membranes and/or the use of nitrifying bacteria (Hammer and Hammer 2011). Copper and lead are typically removed from wastewater by precipitation processes or ion exchange (Hammer and Hammer 2011). Based on those four constituents alone, the leachate would likely require a complex treatment train with multiple treatment processes similar to a centralized wastewater treatment facility to reach the appropriate effluent limitations. Due to the inconsistency of landfill leachate, a universal treatment is difficult to come by. While there are effective treatments available for individual characteristics of leachate, an effective comprehensive treatment process has yet to be established. Removal of individual parameters is possible, and those removal processes are performed routinely in conventional wastewater and drinking water treatment plants. These processes are different for leachate because it has such high concentrations and varied combinations of contaminants that a more universal treatment technique is required to be cost effective. The development of such a technique is still in the stages of research and experimentation. Recent research suggests that advanced oxidation processes have the potential to solve the leachate management dilemma, with their ability to simultaneously oxidize refractory organics, reduce heavy metals, and eliminate ammonia and VOCs (Wang and Xu 2012).

Actual leachate flow data were compiled from cells ranging in size from 18,212m² (4.5 acres) to 80,940 m² (20 acres). For the Monarch Hill Sanitary Landfill in Broward County, FL, three different cells were analyzed for leachate generation rates (FDEP 2007). With total rainfall periods varying from 35-345 inches, the leachate generation rates varied from 604 – 6462 gpd/acre.

2.3 COLLECTION OF LEACHATE SAMPLES

Leachate was collected from the Monarch Hill Class 1 sanitary landfill in Pompano Beach, FL. The facility was opened by Waste Management Inc. in 1965 and was formerly known as Central Disposal Sanitary Landfill (CDSL). The site has a mass-burn facility rated at 2000 tons per day and receives between 4000 tons (2010 data) to 10,000 tons (2007 data) of municipal solid waste (MSW) per day. The site has a footprint of approximately 300 acres, of which about 80 acres is being landfilled currently. The facility is located at 2700 Wiles Road, Pompano Beach, FL. The property spans east to west from Powerline Road to Florida's Turnpike and north to south from Wiles Road to Sample Road as shown previously in Figure 5.

Approval and permission to obtain samples of raw leachate was obtained from Jeff Roccapiore, District Manager, Broward County Monarch Hill, Waste Management Inc. of Florida. Samples were collected with the assistance of Stephen "Leroy" Melton,

Landfill Technician. Figure 5 shows the location of the main sampling point for the southeast corner of the landfill, which is known as the “South East Step-up Station.” This is the location where all the leachate in this work was collected from. A small pressure monitoring valve installed at the port allows for manual leachate sampling. A closer look at this sampling port is shown in Figure 6. It is possible to collect other samples from various locations on the property such as: the NW corner (old leachate), SW corner (new leachate), SE corner (Waste-To-Energy condensate), or from the wastewater treatment plant sump (combined leachate).



Figure 6. Closeup photograph of the South East Step-up Station sampling port.

The leachate from this facility is discharged to a sanitary sewer collection system and sent directly to the Broward County North Regional Wastewater Treatment Plant (Figure 7) located at the intersection of Powerline Road and Copans Road. According to Jeff Roccapriore (District Manager), the county assesses a surcharge on the order of \$350,000 per year for leachate disposal fees. The facility records approximately 3.5 million gallons per month of leachate generation, but the treatment plant flowmeter reads 5-6 million gallons per month, typically.



Figure 7. Aerial photograph of the Broward County North Regional Wastewater Treatment plant

Waste Management, Inc., who owns the landfill facility, has a 5-year agreement with Broward County to accept its leachate provided it meets the industrial pretreatment criteria (see Table 14 and Table 15), but most notably: $TSS < 400 \text{ mg/L}$, $BOD_5 < 400 \text{ mg/L}$, and $COD < 2 \times BOD_5$. The goal of preliminary work is to meet the local wastewater discharge guidelines for sanitary sewer disposal. The Broward County industrial pretreatment requirements are summarized in Table 15. The key issue for the Monarch Hill Sanitary Landfill is the COD requirement, which essentially is set at 800 mg/L .

Table 15. Broward County industrial pretreatment guidelines approved on January 2002.

Parameter	Limit Value (mg/L)
Ammonia	Not regulated
Arsenic	0.1
BOD	400
Boron	1
Cadmium	0.7
CBOD	800
Chromium (Total)	1
COD	Not regulated unless COD > 2 x BOD ₅ value
Copper	2
Cyanide	0.25
Hydrogen Sulfide	1.5
Iron	10
Lead	0.4
Mercury	0.1
Nickel	1.8
Oil and Grease	100
pH	5.5 – 9.5
Silver	0.35
Total Kjeldhal Nitrogen	30
Total Suspended Solids	400
Total Toxic Organics	1
Zinc	148

The first leachate sampling for these experiments took place on September 30, 2011. Three gallons of leachate was taken from the site at this time, in a five-gallon bucket. The second sampling took place on March 9, 2012. Five gallons of leachate was secured from the site during this visit, in a five-gallon gas can (used to minimize spillage). The third sampling date was July 18, 2012. Another five gallons of leachate was acquired using the five gallon gas can (shown in Figure 8). The collected leachate was stored in a refrigerator at 4°C until treated in the laboratory.



Figure 8. Research assistant collecting samples from the South East Step-up Station sampling location at the Waste Management Monarch Hill Landfill in Pompano Beach, FL (07/18/2012)

2.4 PILOT SCALE FALLING FILM REACTOR

The experiments for this pilot scale study were conducted using a falling film reactor. The unit used is the CE 584 Advanced Oxidation System, manufactured by G.U.N.T. Gerätebau GmbH; a company based in Barsbuettel, Germany. The advanced oxidation machine is shown in Figure 9 and Figure 10.



Figure 9. CE 584 Advanced Oxidation pilot treatment platform



Figure 10. Photographs of the falling film pilot reactor (left: close up view of the reaction chamber; right: overall view)

The test rig measures 1510 mm (60 in) \times 790 mm (30 in) \times 1990 mm (80 in) and weighs approximately 330 lbs. The main components of the advanced oxidation machine are labeled in Figure 11. The unit is equipped with a 10-L reservoir, temperature sensor (0-50°C), 260 Lph 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, and a 120W low-pressure, ultraviolet lamp with power source (30-35% efficiency).

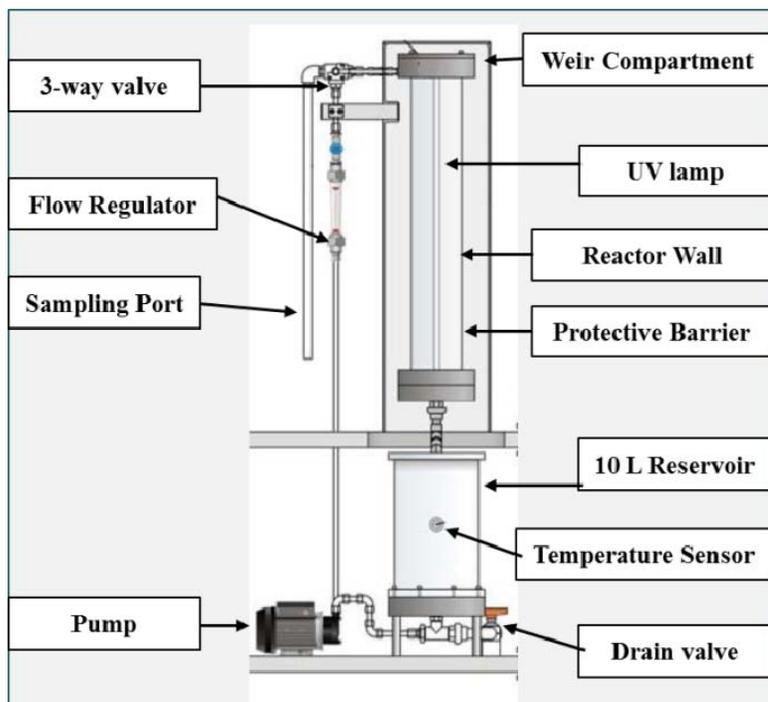


Figure 11. Main components of the CE 584 Advanced Oxidation pilot treatment platform

This unit is designed to oxidize contaminants in water using UV radiation. The process begins by adding the desired liquid to the 10-L reservoir. The liquid is then pumped up through the flow regulator, which allows a flow range of 30 – 320 L/hour. Following the flow regulator, there is a three-way valve which leads to either the sampling port or the weir compartment. The liquid builds up in the weir compartment until it falls over the weir 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 it falls back into the reservoir. Underneath the reservoir is a drain valve to remove the desired liquid from the machine. A schematic drawing displaying the flow path(s) of the machine is shown in Figure 12.

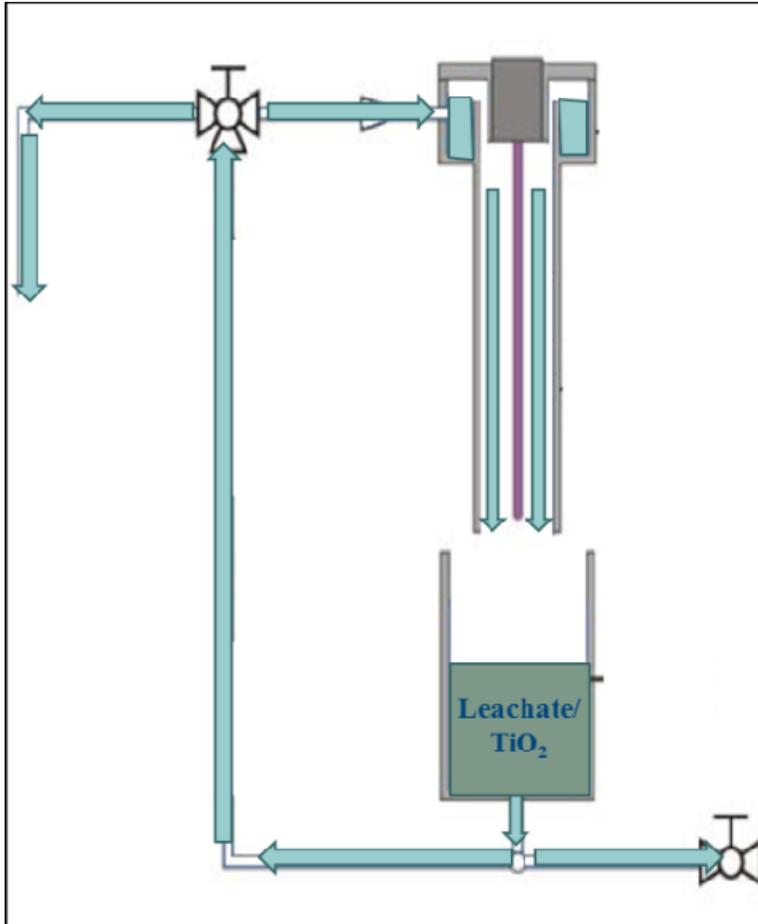


Figure 12. Flow path of advanced oxidation pilot treatment platform

The UV lamp (Strahler NNI 125/84 XL) was purchased from Heraeus Noblelight (Hanau, Germany). The irradiation spectrum (Figure 13) 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.

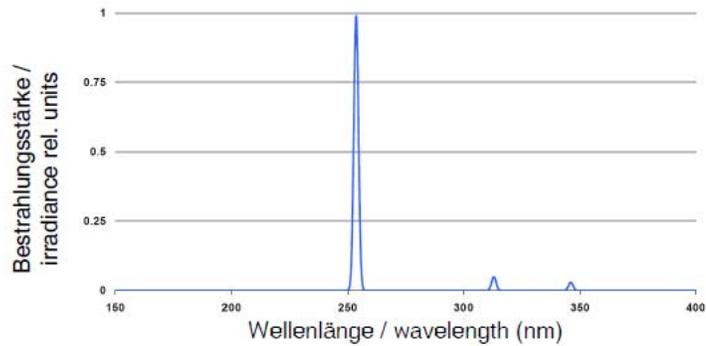


Figure 13. Irradiation spectrum for the Strahler NNI 125/84 XL low pressure UV lamp as provided by the manufacturer

The unit's power options are accessed through the control panel. The power supply for the advanced oxidation unit is a standard 120V outlet. The controls on the panel are shown in Figure 14. The main power switch is in the off position in the image, a quarter turn in the clockwise direction will power up the unit. The pump control and UV lamp control can be used, when the main power switch is in the "on" position. Pushing the green button turns them on and pushing the red button turns them off. Next to those controls is a digital temperature output, which displays the temperature in degrees Celsius.

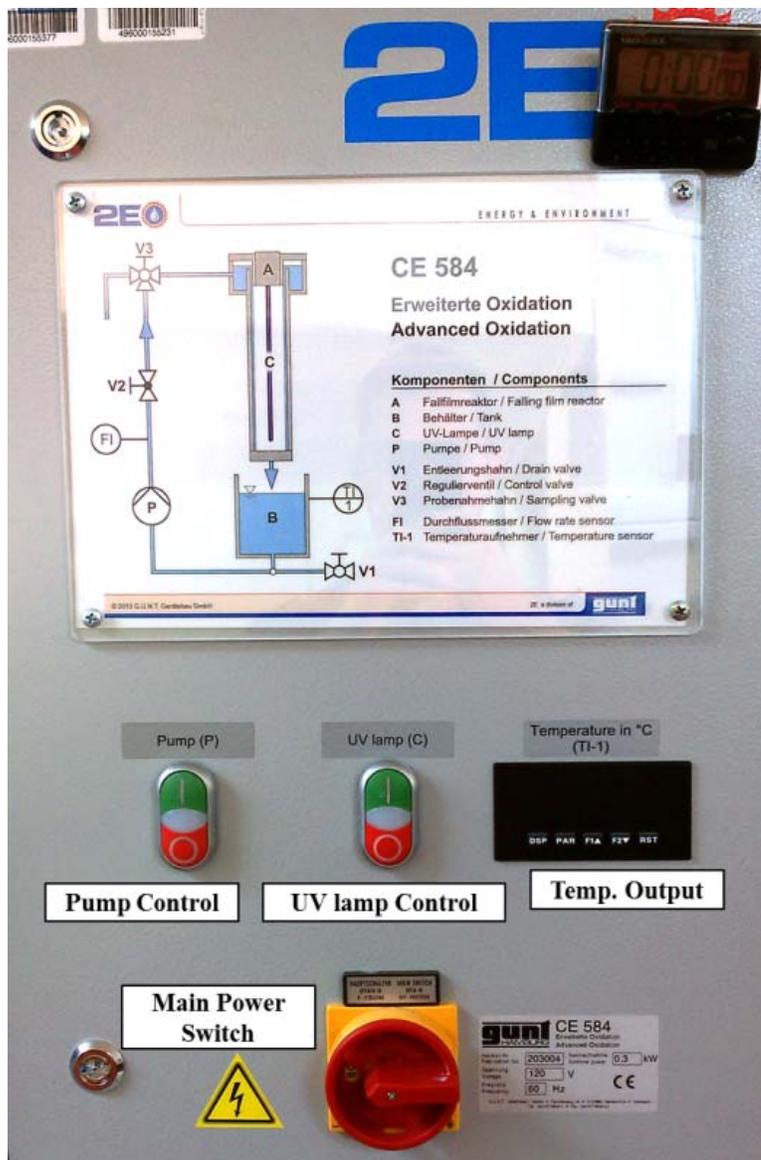


Figure 14. Control panel for the CE 584 Advanced Oxidation System.

2.5 REACTOR IMPROVEMENTS

Before testing the unit with leachate, some mechanical improvements had to be made. The first alteration to the unit was the addition of a 3-way valve between the reservoir and the pump. The necessity of this modification arose from trouble encountered priming the circulation pump. Using a tap water test with TiO_2 particles, the heavy catalyst particles would settle in the pump cavity, dry up and harden around the impeller in the

pump head. This hardening of the catalyst in the pump led to a dry start (see location in Figure 15), such that the pump did not have enough initial torque to break up the dried particles, requiring priming. Prior to this improvement, restart could only be accomplished by taking the pump apart to manually clean and filling the reservoir with water for priming.

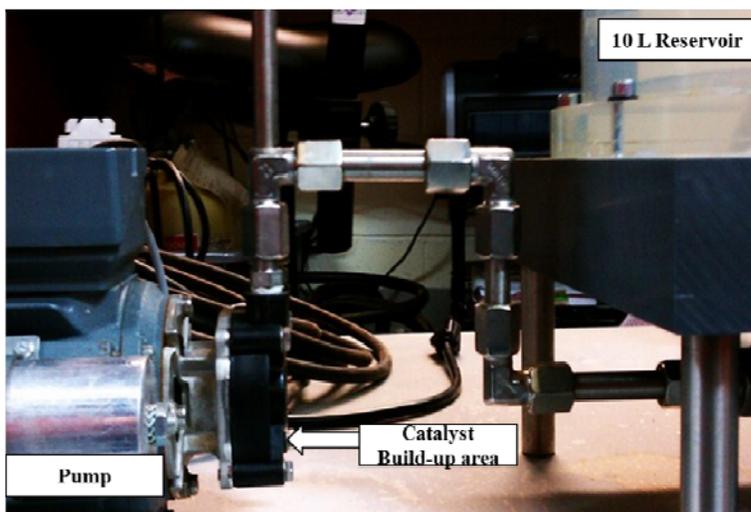


Figure 15. Catalyst settling location in the circulation pump head

A new stainless steel 3-way valve was installed so that the pump could be flushed out after every use without taking apart the unit, limiting the amount of TiO_2 build-up and maintaining proper pump operation. The 3-way valve can be seen in Figure 16. The valve allows us to stop the unit, drain the pump, and recirculate the catalyst so that it will not collect in the pump cavity or in the weir above the falling film reaction zone during long term kinetics experiments in which the unit is stopped overnight for cooling and restarted the next morning.

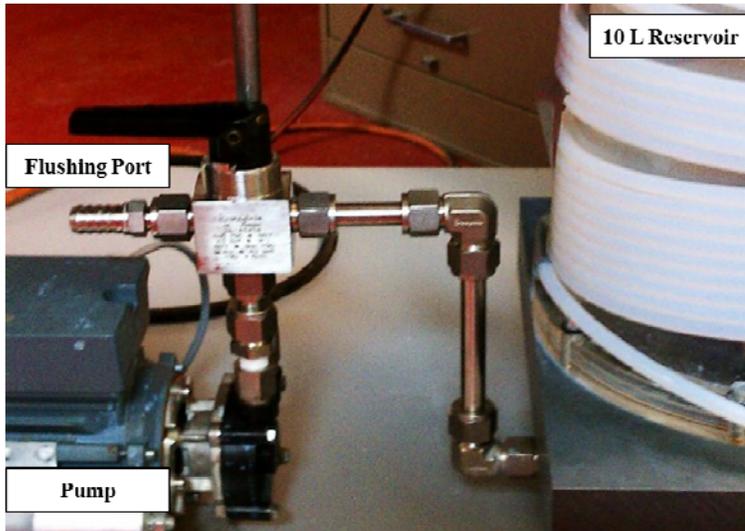


Figure 16. New stainless steel 3-way valve modification to the unit flushing and priming the recirculating pump.

After each experiment, a hose from a bucket of clean tap water is connected to the flushing port. The pump is turned on, and the pump pulls water from the bucket. By opening the 3-way valve (V3) just before the weir compartment, the wash water can be disposed of. A flow diagram of the flushing process is shown below in Figure 17 with the 3-way valves circled.

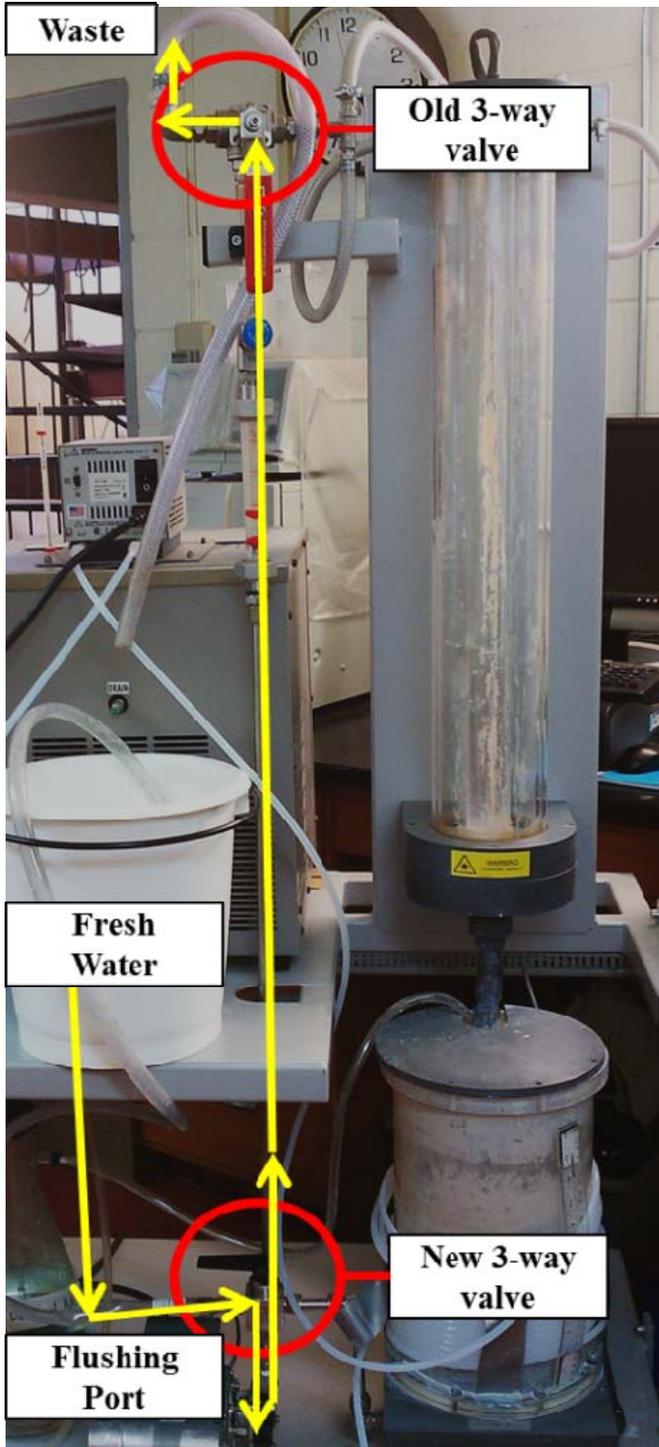


Figure 17. Pump flushing flow path diagram

A second modification to the unit was required to try to maintain constant temperatures throughout the duration of kinetics testing. In tests performed by previous students, it was found that the temperature kept rising over the course of each trial. The temperatures in the reservoir reached nearly 50°C in just 4 hours of treatment. To counteract this rising temperature, a cooling system was installed to limit the heating of liquid in the reservoir. A VWR Recirculating Chiller 1150S with a 13-L capacity was purchased. The chiller unit can circulate fluid at a temperature range of -30°C to 150°C. The circulating fluid used was Dynalene HC-50 (hydrocoolant), which is an aqueous based heat transfer fluid. Dynalene HC-50 works efficiently between a temperature range of -50°C to 218°C. The silicone-based Dynalene HC-50 bath fluid was selected to maximize heat transfer to provide the best thermal stability for the reactor, as possible given the technological limitations. The recirculating cooler has inlet and outlet ports located at the rear of the unit which lead to the 13-L reservoir as shown in Figure 18.

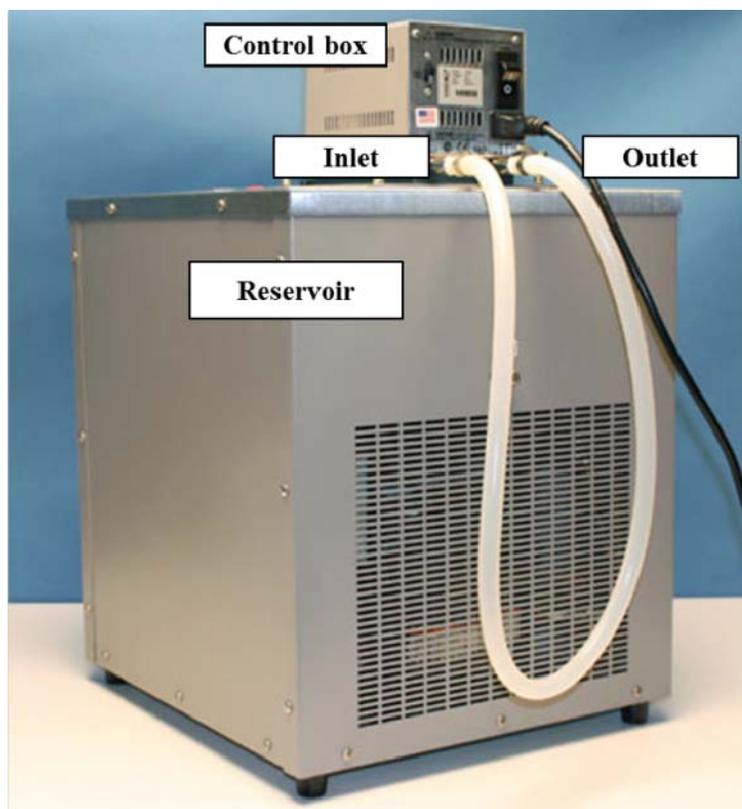


Figure 18. VWR Recirculating Chiller 1150S.

The hose in Figure 18 was replaced with a 50-ft long, 3/8-inch OD polytetrafluoroethylene (PTFE) tubing, which was attached to the inlet port and then

wrapped around the reservoir of the advanced oxidation unit multiple times (see Figure 19) and the opposite end was connected to the outlet port of the cooler to close the loop. As shown, crystalline ice formation occurred on the outside of the tubing due to the temperature of the liquid cycling through it and the humidity in the laboratory. It can also be seen that duct tape was applied to secure the tubing to the reservoir.



Figure 19. Recirculating cooler hose surrounding leachate reservoir (left) and Frank Youngman testing the temperature control system provided by the recirculating chiller unit.

The cooling system limited the increase of the sample temperature to a maximum of 35°C during the 4-hr treatment window, as shown in Figure 20.

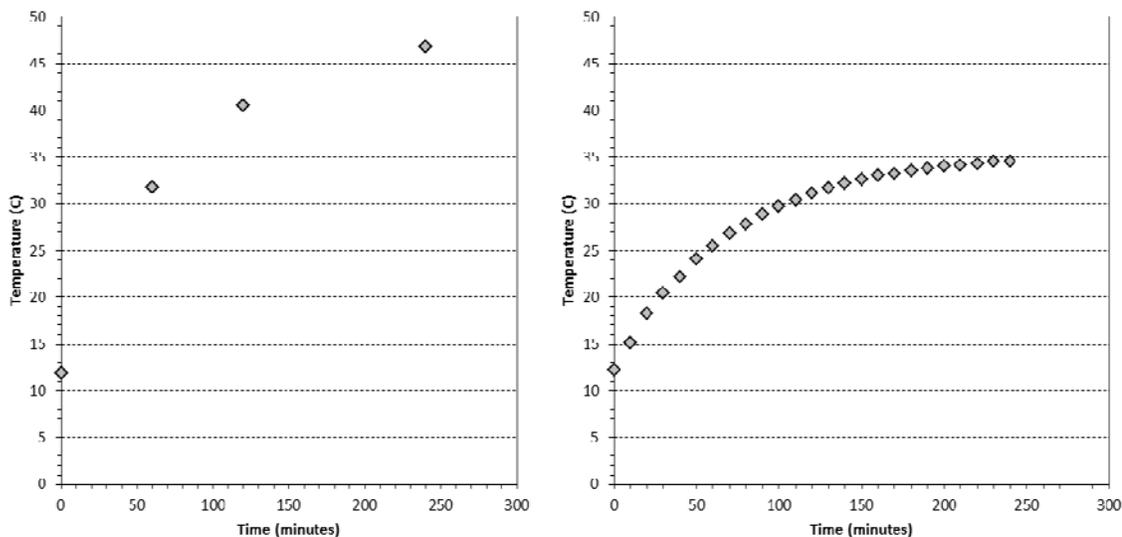


Figure 20. Temperature rise without the cooling system (left) and with the cooling system (right)

A third modification was an air pump. Specifically, the 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) and an air stone in the shape of a rectangular prism to add air directly into the leachate reservoir (see Figure 21). A Y-attachment and two-way valve was installed onto the tubing which the air is pumped through (see Figure 22). Opening the valve allowed a portion of the pressurized air to escape into the open environment, thus reducing the amount of air introduced into the leachate, permitting agitation in the reservoir without causing overflow. No attempt was made to measure the flowrate of air added to the reservoir. There are two main purposes to the addition of the air pump system. The first is to agitate the leachate sample to prevent settling of the heavy TiO_2 particles. The second function is to accelerate oxygenation of the sample. One issue found in prior research was that when the air was pumped into the leachate, the mixture would immediately foam up and overflow the reservoir. So the valve was adjusted mid-experiment, as needed, to limit foaming.

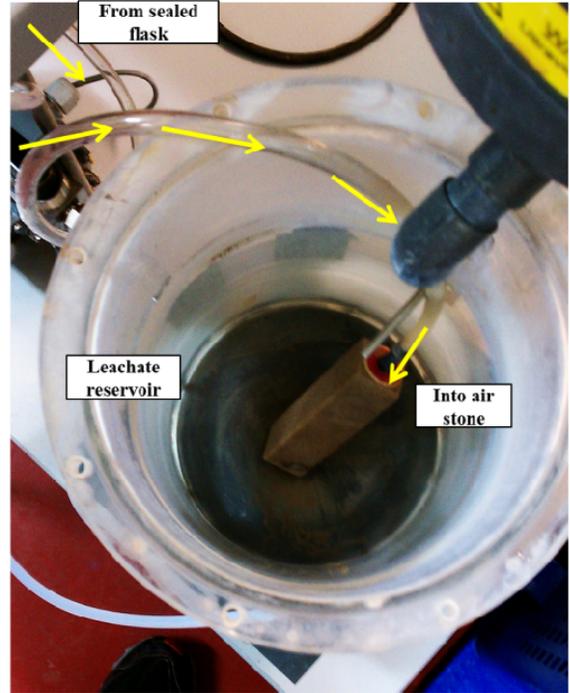
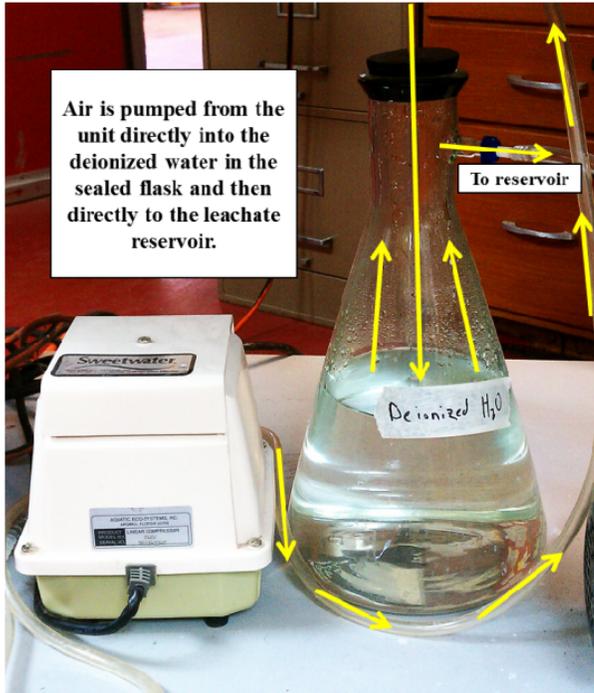


Figure 21. Air pump system.

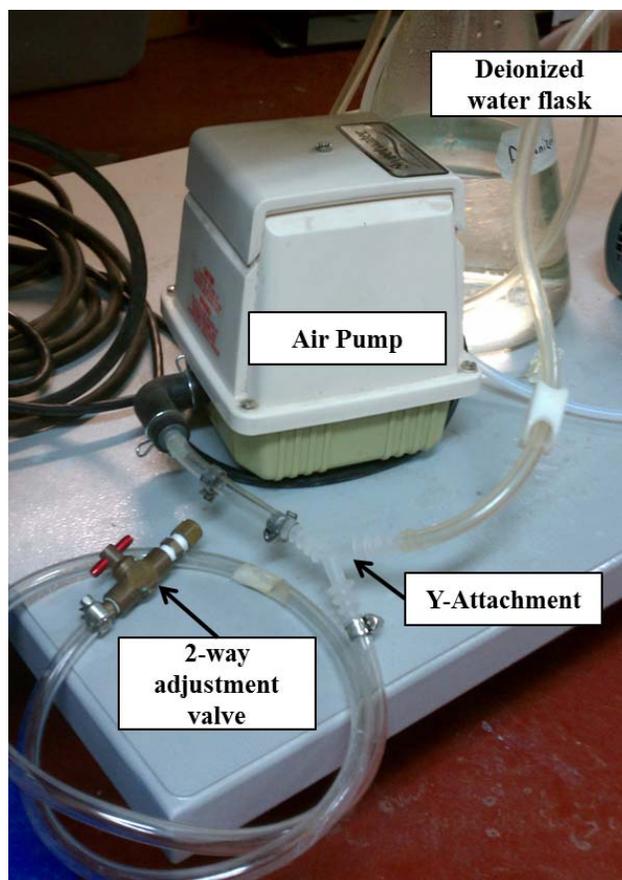


Figure 22. Y-attachment and 2-way adjustment valve for air pump system

Opening the valve allowed a portion of the pressurized air to escape into the open environment, thus reducing the amount of air introduced into the leachate, permitting agitation in the reservoir without causing overflow. No attempt was made to measure the flowrate of air added to the reservoir. There are two main purposes to the addition of the air pump system. The first is to agitate the leachate sample to prevent settling of the heavy TiO_2 particles. The second function is to accelerate oxygenation of the sample. One issue found in prior research was that when the air was pumped into the leachate, the mixture would immediately foam up and overflow the reservoir. So the valve was adjusted mid-experiment, as needed, to limit foaming. Also an antifoaming agent was added drop wise in extreme cases.

2.6 EXPERIMENTAL PROCEDURE

Before beginning the experiments, a review of the work performed by previous students using the falling film reactor was executed. This review led to the initial determination of running the leachate through the advanced oxidation unit in 4-hour segments to limit the increase in reaction temperature. This was to be performed until acceptable temperature control was demonstrated, and then longer test segments would be possible. From the literature and data review, it was found that most processes were evaluated for reaction times less than 24 hours. For completeness, some experiments were carried out for periods well in excess of 24 hours in an attempt to determine the time needed to reach complete mineralization. Prior to each experiment, a sample would be taken from the raw leachate to determine the initial levels of the parameters of interest.

To begin each experiment, the leachate was removed from storage and then 8-L was measured in 2-L increments, using a 2000-mL graduated cylinder as shown in Figure 23 (left). The raw leachate was then added to the advanced oxidation unit's reservoir, as shown in Figure 23 (right). Then a sample of 30-40 mL was taken for testing. Approximately 7 mL of this sample was used up from the leachate for sample testing, and the unused remainder of the sample was poured back into the reservoir.



Figure 23. Measurement of 2L of leachate in a 2000 mL graduated cylinder (left) and then poured into the advanced oxidation unit reservoir (right).

The next step in the process was to add the titanium dioxide photocatalyst. Through analysis of the previous batch scale work, it was determined to add 4 grams of TiO_2 per liter of leachate for the first experiment. Further amounts of catalyst were to be determined by the results of the previous experiment to arrive at an optimum dose at this scale. The catalyst was gathered in a 1000mL HDPE beaker and weighed using Mettler-Toledo's XS204 DeltaRange Analytical Balance.

A widely used, high quality TiO_2 product (Degussa Aeroxide TiO_2 P-25) was used as the photocatalyst for all testing. A breakdown of the composition in Aeroxide TiO_2 P-25 is shown in Table 16.

Table 16: Physical Composition of Degussa Aeroxide TiO₂ P-25

Compound	Unit	Value
Titanium Dioxide	wt. %	≥ 99.5
Al ₂ O ₃	wt. %	≤ 0.300
SiO ₂	wt. %	≤ 0.200
Fe ₂ O ₃	wt. %	≤ 0.010
HCl	wt. %	≤ 0.300
Sieve Residue	wt. %	≤ 0.050

Source: Aeroxide® TiO₂ P 25 Product Information Sheet

The titanium dioxide in the Degussa Aeroxide TiO₂ P-25 is not a pure form of TiO₂. 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 TiO₂ P-25 (used in this study) are listed in Table 17.

Table 17: Properties of anatase and rutile forms of titanium dioxide

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

Source: Pelaez et al. (2012), Hong et al. (2005), Faure et al. (2010), Kosmulski et al. (2009), Evonik Industries (2008)

Once the correct amount of catalyst was measured out, the advanced oxidation unit was turned on, and the centrifugal pump and the air pump were started to begin circulating the leachate. After about 5 minutes, the TiO₂ was slowly added to the leachate allowing it to thoroughly mix into the liquid and prevent clogging of the system. At this point, the color of the liquid changed from a dark coffee color to milky color. In Figure 24 (left), you can see the pilot unit loaded with real leachate, which has a dark coffee color and foul odor. Once the TiO₂ photocatalytic particles are added, the color changes to a light caramel color, as seen in Figure 24 (right). The leachate foams very quickly with the aeration unit

at 50% capacity as seen in Figure 24 (left). Immediately after foaming is noticed, aeration is stopped to allow the photocatalyst to partially settle before starting the recirculation pumping cycle (see Figure 25).



Figure 24. Photograph of the falling film pilot reactor loaded with real leachate. The left picture shows leachate foaming occurring with the aeration unit at 50% capacity. The right picture shows the leachate after TiO_2 addition. Note the color difference between the raw leachate and leachate with TiO_2 .

After the catalyst appeared to be well-mixed (about 5-10 minutes) with the leachate, the pump and air pump were shut off so that a 30-40 mL sample could be collected from the mixture (see Figure 25). This sample is referred to as the initial leachate plus catalyst sample.

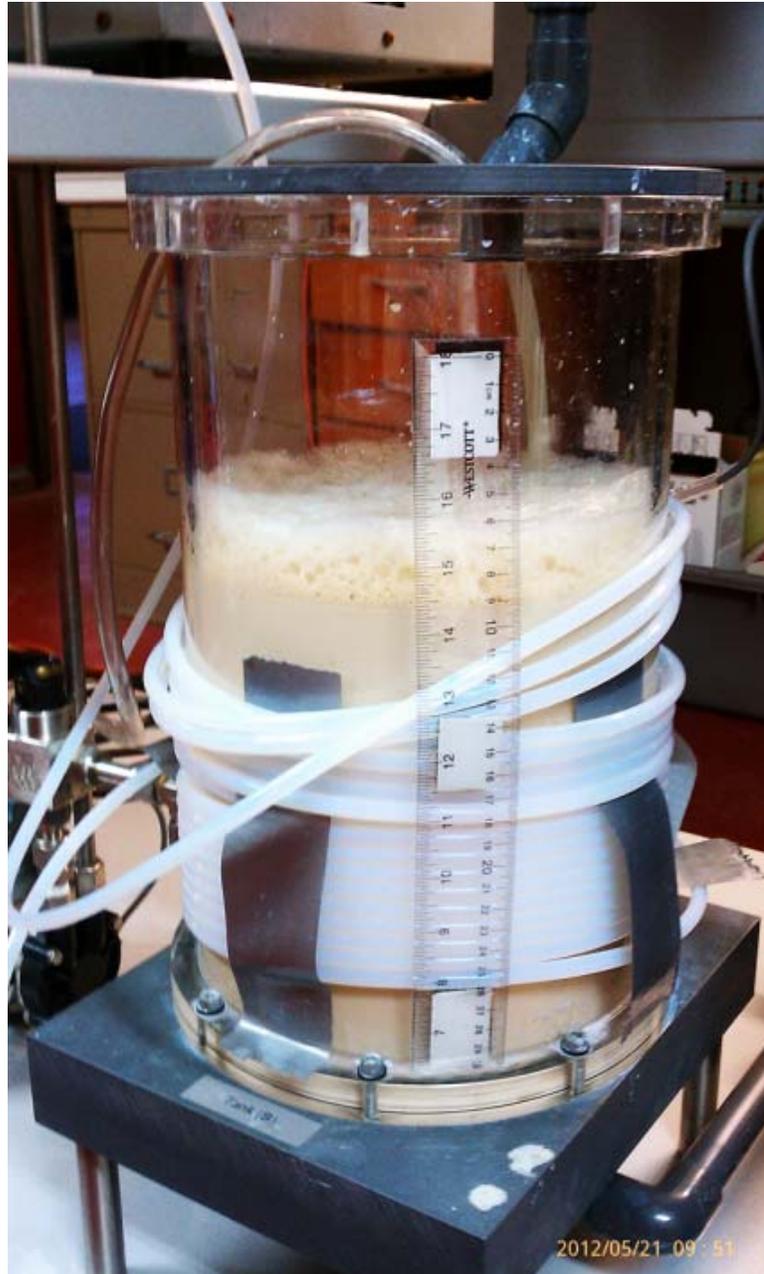


Figure 25. Leachate containing TiO_2 photocatalyst.

At this point, the pump, the UV lamp, the air pump, the recirculating cooler, and a digital timer were all activated. The temperature was recorded from the digital output on the control box of the advanced oxidation unit. Initially, the temperature was recorded every

five minutes to gain an understanding of the temperature control exhibited by the recirculating cooler. Once the behavior pattern of the temperature was established, the interval was extended to every 10 minutes. The advanced oxidation unit was run until the timer reached 4 hours, at which point the pump, the UV lamp, the air pump, the recirculating cooler, and a digital timer were all stopped or switched off. Another 30-40 mL sample was taken for parameter testing.

Then the drain valve was opened to allow the leachate to drain into the desired container so that it could be put back in refrigeration to limit any further breakdown or biological growth from high temperatures. Once the leachate was stored, a bucket full of 8-9 liters of tap water was poured into the leachate reservoir and cycled through the system to collect any catalyst or other constituents remaining in the machine. That flushing process was repeated 3-5 times depending on the clarity of water when it was drained out of the system. After flushing the main system, the pump was flushed as described earlier.

In Figure 26 (left), you can see the pilot unit in operation with the lamp at full power and the recirculation rate set to the minimum value. The photocatalytic particles are sufficiently heavy to rapidly settle when the aeration is shut off (Figure 26 right). With the high alkalinity and temperature conditions in the first set of experiments, calcium carbonate scaling was evident after only a few hours of treatment.



Figure 26. Photograph of the falling film pilot reactor loaded with real leachate and TiO_2 in operation (left). Note the buildup of calcium carbonate on the walls of the reservoir and the rapidly settling photocatalyst when the air is shut off (right).

2.6.1 Measurement of Ultraviolet Intensity

The power of the UV lamp was tested using a Fisher Scientific Traceable UV Light Meter. To perform the measurement, the ultraviolet lamp had to be removed from the unit, away from the protective barriers. The diameter of the UV bulb itself, the protective quartz glass tube and the borosilicate glass reactor wall were all measured and compared to the specifications given in the CE584 Advanced Oxidation manual, shown in Table 18.

Table 18: Technical data on the falling film reactor

Falling film reactor	Material	Diameter (mm)
Inner protective tube	Quartz glass	43
Reactor wall	Borosilicate glass	110
Outer protective tube	PMMA XT	-

To determine the distance between the UV source and the reactor tube (i.e. the distance to the leachate), the radius of the UV lamp was subtracted from the radius of the borosilicate glass reactor wall (Figure 27). This distance was found to be 1.84 inches. The protective quartz barrier sleeve allows UV light to pass but protects the lamp from the corrosive water spray and calcium carbonate precipitation and other dangers.



Figure 27. UV distance from reactor wall. Note the calcium carbonate buildup on the walls of the container.

Once the distance from the UV source was determined, the UV lamp was taped to the back of the oxidation unit. The sensor was then placed at the correct distance from the bulb for 5 – 10 minute readings. The UV sensor showed that the UV lamp reached maximum power output after the lamp had been on for five minutes.

2.6.2 Sub-Sampling Procedure

Preliminary pilot-scale experiments were run for up to 6 hours. For these experiments, the sample collection procedure was as follows. Samples were collected from the sampling port or directly from the reservoir using a 50 mL beaker. Samples were transferred to 15 mL conical centrifuge tubes and centrifuged at 3000 rpm for 5 minutes at 20°C in a refrigerated centrifuge (accuSpin 1R, Fisher Scientific, Pittsburgh, PA) to separate the photocatalyst. After centrifugation, subsamples were decanted leaving the photocatalyst pellet in the tube. The decanted liquid was used to constitute the samples for further laboratory analysis of the parameters of interest.

2.7 ANALYTICAL METHODS FOR PARAMETERS OF INTEREST

The advanced oxidation unit was used to test the removal efficiency of the following constituents: COD, ammonia, alkalinity, color, and pH.

2.7.1 COD

For chemical oxygen demand (COD) testing the Reactor Digestion Method for the Hach DR4000U (Loveland, CO) was used with the High Range COD digestion vials (20 to 1,500 mg/L as O₂). The method involves the reduction of the dichromate ion (Cr₂O₇²⁻) to chromic ion (Cr³⁺), which can be analyzed colorimetrically because the two species of chromium are colored with Cr⁶⁺ being orange and Cr³⁺ being green. Theoretically, since each dichromate ion accepts 6 electrons per molecule and each molecule of molecular oxygen accepts 4 electrons, the COD of 1 g of Cr₂O₇²⁻ is equal to 1.5 g of diatomic oxygen. The COD was tested prior to treatment and then after every subsequent 4 hours of treatment. At least 2 duplicate samples were analyzed for each COD test.

After centrifugation at 6000 rpm to separate the photocatalyst particles, samples were diluted to 2.0 mL using 18.2MΩ-cm deionized water. Throughout the pilot scale testing, a dilution of 1:10 was used. Briefly, 2 mL samples were inverted 20 times to mix and 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 DR/4000U UV-Vis spectrophotometer. The COD value in mg/L was recorded. A certified reference material (Total Organic Carbon Standard 1,000 ppm [Prepared to EPA Method 415-1] Aqua Solutions, Deer Park, TX) was used to check the instrument calibration. This value varied from 0.1-14.7% error. One calibration check standard was analyzed per COD test. It is well known that high levels of chloride in the samples can work as an interferent in this 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. For this reason, the chlorides were tested in the leachate as described in the chloride section.

2.7.2 Ammonia-Nitrogen

For ammonia-nitrogen, the EPA Method # 350.2 (Detection of Ammonia by Colorimetry), Nessler spectrophotometric method was used. An ammonia ion specific meter (Medium Range: 0.00 to 9.99 mg/L as NH₃-N) from Hanna Instruments

(Woonsocket, RI) was used. The test began by adding 10-mL of sample to a 10-mL cuvette. The cuvette was cleaned with a Kim-wipe and placed in the instrument to be zeroed out. Next, four drops of the first reagent?? were added to the cuvette. The cuvette was then swirled and then four drops of the second reagent?? were added (see Figure 28) and the sample was swirled again.



Figure 28. Reagent addition to cuvette for ammonia testing

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 ($\text{NH}_3\text{-N}$) on the liquid crystal display (see Figure 29).



Figure 29. Sample reading from 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. For the purpose of these experiments conversion was not necessary since the Broward County Sewer Use Limitations specify a limit of 25 mg/L as $\text{NH}_3\text{-N}$. Dilution was necessary to lower the concentrations of known interferences, such as organics, sulfides, color, chloramines, aldehydes, and hardness above 1000 mg/L as CaCO_3 . Due to the potency of the ammonia in real leachate a 0.4 – 1% dilution was used.

2.7.3 Alkalinity

For the total alkalinity measurements, SM 2320B was used. A Hach digital titrator was loaded with a 1.600 N H_2SO_4 titrant cartridge for all analyses. First the sample was diluted to 0.4 – 1%, 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 bromocresol 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 bromocresol green methyl-red alkalinity. When the phenolphthalein alkalinity and bromocresol green methyl-red alkalinity values were added together, this corresponded to the total alkalinity value.

2.7.4 Color

The color parameter was monitored with a color wheel comparison method in order to determine the magnitude of color removal. The procedure for this analysis was taken according to SM2120B using a Hach Model C0-1 color comparator (2234-00; lot number: A7984). For each sample, 5.0 mL was placed into the 15 mL sample viewing tube. Leachate samples were diluted 1:25 with deionized water. Samples were compared to deionized water using a color comparator wheel that was rotated against a light source until a color match was obtained. Values were reported in APHA platinum cobalt units.

2.7.5 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 HQ40d Portable Multi-Parameter Meter, with the latter being used for nearly all of the measurements reported. Probes were calibrated periodically with standard pH buffers (4, 7, and 10). Sensors were rinsed with deionized water and dried with Kim-wipes in between sample readings.

2.7.6 Temperature

The temperature was recorded prior to and during all pilot scale experiments. The advanced oxidation unit has a built-in temperature sensor inside the 10-L reservoir. The temperature was recorded from the digital output located on the control box of the unit. Initially, the temperature was recorded every five minutes to gain an understanding of the temperature control exhibited by the recirculating cooler. Once the behavior pattern of the temperature was established, the interval was increased to 10 minutes and then to 30 minutes.

2.7.7 Chloride

The chloride levels of the leachate were tested due to the possibility of interference with the COD measurements. The procedure used was the Hach Silver Nitrate Method 10246. This method has the ability to test levels of chloride within the range of 100 to 200,000 mg/L as Cl⁻. Before the sample could be tested, an estimation procedure was performed to determine the sample size and dilution necessary for the test by starting with a 1:100

dilution in deionized water. A Hach digital titrator was loaded with a 1.128 N Silver Nitrate titrant cartridge for the analyses. The contents of one Chloride 2 Indicator Powder Pillow was added to the sample and mixed thoroughly. The titrant was added to the sample until the end point was reached (yellow to red-brown). The digits added to reach the end point was recorded. The chloride concentration (in mg/L as Cl⁻) was determined by multiplying the number of digits by the given multiplier (determined from Table 2 in the Hach chloride test procedure). An interference of concern for the chloride test was sulfide. For this reason, a test was run using a Sulfide Inhibitor Reagent Powder Pillow to remove this possible interference from the sample. The results of the sulfide inhibitor showed that sulfide was not present at a level which would cause interference. Accuracy checks were performed using Chloride Voluette® Ampule Standard Solution, 12,500 mg/L Cl⁻. The error derived from the standard ranged from 1.3 – 8%.

2.8 CATALYST RECOVERY

An experiment was conducted in an attempt to collect the used catalyst from the treated leachate for reuse. Nylon monofilament filter bags were purchased from Aquatic Eco-Systems in three different sizes: 5-micron (BAG5), 10-micron (BAG10) and 20-micron (BAG20). The bags were placed in a drying oven at 105° C for 45 minutes and subsequently placed in a desiccator for 1 hour. The dried, empty filter bag was placed in a 1000-mL HDPE beaker and weighed using Mettler-Toledo's XS204 DeltaRange Analytical Balance. The leachate used for the experiment (5-L) was diluted with tap water (3-L) and added to the reservoir of the advanced oxidation unit. A catalyst dosage of 5 g/L was added to the leachate. The leachate was treated for 8 hours continuously. Once the 8-hour treatment of the leachate was completed, the machine was shut down so the filter bag could be attached to the spigot above the 10-L reservoir. Once the bag was attached using a single cable tie the machine was powered back up so the leachate could flow into and through the bag (Figure 30).



Figure 30. Nylon monofilament filter bag attached to advanced oxidation unit for catalyst recovery

After all the leachate passed through the filter bag, the bag was removed and placed into an oven at 105° C for one hour and subsequently placed in the desiccator for one hour. The dried filter bag containing the used catalyst was placed in a 1000-mL HDPE beaker and weighed on the balance. The weight of catalyst recovered was determined to be the difference between the weight of the empty bag and the weight of the bag containing the used catalyst.

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 QUALITY CHARACTERIZATION

Table 19 characterizes the Monarch Hill leachate samples for pH, COD, alkalinity, color, and ammonia. Supporting the fact that leachate quality has high variability, the parameter concentrations varied for each sample, even though 3 of the samples were collected in the same year. The COD ranged from 5,270 – 6,560 mg/L. The alkalinity varied from 3,560 – 4,690 mg/L as CaCO₃. The ammonia levels ranged from 1,310 – 1,855 mg/L as NH₃-N and the color ranged from 750 – 1125 PCU.

Table 19. Summary of Leachate Water Quality Testing Results.

Parameter	Units	Composite	SE step up	SE step up	SE step up	SE step up
		sample	station	station	station	station
		03/16/2010	09/30/2011	03/09/2012	07/18/2012	11/2/2012
Alkalinity	mg/L as CaCO ₃	4500	4625	3560	4125	4690
pH	pH units	7.6	7.8	7.4	7.7	7.7
Color	PCU	500	1125	950	760	750
Ammonia	mg/L as NH ₃ -N	1748	1855	1310	1635	1700
COD	mg/L as O ₂	Not recorded	6250	5270	6560	6180

3.2 PRELIMINARY TESTING

Initial screening experiments were conducted to test the efficacy of hydraulic modifications to the pilot testing unit which allowed for longer term experiments. (Meeroff and McBarnette 2011), testing was limited to only 4 hours before the temperatures became excessive (T>60°C). The modifications were described in the previous methodology section. After running the pilot unit for a total of 44 hours over an 11-day period, reaction temperatures below 20 – 35°C were maintained, consistently, as shown in Figure 31. For each experiment, the maximum temperature was recorded as described previously.

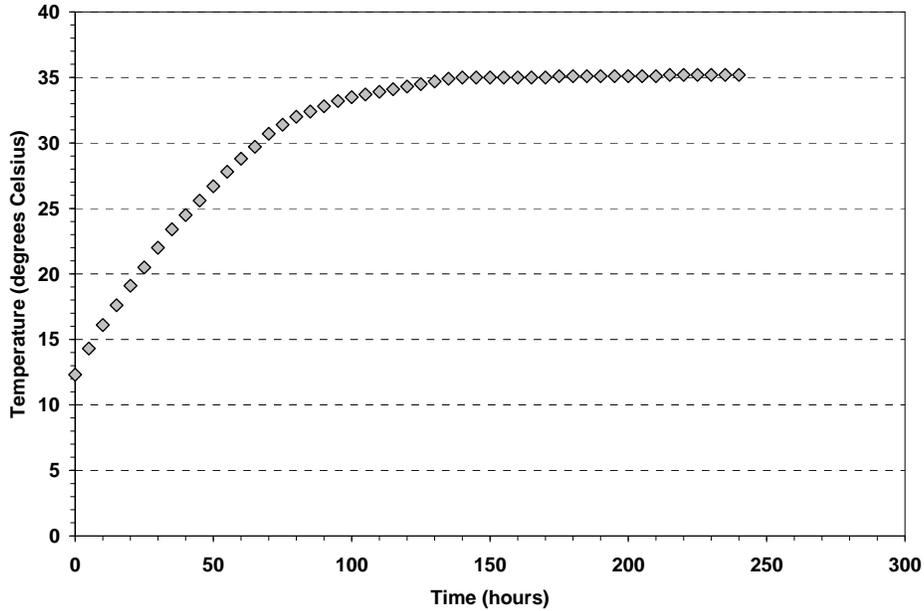


Figure 31. Typical temperature curve collected during one of the 4-hour pilot test runs (January 13, 2012).

The UV radiation intensity was tested in July 2012 by removing the UV lamp from its housing as described earlier. A Fisher Scientific UV light meter was used to measure the intensity of the lamp. Measurements were recorded for approximately ten minutes or once the lamp had stabilized at maximum intensity. The lamp reached maximum intensity at 5-6 minutes. The measurements were taken at two distances from the lamp: 1.84-inches and 5.38-inches. The actual distance from the lamp to the reactor wall is 1.84-inches. Previous UV intensity measurements for the same lamp were conducted in July 2011 by Kelly Horner at a distance of 5.38-inches, so this distance was used to compare data results. A summary of the trial results and comparison to previous data is summarized in Table 20.

Table 20: Summary of maximum UV intensities recorded and doses calculated

	Trial 1	Trial 2	Trial 3	July 2011
Measurement Distance (in)	1.84	1.84	5.38	5.38
Measured Intensity (mW/cm ²)	0.34	0.37	0.14	0.21
Calculated UV dose @ 1.84" (mW/cm ²)	0.34	0.37	1.17	1.78
$I_{(\eta R),z^*}$ (mW/cm ²)	1.16	1.25	4.03	6.12

$I_{(\eta R),z^*}$ = Intensity of incident radiation entering the inner wall of the annulus at $z^* = 0.5$

The intensity measured in July 2011 was higher than the intensity measured one year later. This suggests a decrease in UV intensity over the life of the lamp. The calculated dose was the result of applying the inverse square law by multiplying the measured intensity (mW/cm^2) by the measurement distance squared and then dividing by the sample distance squared. The distances did not need to be converted to centimeters because their units cancel each other out. Measuring from the actual reactor distance resulted in much lower calculated intensities than measuring from far away. This was unexpected since increased light scattering should occur over longer distances in air. During the measurements, the only interference between the UV lamp and UV meter was air. Also, these measurements assumed that the full spectrum of the lamp was being recorded. This was not the case due to the limitation of the UV light meter, which can only measure wavelengths between 320 – 390 nm. The UV lamp in the falling film reactor emits most of its intensity in the 250 – 260 nm range, which was not recorded by the UV light meter. Previous UV testing conducted by André McBarnette on the batch scale reactor UV dose resulted in calculated intensities as high as $130 \text{ mW}/\text{cm}^2$ (Meeroff and McBarnette 2011). The UV doses from the various UV/ TiO_2 experiments presented previously in Table 9 ranged from 1.8 – $10 \text{ mW}/\text{cm}^2$. Compared to these and the batch scale UV intensities, the UV dose is relatively low for this falling film reactor unit. It is recommended to obtain intensity measurements using a meter in the UV-C range for subsequent research studies.

The application of UV radiation to the leachate caused the water to heat up, which could theoretically lead to evaporation losses and difficulties for accurate kinetics experiments. Testing for evaporation losses from the falling film reactor were conducted by previous FAU researchers (Meeroff and McBarnette 2011). The experiment used 8.0-L of deionized water instead of leachate. Temperature and evaporation were recorded during the experiment, and the results were plotted in Figure 32.

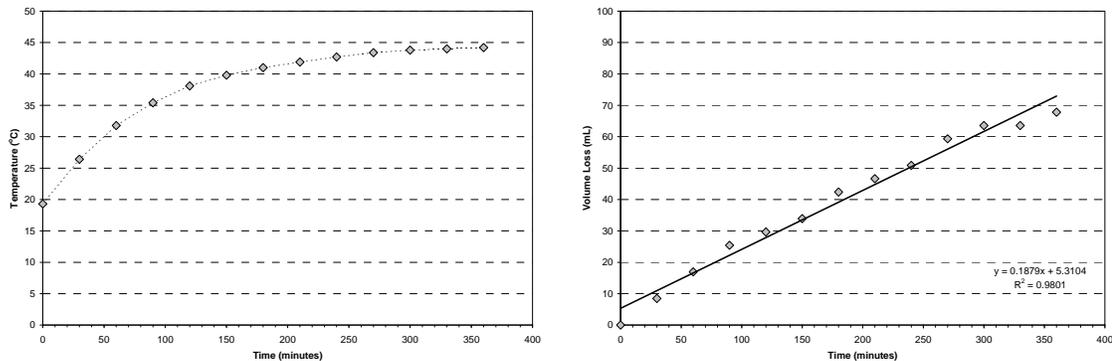


Figure 32. Temperature curve for the falling film pilot reactor (flowrate = 30 Lph) using UV and Aeration (left). Falling film pilot reactor volume loss due to evaporation using UV and aeration with 8 L deionized water (right).

The temperature rose to a maximum of 44.2°C in six hours. The average evaporation rate determined by the data was found to be 11.5 mL/hr. The total volume loss for the six-hour period was 70-mL, which equates to 0.9%. It was determined that evaporation losses can be ignored when less than 2%, so the evaporation losses for the falling film reactor were neglected.

A previous FAU research assistant, Richard Reichenbach, performed a dark test with the falling film reactor. The experiment was performed with 8.0-L of leachate collected from the Monarch Hill landfill SE step-up station. A catalyst dosage of 36.7 g/L TiO₂ was used (ratio of TiO₂:COD = 10.1). The experiment was run for 6 hours with no application of UV radiation. The results of the dark reaction showed no change in pH or removal of COD as demonstrated in Figure 33 (Meeroff and McBarnette 2011). These results clearly establish the requirement to activate the catalyst with UV radiation.

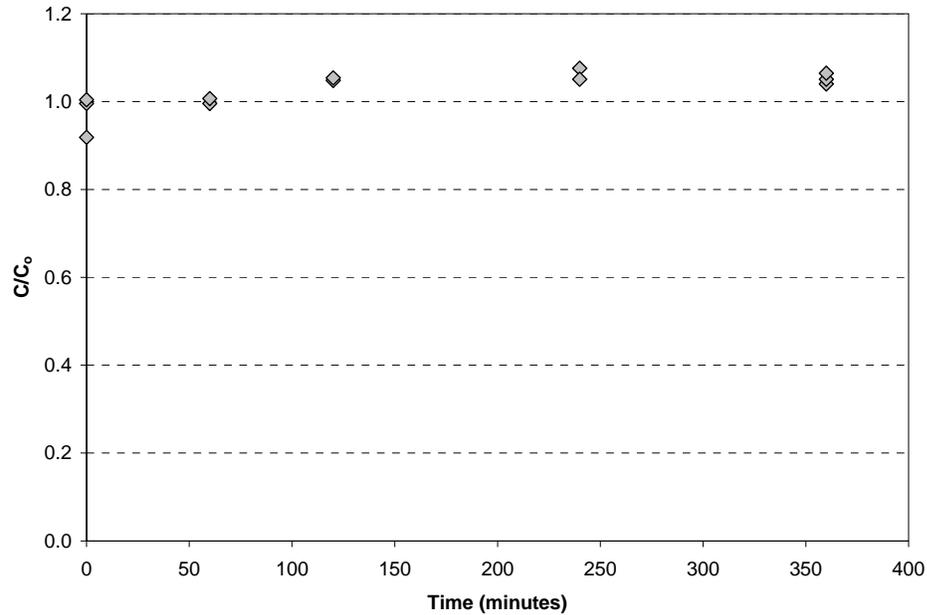


Figure 33. Results of dark reaction for falling film reactor ($\text{TiO}_2 = 36.7 \text{ g/L}$; $\text{UV} = 0$)

3.3 PRELIMINARY ASSESSMENT OF PILOT PERFORMANCE

Preliminary experiments were designed to attempt to optimize the catalyst dosage, understand more about the alkalinity dependence, and learn more about the reaction kinetics, if possible. During operation of the preliminary testing pilot unit, measurements of COD, ammonia, color, alkalinity, and pH were recorded to investigate system performance. Experiments were run at 4-hour intervals at which time the leachate was removed from the unit to cool to room temperature and flush any suspended materials from the pump housing. This was repeated after each 4-hour period. Samples were collected at $t=0$ and $t=4$ hours for each daily run as described in the previous methodology section. The starting point for the catalyst dosage optimization experiments was derived from previous bench scale experiments (Meeroff and McBarnette 2011) which demonstrated 100% COD removal using 4 g/L TiO_2 .

A summary of all the pilot scale experiments performed is presented in Table 21, which displays the catalyst doses used and the parameters measured throughout the study.

Table 21. Summary of all six pilot scale experiments with parameter removal at 24 hours

Exp.	Date started	TiO ₂ (g/L)	Max Temp. (°C)	pH (pH units)		Alkalinity (mg/L as CaCO ₃)		Ammonia (mg/L as NH ₃ -N)		COD (mg/L as O ₂)		Color (PCU)	
				Range	Mean	Initial	Final	Initial	Final	Initial	Final	Initial	Final
1	12/29/11	4	36.7	8.35 – 9.26	8.89	4625	875	1713	306	6246	4890	1125	750
2	05/16/12	16	35.7	7.63 – 9.18	8.84	3560	1375	1310	602	5268	3780	825	575
3	06/18/12	25	36.0	7.54 – 8.96	8.72	3563	1875	1380	700	5360	3540	788	525
4	08/08/12	40	36.7	7.59 – 9.06	8.74	4313	1130	1523	842	6990	4530	756	325
5	09/20/12	30	36.3	7.70 – 9.20	8.87	4125	1013	1635	845	6135	4322	756	425
6	12/10/12	10	37.1	7.66 – 9.09	8.73	4375	700	1700	470	6064	5343	813	600

3.3.1 Experiment 1

For the first extended time treatment trial, real leachate from the SE step-up station collected on September 30, 2011 was used, with an initial COD concentration of 6,250 mg/L and 4 g/L of TiO₂ photocatalyst (0.6:1 TiO₂:COD ratio). Table 22 summarizes the results of the first experiment.

Table 22. Removal of leachate water quality constituents from experiment 1 (4 g/L TiO₂) after 44 hours

Parameter	Units	C ₀	C ₄₄	Removal (%)
COD	mg/L as O ₂	6250	3910	37.4
Ammonia	mg/L as NH ₃ -N	1710	172	89.9
Alkalinity	mg/L as CaCO ₃	4630	500	89.2
Color	PCU	1130	525	55.5

The ammonia and alkalinity degraded at nearly an identical rate until the end of the experiment at which time both constituents approached 90% removal. Slightly more than half of the color was removed in 44 hours. The lowest removal percentage came from the COD at only 37.4%, but 2,350 mg/L of COD was destroyed. The wide difference in removal percentages prompted an investigation of which of the water quality parameters

may be limiting the process. This was determined by comparing the removal rates of COD, alkalinity and ammonia. A graphical display of the comparison is shown in Figure 34.

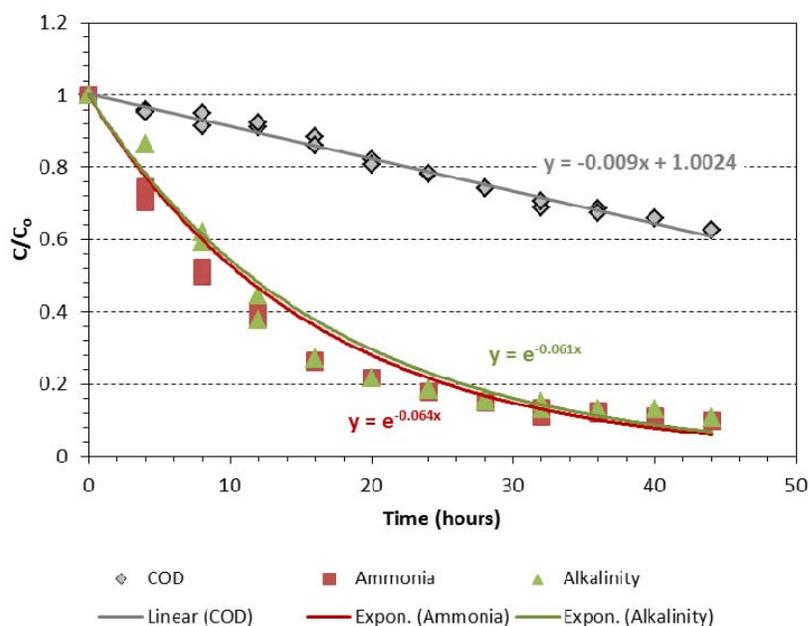


Figure 34. Removal rate comparison of alkalinity, ammonia and COD for experiment 1 (12/29/2011) using 4 g/L TiO₂

Figure 34 clearly shows a more rapid degradation rate for ammonia and alkalinity when compared to the oxidation of COD. It can be deduced that once all of the COD has been oxidized, the ammonia and alkalinity will likely have already been degraded as well. Also, it appears that the destruction of COD follows a linear trend while the degradation of ammonia and alkalinity follow a more complex trend that appears to be pseudo first order. The COD first order removal model exhibits a slope of -0.011 hr^{-1} ($R^2 = 0.984$) while the ammonia and alkalinity have slopes of -0.053 hr^{-1} ($R^2 = 0.944$) and -0.053 hr^{-1} ($R^2 = 0.922$), respectively. This shows that initially, the first order rate of degradation of alkalinity and ammonia is five times that of COD removal. This, again, clearly indicates COD to be the limiting parameter.

3.3.1.1. Experiment 1 COD Removal Kinetics

Since the limiting parameter was determined to be COD, the first set of kinetics investigation experiments was focused on COD removal. Kinetics data was plotted for

zero order (Figure 35), first order (Figure 36) and second order (Figure 37) overall reaction kinetics.

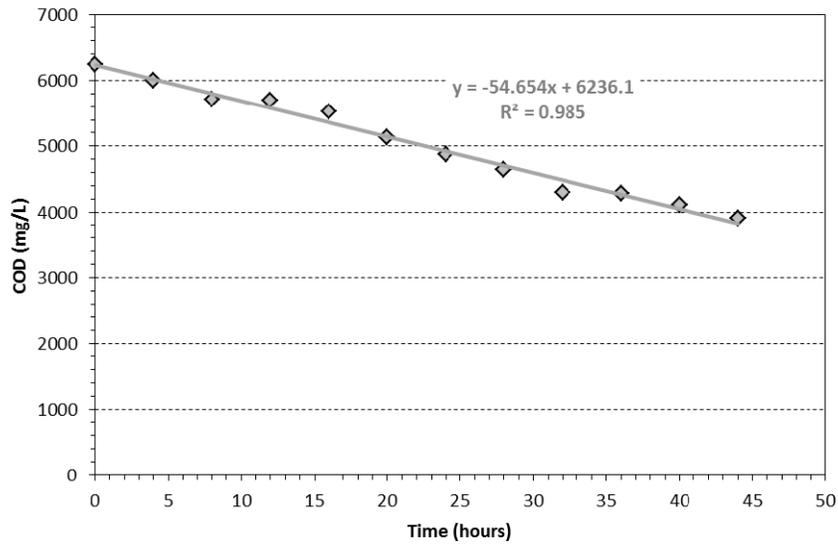


Figure 35: Zero order COD kinetics plot for experiment 1 (4 g/L TiO₂)

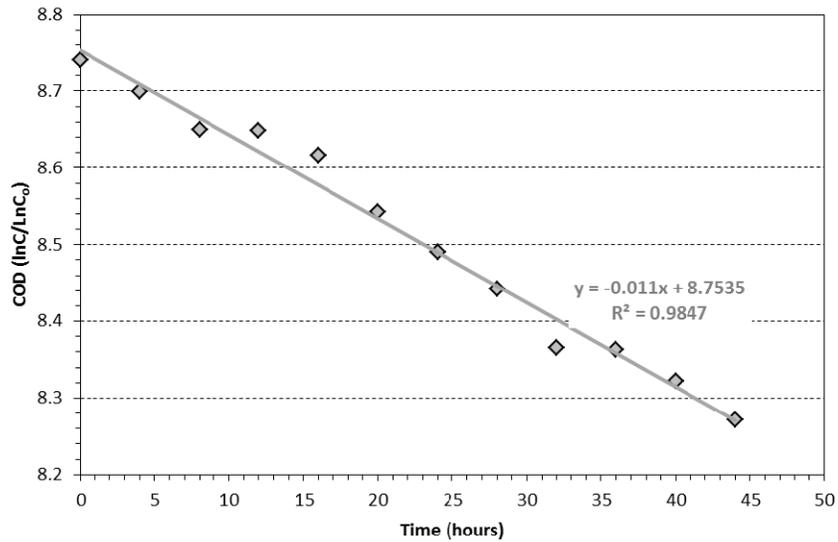


Figure 36. First order COD kinetics plot for experiment 1 (4 g/L TiO₂)

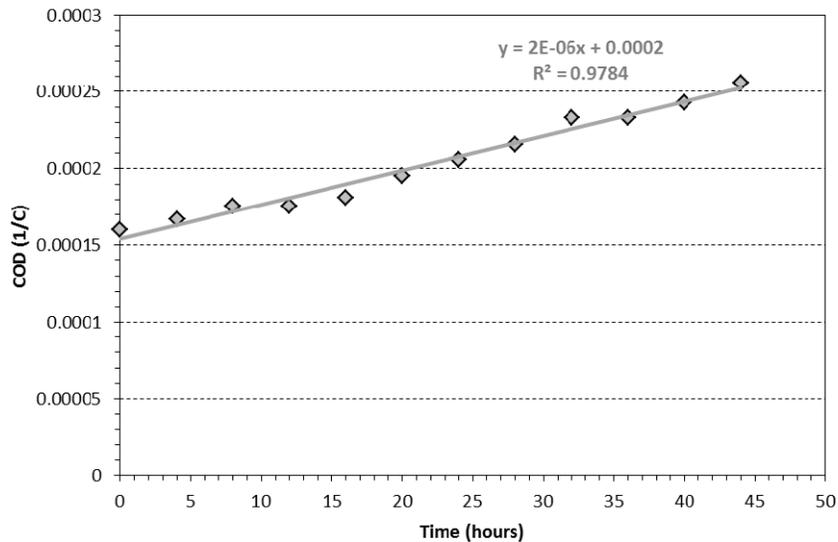


Figure 37. Second order COD kinetics plot for experiment 1 (4 g/L TiO₂)

As shown in previous testing by the FAU Laboratories for Engineered Environmental Solutions (Lab.EES) (Meeroff and McBarnette 2011) and according to Chong et al. (2010), some researchers found that zero order or first order kinetics is sufficient to model the photomineralization of certain organic compounds. Though, zero order assumes that the degradation rate is constant with time, which does not seem to be possible since the catalyst has reported issues with deactivation when it is swamped with contaminants on the reaction surface, which slows down the reaction process (Carneiro et al. 2010). First order reactions assume that the degradation rate is concentration-dependent, which fits with the experimental results and follows a behavior of multiple reactions taking place (an overall pseudo first-order behavior). For example, adsorption of organics on the TiO₂ surface reduces the active area for UV radiation to penetrate and excite the catalyst, which in turn decreases the reaction rate. Initially there is a high concentration of COD in the complex leachate matrix, which increases the probability that free radicals will collide with COD molecules as opposed to competing compounds. As the COD concentration decreases, it can be assumed that the likelihood of free radicals and/or photons colliding with COD particles in the matrix is decreased as well. From inspection of the data collected in this experiment, the coefficient of determination (R^2) is ≈ 0.985 for both zero and first order reactions suggesting an equal possibility of either zero or first order kinetics for COD degradation. Rearranging the kinetics equations to solve for the time needed for the actual removal percentage can provide further insight on the estimated reaction time for target removal of COD (800 mg/L COD). Using zero order kinetics this critical time value is calculated by the following:

$$t = \frac{C_t - C_0}{-k} = \frac{6246 - 800}{-56.23} = 96.9 \text{ hours}$$

The estimated critical time for target removal using first order kinetics is calculated by the following:

$$t = \frac{\ln\left(\frac{C_t}{C_0}\right)}{-k} = \frac{\ln\left(\frac{800}{6246}\right)}{-0.0102} = 201.5 \text{ hours}$$

Finally, the estimated critical time for target removal using second order kinetics is calculated by the following:

$$t = \frac{\left(\frac{C_0}{C_t} - 1\right)}{kC_0} = \frac{\left(\frac{6246}{800} - 1\right)}{0.000002 \times 6246} = 545 \text{ hours}$$

The time for the target achievement of 800 mg/L COD using 4 g/L TiO₂ under these conditions are estimated by zero order and first order calculations as 97 and 202 hours, respectively. Further investigation of the reaction order can be accomplished by fitting the data to the three models. If the data follows the zero, first or second order model, then it can be said that the data are consistent with that particular reaction rate, within the limits of observation (Hemond and Fechner-Levy 2000). The actual COD removal in 44 hours was 37.4%. Solving the zero order reaction equation for 37.4% removal results in a time of 41.5 hours (5.7% error). The times calculated for first and second order are 45.9 hours (4.3% error) and 47.8 hours (8.6% error), respectively. According to these results, the Cod removal data appear to more closely follow (pseudo-) first order reaction kinetics.

3.3.1.2. Experiment 1 Alkalinity Removal Kinetics

The same process was conducted for alkalinity, ammonia and color. The reaction kinetics plots for alkalinity can be seen in Figure 38 (zero order), Figure 39 (first order) and Figure 40 (second order).

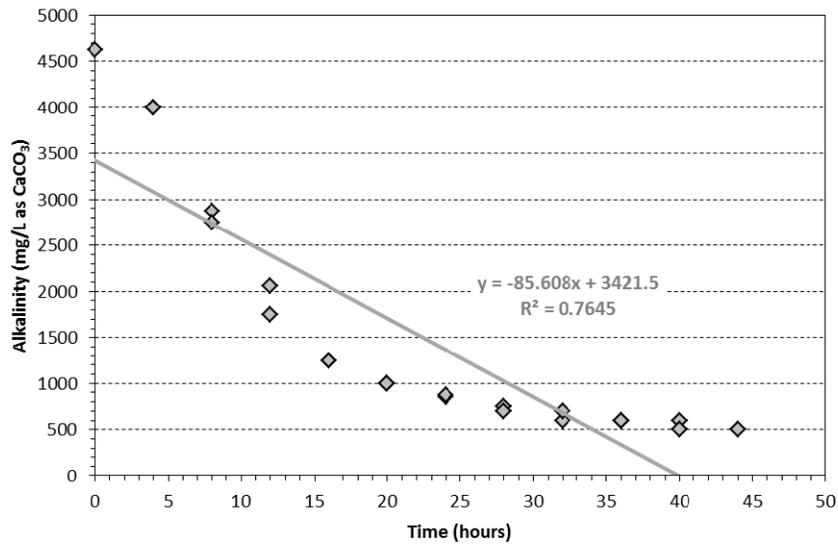


Figure 38. Zero order alkalinity kinetics plot for experiment 1 (4 g/L TiO₂)

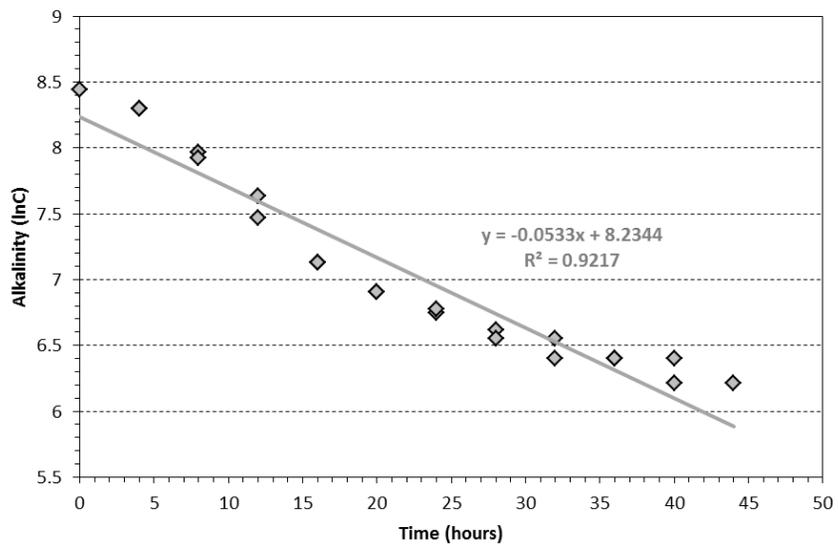


Figure 39. First order alkalinity kinetics plot for experiment 1 (4 g/L TiO₂)

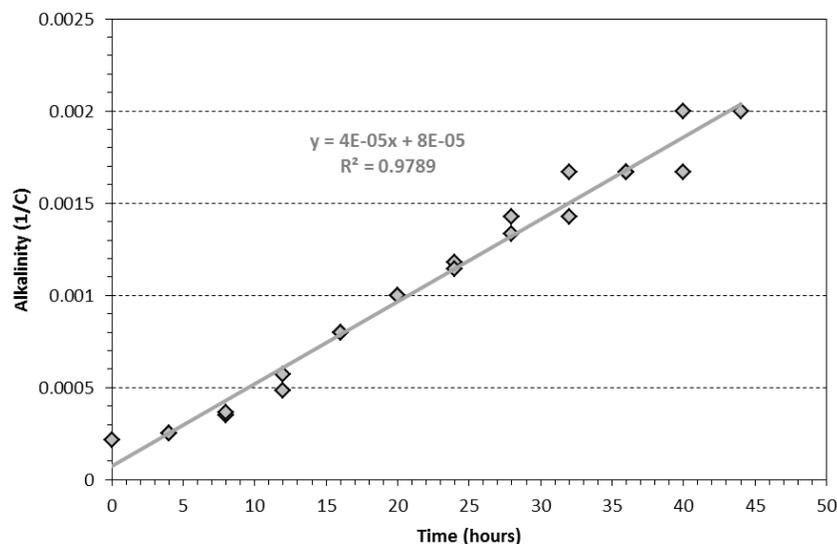


Figure 40. Second order alkalinity kinetics plot for experiment 1 (4 g/L TiO₂)

Inspection of the kinetics plots shows that the largest coefficient of determination is found with the second order kinetics data ($R^2 = 0.979$) followed by the first order reaction ($R^2 = 0.922$). The zero order kinetics can be ruled out since the shape of the data points clearly do not follow an acceptable linear relationship ($R^2 = 0.765$) and appear to create an exponential curve. Due to the high R^2 value of the first order plot, it is difficult to rule out first order even though the data points appear to have a slight curve to them as well. Following these data sets, it would take approximately 30 hours for 90% removal of alkalinity using first order kinetics and 43 hours modeling the second order reaction. Since the experiment actually showed 89% removal at 44 hours, the second order plot is the better fit to the observed data. Kwon et al. (2009) suggested that hydroxyl radical reactions follow second order reaction kinetics for organic compounds and alkalinity in the form of carbonate and bicarbonate. They compared their experimental rate constant to reported rate constants and found similar results. They found a bicarbonate rate constant of $1.93 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$ versus the expected value of $8.5 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$. By converting the k -value from Figure 40 to the same units, the result is $k = 7.6 \times 10^{-4} \text{ M}^{-1}\text{s}^{-1}$, which is approximately 10 orders of magnitude different. A major difference is that Kwon et al. (2009) studied the reaction constants strictly for hydroxyl radical attack of a laboratory solution of bicarbonate in pure water. In the photocatalytic degradation of landfill leachate, the sample matrix is substantially more complex. Bicarbonate alkalinity is known to be a hydroxyl radical scavenger (Kishimoto et al. 2007). Also, the relatively fast degradation of alkalinity could also be a result of aeration acting as an air stripping mechanism to release CO₂ from the leachate (Kishimoto et al. 2007), but this should only be significant at low pH, which was not the case in these experiments (pH > 7.54).

At circumneutral pH, the vast majority of alkalinity is present in the form of bicarbonate. The range of pH throughout all six experiments stayed within $\text{pH} > 6.35$ and < 10.33 , where the bicarbonate species dominates the carbonate system. The theoretical hydroxyl radical scavenging mechanism of bicarbonate is thought to occur as follows:



The bicarbonate ions react with hydroxyl radicals to form a significantly less effective carbonate radical and water. Due to the scavenging effects, Jia et al. (2011) suggests that removing alkalinity prior to photocatalytic treatment is necessary to increase degradation efficiency for other parameters of interest. The alkalinity plays a role in the rate-determination step for photocatalytic degradation due to its hydroxyl radical scavenging, inhibition of reactions at the catalyst surface on account of an increase in negative charge, pH effects, and promotion of catalyst aggregation (Autin et al. 2013). Also, in strongly alkaline waters (which was not the case in these experiments), OH^\bullet is rapidly converted to its conjugate base $^\bullet\text{O}^-$ (Buxton et al. 1988).

3.3.1.3. Experiment 1 Ammonia Removal Kinetics

The reaction kinetics plots for ammonia are shown in Figure 41 (zero order), Figure 42 (first order) and Figure 43 (second order).

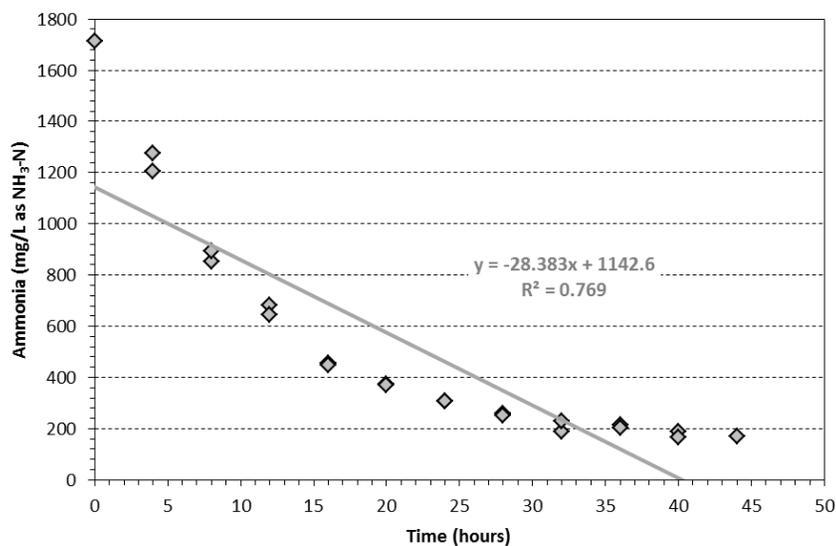


Figure 41. Zero order ammonia kinetics plot for experiment 1 (4 g/L TiO_2)

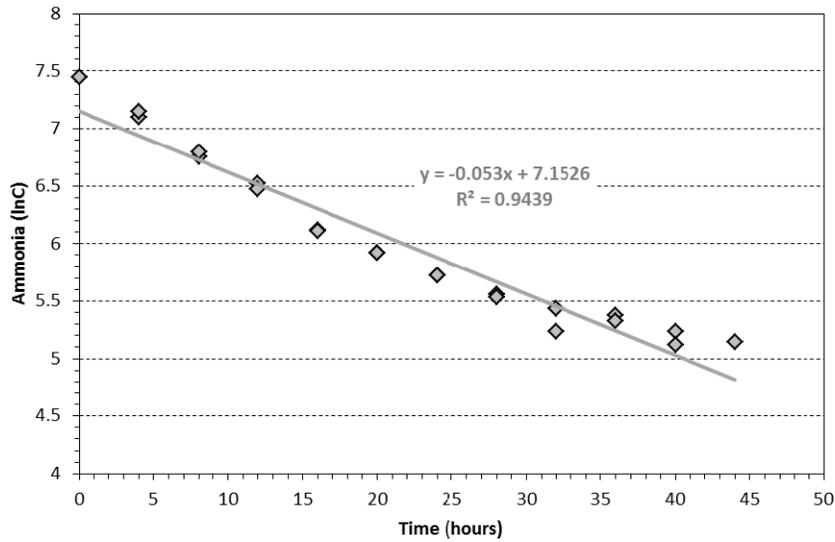


Figure 42. First order ammonia kinetics plot for experiment 1 (4 g/L TiO₂)

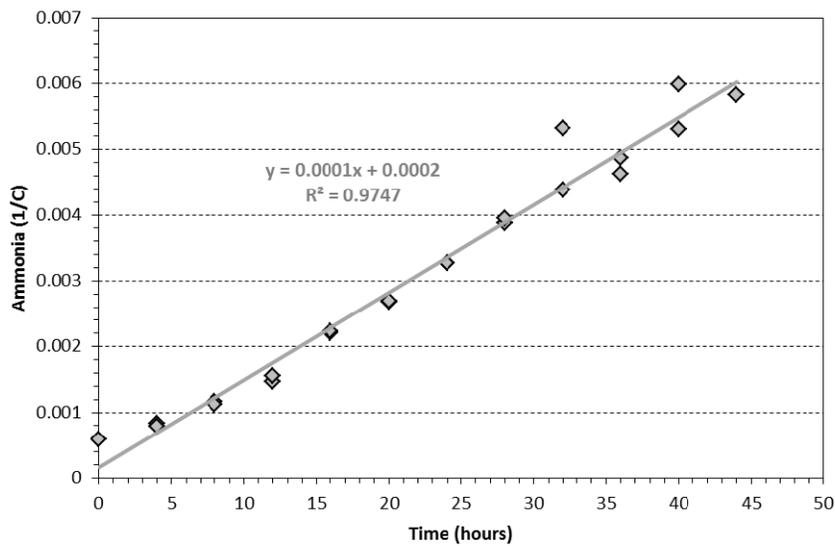


Figure 43. Second order ammonia kinetics plot for experiment 1 (4 g/L TiO₂)

Inspection of the kinetics data shows that the ammonia degradation closely mimics the alkalinity degradation. Again, the largest coefficient of determination was found for the second order kinetics plot ($R^2 = 0.975$) followed closely by the first order reaction ($R^2 =$

0.944). Zero order kinetics can be ruled out since the shape of the data points clearly do not follow a linear relationship ($R^2 = 0.769$) and appear to create an exponential curve. Similar to the alkalinity data, the high R^2 value of the first order plot makes it difficult to rule out first order even though the data points appear to have a slight curve to them. Following these data sets, it would take approximately 58 hours to achieve the 25 mg/L $\text{NH}_3\text{-N}$ target for sewer disposal using first order kinetics and 331 hours using second order kinetics. The experiment was stopped at 44 hours of elapsed time, at which the ammonia had been reduced to 172 mg/L $\text{NH}_3\text{-N}$ from an initial value of 1710 mg/L $\text{NH}_3\text{-N}$.

3.3.1.4. Experiment 1 Color Removal Kinetics

The reaction kinetic plots for color can be seen in Figure 44 (zero order), Figure 45 (first order) and Figure 46 (second order).

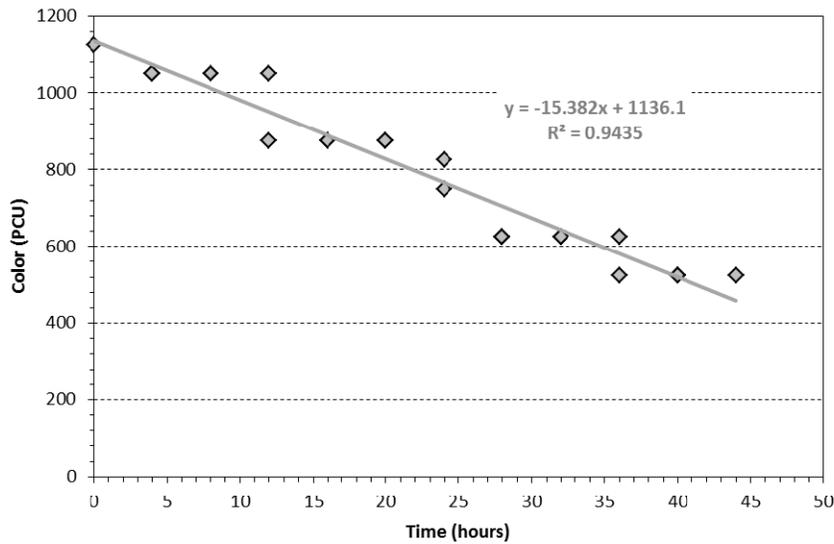


Figure 44. Zero order color kinetics plot for experiment 1 (4 g/L TiO_2)

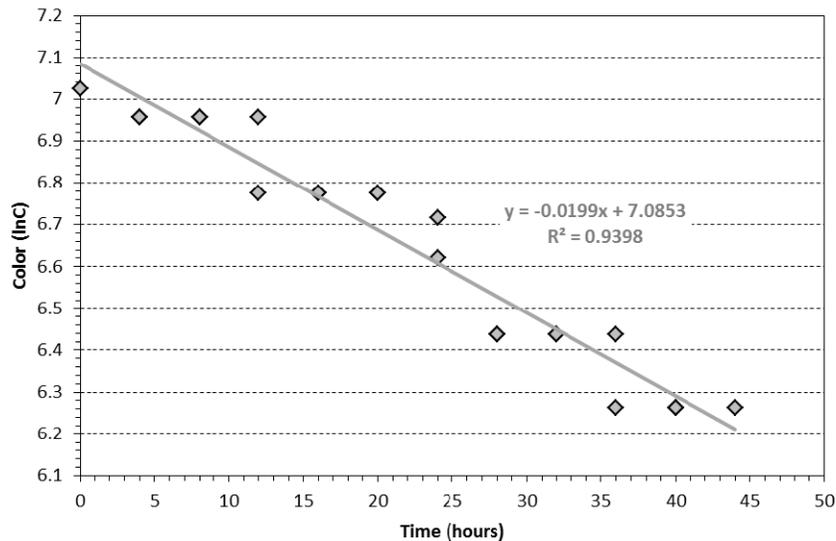


Figure 45. First order color kinetics plot for experiment 1 (4 g/L TiO₂)

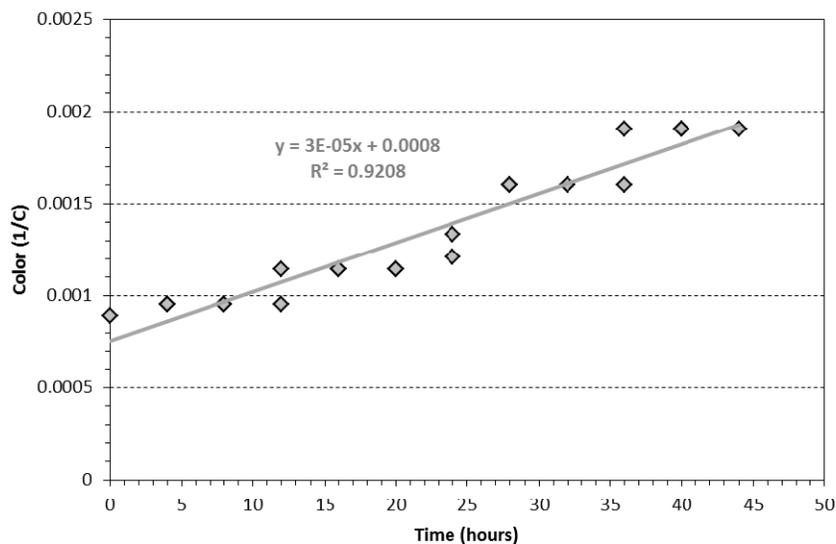


Figure 46. Second order color kinetics plot for experiment 1 (4 g/L TiO₂)

Analysis of the color removal data shows close linear trends for zero, first and second order ($R^2 = 0.944$, 0.940 and 0.921 , respectively). The results do not allow for the elimination of any of the possible reaction orders for color removal. Following these trends, 90% color removal is estimated at approximately 74 hours for zero order, 158

hours for first order and 500 hours for second order reactions. After 44 hours of treatment, the color value had been reduced to 525 PCU from an initial color of 1130 PCU.

3.3.2 Experiment 2

After the first 44-hour test (Experiment 1), the next step was increasing the TiO_2 dosage incrementally to attempt to improve efficiency. The starting point was the 4 g/L dose that gave 100% removal in 4 hours at the bench scale in previous testing (Meeroff and McBarnette 2011), but as described earlier, the pilot falling film reactor has a lower UV intensity and much lower contact time in the reaction zone compared to the bench scale testing conditions. Previous pilot testing conducted in FAU's Lab.EES with 28 g/L TiO_2 did not show promising results with respect to COD removal (Meeroff and McBarnette 2011). It was hypothesized that an effective TiO_2 dose would be from 4 g/L to 16 g/L.

This second extended-time experiment used leachate from Monarch Hill SE step-up station collected on March 9, 2012. The initial COD was 5,270 mg/L and the TiO_2 dose was 16 g/L. Samples were collected for parameter measurement at $t=0$ and $t=4$ for each daily run for a total of 10 days (or 40 total hours of treatment). The results of this experiment are summarized in Table 23.

Table 23. Summary of removal of selected water quality parameters from experiment 2 (16 g/L TiO₂) after 40 hours

Parameter	Units	C ₀	C ₄₀	Removal (%)
COD	mg/L as O ₂	5270	3160	40.0
Ammonia	mg/L as NH ₃ -N	1310	408	68.9
Alkalinity	mg/L as CaCO ₃	3560	1000	71.9
Color	PCU	825	425	48.5

Similar to experiment 1, the ammonia and alkalinity degraded at a comparable rate (within 3%), achieving approximately 70% removal. Slightly less than 50% of the color was removed in 40 hours. Again, the lowest removal percentage came from the COD at 40%, which represents 2,110 mg/L of COD that was destroyed. The high removal percentage of alkalinity and ammonia compared to the lower degradation rate of COD supports the limiting parameter hypothesis from experiment 1.

3.3.3.1. Experiment 2 COD Removal Kinetics

Kinetics data for COD removal was plotted for zero order (Figure 47), first order (Figure 48) and second order (Figure 49).

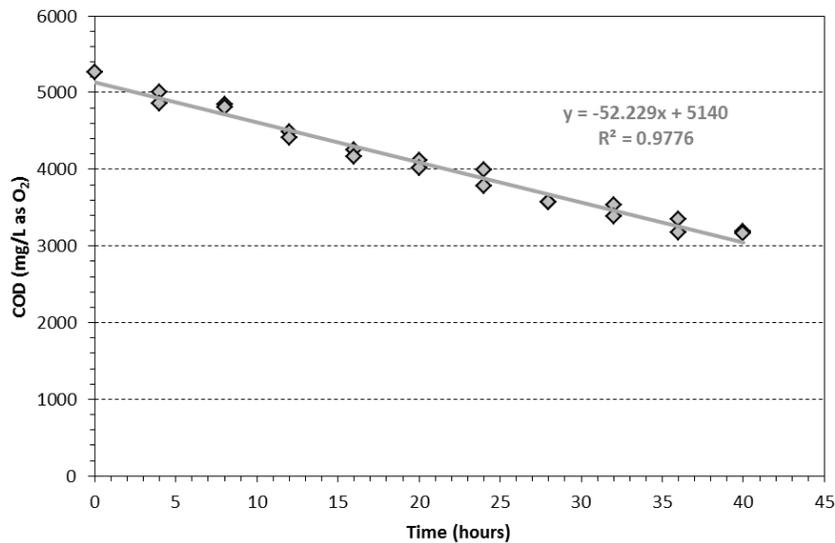


Figure 47. Zero order COD kinetics plot for experiment 2 (16 g/L TiO₂)

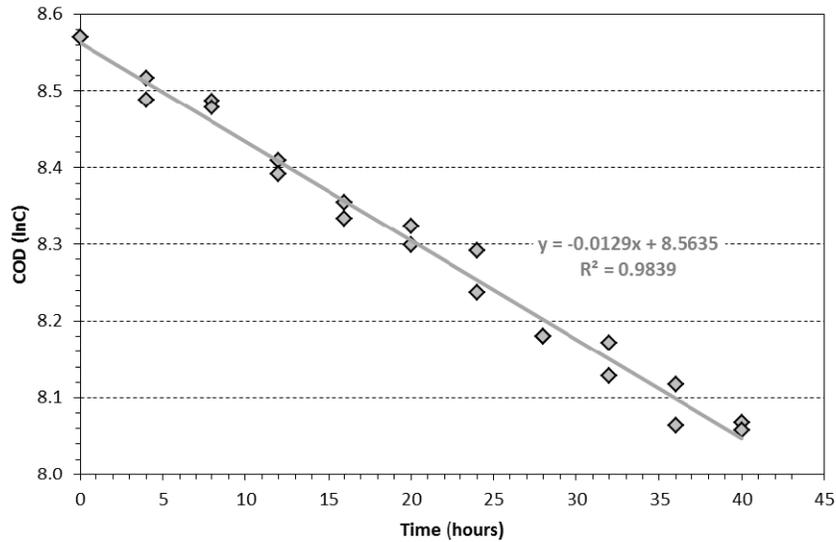


Figure 48. First order COD kinetics plot for experiment 2 (16 g/L TiO₂)

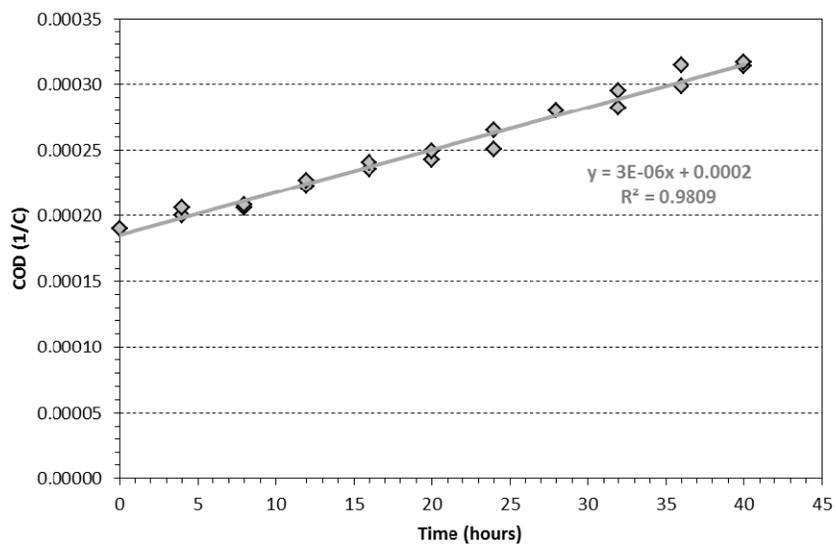


Figure 49. Second order COD kinetics plot for experiment 2 (16 g/L TiO₂)

The kinetics from this experiment appear to follow first order kinetics ($R^2 = 0.984$). However, zero and second order also cannot be ruled out, $R^2 = 0.978$ and 0.981 , respectively. Using this data, the removal time to achieve 800 mg/L COD is estimated to

take 78 hours for zero order, 148 hours for first order and 353 hours for second order kinetics. The actual removal of COD was 40% in 40 hours, which corresponds to a removal of 2,110 mg/L of COD.

Solving the first order reaction for the time to remove 40% COD results in 40.2 hours (0.5% error). The zero order and second order estimations result in times of 36.9 hours (7.8% error) and 42.2 hours (5.5% error), respectively. Similarly to experiment 1, the first order estimation equates better to the actual removal, strongly supporting COD degradation as a pseudo-first order reaction.

3.3.3.2. Experiment 2 Alkalinity Removal Kinetics

Further investigation of the kinetics for alkalinity was conducted by plotting the zero order (Figure 50), first order (Figure 51) and second order (Figure 52) data.

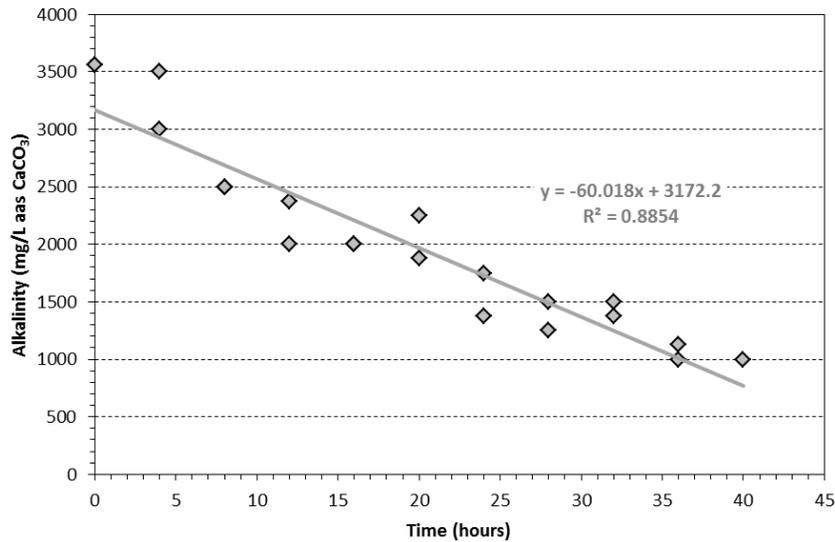


Figure 50. Zero order alkalinity kinetics plot for experiment 2 (16 g/L TiO₂)

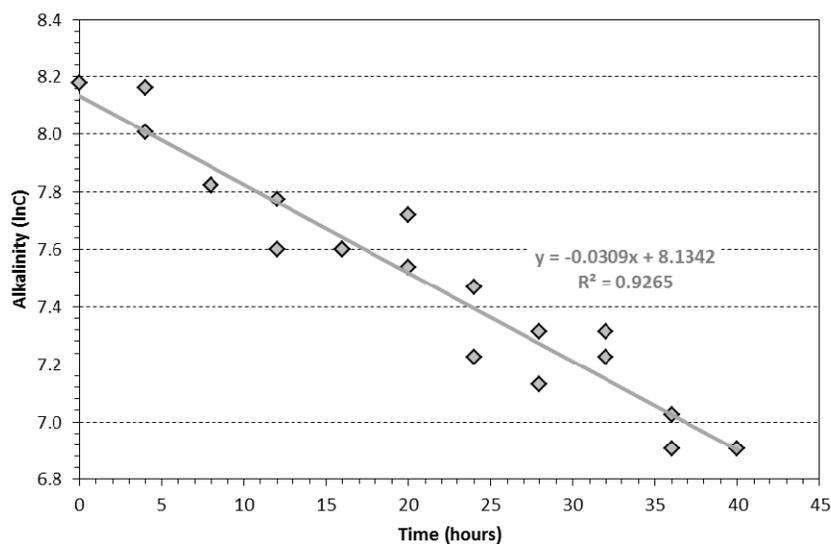


Figure 51. First order alkalinity kinetics plot for experiment 2 (16 g/L TiO₂)

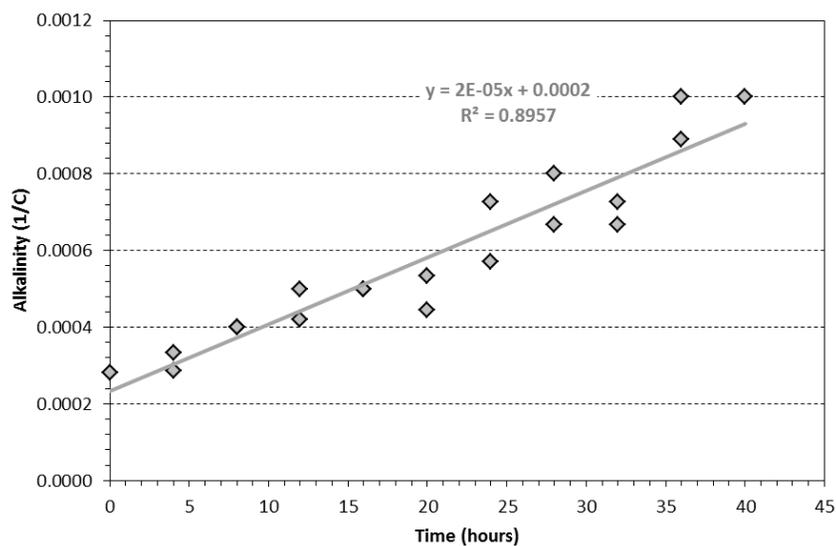


Figure 52. Second order alkalinity kinetics plot for experiment 2 (16 g/L TiO₂)

The data show the highest coefficient of determination is found with the first order reaction kinetics ($R^2 = 0.927$) followed closely by second order reaction ($R^2 = 0.896$).

The zero order reaction has a slightly higher linear correlation in this test than in experiment 1 ($R^2 = 0.885$ vs. $R^2 = 0.765$, respectively). However, the zero order reaction plot appears to have a slight curve, whereas the data for the second order plot appears to be randomly scattered from the mean. Using the second order kinetics formulas to solve for 71.9% removal (actual removal achieved by the experiment) of alkalinity, the time was found to be 51 hours which is 11 hours above the actual time. Following first order kinetics, 71.9% removal was estimated to be 40 hours, which coincides with the experimental value. This highly supports alkalinity degradation following first order kinetics. Using the same first order kinetics, the time for 90% removal is approximately 72 hours.

3.3.3.3. Experiment 2 Ammonia Removal Kinetics

The reaction kinetics of ammonia removal was further studied by plotting the zero order (Figure 53), first order (Figure 54) and second order (Figure 55) kinetics data.

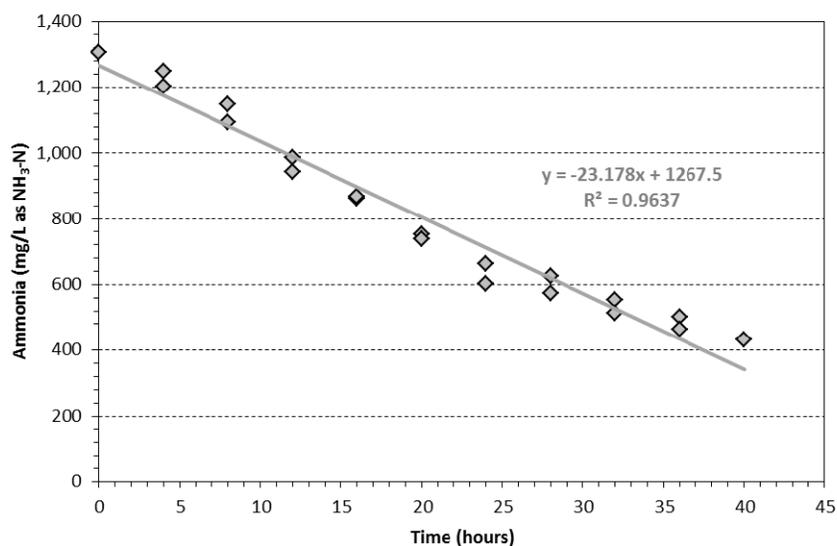


Figure 53. Zero order ammonia kinetics plot for experiment 2 (16 g/L TiO₂)

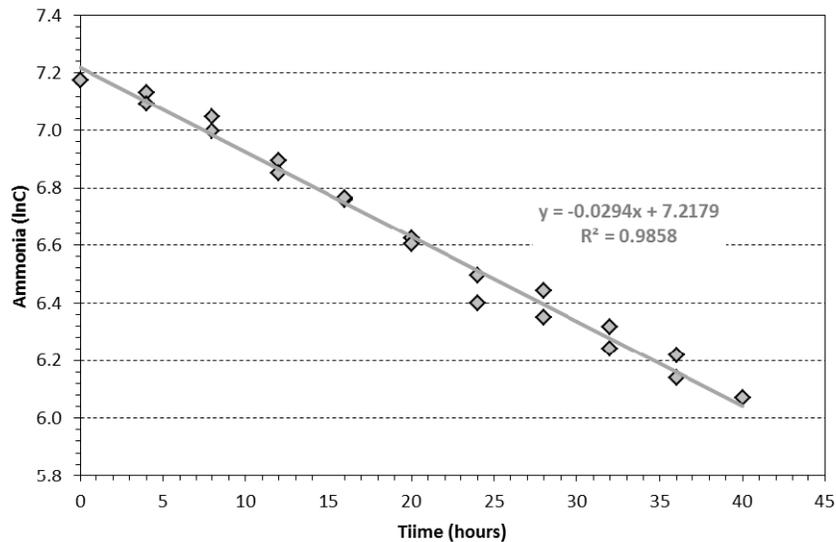


Figure 54. First order ammonia kinetics plot for experiment 2 (16 g/L TiO₂)

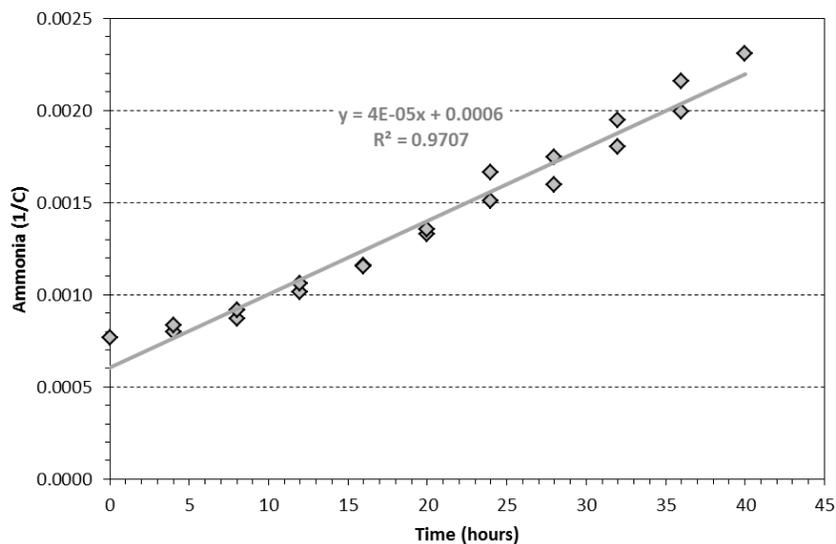


Figure 55. Second order ammonia kinetics plot for experiment 2 (16 g/L TiO₂)

Similarly to the alkalinity results, the ammonia degradation shows the strongest linear relationship with first order kinetics ($R^2 = 0.986$) followed closely by second order ($R^2 = 0.971$). The zero order plot shows the data following a slight curve, while the first order and second order show a trendline characterized by more randomized scatter about the mean. The actual removal of ammonia achieved in 40 hours was 68.9%. Modeling

second order kinetics to estimate the time necessary for 68.9% removal returns a value of 48 hours, which is 8 hours higher than the actual time. For 68.9% removal using first order kinetics, only 37 hours was estimated, which is just 3 hours shy of the actual value. Ammonia appears to primarily follow first order kinetics. Using the first order kinetics, achieving the 25 mg/L goal is estimated to take 125 hours of treatment under these conditions.

3.3.3.4. Experiment 2 Color Removal Kinetics

The reaction order kinetics plots for color removal are shown in Figure 56 (zero order), Figure 57 (first order) and Figure 58 (second order).

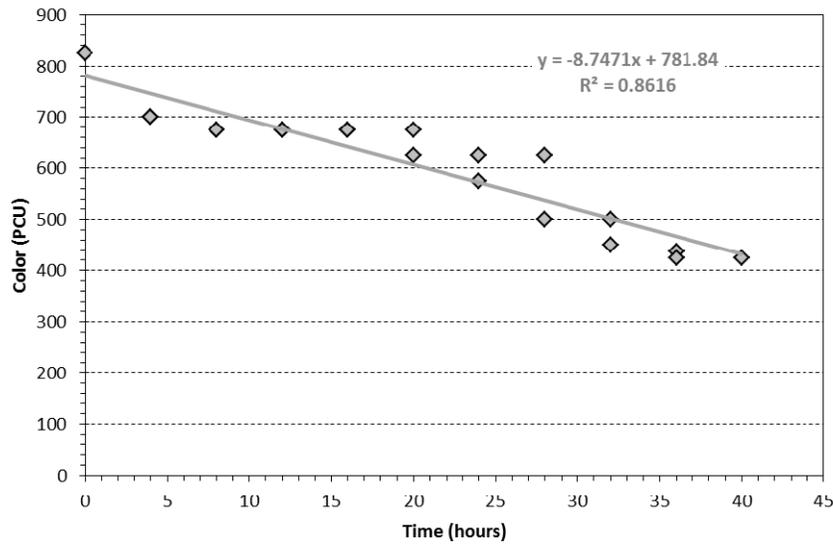


Figure 56. Zero order color kinetics plot for experiment 2 (16 g/L TiO₂)

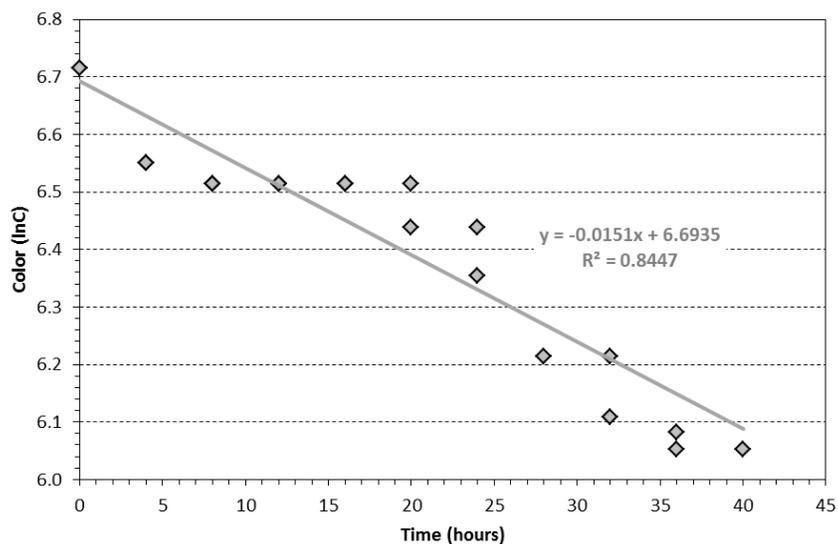


Figure 57. First order color kinetics plot for experiment 2 (16 g/L TiO₂)

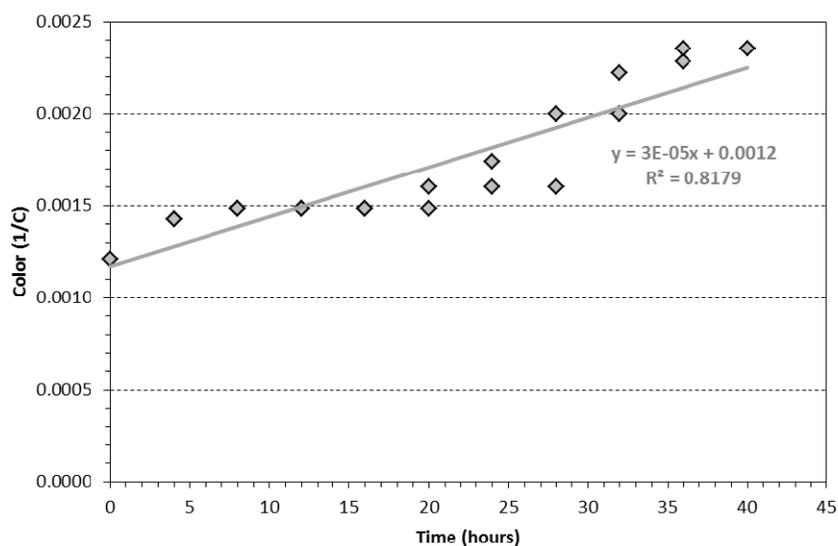


Figure 58. Second order color kinetics plot for experiment 2 (16 g/L TiO₂)

The strongest linear relationship for color falls on the zero order plot ($R^2 = 0.862$) followed closely by the first order plot ($R^2 = 0.845$). The second order reaction kinetics have the smallest coefficient of determination ($R^2 = 0.818$), suggesting the color

degradation is not second order. In 40 hours, 48.5% of the color was removed. Using the zero, first and second order kinetics equations to solve for the time to remove 48.5% of the color, it would take 46, 44, and 38 hours, respectively. None of these times correlate with the actual data, making the reaction kinetics difficult to determine. This is attributed to the limitation of the color testing method, which relies on the perception of color from the naked eye. Also, the color wheel markings were spaced too far away to allow for accurate estimates to be made at the dilution levels used (1:25). Cortes et al. suggests that color removal from a TiO₂/UV AOP follows a zero order decolorization reaction rate (2008); however, this pilot testing cannot confirm this relationship. It is recommended to record an absorbance value at $\lambda = 254$ nm to obtain a more sensitive value for measuring the kinetics relationship for apparent color.

3.3.3 Experiments 3 through 6

Experiments 1 and 2 allowed for the reaction kinetics determination for ammonia, alkalinity, COD and color. These parameters were all found to follow varying reaction orders and thus were modeled using overall first order kinetics for the remainder of testing. Prior to beginning experiment 3, calculations using the kinetics equations were made with the removal data for each parameter to predict the removal at any given time. The results of the COD prediction modeling with overall first order kinetics are shown in Table 24.

Table 24: COD removal predictions for experiments 1 and 2 using 24 hour k-values from first order kinetics

TiO ₂ (g/L)	k-value (hr ⁻¹)	C ₀ (mg/L as O ₂)	t (hr)	Concentration (mg/L)		% Removal		% error
				calculated	actual	calculated	actual	
4	-0.0102	6246	44	3990	3910	36.2	37.4	1.98
16	-0.0127	5268	40	3170	3160	39.8	40.0	0.32

The results showed that using the k-value from the experiments at 24 hours provided an accurate representation of the actual removal at the end of the extended-term experiments (40 – 44 hrs) using first order kinetics. Using the 24-hour k-values for first order reactions allow for prediction of the COD concentration with less than 2% error (see Table 24). This demonstrates that the removal pattern does not effectively change after 24 hours. Similar prediction tables were made for the other parameters (Appendix C). Since the results were similar, subsequent experiments were performed for a total of 24 hours, rather than 40 or more.

Experiments 3 – 6 investigated removal efficiencies at various catalyst dosages, varying from 10 – 40 g/L TiO₂. The results of each experiment determined the catalyst dosage for the next experiment. The removal efficiencies for all the parameters of interest for all six experiments can be seen in Table 25, in order of increasing TiO₂ dose.

Table 25: Summary of water quality indicator removal at 24 hours for experiments 1 – 6

Experiment		1	6	2	3	5	4
	TiO ₂ (g/L)	4	10	16	25	30	40
	Max Temp. (°C)	36.7	37.1	35.7	36.0	36.3	36.7
pH	Min	8.35	7.66	7.63	7.54	7.70	7.59
	Max	9.26	9.09	9.18	8.96	9.20	9.06
	Mean	8.89	8.73	8.84	8.72	8.87	8.74
COD	C ₀ (mg/L as O ₂)	6,250	6,060	5,270	5,360	6,140	6,990
	C ₂₄ (mg/L as O ₂)	4,880	4,510	3,890	3,540	4,320	4,560
	Removal (%)	22	26	26	34	30	34
	k-value (hr ⁻¹)	0.0102	-0.0125	-0.0127	-0.0167	-0.0146	-0.0160
Alkalinity	C ₀ (mg/L as CaCO ₃)	4,630	4380	3,560	3,560	4,130	4,310
	C ₂₄ (mg/L as CaCO ₃)	860	700	1,560	1,940	1,010	1,190
	Removal (%)	81	84	56	46	75	72

Experiment	1	6	2	3	5	4
k-value (hr⁻¹)	- 0.0780	-0.0794	-0.0319	-0.0228	-0.0585	-0.0496
C₀ (mg/L as NH₃-N)	1,710	1,700	1,310	1,380	1,640	1,520
C₂₄ (mg/L as NH₃-N)	306	470	602	700	850	850
Ammonia Removal %	82	72	52	49	48	44
k-value (hr⁻¹)	- 0.0726	-0.0580	-0.0316	-0.0271	-0.0275	-0.0227
C₀ (PCU)	1,130	813	825	788	756	756
C₂₄ (PCU)	788	600	600	525	450	325
Color Removal (%)	30	26	27	33	40	57
k-value (PCU/hr)	- 13.735	-5.9390	-7.0910	-16.809	-9.2500	-8.8170

As shown in Table 25, COD removal generally increased with increasing TiO₂ dose, but for the other water quality parameters, this was not the case. The ammonia removal actually decreased with an increase in catalyst concentration. The overall pH range throughout all of the experiments was 7.54 – 9.26. The mean pH values for each experiment were within 0.2 pH units of each other. Comparing the pH to the removal of each individual parameter does not show any obvious trend. Even in the high destruction of alkalinity, it was expected to see relatively greater changes in pH, but this was not the case. As the literature suggested, higher pH levels demonstrated greater destruction of ammonia compared to COD, which is reported to degrade faster in acidic conditions (Chemlal 2013).

3.3.3.1. Experiment 3 – 6 COD Removal Kinetics

Taken together, the six 24-hour treatment experiments showed a range of COD destruction from 22% to 34%. The largest removal efficiency for COD is observed using 25 g/L and 40 g/L of catalyst, which both achieved 34% removal. More mass of COD was removed with the 40 g/L dose (2430 mg/L vs. 1820 mg/L), but the final concentration for the 25 g/L dose was lower (3540 mg/L vs. 4560 mg/L). The removal efficiency was increasing with catalyst dosage until the 25 g/L dose. Catalyst doses in excess of 25 g/L demonstrated similar removal efficiency but at a cost of using much more TiO₂ photocatalytic particles. To compare the first order destruction rates for each catalyst dosage, a plot was created (Figure 59). Figure 59 shows that the highest degradation rate takes place at the TiO₂ dose of 25 g/L ($k = -0.0167 \text{ hr}^{-1}$), followed closely by 40 g/L ($k = -0.0160 \text{ hr}^{-1}$). The slowest rate of COD destruction was from the first experiment using 4 g/L TiO₂ ($k = -0.0102 \text{ hr}^{-1}$).

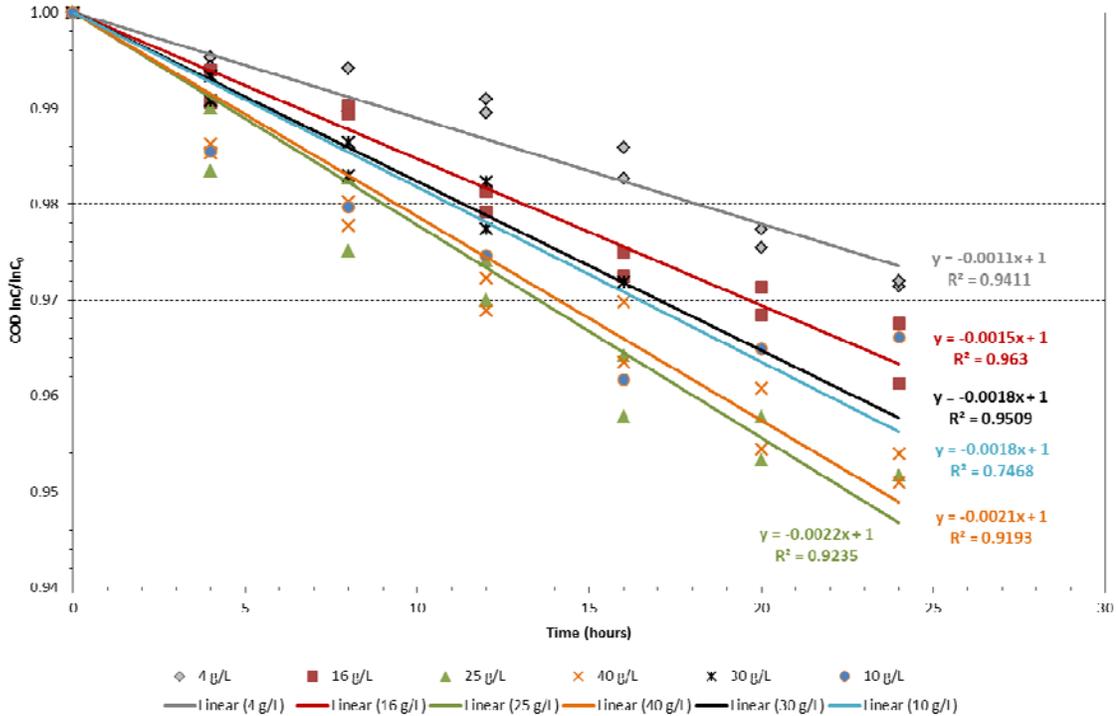


Figure 59. Comparison plot of first order COD removal after 24 hours for the catalyst dosages from six experiments

Since the removal target for COD (800 mg/L) was not technically achieved by any of the experiments so far, based on the 24 – 44 hour tests, predictions for the time necessary to reach 800 mg/L COD were made. Using the first order kinetics plots to get a k -value for each experiment, the times to achieve the target COD (800 mg/L as O₂) were compared in Table 26.

Table 26. Comparison of times to achieve target level COD removal using first order decay rates from six experiments

Experiment	TiO ₂ (g/L)	k -value (hr ⁻¹)	C ₀ (mg/L as O ₂)	C _t (mg/L as O ₂)	t (hr)
1	4	-0.0102	6246	800	201.5
2	16	-0.0127	5268	800	148.4
3	25	-0.0167	5360	800	113.9
4	40	-0.0160	6980	800	135.4
5	30	-0.0146	6135	800	139.5
6	10	-0.0125	6064	800	162.0

Just as the comparison plot (Figure 59) demonstrated, Table 26 concludes that the catalyst dosage of 25 g/L achieved the fastest degradation rate ($k = -0.0167 \text{ hr}^{-1}$) and therefore had the lowest time ($t = 113.9$ hours) to reach the target COD. The k -values ranged from -0.0102 to -0.0167 hr^{-1} . These values were less than the k -values from the batch scale reactor with real leachate experiments performed by André McBarnette (2011), who observed k -values ranging from -0.027 to -0.125 hr^{-1} , double to nearly 10 times the rates from this pilot study. The most rapid degradation in those previous experiments ($k = -0.125 \text{ hr}^{-1}$) took place in a six-hour treatment time with an initial COD concentration of 5,218 mg/L and used 35.5 g/L TiO_2 plus lime and sulfuric acid addition. Also, the maximum temperature reached nearly 60°C . In six hours of treatment, 55% of the COD was mineralized. Using the first order kinetics for the batch scale reactor, the lowest estimated time to achieve the target COD (800 mg/L) was 15 hours or about one tenth of the fastest time observed with the falling film pilot scale reactor. Literature review revealed photocatalytic destruction of COD to have first order reaction rate constants ranging from -0.026 hr^{-1} to -0.456 hr^{-1} (Vineetha et al. 2012, Ghaly et al. 2011, Chemlal et al. 2013). Although the study which showed the lowest k values (-0.026 hr^{-1} to -0.061 hr^{-1}) was the only one conducted with real landfill leachate, indicating lower removal rates in the treatment of leachate versus other wastewaters. From inspection of Table 26, the pilot scale degradation rates are similar in value and do not show a clear correlation between the rate of removal and initial concentration of COD.

3.3.3.2. Experiment 3 – 6 Alkalinity Removal Kinetics

The alkalinity in all six experiments existed primarily as bicarbonate species since the pH extremes ranged from 7.4 – 9.3, which are levels where bicarbonate is the dominant species of the carbonate system. The destruction of alkalinity for the six experiments ranged from 46% to 84% (see Table 25). Experiment #6 (10 g/L TiO_2) demonstrated the greatest efficiency by removing 84% of the alkalinity in 24 hours. The lowest removal was exhibited in the third experiment (25 g/L TiO_2) with 46% removal. The removal efficiency of alkalinity did not seem to correlate with the catalyst dosage as there were high amounts of alkalinity reduction with higher and lower dosages of TiO_2 . A graphical comparison for the alkalinity destruction in all six experiments is shown in Figure 60.

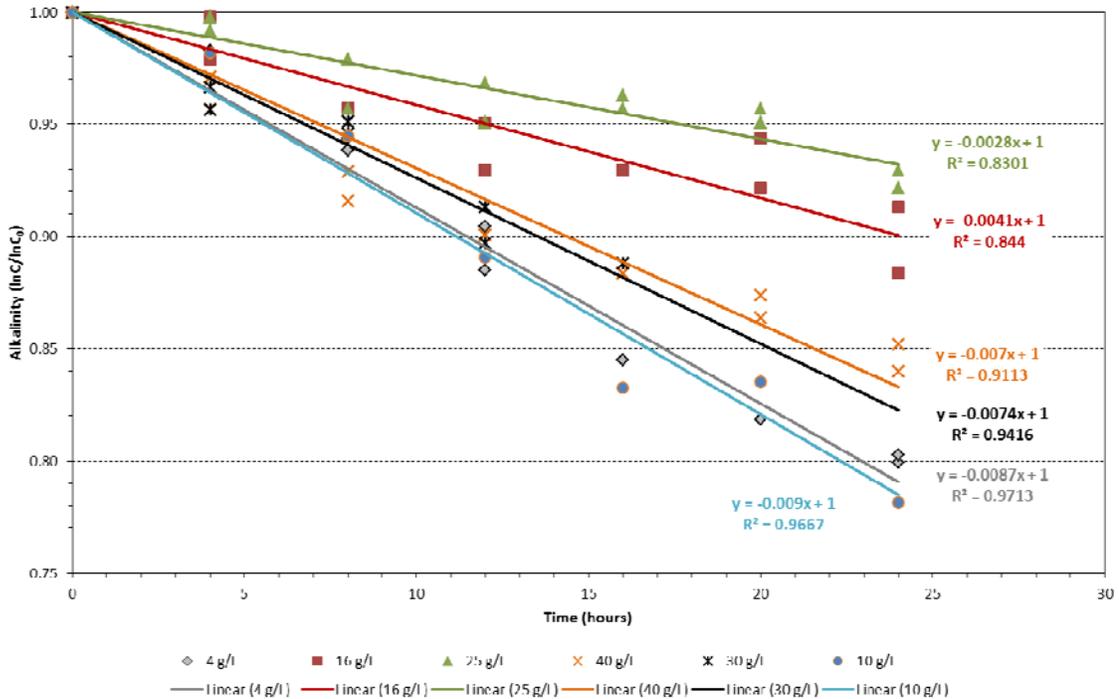


Figure 60. Comparison plot of first order alkalinity removal after 24 hours for the catalyst dosages from six experiments

Figure 60 shows that the fastest alkalinity removal rate occurs at a catalyst dosage of 10 g/L ($k = -0.0794 \text{ hr}^{-1}$), closely followed by 4 g/L ($k = -0.0780 \text{ hr}^{-1}$). The slowest destruction rate of alkalinity came from the experimental catalyst dose of 25 g/L ($k = -0.0228 \text{ hr}^{-1}$). There does not appear to be any clear relationship between the catalyst dosage and removal rate of alkalinity, although it was observed that a film of carbonate was deposited at an accelerated rate on the falling film column with increasing temperatures and operating times.

Experiment 1 nearly achieved a 90% reduction in alkalinity in 44 hours of treatment. None of the other experiments approached 90% removal although it is likely that experiment 6 would have exceeded 90% if run for 44 hours. To estimate the time required for this experiment, as well as the other five experiments, to achieve 90% alkalinity reduction a summary was made using first order degradation constants (see Table 27).

Table 27. Comparison of times to achieve 90% alkalinity removal using first order decay rates from six experiments

Experiment	TiO ₂ (g/L)	k-value (hr ⁻¹)	C ₀ (mg/L as CaCO ₃)	C _t (mg/L as CaCO ₃)	t (hr)
1	4	-0.0780	4625	463	29.5
2	16	-0.0319	3560	356	72.2
3	25	-0.0228	3563	357	101.0
4	40	-0.0496	4313	431	46.4
5	30	-0.0585	4125	413	39.4
6	10	-0.0794	4375	438	29.0

Table 27 demonstrates that the catalyst dosage of 10 g/L achieved the fastest degradation rate ($k = -0.0794 \text{ hr}^{-1}$) and therefore had the lowest time ($t = 29$ hours) to reach 1-log removal of alkalinity. The slowest rate of alkalinity reduction ($k = -0.0228 \text{ hr}^{-1}$) was exhibited by the experimental dosage of 25 g/L TiO₂, resulting in an estimation of 101 hours for target removal. The removal of alkalinity to the goal of 90% has the lowest removal times of all the measured parameters, which may show a preferential reaction with bicarbonate species, which act as hydroxyl radical scavengers (Holmes 2003), even though alkalinity was needed to initiate the reaction in laboratory tests of artificial leachates containing KHP and water (Meeroff and McBarnette 2011). The two samples that had initial alkalinity concentrations under 4,000 mg/L as CaCO₃ had lower degradation rates and lower overall percentage removal compared to the samples with higher initial alkalinity. This suggests that the degradation of alkalinity has some dependence on the initial concentration, which is an indicator of first-order reaction kinetics.

3.3.3.3. Experiment 3 – 6 Ammonia Removal Kinetics

The six experiments showed a range of ammonia destruction from 44% to 82%, with a 38% difference between the highest and lowest removal percentage (see Table 25). Experiment #1 (4 g/L TiO₂) demonstrated the greatest efficiency with 82% removal in 24 hours. The lowest removal was exhibited by the highest catalyst dose (40 g/L). The removal efficiency of ammonia consistently decreased as the catalyst dosage increased. A graphical comparison for the ammonia destruction in all six experiments is shown in Figure 61.

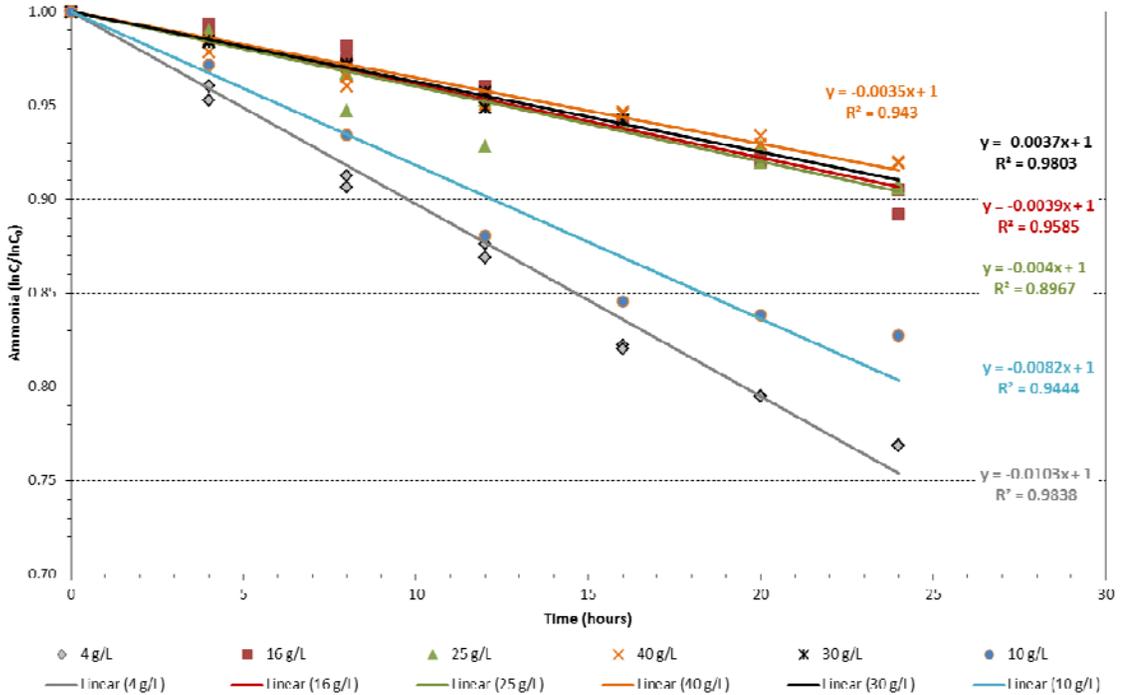


Figure 61. Comparison plot of first order ammonia removal after 24 hours for the catalyst dosages from six experiments

Inspection of Figure 61 shows that the highest ammonia removal rate takes place at the lowest TiO_2 dose of 4 g/L ($k = -0.0726 \text{ hr}^{-1}$), followed by 10 g/L ($k = -0.0580 \text{ hr}^{-1}$). These two doses exhibited removal rates much higher than the other four experiments. In fact, the reaction rate decreases with increasing catalyst. The slowest rate of ammonia destruction ($k = -0.0227 \text{ hr}^{-1}$) came from the highest amount of catalyst application (40 g/L TiO_2). The Broward County Sewer Use Limitations state that ammonia levels need to be less than or equal to 25 mg/L as $\text{NH}_3\text{-N}$ to avoid exceedance fees. Since none of the experiments were able to achieve this goal, the time necessary to do so had to be estimated from kinetics data. Using the first order kinetics plots to get a k-value for each experiment, the times to achieve the target ammonia (25 mg/L as $\text{NH}_3\text{-N}$) were compared in order of increasing catalyst (Table 28).

Table 28. Comparison of times to achieve target level ammonia removal using first order decay rates from six experiments

Experiment	TiO ₂ (g/L)	pH range (pH units)	k-value (hr ⁻¹)	C ₀ (mg/L as NH ₃ -N)	C _t (mg/L as NH ₃ -N)	t (hr)
1	4	8.35 – 9.26	-0.0726	1713	25	58.2
6	10	7.66 – 9.09	-0.0580	1700	25	72.7
2	16	7.63 – 9.18	-0.0316	1310	25	125.3
3	25	7.54 – 8.96	-0.0271	1380	25	148.0
5	30	7.70 – 9.20	-0.0275	1635	25	152.0
4	40	7.59 – 9.06	-0.0227	1523	25	181.0

Just as Figure 61 displayed, Table 28 demonstrates that the catalyst dosage of 4 g/L achieved the fastest degradation rate ($k = -0.0726 \text{ hr}^{-1}$) and therefore had the lowest time ($t = 58.2$ hours) to reach the target ammonia concentration. Also, it can be seen that an increase in catalyst dosage results in a decrease of ammonia removal efficiency. The slowest rate of ammonia reduction was observed at the highest dose of TiO₂, resulting in an estimate of 181 hours for target removal. The degradation rates appear to have no observable correlation to the initial concentration. However, since the degradation of ammonia decreased with increasing levels of catalyst it can be noted that the optimum catalyst dose for ammonia removal may actually be lower than 4 g/L, which was the smallest amount used during pilot testing.

Ammonia removal is highly dependent on the pH (Yuzawa et al. 2012). The dissociation of the ammonium ion (NH₄⁺) to free ammonia (NH₃) occurs at a high pH ($\text{pK}_a = 9.24$). The most rapid photodecomposition of ammonia occurs when it exists in the form of NH₃ (Nemoto et al. 2007). The first experiment exhibited a maximum pH of 9.26 and also showed the fastest degradation rate of ammonia. So to further investigate the relationship between ammonia and pH, a table was constructed to compare the pH range for each time interval up to 24 hours for the three lowest catalyst doses (Table 29).

Table 29. Comparison of pH range and ammonia removal for every 4 hour time interval up to 24 hours

Time (hr)	TiO ₂ = 4 g/L		TiO ₂ = 10 g/L		TiO ₂ = 16 g/L	
	pH	NH ₃ -N % removal	pH	NH ₃ -N % removal	pH	NH ₃ -N % removal
0 – 4	8.35 – 9.20	29.63	7.66 – 9.07	19.00	7.63 – 8.85	29.64
4 – 8	9.04 – 8.98	20.55	9.07 – 9.04	19.66	8.97 – 8.88	7.79
8 – 12	9.26 – 9.10	10.03	9.04 – 9.09	20.25	9.01 – 8.99	12.44
12 – 16	9.22 – 9.03	13.21	9.09 – 9.01	9.41	9.16 – 9.02	9.39
16 – 20	9.18 – 8.91	4.82	9.01 – 8.61	1.62	9.12 – 9.01	8.32
20 – 24	9.09 – 8.91	3.87	8.61 – 8.62	2.39	9.18 – 9.01	6.95
Total	8.35 – 9.26	82.13	7.66 – 9.09	72.33	7.63 – 9.18	74.53

It was expected that the time intervals with the highest pH ranges would provide the most removal, but that was not the case. For example, the highest amount of removal was expected to be the 8-12 hour time interval for the 4 g/L experiment since the pH ranged from 9.10 to 9.26, but the table shows it only achieved about 1/3 of the maximum removal for any of the 4-hour time periods. Table 29 shows that the majority of the degradation actually occurs in the first 12 hours of treatment, regardless of pH. This is another indicator of first order reaction kinetics since the removal decreases at lower total concentration. Although it is known that ammonia removal is greater at higher pH, the data collected in this study did not support an observable trend.

3.3.3.4. Experiment 3 – 6 Color Removal Kinetics

Decolorization efficiencies ranged from 26 – 57%, as seen in Table 25. The highest removal of color in 24 hours was achieved with the largest amount of catalyst (40 g/L). However, this may actually be an artifact attributed to a whitening effect of the catalyst on the initial color of the leachate. Figure 62 shows the comparison of color between raw leachate and raw leachate mixed with TiO₂.



Figure 62. Color comparison for raw leachate (left) vs. leachate w/ TiO₂ (right)

The raw leachate has the appearance of black coffee, but once it is mixed with the catalyst, it looks much lighter in color. As shown in Table 30, every experiment showed that just the addition of catalyst to the leachate, prior to any treatment, resulted in a lower color reading than the raw leachate even though the samples were centrifuged at 6000 rpm for 5 minutes to remove the photocatalytic particles from solution.

Table 30. Color concentration change after adding TiO₂ to raw leachate insert a column with percent change

Sample	TiO ₂ (g/L)	Concentration (PCU)	
		Raw Leachate	Leachate w/ TiO ₂
1	4	1175	1125
2	10	950	700
3	16	950	625
4	25	875	625
5	40	925	575
6	30	550	475

The color change from simply adding catalyst ranged from 50 to 350 PCU. Higher doses of catalyst generally resulted in greater initial color change. This is possibly due to

immediate adsorption of particles which contribute to the color of leachate when adding the TiO₂.

If the catalyst does indeed provide a false color removal effect then the variance in the color readings can also be related to the lack of homogeneity between the catalyst and the leachate. Since the TiO₂ nanoparticles are heavy and begin to settle in the leachate rather quickly, the ratio of catalyst to leachate can be different in every sample, resulting in a variety of measurement values. The relative degradation rates of color are summarized in Figure 63 and Table 31.

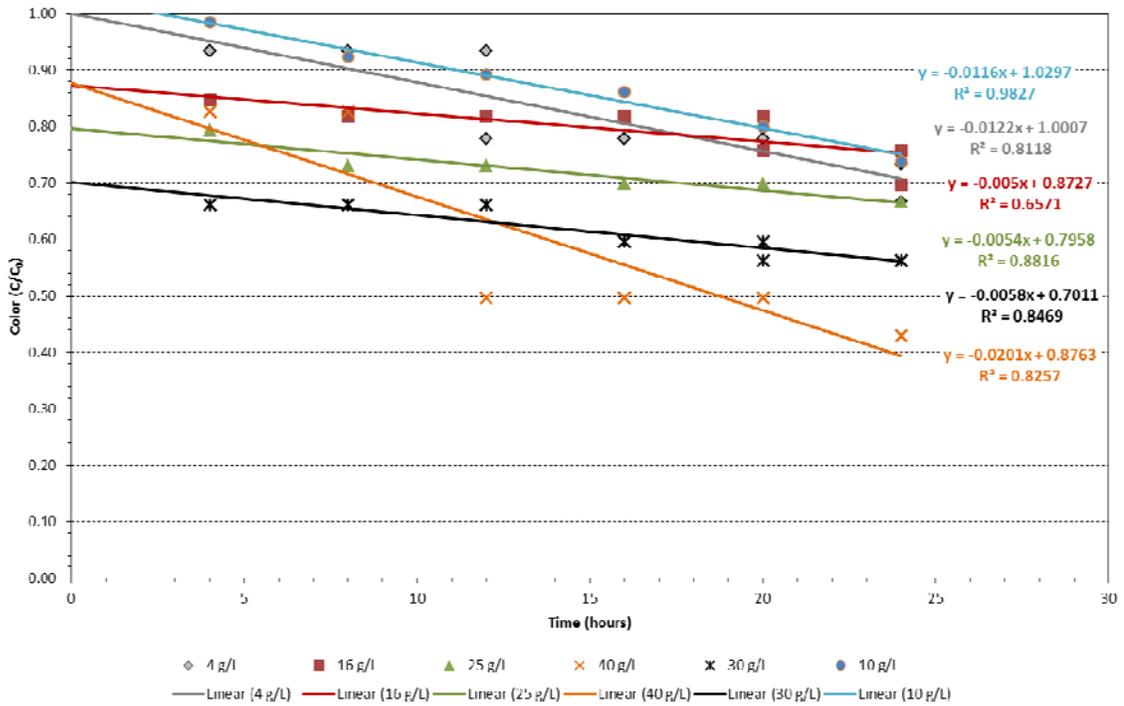


Figure 63. Comparison plot of zero order color removal after 24 hours for the catalyst dosages from six experiments

The data for the color removal does not allow for a good estimate by forcing the comparative trendlines through the point (0, 1). Instead, the C/C₀ values were plotted without alteration. To assist in the interpretation of the data the slopes and R² values for each experiment were tabulated in Table 31.

Table 31. Slopes and R² values for color comparison graph

Experiment	TiO ₂ (g/L)	Slope (PCU/hr)	R ² value
1	4	-0.0122	0.8118
6	10	-0.0116	0.9827
2	16	-0.0050	0.6571
3	25	-0.0054	0.8816
5	30	-0.0058	0.8469
4	40	-0.0201	0.8257

Figure 63 and Table 31 shows that the highest color removal rate correlates with the highest catalyst dose, showing a slope of -0.0201. The degradation slopes for 4 g/L and 10 g/L are almost identical at -0.0122 and -0.0116, respectively. It is interesting to note that the smallest two catalyst doses showed the second and third largest degradation rates. The “middle” doses (10, 16 and 25 g/L) also had similar slopes in relation to each other, which ranged from -0.0050 to -0.0058. From the data, it is determined that further investigation is needed to better understand the color removal mechanism.

None of the experiments were able to achieve 90% removal of color within the treatment times tested. As a result, the time necessary to do so had to be predicted from kinetics data. Using the zero order kinetics plots to get a k-value for each experiment, the times to achieve the 90% decolorization were compared in Table 32.

Table 32. Comparison of times to achieve 90% color removal using zero order decay rates from six experiments

Experiment	TiO ₂ (g/L)	k-value (PCU/hr)	C ₀ (PCU)	C _t (PCU)	t (hr)
1	4	-13.735	1125	112.5	73.7
6	10	-8.817	475	47.5	82.9
2	16	-3.758	700	70.0	167.6
3	25	-4.257	625	62.5	132.1
5	30	-5.160	575	57.5	100.3
4	40	-14.525	625	62.5	38.7

Table 32 demonstrates that the catalyst dosage of 40 g/L achieved the fastest degradation rate (k = -14.525 PCU/hr) and therefore had the lowest time (t = 38.7 hours) to reach the 10% of the initial color concentration. The slowest rate of color removal was exhibited by

the experimental dosage of 16 g/L TiO₂, resulting in an estimated 168 hours for target removal. The degradation rates appear to have no significant correlation to the initial concentration.

3.4 CATALYST OPTIMIZATION

In the investigation of the most effective catalyst dose for maximum destruction of COD at 24 hours of treatment based on first order kinetics for all six experiments, a catalyst optimization plot was created (Figure 64).

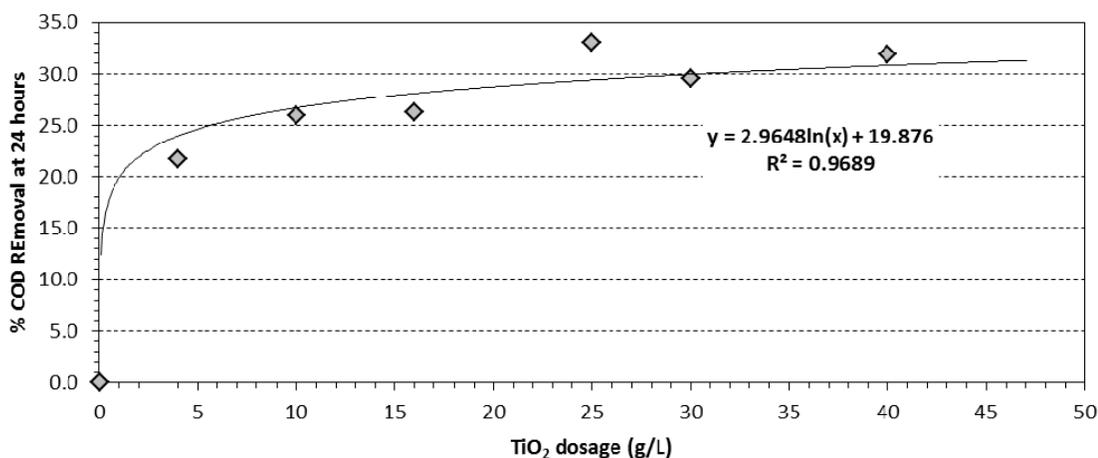


Figure 64. Catalyst optimization curve for COD removal at 24 hours for six experiments

The data from experiments 1 (4 g/L) and 2 (16 g/L) supported the hypothesis that more catalyst generated a higher COD destruction rate. So, for the third experiment the catalyst dose was increased to 25 g/L, which again showed higher COD removal (34%) than the lower doses. Again, the catalyst dose was increased to 40 g/L for the fourth experiment. The degradation that took place in the fourth experiment was not the increase that was expected; only 34% of the COD was mineralized, suggesting a plateau. This led to the expectation of a peak in between 25 and 40 g/L TiO₂ and the use of 30 g/L in experiment 5, which only reached 30% mineralization. The data seemed to follow the asymptotic curve pretty closely ($R^2 = 0.9697$) prior to the sixth experiment. Proceeding from there, 10 g/L TiO₂ was tested to see if the result would fall on the curve as well. The results of the sixth experiment were as expected, and the data point landed directly on the existing curve, which barely changed once the sixth experiment data was included in the graph as seen in Figure 64.

The optimum catalyst dosage range was deduced from this curve to be between 4 – 10 g/L taking into account the diminishing returns of increasing the amount of photocatalyst. At TiO₂ levels higher than 10 g/L there is a large increase in catalyst amount without a correspondingly large increase in removal efficiency. Both alkalinity and ammonia exhibited their two highest levels of degradation from 4 and 10 g/L TiO₂ as well. This amount of catalyst corresponds to a ratio of 0.6-1.5 TiO₂:COD.

3.5 CATALYST RECOVERY

Once the optimum catalyst dosage was found, the next step was to design a system to add on to the advanced oxidation treatment unit in an effort to recover the TiO₂ photocatalytic particles after each treatment cycle. A number of nylon monofilament filter bags were obtained for this purpose. The three bag sizes to be tested were 5-micron, 10-micron and 20-micron. Prior to attempting to recover the catalyst using this method, a preliminary test was performed to see how leachate liquid flows through the bag and if noticeable filtration of the catalyst actually takes place. The 10-micron bag was used to filter 100-mL of tap water containing 0.73 g of TiO₂. When the water was poured into the filter bag, it collected in the bottom of bag and dripped out slowly. The filtered water appeared just as cloudy as it did before filtering. The average primary size of Aeroxide P25 TiO₂ nanoparticles is reported to be 21 nm on Aerosil's specifications sheet (Appendix D). Therefore, the smallest filter bag (5-micron) was used for the recovery trial with actual leachate. The results of attempting to collect the TiO₂ from the treated leachate are summarized in Table 33.

Table 33. Summary of results from catalyst recovery experiments

Item	Weight (g)
TiO ₂ added to leachate	40.08
Filter bag (empty)	38.04
Filter bag (full)	91.93
Estimated TiO ₂ captured	56.63
Recovery (%)	141.30

The recovery experiment using the nylon monofilament filter bag did not provide usable data results. The leachate did not flow through the bag at a rate that would allow the unit to keep running. The filter bag filled up with leachate and slowly dripped into the reservoir (Figure 65).



Figure 65. Photograph of the 5-micron nylon monofilament filter bag filled with treated leachate

As the pressure head in the bag diminished and the leachate levels went down, so did the flow. After just over an hour of allowing the bag to hang and drip, manual pressure had to be applied to remove the leachate from the filtration bag. During the application of pressure, it was noted that the outside of the filter bag was covered in TiO_2 . Visual inspection revealed that the catalyst particles had the ability to pass through the bag with ease. However, the filtered leachate in the reservoir still had a chocolate milk appearance compared to the coffee appearance of raw leachate. Also, some colored particles, possibly in the form of organics adsorbed onto the catalyst surface were on the inside and outside surfaces of the bag. These particles could also be leachate TSS. Every surface the filter bag touched had remnants of catalyst on it. It appears the catalyst may have a charge affinity for the bag or settled out due to the slowing of the flow conditions caused by the bag itself. The filter bag was put in a drying oven at 100°C for approximately 75 minutes and then into a desiccator for one hour. The weight of the recovered catalyst was found to be 56.634 grams, which was greater than the amount of catalyst added to the leachate (40.084 g). This showed greater than 100% recovery, which obviously means that the bag retained more than just TiO_2 particles. The extra material is likely native

leachate TSS, which must be measured and subtracted out. By visual inspection, it was observed that the filter bag did not in fact retain 100% of the catalyst. The testing method had no way of accounting for additional particles that may have been caught in filtration.

The catalyst has a heavy molecular weight which allows the particles to settle quickly in water or leachate. Recovery of the catalyst should incorporate a sedimentation system to collect the catalyst rather than filtration. The amount of energy required to filter out particles averaging 21 nm would not be cost efficient. Suryaman and Hasegawa (2010) recovered the TiO₂ by adding a separate sedimentation tank to the treatment cycle. The overflow of the tank was the treated effluent while the settled particles were pumped back into the mixing tank for reuse. Cho et al. (2004) used a centrifuge to recover the catalyst from their samples for reuse. After which, the catalyst was washed with deionized water and dried. Washing the catalyst may have been a good technique to purge any other compounds adsorbed to the catalyst surface. In this experiment, removing the catalyst from the filter bag and washing the TiO₂ may have eliminated the excess weight and given a true weight of catalyst recovery. Although, collecting the catalyst from the surface of the filter bag for washing would have been a challenge.

To develop the design of a sedimentation system to recover the catalyst, it was necessary to determine the surface area requirement. The settling behavior of the catalyst was determined using a sedimentation test. Assuming discrete settling (Type 1) using Stoke's Law, an initial settling velocity (v_s) was calculated as follows:

$$v_s = \frac{g d^2 (\rho_s - \rho)}{18 \mu} = \frac{9.81 \times 0.000000021^2 (3800 - 995.7)}{18 \times 0.000798} = 8.4 \times 10^{-10} \text{ m/s}$$

where g = acceleration due to gravity (m/s^2), d = particle diameter (m), ρ_s = density of catalyst (kg/m^3), ρ = density of water (kg/m^3), and μ = absolute viscosity ($\text{kg/m}\cdot\text{s}$)

Since Stoke's Law is highly dependent on the average catalyst particle size (21 nm), the settling velocity was found to be extremely low. To be sure that Stoke's Law could be used as opposed to Newton's Law, the Reynold's number (N_R) was calculated as follows:

$$N_R = \frac{v_s \rho d}{\mu} = \frac{8.446 \times 10^{-10} \times 995.7 \times 0.000000021}{0.000798} = 2.21 \times 10^{-11} < 1$$

Since the theoretical Reynold's number was found to be less than 1, laminar flow conditions are indicated, which is a requirement for using Stoke's Law. From the settling velocity obtained using Stoke's Law, the area of the tank necessary to settle out the catalyst was calculated using the 300 L/hr flow of the reactor and found to be approximately 350,000,000 m^2 . This erroneous result shows that the catalyst clearly does

not follow simple discrete settling. Therefore, a small experiment was conducted to test hindered settling (Type 3) using the Talmadge and Fitch method. First, 50-mL of leachate with 5 g/L TiO_2 was added to a graduated cylinder and the height of the clearwater interface was recorded at ten-minute intervals. The results were plotted in Figure 66.

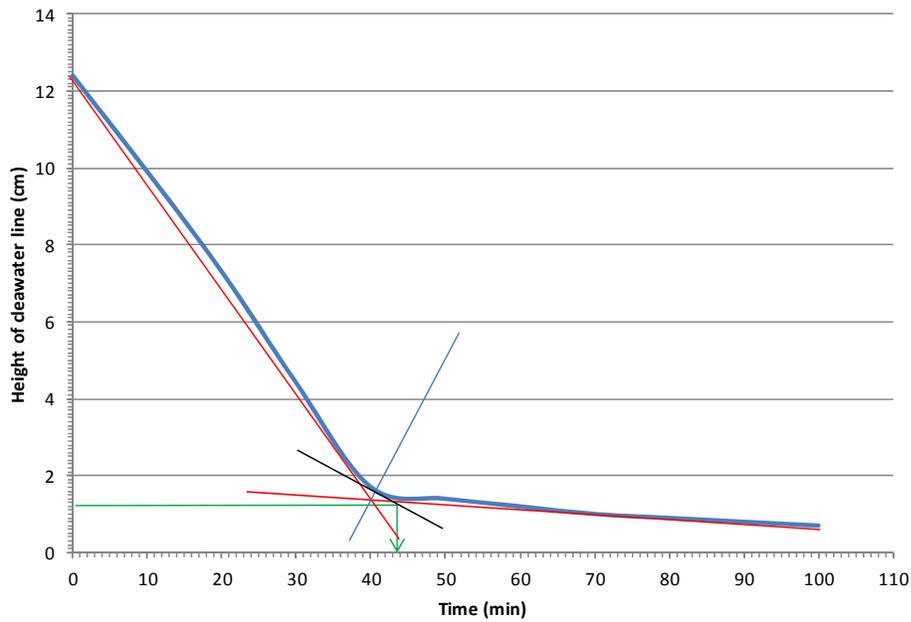


Figure 66: Interface height vs. Time plot for Talmadge and Fitch method

The resulting time (t_u) to the desired underflow concentration ($C_u = 10C_0$) was found to be 43.3 minutes as seen in Figure 66. The calculated area required for thickening based on the 300 L/hr flow of the reactor was found to be 1.74 m^2 . This result proved to be more reasonable than Stoke's Law and indicates that the catalyst may more closely follow Type 3 hindered settling behavior, although it is difficult to confirm this due to factors that affect the settling of the catalyst particles. For example, alkalinity is reported to promote aggregation of the catalyst particles, thereby increasing the effective particle diameter. Also, the adsorption of particles onto the catalyst surface increases the weight and the diameter, which in turn increases the settling velocity. Further investigation is necessary to develop more accurate predictions of the catalyst's settling dynamics. It would also help to determine the effective particle size distribution of the spent photocatalyst by some direct measurement method.

4. CONCLUSIONS AND RECCOMENDATIONS

In this section, the major findings are summarized and recommendations for further study are presented.

4.1 SUMMARY OF FINDINGS

Landfill leachate is highly polluted water that, if released into the environment, can have deleterious effects on groundwater and soil and therefore must be managed properly. Multiple methods of leachate management have been reviewed, revealing a number of issues. One important concern is the biological, chemical and physical contaminants in the leachate, such as ammonia, COD, BOD, heavy metals, TSS and TDS. Also, the variability of the volume and constituent concentrations cannot be governed, since they are dependent on precipitation, landfill area, landfill age and design, waste composition, etc. Alternative methods of dealing with landfill leachate in the future must be able to destroy many different types of constituents, some of which are present in very high concentrations, simultaneously and inexpensively, to be able to safely discharge this water back to the environment.

Advanced oxidation processes, especially those which harness the oxidation potential of the hydroxyl radical, have shown promising results in research performed at laboratory and pilot scales. TiO₂ photocatalytic oxidation is among these emerging techniques. The process involves the generation of hydroxyl radicals and superoxide anions which have the capacity to decontaminate wastewaters by removing ammonia, organics, common inorganics, color and heavy metals simultaneously, as explained in detail in Chapter 1.

The purpose of this study was to follow up batch scale testing performed by McBarnette (2011) with the testing of a pilot scale falling film reactor utilizing TiO₂ photocatalysis to treat landfill leachate. The main objective was to determine an optimum dosage of catalyst without the use of any chemical addition or pretreatment, with the goal of meeting the Broward County sewer use limitations for COD (<800 mg/L s O₂) and ammonia (<25 mg/L as NH₃-N).

The previous batch scale studies achieved 100% mineralization of COD, 79% removal of copper and 50% degradation of ammonia in simulated leachate using 4 g/L TiO₂ (3.88 TiO₂:COD). This catalyst dose became the starting point for the pilot studies presented in this document. TiO₂ dosages were tested from 4 – 40 g/L (0.64 – 5.73 TiO₂:COD). No pH control was implemented and thus ranged from 7.5 – 9.3 throughout the duration of all experiments. The mean pH for all experiments ranged from 8.72 – 8.89. The consistency of the average pH demonstrated that the pH had minimal effect on the

varying removal efficiencies for all parameters. Overall, treatment in the ambient pH conditions resulted in higher degradation of ammonia compared to COD for all experiments, as expected. Maximum COD mineralization (34%) was carried out at catalyst doses of 25 and 40 g/L after 24 hours of treatment. Ammonia reached maximum removal (82%) with 4 g/L TiO₂ after 24 hours of treatment. The highest alkalinity destruction in 24 hours was 84%, occurring with a catalyst dosage of 10 g/L. Maximum color removal in 24 hours was 57% with a catalyst dose of 40 g/L.

To find the desired amount of catalyst, it was necessary to balance the removal percentages of COD versus ammonia, color, and alkalinity. It was found that catalyst dosages above 10 g/L reduced ammonia removal by 32 – 38% and alkalinity removal by 9 – 12% below their respective maximum values. For COD, catalyst doses less than 25 g/L exhibited only 8 – 12% less removal than the maximum. Since large increases in catalyst provided minimal increases in COD mineralization and great decreases in ammonia and alkalinity degradation, optimization of the catalyst resulted in a preferred dose range of 4 – 10 g/L TiO₂. In this optimum range at 24 hours, 22 – 26% of COD, 72 – 82% of ammonia, 81 – 84% of alkalinity, and 26 – 30% of color was removed from the leachate. The parameters that incurred the most exceedance fees for the Monarch Hill landfill were COD and ammonia, which in the optimum range degrade to the target levels in 160 – 200 hours and 55 – 75 hours of treatment, respectively.

The study of reaction kinetics is very complicated with respect to advanced oxidation processes. A chain of reactions is set in motion by the UV radiation and the TiO₂ photocatalyst. The kinetics studies within this manuscript did not monitor the individual processes occurring, but the overall reaction order, which is defined by the slowest reaction in the matrix (the rate limiting step). The results determined that the photocatalytic degradation of COD followed overall first order behavior closer than zero or second order. Using the optimum range of catalyst (4 – 10 g/L) the decay rates of COD ranged from -0.0102 to -0.0127 hr⁻¹. Based on the data and literature, ammonia and alkalinity were recommended to also be modeled as overall first order reactions at ambient pH levels. The optimum range of catalyst gave decay rates for ammonia ranging from -0.058 to -0.073 hr⁻¹ and alkalinity ranging from -0.078 to -0.079 hr⁻¹. From the data analysis and literature review, it was suggested to model color removal as an overall zero order reaction. Under the optimum range of TiO₂ (4 – 10 g/L) color was degraded at -13.7 to -8.82 PCU/hr. At these rates and these conditions, the goal of meeting the Broward County sewer use limitations is not met in less than 24 hours of treatment for the raw composite leachate sampled at Monarch Hill landfill.

Attempts to recover the used catalyst after 8 hours of treatment using nylon monofilament filter bags were unsuccessful. The average primary size of Aeroxide P25 TiO₂ nanoparticles is reported to be 21 nm. It was expected that this size would increase

due to adsorption of organics and other compounds. The 5-micron bag did not catch many catalyst particles as the filtered leachate clearly still contained a large amount of TiO₂. Some catalyst particles, among other constituents, did adsorb to the inner and outer surfaces of the filter bag. The addition of the other non-TiO₂ particles on the bag surface resulted in a larger estimate (141.3 % recovery) of the catalyst recovered when weighed on a scale. The test method did not have a way to account for additional particles caught in the filtration. Also, the amount of energy required to filter out catalyst particles averaging 21 nm would not be cost efficient and thus, the bag filter system was determined to be an inefficient method of catalyst recovery. Instead, a sedimentation trap or centrifugation are recommended.

4.2 PRELIMINARY COST ANALYSIS

The Monarch Hill Landfill currently pays disposal fees based on annual volumetric flow rates and constituent concentrations above a certain threshold. It was reported that the average leachate production is 42 – 96 million gallons per year (Meeroff and McBarnette 2011), with the first 12 million gallons per year being free of charge, as per the agreement between Broward County and Waste Management. The high constituent concentrations (i.e. COD > 800 mg/L and NH₃-N > 25 mg/L) of the leachate also add on exceedance fees averaging \$350,000 per year in FY2010. A goal of the photocatalytic study is to develop a leachate treatment process that can achieve operating costs lower than these exceedance fees. Therefore, an attempt will now be made to speculate the cost of the leachate treatment unit at full scale.

Assuming that the sewer disposal costs will remain the same between the current option and the proposed photocatalytic oxidation treatment option, the current disposal option cost is calculated by the exceedance fees and the leachate generation as follows:

$$\frac{\$350,000}{96,000,000 \text{ gal}} = \frac{\$3.65 \times 10^{-6}}{\text{gal}} = \frac{\$3.65}{1000 \text{ gal}}$$

and,

$$\frac{\$350,000}{42,000,000 \text{ gal}} = \frac{\$8.33 \times 10^{-6}}{\text{gal}} = \frac{\$8.33}{1000 \text{ gal}}$$

So, the current cost ranges from \$3.65 – \$8.33 per 1000 gallons plus the cost of sewer disposal. This value will be compared to an estimated cost of the reactor operated at full scale.

Using the leachate generation rates of 115,000 to 262,000 gallons of leachate per day, on average, and a treatment cycle of 200 hours (based on the pilot reactor treatment time to reach the sewer use limitation for COD), the reactor volume would need to be on the order of 960,000 – 2,200,000 gallons. Currently a 22 lb (10 kg) bag of TiO₂ costs \$600. The batch reactor optimization was on the order of 13.3 g/L of TiO₂, but the pilot optimization was closer to 4 g/L. Therefore the amount of TiO₂ needed would be on the order 14,500 – 33,200 kg. Without factoring in the economies of scale, the total first cost of photocatalyst is \$870,000 - \$1,990,000. Since the catalyst is reusable, this can be taken as a one-time expenditure.

Further estimates are needed regarding the reservoir size, UV lamps and pumps in order to establish a capital cost. To account for a 200-hour treatment cycle, the daily tank volume should be on the order of 1.0 – 2.5 MG to account for the worst case scenario. Currently the UV lamp in the pilot reactor produces 120 watts. The wattage of the lamp for a full scale operation was determined based on the assumption that the system will treat the amount of leachate produced per day. After adding in all of the pumps, blowers, and appurtenances, the capital cost is amortized at 6% interest per year for 20 years. The preliminary cost analysis is summarized in Table 34.

Table 34. Preliminary cost analysis based on pilot reactor optimal catalyst dose

Costs	42 MG/year	96 MG/year
TiO ₂ chemical costs (one time only)	\$871,068	\$1,991,014
2 x 1.0 MG tanks (one spare)	\$1,736,020	
2 x 2.5 MG tanks (one spare)		\$3,088,180
UV lamps/ballast/power supply	\$250,000	\$500,000
Pumps/blowers/plumbing/etc.	\$89,000	\$136,000
Total capital cost	\$2,946,088	\$5,715,194
Annualized (6%, 20 years)	\$256,899	\$498,365
O&M costs (est. 10% of capital)	\$294,609	\$571,519
Total annual costs	\$551,508	\$1,069,884
Cost per 1000 gallons	\$13.13	\$11.14

A similar cost analysis was made for the batch scale treatment process using optimum batch scale conditions of 13.3 g/L TiO₂ and a 20-hour treatment process time (Table 35).

Table 35: Preliminary cost analysis based on batch reactor optimal catalyst dose

Costs	42 MG/year	96 MG/year
TiO ₂ chemical costs (one time only)	\$289,630	\$662,013
2 x 0.2 MG tanks	\$90,000	
2 x 0.3 MG tanks		\$140,000
UV lamps/ballast/power supply	\$40,000	\$70,000
Pumps/blowers/plumbing/etc.	\$21,000	\$36,000
Total capital cost	\$440,630	\$908,013
Annualized (6%, 20 years)	\$38,423	\$79,179
O&M costs (est. 10% of capital)	\$44,063	\$90,801
Total annual costs	\$82,486	\$169,980
Cost per 1000 gallons	\$1.96	\$1.77

The resulting cost analysis shows that the batch scale process provided a cost efficient option while the scale up of the current pilot process currently does not. While the falling film reactor showed promising results, the pilot scale treatment still needs to be further developed in order to be cost effective in practical applications. The main goal in the effort to keep the cost down is to reduce the treatment time, which is the main difference between the two cost estimates. This is because reducing the treatment time will reduce the size of the tanks needed, the amount of UV lamps necessary, the quantity of pumps, blowers and plumbing needs, and even the operations costs. This study provides a baseline for the further development in the pilot scale research. The optimal catalyst dosage has been narrowed down, so that further testing and process modifications can be implemented to reduce the treatment costs and increase overall efficiency by lowering the residence time to less than 24 hours.

4.3 RECOMMENDATIONS

The following recommendations can be made from the completed study:

- Experiments should be conducted to investigate UV intensity effects by varying the lamp power. The UV intensity issue must also be optimized because the higher the energy output required, the higher the cost of the system. The UV lamp in the pilot reactor emits most of its intensity in the UV-C range, which is not received at the earth's surface from the sun. The use of a lamp which mimics the wavelengths of solar radiation received at the surface should be investigated. The efficiencies between both lamps should be compared. Once the optimal UV intensity is found and compared to solar radiation along a wide scale of wavelengths, the research and development of a means to focus the solar energy should begin. The sole use of solar

radiation provides a sustainable resource that produces no waste and requires no additional energy. This is a main attraction of photocatalytic processes.

- As stated in the literature review section, applications using solar radiation instead of UV lamps would be more sustainable because UV lamps typically contain mercury and spent lamps must be treated as a hazardous waste. Use of focused solar radiation would be a solution that requires zero energy and produces zero waste. The potential of using solar energy is particularly attractive since Florida landfills may have considerable acreage available in closed or inactive areas for solar utilization. The substantial cost savings of solar over UV lamps cost make the costs more competitive.
- The decline of the efficiency of the UV source over time can influence results. According to the manufacturer, the average lifetime of the lamps used in this study is 1000 hours, but the energy measured during this study declined in less time. To determine the precise effect, a lamp emitting only narrow band UV radiation could also improve the productivity of the process. Instead of using a UV intensity probe that only measures a narrow wavelength band, a more efficient means of determining the dosimetry of the lamp is needed. Compared to previous UV testing conducted by André McBarnette on a batch scale reactor (Meeroff and McBarnette 2011), the UV dose is relatively low for this falling film reactor unit (130 vs. 2-10 mW/cm²).
- The pilot reactor lamp emits most of its power between 250 – 260 nm. Obtain a UV sensor which measures wavelengths between 250 – 260 nm (UV-C) to develop a better understanding of the radiation intensity applied to the leachate. Also, this will allow tests to be performed on the germicidal irradiation range and the effects it has on parameter removal.
- Develop a more efficient means to maintain constant temperature in the reactors to allow for experiments with longer contact times. If no feasible solution is found, we could investigate the effects of running the reaction in stages (i.e. 240 minutes on, 360 minutes off, and repeat until 100% mineralization is achieved).
- This study found that an increase in TiO₂ led to a decrease in ammonia removal. Investigation of the effect of the catalyst concentration on ammonia removal should be performed. In this experiment, escape of gaseous ammonia should be monitored, as well. A system to catch and measure gases being released from the pilot scale reactor should be devised. Determination of the amount of CO₂ being released can provide further insight to the degradation kinetics of COD as well as information on potential greenhouse gas emissions. Determining the volume of H₂ and N₂ can provide valuable information on the photocatalytic breakdown of ammonia.
- Further investigation of the pH effects should be conducted. Experiments should be run at multiple pH values to compare the removal efficiencies of COD, ammonia and/or other parameters of interest with pH adjustment.
- Further studies should be conducted on the catalyst dosage to find the minimal amount of TiO₂ necessary for acceptable removal efficiency in less than 20 hours of

reaction time, if possible. Also, the TiO_2/COD ratio should be studied as a means in determining the most effective catalyst dose.

- It is critical to develop methods to capture the photocatalyst after batch processing for reuse in the next batch. Based on the results of the catalyst recovery trial in this study (bag filter), a new recovery study should be conducted. Due to the weight of the TiO_2 particles, the use of a sedimentation process (sediment trap or similar) should provide adequate recovery percentages. A size distribution analysis of the photocatalytic particles should be obtained or measured directly to better understand the sedimentation dynamics. Experiments to determine the recovery efficiency and potential cost implications should be conducted.
- Studies should be performed on the reuse of TiO_2 . These studies will help determine the lifetime of the catalyst or the point to which a regeneration process is necessary. Furthermore, the number of times the photocatalyst can be reused before it is fouled, denatured, or otherwise in need of replacement must be determined. This can then be included in the cost analysis.
- Investigate the photo-inhibitory effect of alkalinity and pH so as to determine the optimum values for maximum decomposition.
- Process modifications such as the addition of hydrogen peroxide and/or potassium persulfate to increase the production of radical species and the addition of sulfuric acid to control the pH should be investigated to increase the efficiency of the photocatalytic process.
- Further investigation of COD removal should be performed by measuring the BOD/COD ratio during testing. The change in the BOD/COD ratio will provide insight to the type of oxygen demand present in the leachate.
- Since the composition of landfill leachate varies with time and location, experiments should be conducted to study concentration dependence on COD, ammonia, and other parameters of interest (such as BOD, color, TDS, TSS, TKN, phosphorus, heavy metals, etc.). The determination of concentration dependence for these parameters, among others, will provide valuable information on the overall reaction kinetics, which can be used to optimize the removal efficiency of said parameter(s). The knowledge of the reaction kinetics for individual parameters can be used to develop more efficient congruent treatments for multiple parameter destruction. Without viable reaction order kinetics tests, it is not possible at this time to develop accurate cost estimates, process footprint, pre-treatment requirements, and operation and maintenance issues.
- The color testing method used in this study relies on the perception of color from the naked eye. Also, the color wheel markings are spaced too far away to allow for accurate estimates to be made at the high dilution levels used (1:25), which may have artificially elevated the error in this method. It is recommended to record an absorbance value at $\lambda = 254 \text{ nm}$ to obtain a more sensitive and less subjective measurement of apparent color.

- In addition to COD, optimization studies should be conducted on BOD₅, dissolved solids, conductivity, or heavy metals (i.e. arsenic, lead). Regarding metals and other inorganics, understanding the mechanism of removal is important because if surface precipitation, redox plating, or adsorption is significant, these mechanisms would reduce the active surface area of the photocatalyst, effectively poisoning the surface and reducing treatment efficiency. If these mechanisms can be better understood, then the system can be modified to meet the treatment objectives without compromising process efficiency.
- The effect of aeration should also be monitored by conducting some experiments without the air supply to see if it is actually needed because the TiO₂ particles can be theoretically mixed by recirculation, so air would only be necessary if it truly participates in the reaction.
- Investigate the ecotoxicity of treated effluents and spent catalysts.
- The cost analysis should take into account peak seasonal leachate generation, which may be five times or more compared to the annual average.
- Since the COD removal process efficiency of the pilot plant did not meet the target removal goal for this study, the process can be used as a pretreatment followed by post-treatment or a polishing step, such as wetlands treatment (which requires low levels of ammonia for efficacy) to allow final discharge to onsite surface water if local regulations allow.
- Future pilot tests are needed to interpret the concentration dependence on COD efficiency. Without these tests, it is not possible at this time to develop detailed cost estimates, process footprint, pre-treatment requirements, residuals generation, reactor volume, appropriate treatment targets, and operation and maintenance issues. Once the above items are addressed, design of a system to retrofit into existing leachate storage tanks can be tested.

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APPENDIX A: Data for Experiments 1 – 6

Table 36: Data for Experiment 1 (4 g/L TiO₂)

Experiment #1					
Date Leachate Collected:	9/30/2011				
Volume of Leachate:	8 Liters				
Catalyst Dose:	4 g/L TiO ₂				
Maximum Temperature:	36.7 °C				
Time (hr)	pH (pH units)	COD (mg/L as O ₂)	Ammonia (mg/L as NH ₃ -N)	Alkalinity (mg/L as CaCO ₃)	Color (PCU)
0	8.35	6246.25	1712.50	4625.0	1125
4	9.20	5996.67	1205.00	4000.0	1050
4	9.04	5946.67	1275.00	4000.0	1050
8	8.98	5706.67	853.00	2875.0	1050
8	9.23	5935.00	892.50	2750.0	1050
12	9.10	5700.00	681.25	2062.5	1050
12	9.22	5770.00	645.83	1750.0	875
16	9.03	5520.00	455.00	1250.0	875
16	9.18	5370.00	448.75	1250.0	875
20	8.91	5126.67	372.50	1000.0	875
20	9.09	5040.00	371.00	1000.0	875
24	8.91	4866.67	306.25	850.0	825
24	8.94	4890.00	306.00	875.0	750
28	8.72	4636.67	258.00	750.0	625
28	8.77	4640.00	253.33	700.0	625
32	8.69	4295.00	188.00	600.0	625
32	8.67	4410.00	228.50	700.0	625
36	8.62	4286.67	216.33	600.0	625
36	8.65	4215.00	205.00	600.0	525
40	8.62	4113.33	188.50	600.0	525
40	8.63	4215.00	167.00	500.0	525
44	8.61	3910.00	171.50	500.0	525
Removal	N/A	37.40%	89.99%	89.19%	53.33%

Table 37: Data for Experiment 2 (16 g/L TiO₂)

Experiment #2					
Date Leachate Collected:	3/09/2012				
Volume of Leachate:	8 Liters				
Catalyst Dose:	16 g/L TiO ₂				
Maximum Temperature:	35.7 °C				
Time (hr)	pH (pH units)	COD (mg/L as O ₂)	Ammonia (mg/L as NH ₃ -N)	Alkalinity (mg/L as CaCO ₃)	Color (PCU)
0	7.63	5268	1306	3563	825
4	8.85	5000	1250	3500	700
4	8.97	4860	1203	3000	700
8	8.88	4850	1148	2500	675
8	9.01	4810	1092	2500	675
12	8.99	4490	985	2375	675
12	9.16	4410	944	2000	675
16	9.02	4250	862	2000	675
16	9.12	4160	868	2000	675
20	9.01	4120	753	1875	675
20	9.18	4020	738	2250	625
24	9.01	3990	662	1750	625
24	8.97	3780	602	1375	575
28	8.65	3570	573	1250	625
28	8.84	3570	627	1500	500
32	8.61	3540	554	1500	500
32	8.84	3390	513	1375	450
36	8.56	3350	502	1125	438
36	8.79	3180	463	1000	425
40	8.66	3160	433	1000	425
Removal	N/A	40.02%	66.85%	71.93%	48.48%

Table 38: Data for Experiment 3 (25 g/L TiO₂)

Experiment #3					
Date Leachate Collected:	3/09/2012				
Volume of Leachate:	8 Liters				
Catalyst Dose:	25 g/L TiO ₂				
Maximum Temperature:	36.0 °C				
Time (hr)	pH (pH units)	COD (mg/L as O ₂)	Ammonia (mg/L as NH ₃ -N)	Alkalinity (mg/L as CaCO ₃)	Color (PCU)
0	7.54	5360	1380	3562.5	787.5
4	8.59	4920	1280	3330.0	625.0
4	8.86	4650	1270	3500.0	625.0
8	8.84	4620	940	2500.0	575.0
8	8.89	4330	1090	3000.0	575.0
12	8.88	4290	820	2380.0	575.0
12	8.91	4140	980	2750.0	575.0
16	8.79	3940	900	2630.0	550.0
16	8.96	3730	890	2500.0	550.0
20	8.78	3730	820	2500.0	550.0
20	8.86	3590	770	2380.0	550.0
24	8.73	3540	710	2000.0	525.0
24	8.85	3540	700	1875.0	525.0
Removal	N/A	33.96%	49.28%	47.37%	33.33%

Table 39: Data for Experiment 4 (40 g/L TiO₂)

Experiment #4					
Date Leachate Collected:	7/18/2012				
Volume of Leachate:	8 Liters				
Catalyst Dose:	40 g/L TiO ₂				
Maximum Temperature:	37.7 °C				
Time (hr)	pH (pH units)	COD (mg/L as O ₂)	Ammonia (mg/L as NH ₃ -N)	Alkalinity (mg/L as CaCO ₃)	Color (PCU)
0	7.59	6990	1523	4312.5	756
4	8.63	6190	1370	3380.0	625
4	8.84	6140	1300	3000.0	625
8	8.65	5870	1140	2380.0	625
8	9.06	5740	1180	2130.0	500
12	8.83	5470	1050	1880.0	500
12	9.05	5310	1060	1880.0	375
16	8.82	5350	1030	1630.0	375
16	9.01	5060	1020	1630.0	375
20	8.62	4940	938	1500.0	375
20	8.96	4670	908	1380.0	375
24	8.72	4650	849	1250.0	325
24	8.90	4530	842	1130.0	325
Removal	N/A	35.19%	44.71%	73.80%	57.01%

Table 40: Data for Experiment 5 (30 g/L TiO₂)

Experiment #5					
Date Leachate Collected:	7/18/2012				
Volume of Leachate:	8 Liters				
Catalyst Dose:	30 g/L TiO ₂				
Maximum Temperature:	36.8 °C				
Time (hr)	pH (pH units)	COD (mg/L as O ₂)	Ammonia (mg/L as NH ₃ -N)	Alkalinity (mg/L as CaCO ₃)	Color (PCU)
0	7.70	6135	1635	4125	756
4	9.02	5790	1460	2875	500
4	9.19	5660	1450	3125	500
8	8.96	5450	1330	2625	500
8	9.20	5290	1320	2750	500
12	9.01	5260	1190	2000	500
12	8.98	5040	1120	1750	500
16	8.92	4800	1065	1625	450
16	9.08	4767	1020	1605	450
20	8.94	4660	980	1357	450
20	9.06	4590	933	1277	425
24	8.83	4418	855	1110	425
24	9.01	4322	845	1013	425
Removal	N/A	29.55%	48.32%	75.44%	43.78%

Table 41: Data for Experiment 6 (10 g/L TiO₂)

Experiment #6					
Date Leachate Collected:	11/26/2012				
Volume of Leachate:	8 Liters				
Catalyst Dose:	10 g/L TiO ₂				
Maximum Temperature:	37.1 °C				
Time (hr)	pH (pH units)	COD (mg/L as O ₂)	Ammonia (mg/L as NH ₃ -N)	Alkalinity (mg/L as CaCO ₃)	Color (PCU)
0	7.71	5947.5	1670	4375	813
4	9.07	5343.3	1380	3750	800
8	9.04	5080.0	1040	2750	750
12	9.05	5036.7	721	1750	750
12	9.14	4686.7	698	1750	700
16	8.94	4560.0	546	1000	700
16	9.08	4466.7	531	1150	700
20	8.61	4473.3	511	1100	650
24	8.62	4323.3	470	700	600
24	8.89	4327.2	412	600	450
Removal	N/A	27.24%	75.33%	86.29%	44.65%

APPENDIX B: Typical Temperature Recordings

Table 42: Experiment 1 Day 8 Temperature recordings

Time (min)	Temp. (°C)
0	14.3
10	17.3
20	20.0
30	22.4
40	24.5
50	26.3
60	27.8
70	29.1
80	30.3
90	31.6
100	32.5
110	33.3
120	33.9
130	34.5
140	35.0
150	35.4
160	35.7
170	35.9
180	36.1
190	36.2
200	36.3
210	36.4
220	36.5
230	36.6
240	36.7

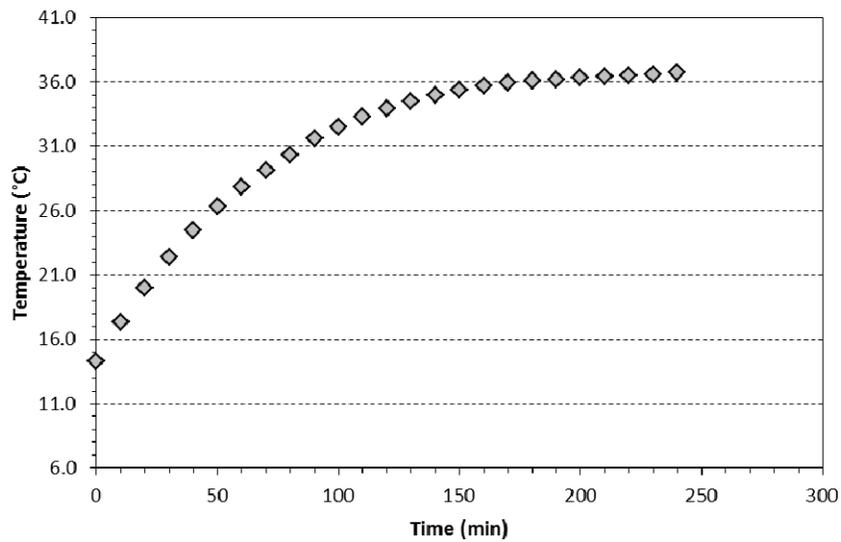


Figure 67: Temperature curve for Experiment 1 Day 8

Table 43: Experiment 2 Day 5 Temperature recordings

Time (min)	Temp. (°C)
0	14.0
10	16.8
20	19.3
30	21.5
40	23.4
50	25.1
60	26.6
70	27.8
80	29.0
90	30.0
100	30.9
110	31.6
120	32.3
130	32.8
140	33.3
150	33.7
160	34.0
170	34.3
180	34.5
190	34.7
200	34.9
210	35.1
220	35.3
230	35.6
240	35.7

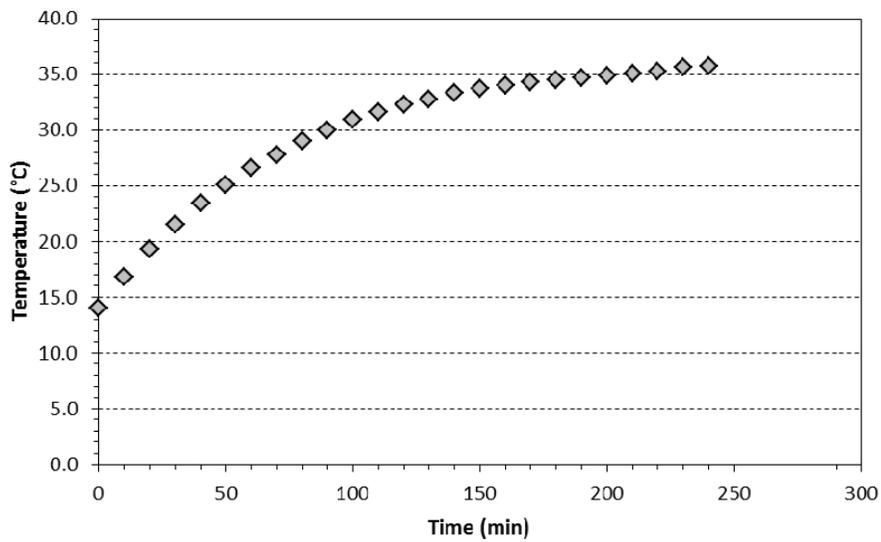


Figure 68: Temperature curve for Experiment 2 Day 5

Table 44: Experiment 3 Day 5 Temperature recordings

Time (min)	Temp. (°C)
0	11.1
10	14.2
20	17.3
30	19.6
40	21.6
50	23.5
60	25.1
70	26.7
80	27.9
90	28.9
100	30.1
110	30.8
120	31.4
130	32.1
140	32.7
150	33.0
160	33.6
170	33.9
180	34.2
190	34.5
200	34.8
210	35.0
220	35.3
230	35.7
240	35.8

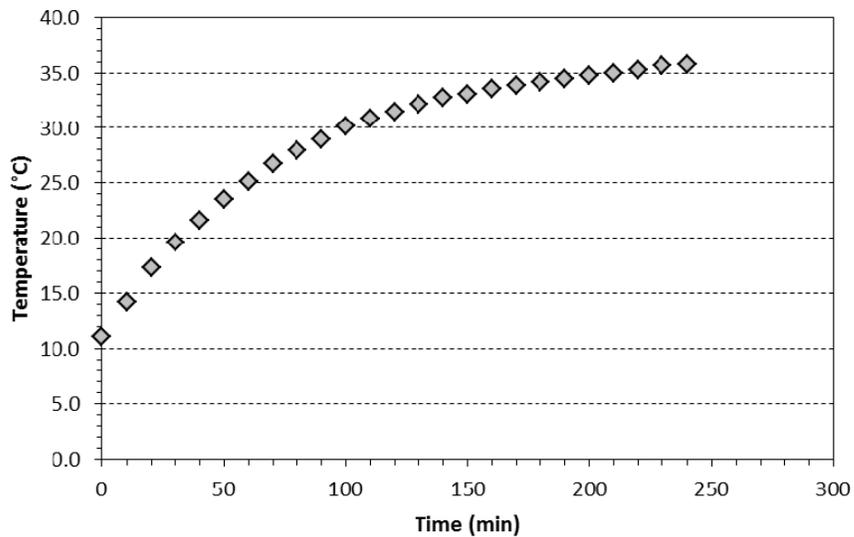


Figure 69: Temperature curve for Experiment 3 Day 5

Table 45: Experiment 4 Day 2 Temperature recordings

Time (min)	Temp. (°C)
0	11.2
10	14.7
20	18.2
30	21.1
40	23.9
50	26.5
60	28.0
70	29.6
80	30.9
90	31.9
100	32.7
110	33.3
120	33.9
130	34.4
140	34.9
150	35.3
160	35.9
170	36.0
180	35.9
190	35.7
200	35.9
210	36.0
220	36.2
230	36.6
240	36.7

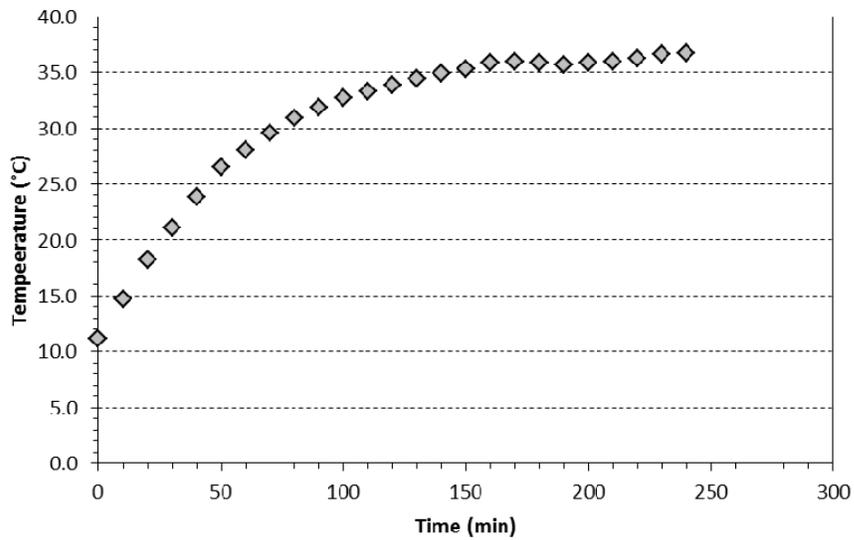


Figure 70: Temperature curve for Experiment 4 Day 2

Table 46: Experiment 5 Day 4 Temperature recordings

Time (min)	Temp. (°C)
0	13.5
10	17.0
20	20.0
30	22.1
40	24.0
50	25.8
60	27.5
70	28.9
80	30.1
90	31.0
100	31.8
110	32.5
120	33.2
130	33.7
140	34.2
150	34.6
160	34.9
170	35.2
180	35.4
190	35.6
200	35.8
210	36.0
220	36.2
230	36.3
240	36.3

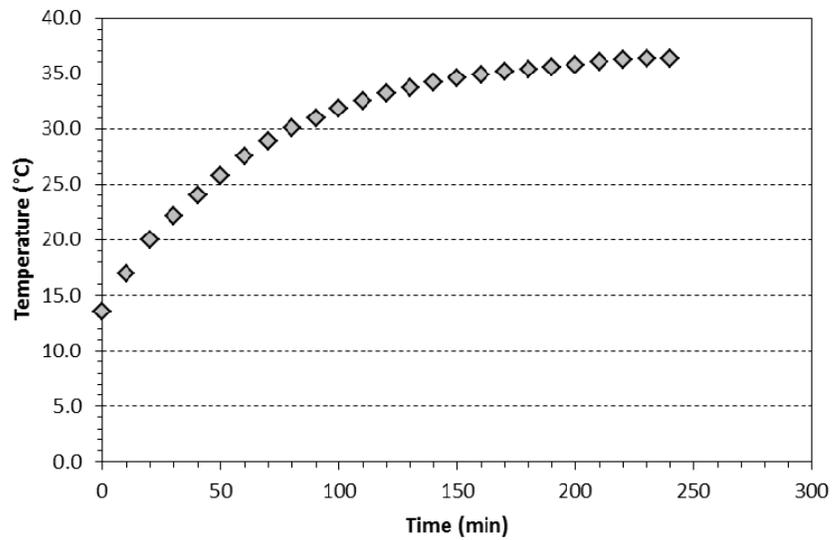


Figure 71: Temperature curve for Experiment 5 Day 4

Table 47: Experiment 6 Day 1 Temperature recordings

Time (min)	Temp. °C
0	11.2
10	14.7
20	18.2
30	21.1
40	23.9
50	26.5
60	28.0
70	29.6
80	30.9
90	31.9
100	32.7
110	33.3
120	33.9
130	34.4
140	34.9
150	35.3
160	35.9
170	36.1
180	35.9
190	35.7
200	35.9
210	36.0
220	36.4
230	36.6
240	36.7
250	36.8
260	36.9
270	37.0
280	37.0
290	37.0
300	37.0
310	37.0
320	37.0
330	37.0
340	37.0
350	37.1
360	37.1
370	37.1
380	37.1
390	37.1
400	37.1
410	37.1
420	37.1
430	37.1
440	37.1

450	37.2
460	37.2
470	37.2
480	37.2
490	37.1
500	37.1
510	37.1
520	37.1
530	37.1
540	37.1
550	37.1
560	37.1
570	37.1
580	37.1
590	37.2
600	37.2
610	37.2
620	37.2
630	37.3
640	37.2
650	37.2
660	37.2
670	37.1
680	37.1
690	37.1
700	37.1
710	37.1
720	37.1

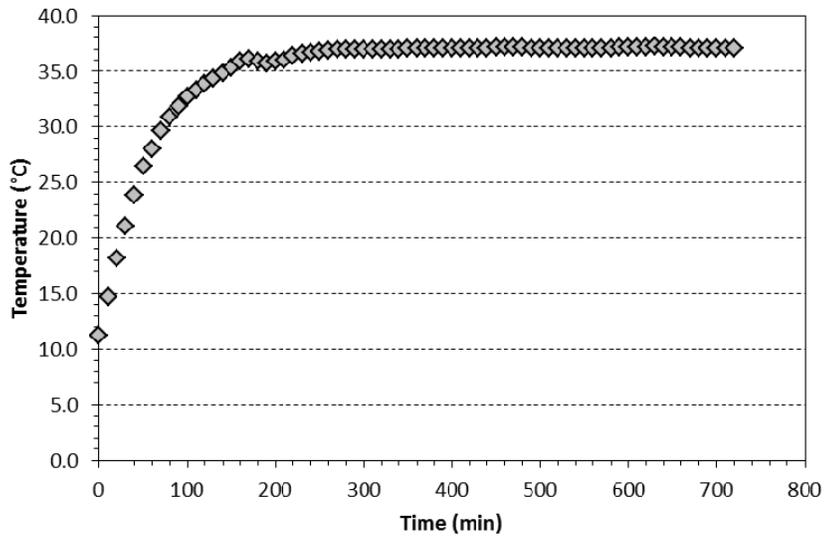


Figure 72: Temperature curve for Experiment 6 Day 1

APPENDIX C: Prediction Tables

Table 48: Alkalinity removal predictions for experiments 1 and 2 using 24 hour k-values from first order kinetics

TiO ₂ (g/L)	k-value (hr ⁻¹)	C ₀ (mg/L as CaCO ₃)	t (hr)	Concentration (mg/L)		% Removal		% error
				calculated	actual	calculated	actual	
4	-0.0780	4625	44	149.5	500	96.7	89.2	70.1
16	-0.0319	3560	40	993.8	1000	72.1	71.9	0.62

Table 49: Ammonia removal predictions for experiments 1 and 2 using 24 hour k-values from first order kinetics

TiO ₂ (g/L)	k-value (hr ⁻¹)	C ₀ (mg/L as NH ₃ -N)	t (hr)	Concentration (mg/L)		% Removal		% error
				calculated	actual	calculated	actual	
4	-0.0726	1713	44	70.2	171.5	95.9	90.0	59.1
16	-0.0316	1310	40	370.1	433.0	71.7	66.9	14.5

Table 50: Color removal predictions for experiments 1 and 2 using 24 hour k-values from zero order kinetics

TiO ₂ (g/L)	k-value (PCU/hr)	C ₀ (PCU)	t (hr)	Concentration (PCU)		% Removal		% error
				calculated	actual	calculated	actual	
4	-0.0780	1125	44	520.7	525	53.7	53.3	0.83
16	-0.0319	700	40	462.5	425	33.9	39.3	8.81

APPENDIX D: UV data recordings

Table 51: Trial 1 of UV measurements

Trial 1
Distance from UV lamp: 1.844”
Angle of sensor to UV source: 0°

Time (min)	UV intensity (mW/cm ²)
0	0.004
1	0.208
2	0.293
3	0.328
4	0.336
5	0.338
6	0.338
7	0.338
8	0.338
9	0.336
10	0.337

Table 52: Trail 2 of UV measurements

Trial 2
Distance from UV lamp: 1.844”
Angle of sensor to UV source: 0°

Time (min)	UV intensity (mW/cm ²)
0	0.009
1	0.145
2	0.302
3	0.352
4	0.361
5	0.365
6	0.364
7	0.365
8	0.365
9	0.365
10	0.365

Table 53: Trial 3 of UV measurements, taken at 45° angle

Trial 3
Distance from UV lamp: 1.844”
Angle of sensor to UV source: 45°

Time (min)	UV intensity (mW/cm ²)
0	0.001
1	0.158
2	0.258
3	0.287
4	0.293
5	0.293
6	0.293
7	0.293
8	0.293
9	0.293
10	0.293

Table 54: Trial 4 of UV measurements, taken at 5.38” from source

Trial 4
Distance from UV lamp: 5.38”
Angle of sensor to UV source: 0°

Time (min)	UV intensity (mW/cm ²)
0	0.001
1	0.049
2	0.109
3	0.129
4	0.135
5	0.138
6	0.138
7	0.138
8	0.138
9	0.138
10	0.138

APPENDIX E: MSDS

SAFETY DATA SHEET (EC 1907/2006)**AEROXIDE® TiO2 P 25**

Material no.		Version	3.8 / REG_EU
Specification	132843	Revision date	29.08.2008
VA-Nr		Print Date	30.08.2008
		Page	1 / 6

1. IDENTIFICATION OF THE SUBSTANCE/PREPARATION AND OF THE COMPANY/UNDERTAKING**Product information**

Trade name	:	AEROXIDE® TiO2 P 25
Company	:	Evonik Degussa GmbH Inorganic Materials Produktsicherheit IM-IM-PS Postfach 1345 D-63403 Hanau
Telephone	:	+49 (0)6181 59-4787
Telefax	:	+49 (0)6181 59-4205
Email address	:	sds.asfp@evonik.com
Emergency telephone number	:	+49 (0)7623-919191
Use of the Substance / Preparation	:	Catalyst support Stabilizer UV-filters

2. HAZARDS IDENTIFICATION**Additional safety information for humans and the environment**

On the basis of our data the product is not a hazardous substance as defined by the Chemicals Act or Hazardous Substance Ordinance in the currently valid versions.

3. COMPOSITION/INFORMATION ON INGREDIENTS**Information on ingredients / Hazardous components**

• Titanium dioxide			
CAS-No.	13463-67-7	EC-No.	236-675-5

See chapter 16 for text of risk phrases

4. FIRST AID MEASURES**Inhalation**

In case product dust is released:
Possible discomfort: cough, sneezing
Move victims into fresh air.

Skin contact

Wash off with plenty of water and soap.

Eye contact

Possible discomfort is due to foreign substance effect.
Rinse thoroughly with plenty of water keeping eyelid open.
In case of persistent discomfort: Consult an ophthalmologist.

SAFETY DATA SHEET (EC 1907/2006)**AEROXIDE® TiO2 P 25**

Material no.		Version	3.8 / REG_EU
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Ingestion

Clean mouth with water and drink afterwards plenty of water.

After absorbing large amounts of substance / In case of discomfort: Supply with medical care.

Notes to physician

No hazards which require special first aid measures.

5. FIRE-FIGHTING MEASURES**Suitable extinguishing media**

All extinguishing substances suitable.

Specific hazards during fire fighting

None known

Further information

Water used to extinguish fire should not enter drainage systems, soil or stretches of water.

Ensure there are sufficient retaining facilities for water used to extinguish fire.

Fire residues and contaminated fire extinguishing water must be disposed of in accordance with local regulations.

6. ACCIDENTAL RELEASE MEASURES**Personal precautions**

Wear personal protective equipment.

Environmental precautions

Do not allow entrance in sewage water, soil stretches of water, groundwater, drainage systems.

Methods for cleaning up

Sweep up or vacuum up spillage and collect in suitable container for disposal.

Avoid dust formation.

7. HANDLING AND STORAGE**Handling****Safe handling advice**

If necessary: Local ventilation.

Advice on protection against fire and explosion

Take precautionary measures against static discharges.

Storage**Requirements for storage areas and containers**

Keep in a dry place.

SAFETY DATA SHEET (EC 1907/2006)**AEROXIDE® TiO2 P 25**

Material no.		Version	3.8 / REG_EU
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8. EXPOSURE CONTROLS / PERSONAL PROTECTION**Components with workplace control parameters****Personal protective equipment****Respiratory protection**

No special protective equipment required.
If dust occurs: Dust mask with P2 particle filter

Hand protection

Wear protective gloves made of the following materials: nitrile rubber (NBR), butyl rubber, PVC.
The material thickness and rupture time data do not apply to non-solute solids / dusts.

Eye protection

Safety glasses with side-shields
If dust occurs: basket-shaped glasses

Skin and body protection

No special protective equipment required.
preventive skin protection
Cleanse and apply cream to skin after work.

Hygiene measures

When using, do not eat, drink or smoke. Wash face and/or hands before break and end of work.
Avoid contaminating clothes with product. Wash contaminated clothing after use.

Protective measures

Handle in accordance with good industrial hygiene and safety practices.
If there is the possibility of skin/eye contact, the indicated hand/eye/body protection should be used.
If the limits at the workplace are exceeded and/or larger amounts are released (leakage, spilling, dust) the indicated respiratory protection should be used.

9. PHYSICAL AND CHEMICAL PROPERTIES**Appearance**

Form	powder
Colour	white
Odour	odourless

Safety data

pH	3.5 - 4.5	(40 g / l)	(20 °C)
Melting point/range	ca. 1850 °C		
Boiling point/range	not applicable		
Flash point	not applicable		
Flammability	not applicable		
Ignition temperature	not applicable		
Autoinflammability	not applicable		

SAFETY DATA SHEET (EC 1907/2006)**AEROXIDE® TiO2 P 25**

Material no.		Version	3.8 / REG_EU
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Lower explosion limit	not applicable
Upper explosion limit	not applicable
Minimum ignition energy	> 10 Joule
Vapour pressure	not applicable
Density	ca. 3.8 g/cm ³ (20 °C)
Tapped density	ca. 130 g / l Method: DIN 53 194
Water solubility	insoluble
Partition coefficient (n-octanol/water)	not applicable
Viscosity, dynamic	not applicable

10. STABILITY AND REACTIVITY

Hazardous decomposition products	None known
Thermal decomposition	> 2000 °C

11. TOXICOLOGICAL INFORMATION

Acute oral toxicity	LD50 Rat: > 10000 mg/kg Method: literature (limit test)
Acute dermal toxicity	LD50 Rabbit: >= 10000 mg/kg Method: literature
Skin irritation	Rabbit / literature not irritating
Eye irritation	Rabbit / literature not irritating
Sensitization	Optimizations-test guinea pig: not sensitizing Method: literature Patch test : not sensitizing Method: literature
Gentoxicity in vitro	Microorganisms, cell cultures Shown no mutagenic/genotoxic effect., literature
Gentoxicity in vivo	Microorganisms, cell cultures Shown no mutagenic/genotoxic effect., literature
Carcinogenicity	Oral rat, mouse: 103 weeks

SAFETY DATA SHEET (EC 1907/2006)**AEROXIDE® TiO2 P 25**

Material no.		Version	3.8 / REG_EU
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no evidence that cancer may be caused, literature.
Feeding experiments

inhalative Rat: 2 years
Method: literature
Increased incidence of lung tumors.

The scientific discussion of the tumorigenic effect of sparingly soluble inorganic particles (fine dusts)- such as titanium dioxide - is ongoing. It is the opinion of many inhalation toxicologists that the tumor formation observed in rats results from a species-specific mechanism involving overloading of the rat lung (overload phenomenon). Corresponding findings resulting from exposure of humans have not been observed to date. On the other hand, the International Agency for Research on Cancer (IARC) assessed, in February of 2006, the available rat model studies as constituting sufficient proof of the carcinogenicity of titanium dioxide in animal models. For humans, the IARC does not see sufficient evidence of a carcinogenic effect of titanium dioxide. However, the IARC evaluation scheme results in an overall assessment of titanium dioxide as "possibly carcinogenic to humans" (Group 2B).

inhalative (mouse): 2 years
no evidence that cancer may be caused, literature.

Human experience

Epidemiological studies to date have not revealed any evidence of a relation between exposure to titanium dioxide and diseases of the respiratory tract beyond general effects of dust.

12. ECOLOGICAL INFORMATION**Elimination information (persistence and degradability)****Behaviour in environmental compartments****Ecotoxicity effects**

Toxicity to fish	LC50 Fundulus heteroclitus: > 1000 mg/l / 96 h Method: literature
Toxicity to daphnia	EC0 Daphnia magna: 1000 mg/l / 48 h Method: literature
Toxicity to bacteria	EC0 Pseudomonas fluorescens: 10000 mg/l / 24 h Method: DEV, DIN 38412, T. 8 (modified).

13. DISPOSAL CONSIDERATIONS**Product**

Disposal according to local authority regulations.

Uncleaned packaging

Offer rinsed packaging material to local recycling facilities.
Other countries: observe the national regulations.

MATERIAL SAFETY DATA SHEET

1. CHEMICAL PRODUCT AND COMPANY IDENTIFICATION

Product Name: Digestion Solution for COD 20-1500 mg/l Range
Catalog Number: 2125915

Hach Company
P.O. Box 389
Loveland, CO USA 80539
(970) 669-3050

Emergency Telephone Numbers:
(Medical and Transportation)
(303) 623-5716 24 Hour Service
(515)232-2533 8am - 4pm CST

MSDS Number: M00485
Chemical Name: Not applicable
CAS Number: Not applicable
Additional CAS No. (for hydrated forms): Not applicable
Chemical Formula: Not applicable
Chemical Family: Not applicable
Intended Use: Laboratory Use Determination of Chemical Oxygen Demand

2. HAZARDS IDENTIFICATION

GHS Classification:

Hazard categories: Acute Toxicity: Acute Tox. 4-Orl Acute Toxicity: Acute Tox. 3-Derm Skin Corrosion/Irritation:
Skin Corr. 1A Germ Cell Mutagenicity: Muta. 1B Carcinogenicity: Carc. 1A Specific Target Organ Toxicity -
Repeated Exposure: STOT RE. 2 Hazardous to the Aquatic Environment: Aquatic Chronic 1

GHS Label Elements:



Hazard statements: May be corrosive to metals. Harmful if swallowed. Toxic in contact with skin. Causes severe skin burns and eye damage. May cause genetic defects. May cause cancer. May cause damage to organs through prolonged or repeated exposure. Very toxic to aquatic life with long lasting effects.

Precautionary statements: Obtain special instructions before use. Wear protective gloves / protective clothing / eye protection / face protection. IF SWALLOWED: rinse mouth. Do NOT induce vomiting. IF ON SKIN (or hair): Remove/Take off immediately all contaminated clothing. Rinse skin with water/shower. IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing. IF exposed or if you feel unwell: Call a POISON CENTER or doctor/physician.

HMIS:

Health: 3*
Flammability: 0
Reactivity: 2
Protective Equipment: X - See protective equipment, Section 8.

NFPA:

Health: 3
Flammability: 0
Reactivity: 2
Symbol: Water Reactive

3. COMPOSITION / INFORMATION ON INGREDIENTS

Hazardous Components according to GHS:

Sulfuric Acid

CAS Number: 7664-93-9
Chemical Formula: H₂SO₄
GHS Classification: Met. Corr. 1 H290; Skin Corr. 1A, H314
Percent Range: 80.0 - 90.0
Percent Range Units: weight / weight
PEL: 1 mg/m³
TLV: 1 mg/m³ (TWA); 3 mg/m³ (STEL)

Silver Sulfate

CAS Number: 10294-26-5
Chemical Formula: Ag₂SO₄
GHS Classification: Eye Dam.1, H318; Aquatic Acute 1, H400
Percent Range: 0.5 - 3.0
Percent Range Units: weight / volume
PEL: 0.01 mg/m³ (Ag)
TLV: 0.01 mg/m³ (Ag)

Mercuric Sulfate

CAS Number: 7783-35-9
Chemical Formula: HgSO₄
GHS Classification: Acute Tox. Inh. 2, H330; Acute Tox Der. 1, H310; Acute Tox. Or. 2, H300; STOT RE 2, H373X, Aquatic Acute 1, H400; Aquatic Chron. 1, H410
Percent Range: 0.1 - 1.0
Percent Range Units: weight / weight
PEL: 0.1 mg/m³ (Hg)
TLV: 0.05 mg/m³ (Hg)

Chromic Acid

CAS Number: 13530-68-2
Chemical Formula: H₂Cr₂O₇
GHS Classification: Ox. Sol.2,H272; Carc.1B,H350; Muta.1B, H340; Repr.1B, H360FD; Acute Tox.2-Inh, H330; Acute Tox.3-Orl, H301; Acute Tox.4-Derm, H312; STOT RE 1, H372; Skin Corr.1B, H314; Resp. Sens.1, H334; Skin Sens.1, H317; Aquatic Acute 1, H400; Aquatic Chronic 1, H410
Percent Range: 0.1 - 1.0
Percent Range Units: weight / volume
PEL: 5 µg/m³ (0.00235 ppm Cr⁺⁶), 8 Hr TWA; Action Level is 2.5 µg/m³ (0.00117 ppm), 8 Hr TWA
TLV: 0.05 mg/m³ (0.0235 ppm as Cr⁺⁶)

Hazardous Components according to GHS: No

Demineralized Water

CAS Number: 7732-18-5
Chemical Formula: H₂O
GHS Classification: Not applicable
Percent Range: 10.0 - 20.0
Percent Range Units: weight / weight
PEL: Not established
TLV: Not established

4. FIRST AID MEASURES

General Information: In the event of exposure, show this Material Safety Data Sheet and label (where possible) to a doctor.

Advice to doctor: Treat symptomatically.

Eye Contact: Immediately flush eyes with water for 15 minutes. Call physician.

Skin Contact (First Aid): Wash skin with plenty of water for 15 minutes. Remove contaminated clothing. Call physician immediately.

Inhalation: Remove to fresh air. Give artificial respiration if necessary. Call physician.

Ingestion (First Aid): Do not induce vomiting. Give large quantities of water. Never give anything by mouth to an unconscious person. Call physician immediately.

5. FIRE FIGHTING MEASURES

Flammable Properties: Not Flammable, but reacts with most metals to form flammable hydrogen gas. During a fire, corrosive and toxic gases may be generated by thermal decomposition.

Fire Fighting Instruction: As in any fire, wear self-contained breathing apparatus pressure-demand and full protective gear. Evacuate area and fight fire from a safe distance. Water runoff can cause environmental damage. Dike and collect water used to fight fire.

Extinguishing Media: Use media appropriate to surrounding fire conditions

Extinguishing Media NOT To Be Used: Not applicable

Fire / Explosion Hazards: Contact with metals gives off hydrogen gas which is flammable. May react violently with: strong bases water

Hazardous Combustion Products: This material will not burn.

6. ACCIDENTAL RELEASE MEASURES

Spill Response Notice:

Only persons properly qualified to respond to an emergency involving hazardous substances may respond to a spill according to federal regulations (OSHA 29 CFR 1910.120(a)(v)) and per your company's emergency response plan and guidelines/procedures. See Section 13, Special Instructions for disposal assistance. Outside of the US, only persons properly qualified according to state or local regulations should respond to a spill involving chemicals.

Containment Technique: Releases of this material may contaminate the environment. Absorb spilled liquid with non-reactive sorbent material. Stop spilled material from being released to the environment. Dike the spill to contain material for later disposal.

Clean-up Technique: Mercury and its compounds are extremely toxic! Be extremely careful not to contact the spill or breathe any vapors. Absorb spilled liquid with non-reactive sorbent material. Dispose of all mercury contaminated material at a government approved hazardous waste facility. Dispose of material in government approved hazardous waste facility. Decontaminate area with commercially available mercury absorbing compounds.

Evacuation Procedure: Evacuate general area (50 foot radius or as directed by your facility's emergency response plan) when: any quantity is spilled. Deny access to unnecessary and unprotected personnel. Remain up-wind from spilled material. If conditions warrant, increase the size of the evacuation.

DOT Emergency Response Guide Number: 137

7. HANDLING AND STORAGE

Handling: Avoid contact with eyes skin clothing Do not breathe mist or vapors. Use with adequate ventilation. Maintain general industrial hygiene practices when using this product.

Storage: Protect from: light contamination by organic materials (will affect product stability) heat

Flammability Class: Not applicable

8. EXPOSURE CONTROLS / PERSONAL PROTECTION

Engineering Controls: Use a fume hood to avoid exposure to dust, mist or vapor. Maintain general industrial hygiene practices when using this product. Maintain adequate ventilation to keep vapor level below TWA for chemicals in this product. Refer to the OSHA Standard at 29CFR1910.1026 for Cr (VI) (See Federal Register 28 February 2006 Page 10100.)

Personal Protective Equipment:

Eye Protection: chemical splash goggles

Skin Protection: disposable latex gloves lab coat

Inhalation Protection: laboratory fume hood

Precautionary Measures: Avoid contact with: eyes skin clothing Do not breathe: mist/vapor Wash thoroughly after handling. Use with adequate ventilation. Protect from: heat light organic materials Keep away from: alkalis metals other combustible materials oxidizers reducers

TLV: Not established. 0.05 mg/m³ (0.0235 ppm as Cr⁺⁶).

PEL: Not established. 5 µg/m³ (0,00235 ppm Cr⁶⁺), 8 Hr TWA; Action Level is 2,5 µg/m³ (0,00117 ppm), 8 Hr TWA
For Occupational Exposure Limits (OEL) for ingredients, see section 3 - Composition/Information on Ingredients.:

9. PHYSICAL AND CHEMICAL PROPERTIES

Appearance: Turbid, light orange liquid

Physical State: Liquid

Molecular Weight: Not applicable

Odor: Not determined

Odor Threshold: Not applicable

pH: < 0.5

Metal Corrosivity:

Corrosivity Classification: Classified as corrosive to metals.

Steel: Corrosive

Aluminum: Corrosive

Specific Gravity/Relative Density (water = 1; air =1): > 1.0

Viscosity: Not determined

Solubility:

Water: Miscible

Acid: Not determined

Other: Not determined

Partition Coefficient (n-octanol / water): Not applicable

Coefficient of Water / Oil: Not applicable

Melting Point: Not applicable

Decomposition Temperature: Not determined

Boiling Point: > 100°C (> 212°F)

Vapor Pressure: Not determined

Vapor Density (air = 1): Not determined

Evaporation Rate (water = 1): Not determined

Volatile Organic Compounds Content: Not applicable

Flammable Properties: Not Flammable, but reacts with most metals to form flammable hydrogen gas. During a fire, corrosive and toxic gases may be generated by thermal decomposition.

Flash Point: Not applicable

Method: Not applicable

Flammability Limits:

Lower Explosion Limits: Not applicable

Upper Explosion Limits: Not applicable

Autoignition Temperature: Not applicable

Explosive Properties:

Not classified according to GHS criteria.

Oxidizing Properties:

Not classified according to GHS criteria.

Reactivity Properties:

Not classified as self-reactive, pyrophoric, self-heating or emitting flammable gases in contact with water according to GHS criteria.

Gas under Pressure:

Not classified as gas under pressure according to GHS.

10. STABILITY AND REACTIVITY

Chemical Stability: Stable when stored under proper conditions.

Mechanical Impact: None reported

Static Discharge: None reported.

Reactivity / Incompatibility: May react violently in contact with: caustics

Hazardous Decomposition: Heating to decomposition releases toxic and/or corrosive fumes of: mercury compounds
sulfur oxides

Conditions to Avoid: Exposure to light or contamination by organic materials will affect this product's stability.

11. TOXICOLOGICAL INFORMATION

Toxicokinetics, Metabolism and Distribution: No information available

Toxicologically Synergistic Products: None reported

Acute Toxicity:

Oral rat LD50 = 496 mg/kg.

Dermal LD50 = 614 mg/kg.

Inhalation LC50 = 32 mg/L.

Specific Target Organ Toxicity - Single Exposure (STOT-SE): Based on classification principles, the classification criteria are not met.

Specific Target Organ Toxicity - Repeat Exposure (STOT-RE): Target Organs Respiratory Tract Kidneys Liver
Reproductive system Central nervous system

Skin Corrosion/Irritation: Corrosive to skin.

Eye Damage: Corrosive to eyes.

Sensitization: Based on classification principles, the classification criteria are not met.

CMR Effects/Properties (carcinogenic, mutagenic or toxic to reproduction): Contains Listed Carcinogen Data supporting mutagenicity was found.

An ingredient of this mixture is: NTP Listed Group 1: Recognized Carcinogen

Hexavalent Chromium Compounds

An ingredient of this product is an OSHA listed carcinogen.

Hexavalent chromium (Cr⁶⁺) compounds

Symptoms/Effects:

Ingestion: Causes: severe burns May cause: abdominal pain circulatory disturbances diarrhea loosening of the teeth
nausea vomiting rapid pulse and respirations toxic nephritis (inflammation of the kidneys) shock collapse kidney
damage death Toxic

Inhalation: Causes: severe burns May cause: difficult breathing mouth soreness teeth erosion Effects similar to those
of ingestion. Toxic

Skin Absorption: Toxic Will be absorbed through the skin. Effects similar to those of ingestion

Chronic Effects: Chronic overexposure may cause destruction of any tissue contacted difficult breathing mouth
soreness erosion of the teeth accumulation of silver in body tissues which causes a slate-gray to bluish discoloration.
cancer Chromate and dichromate salts may cause ulceration and perforation of the nasal septum, severe liver damage,
central nervous system effects, and lung cancer. Mercury is a general protoplasmic poison; it circulates in the blood and
is stored in the liver, kidneys, spleen and bones. Main symptoms are sore mouth, tremors and psychic disturbances.

Medical Conditions Aggravated: Pre-existing: Respiratory conditions Eye conditions Skin conditions Allergies or
sensitivity to chromates or chromic acid. Allergies or sensitivity to mercury.

12. ECOLOGICAL INFORMATION

Product Ecological Information: Calculated: Crustacea 48 hr EC50 = 0.0045 mg/L.

Mobility in soil: No data available

Method Used for Estimation of Aquatic Toxicity of Mixture M-factor (Multiplier) for highly toxic ingredients: 100

Ingredient Ecological Information: Silver sulfate: Crustacea 48 hr EC50 = 0.0045 mg/L; mercuric sulfate: Algae: EC50 -
Pseudokirchneriella subcapitata - 0.033 mg/L - 14 d; chronic acid: Daphnia magna (Water flea) 48 hr EC50 = 0.8 mg/L.

13. DISPOSAL CONSIDERATIONS

EPA Waste ID Number: D002 D007 D009 D011

Special Instructions (Disposal): Dispose of all mercury contaminated material at an E.P.A. hazardous waste facility.

Dispose of material in an E.P.A. approved hazardous waste facility.

Empty Containers: Rinse three times with an appropriate solvent. Dispose of empty container as normal trash. Rinsate
from empty containers may contain sufficient product to require disposal as hazardous waste.

NOTICE (Disposal): These disposal guidelines are based on federal regulations and may be superseded by more stringent
state or local requirements. Please consult your local environmental regulators for more information. In Europe: Chemical
and analysis solutions must be disposed of in compliance with the respective national regulations. Product packaging must
be disposed of in compliance with the country-specific regulations or must be passed to a packaging return system.

14. TRANSPORT INFORMATION

D.O.T.:

D.O.T. Proper Shipping Name: Sulphuric Acid

--

Hazard Class: 8

Subsidiary Risk: NA

ID Number: UN1830

Packing Group: II
I.D.G.:
Proper Shipping Name: Sulphuric Acid
--
Hazard Class: 8
Subsidiary Risk: NA
UN Number/PIN: 1830
Packing Group: II
I.C.A.O.:
I.C.A.O. Proper Shipping Name: Sulphuric Acid
--
Hazard Class: 8
Subsidiary Risk: NA
ID Number: UN1830
Packing Group: II
I.M.O.:
Proper Shipping Name: Sulphuric Acid
--
Hazard Class: 8
Subsidiary Risk: NA
ID Number: UN1830
Packing Group: II

Additional Information: There is a possibility that this product could be contained in a reagent set or kit composed of various compatible dangerous goods. If the item is NOT in a set or kit, the classification given above applies. If the item IS part of a set or kit, the classification would change to the following: UN3316 Chemical Kit, Class 9, PG II or III. If the item is not regulated, the Chemical Kit classification does not apply.

15. REGULATORY INFORMATION

U.S. Federal Regulations:

O.S.H.A.: This product meets the criteria for a hazardous substance as defined in the Hazard Communication Standard. (29 CFR 1910.1200)

E.P.A.:

S.A.R.A. Title III Section 311/312 Categorization (40 CFR 370): Immédiat (aigu) Danger pour la santé Delayed (Chronic) Health Hazard Reactive

S.A.R.A. Title III Section 313 (40 CFR 372): This product contains a chemical(s) subject to the reporting requirements of Section 313 of Title III of SARA.

Mercury compounds, Silver compounds, Chromium Compounds, Sulfuric acid (acid aerosols including mists, vapors, gas, fog and other airborne forms).

302 (EHS) TPQ (40 CFR 355): Sulfuric Acid 1000 lbs.

304 CERCLA RQ (40 CFR 302.4): Chromic acid and Mercuric sulfate (each) = 10 lbs. Sulfuric Acid 1000 lbs.

304 EHS RQ (40 CFR 355): Sulfuric Acid - RQ 1000 lbs.

Clean Water Act (40 CFR 116.4): Chromic acid - RQ 10 lbs. Mercuric sulfate - RQ = 10 lbs. (4.54 kgs.) Sulfuric acid - RQ 1000 lbs.

RCRA: Contains RCRA regulated substances. See Section 13, EPA Waste ID Number.

State Regulations:

California Prop. 65: WARNING - This product contains a chemical known to the State of California to cause cancer.

WARNING - This product contains a chemical known to the State of California to cause birth defects or other reproductive harm.

Identification of Prop. 65 Ingredient(s): Chromium (hexavalent compounds); Mercury and mercury compounds.

California Perchlorate Rule CCR Title 22 Chap 33: Not applicable

Trade Secret Registry: Not applicable

National Inventories:

U.S. Inventory Status: All ingredients in this product are listed on the TSCA 8(b) Inventory (40 CFR 710).

CAS Number: Not applicable

Canadian Inventory Status: All ingredients of this product are DSL Listed.

EEC Inventory Status: All ingredients used to make this product are listed on EINECS / ELINCS.

Australian Inventory (AICS) Status: All ingredients are listed.

New Zealand Inventory (NZIoC) Status: All components either listed or exempt.

Korean Inventory (KECI) Status: All components of this product are either listed, listed as the anhydrous compound or exempt.

Japan (ENCS) Inventory Status: All components either listed or exempt.

China (PRC) Inventory (MEP) Status: All components either listed or exempt.

16. OTHER INFORMATION

References: 29 CFR 1900 - 1910 (Code of Federal Regulations - Labor). Air Contaminants, Federal Register, Vol. 54, No. 12. Thursday, January 19, 1989. pp. 2332-2983. CCINFO RTECS. Canadian Centre for Occupational Health and Safety. Hamilton, Ontario Canada: 30 June 1993. Fire Protection Guide on Hazardous Materials, 10th Ed. Quincy, MA: National Fire Protection Association, 1991. IARC Monographs on the Evaluation of the Carcinogenic Risks to Humans. World Health Organization (Volumes 1-42) Supplement 7. France: 1987. List of Dangerous Substances Classified in Annex I of the EEC Directive (67/548) - Classification, Packaging and Labeling of Dangerous Substances, Amended July 1992. Outside Testing. Sixth Annual Report on Carcinogens, 1991. U.S. Department of Health and Human Services. Rockville, MD: Technical Resources, Inc. 1991. Technical Judgment. Verschueren, Karel. Handbook of Environmental Data on Organic Chemicals. New York: Van Nostrand Reinhold Co., 1977.

Complete Text of H phrases referred to in Section 3: H290 May be corrosive to metals. H302 Harmful if swallowed. H311 Toxic in contact with skin. H314 Causes severe skin burns and eye damage. H340 May cause genetic defects. H350 May cause cancer. H373 May cause damage to organs through prolonged or repeated exposure. H410 Very toxic to aquatic life with long lasting effects.

Revision Summary: Substantial revision to comply with EU Reg 1272/2008, Reg 1907/2006 and UN GHS (ST/SG/AC.10/36/Add.3).

Date of MSDS Preparation:

Day: 08

Month: October

Year: 2012

MSDS Prepared: MSDS prepared by Product Compliance Department extension 3350

CCOHS Evaluation Note: This product has been classified and labeled in accordance with the requirements of GHS (ST/SG/AC.10/36/Add.3). It is offered under the interim policy that was established by Health Canada permitting use of GHS-formatted safety data sheets in Canada prior to revision of CPR to GHS. It is offered under exemption from WHMIS labeling as specified in the Controlled Products Regulation (CPR) Section 17.

Legend:

NA - Not Applicable

ND - Not Determined

NV - Not Available

w/w - weight/weight

w/v - weight/volume

v/v - volume/volume

USER RESPONSIBILITY: Each user should read and understand this information and incorporate it in individual site safety programs in accordance with applicable hazard communication standards and regulations.

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Figure 74: MSDS for COD digestion vials