
**ENERGIZED PROCESSES FOR
ONSITE TREATMENT OF LEACHATE**

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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 State 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
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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 socially and environmentally responsible management of solid waste, new technologies may be 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. This study describes the development of pilot scale onsite treatment systems capable of detoxifying leachate with the power of ultraviolet light and advanced oxidation. The objective of the proposed research is to test photooxidative processes at pilot scale for the removal of COD/BOD, ammonia, heavy metals, color, and pathogens.

EXECUTIVE SUMMARY

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OBJECTIVES

The objective of the proposed research is to pilot test an energized treatment process for the removal of parameters of interest including COD/BOD, ammonia, heavy metals, color, and pathogens using non-biological methods that landfill operators with little training can routinely and reliably employ without spending too much time on the task. The main focus was to validate 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. 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 management of landfill leachate has been the lack of effective methods to guarantee 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. Furthermore, the continual introduction of new chemicals from industry and the ubiquitous detection of pharmaceuticals and endocrine disruptors in natural waters make matters worse.

One attractive option for landfill managers is hauling. Off-site hauling does not directly address water pollution issues because the leachate is merely moved to another location (generally to a wastewater treatment plant). 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 Çakiroglu 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.

Another attractive disposal option for managing leachate is deep well injection, if the appropriate aquifer conditions exist and permitting is available. However, 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 hydrogeologic demonstration and advanced treatment, as necessary. 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, which include treatment limits of 20 mg/L BOD₅ and 5.0 mg/L of TSS before the application of the disinfectant. 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 continue accepting leachate. This would cause problems for another important leachate management option: 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. 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.

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 first step in this project was to compile the available information and update the technical literature review to develop an extensive list of available and experimental alternatives for dealing with landfill leachate in the long-term, ranked according to selection criteria based on environmental sustainability, efficiency, risk, feasibility, and economic factors.

The next step was to conduct baseline water quality studies of the participating landfill leachate. These results were compiled from historical data from NELAC-certified labs, operating reports, and lab tests conducted by FAU Lab.EES. After determining the starting water quality, simulated leachates were prepared for laboratory-scale conceptual design tests using a batch reactor type. This preliminary testing investigated the optimum dose of photocatalytic particles, the optimum alkalinity and pH ranges, and expected treatment performance. Laboratory tests for the effects of pre-treatment using filtration, lime addition, and both were conducted.

Finally two pilot reactors were constructed. The first one was a falling film reactor and the second one was a flow through plug flow coil reactor. Initial tests were conducted with the falling film reactor to determine process design parameters for scale-up. Photocatalytic oxidation tests were conducted to determine process removal efficiency for COD, BOD₅, ammonia-nitrogen, color, and certain trace metals (Cu, As, etc.). Alkalinity and pH were monitored to investigate their effects.

RESULTS

From laboratory scale tests, the optimum dosage of photocatalyst for simulated leachate with initial COD of 1000 mg/L and alkalinity of 4300 mg/L as CaCO₃ is on the order of 3.3 – 3.8 gTiO₂ per gCOD. At 1000 mg/L COD, the optimum alkalinity range occurs between 4100 – 4700 mg/L as CaCO₃. To test if the value is independent of initial COD concentration, another experiment was conducted in which the alkalinity level was in the optimum range, but the initial COD concentration was six times larger. Under these conditions, the COD removal was only 10.5%, which demonstrates a strong concentration dependence that will likely complicate scale-up without extensive pilot testing.

Pre-treatment experiments with lime and filtration and pH adjustment improved the reaction times by a small factor. BOD, ammonia, metals, and color could be effectively removed in simulated and real leachates using the optimum TiO₂ and alkalinity levels developed for COD. The effects of pH and alkalinity were investigated. The process can be effective at ambient pH and alkalinity levels as long as the reaction time can be extended. The reactor data seem to follow zero order or first order kinetics, but modeling is complicated due to the lack of temperature control and the inability to extend the reaction times due to limitations of the reactor design. During pilot tests, the maximum reaction time tested was limited to 6 hours. In future testing, we will run the pilot unit in multiple 6 hour cycles.

CONCLUSIONS

For the photocatalytic oxidation process with commercially available TiO₂ particles (Degussa P25) with simulated and real leachates resulted in COD removal on the order of 4-6 hours, and 100% mineralization of COD to carbon dioxide and water was observed in simulated leachate with initial COD concentrations on the order of 1000 mg/L. In addition, removal of 79% copper and 50% ammonia was also achieved. The optimum dose of TiO₂ particles at pH 7.1 – 9.2 was found to be 4.0 g/L for initial COD concentrations of 1000 mg/L with an initial alkalinity of 4333 mg/L as CaCO₃. It was determined that alkalinity potentially acts as a photosensitizer or facilitates adsorption to the photoactive sites on the catalyst surface, but it also is a known radical scavenger, which inhibits the reaction at elevated alkalinity levels.

Using real leachates at the laboratory-scale, 53% mineralization of COD, 74% ammonia, 34% BOD₅, 52% arsenic removal was demonstrated after 360 minutes of contact time using the optimal conditions developed for the simulated leachate. The BOD/COD ratio began at 0.12, which is considered difficult to biodegrade, and after treatment was converted to 0.21, which is considered partially biodegradable. Scale-up has been complicated due to an observed concentration dependence and the inability to run the reaction longer than 360 minutes due to the effect of large temperature increases.

Scaling up to pilot tests from the laboratory results proved to be a challenge because the kinetics of the reaction are not completely understood due to issues resulting from the inability to precisely control the reaction temperatures. LiPuma et al. (2004) note that “the application of photocatalytic oxidation for wastewater treatment on an industrial scale is currently hindered by a lack of simple mathematical models that can be readily applied to reactor design.” However, work is underway to address this issue.

**ENERGIZED PROCESSES FOR
ONSITE TREATMENT OF LEACHATE**

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1. INTRODUCTION

Over 100 sanitary landfills currently exist in Florida. Of those, 64 are required to have liners and leachate collection systems to prevent leachate migration into drinking water supplies. This number is expected to continue to grow. At the same time, the nature of landfill wastes is undergoing a fundamental change as the amount of incinerator ash and residues increases, particularly in Florida, which has the largest number of waste-to-energy (WTE) plants in operation, generating over 1.5 million tons of ash per year (FDEP 2002). This amounts to 23% of the WTE ash generated annually in the United States (USEPA 2003). Whereas sanitary landfill leachate is characterized by elevated levels of recalcitrant organic material, color, and ammonia, incinerator ash leachate contains important concentrations of organochlorine compounds and heavy metals (i.e. Pb, Hg, and Cd), which must be removed for safe discharge to the environment.

A historical survey of Class 1 landfills in Florida (Tedder 1997; FDEP 2002) found that approximately 750 gallons per acre of variable quality high strength leachate is collected daily. Leachate generation is typically calculated based upon the worst case scenario when the lined portion of the landfill has completed construction and has placed the first lift of garbage in the cell with no cover material and the highest rainfall event ever recorded in the area hits the opened faced landfill. The site runoff and the rainfall that percolates through the waste are considered leachate in this scenario. The HELP model gives a theoretical value in the South Florida area of 2,000 to 3,000 gpd/acre. This value is the design value for most landfills in the Southeast Florida region; however, most landfills do not have calibrated flow meters for recording actual leachate volumes, and most are generating leachates from partially lined cells or older systems (Lurix 2009, personal communication). The Okeechobee landfill (Facility ID: 00070436) has the most accurate flow meters in the southeast district, and is a more modern landfill in that it does not have older cells with partial liner systems or contributing cells without flow meters. The Okeechobee landfill is double-lined, double composite with dual leachate force main piping. The leachate pump stations are controlled with electrical equipment that automatically records leachate production data via satellite to corporate management. So, leachate volume data collected from this landfill is likely the most accurate (2631 gpd/acre). The problem with using this value is that the Okeechobee landfill is considered a very large facility (3200-3500 ton/day), and we do not have data for smaller sized facilities. According a recent survey conducted by FAU (Meeroff and Teegavarapu 2010), leachate production varies widely across the state of Florida from less than 100 – 3000 gpd/acre (see Table 1).

Table 1. Distribution of landfill leachate production in gallons per day per acre for the 52 representative Florida landfills surveyed.

Capacity Class	Range (gpd/acre)	Number
Small	< 100	14
Medium	100 – 300	9
Large	300 – 850	6
Super	> 850	2
Not determined	--	21

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. Different data sets are available from different parts of the world (Akesson and Nilsson 1997, Al-Yaqout et al. 2005, Amokrane et al. 1997, Bekbölet et al. 1996, Bernard et al. 1997, Bila et al. 2005, Calli et al. 2005, Geenens et al. 2000, Gonze et al. 2003, Hickman 2003, Imai et al. 1998, Ince 1998, Kim et al. 1997, Kjeldsen et al. 2002, Lin et al. 2000, Mohammad et al. 2004, Moraes and Bertazzoli 2005, de Morais and Zamora 2005, O’Leary and Walsh 1995, Oweis and Kehra 1998, Tammemagi 1999, Tatsi et al. 2003, Tchobanoglous and Kreith 2002, Reinhart and Grosh 1998, Reinhart and Townsend 1998, Silva et al. 2004, Silva et al. 2004, Statom et al. 2004, Steensen 1997, Ward et al. 2002, Westlake and Phil 1995, Wichitsathian et al. 2004, Wu et al. 2004, Youcai et al. 2002) and are summarized in Table 2.

Table 2. Typical leachate water quality data from young and mature landfills (Tchobanoglous, Theisen, and Vigil 1993)

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 (CH₄) to volatile fatty acids (VFA) to more refractory humics and fulvics; ii) inorganic constituents, such as calcium (Ca²⁺), magnesium (Mg²⁺), sodium (Na⁺), potassium (K⁺), ammonium (NH₄⁺), iron (Fe²⁺), manganese (Mn²⁺), chloride (Cl⁻), sulfates (SO₄²⁻) and bicarbonates (HCO₃⁻) 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. Table 3 summarizes the variability of constituents found in leachate. Specific conditions are not indicated in the table, as the summary serves point out the wide variety of leachate water quality that can be found.

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

Parameters	Units	Range	Concentration	
			Average	Median
Ammonia	mg/L as NH ₃ -N	BDL* - 8750	830	750
BOD ₅	mg/L as O ₂	BDL* - 80,800	4000	190
COD	mg/L as O ₂	0.4 – 152,000	10,300	4200
Conductivity	μS/cm	5.2 – 95,000	13,100	8,600
Lead (Pb)	mg/L	BDL* - 5.0	0.1	0.1
pH	pH units	2.0 – 11.3	7.5	7.5
TDS	mg/L	0.1 – 88,000	11,000	7600

Parameters	Units	Range	Concentration	
			Average	Median
TSS	mg/L	10 – 45,000	840	950

BDL* = below detection limit.

Source: Adapted from Akesson and Nilsson (1997), Al-Yaqout et al. (2005), Amokrane et al. (1997), Bekbölet et al. (1996), Bernard et al. (1997), Bila et al. (2005), Calli et al. (2005), Geenens et al. (2000), Gonze et al. (2003), Hickman (2003), Imai et al. (1998), Ince (1998), Kim et al. (1997), Kjeldsen et al. (2002), Lin et al. (2000), Mohammad et al. (2004), Moraes and Bertazzoli (2005), Morais and Zamora (2005), O’Leary and Walsh (1995), Oweis and Kehra (1998), Tammemagi (1999), Tatsi et al. (2003), Tchobanoglous and Kreith (2002), Reinhart and Grosh (1998), Reinhart and Townsend (1998), Silva et al. (2003), Silva et al. (2004), Solid Waste Authority of Palm Beach County (2006), Statom et al. (2004), Steensen (1997), Ward et al. (2002), Westlake and Phil (1995), Wichitsathian et al. (2004), Wu et al. (2004), Youcai et al. (2002).

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.

One attractive option for landfill managers is hauling. Off-site hauling does not directly address water pollution issues because the leachate is merely moved to another location (generally to a wastewater treatment plant). 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. In 2005, Polk County, FL reported a cost of \$110 per 1,000 gallons for transportation and pre-treatment prior to discharge into a wastewater treatment system that would accept their leachate. 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.

Another attractive disposal option for leachate is deep well injection, if the appropriate aquifer conditions exist and permitting is available. However, 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 hydrogeologic 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.

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. 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 semi-conductor (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.

1.1 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 4 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. 1998; 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; Morais and Zamora 2005).

Table 4. 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 \cdot)	2.05
Ozone	(O $_3$)	1.52
Hydrogen peroxide	(H $_2$ O $_2$)	1.31
Permanganate	(MnO $_4^-$)	1.24
Hypochlorous acid	(HOCl)	1.10
Chlorine	(Cl $_2$)	1.00

An energized process is based on similar mechanisms as the AOPs but with the additional action of ultraviolet light, which may be either from a UV lamp or from natural sunlight. Addition of ultraviolet energy has been shown to enhance the production of the hydroxyl radical. Steensen (1997) explained that the use of iron (catalyst) or photo-energy (EP) improves oxidation power by accelerating the formation of hydroxyl radicals. Staehelin and Hoigné (1983) pointed out however, that “radical scavengers,” such as: carbonates species (CO $_3^{2-}$ / HCO $_3^-$) or alkyl compounds slow down the reaction rate because they interrupt the chain reaction. Maintaining a low pH to shift the carbonate equilibrium toward carbonic acid is important for these types of processes. Nevertheless, AOPs and EPs offer a robust and increasingly economically favorable alternative for treatment of wastewater contaminated with highly toxic organic constituents (Feitz et al. 1998). AOPs and EPs are known to handle many of the constituents typically found in leachate:

1. **Elevated ammonia:** EPs convert ammonia to nitrate through aeration or promote stripping of dissolved ammonia gases at suitably high pH (AWWA 1999).
2. **High COD/BOD ratios:** EPs convert refractory COD into readily biodegradable BOD (Suty et al. 2004), which is then mineralized by oxidation to simple products such as CO $_2$, H $_2$ O, etc. (Metcalf and Eddy 2003).
3. **Heavy metals:** EPs remove heavy metals such as: lead, arsenic, mercury, and cadmium through co-precipitation, adsorption, and redox mechanisms (Englehardt et al. 2002 and references therein).
4. **pH toxicity:** EPs limit pH impacts as a byproduct of aeration treatment via the natural buffering capacity of the carbonate system (AWWA 1999; Metcalf and Eddy 2003).
5. **Volatile organic compounds:** EPs can destroy recalcitrant organics and, because of their volatility or promote the stripping of VOCs during aeration, provided the appropriate conditions (AWWA 1999, Suty et al. 2004).

Advanced oxidation processes can occur both with and without the addition of energy. If AOPs or EPs are used as a pre-treatment step before a biological treatment, it has been demonstrated that these types of oxidation processes can reduce the detention time required for subsequent biological treatment (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

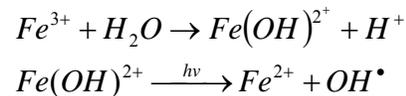
drawback of AOPs is the high demand for electrical energy (e.g. ozonizers, UV lamps, ultrasound, etc.), which increases cost (Lopez et al. 2004). Also, for complete mineralization of pollutants to occur, high oxidant doses may be required. Silva et al. (2004) needed 3.0 g/L of ozone to attain significant toxicity decrease. Furthermore, some intermediate oxidation byproducts generated by incomplete mineralization can increase the toxicity of leachate.

In the following discussion, the use of various advanced oxidation methods is reviewed with respect to photo-Fenton, UV/H₂O₂, photocatalytic oxidation, iron-mediated aeration, and photochemical iron-mediated aeration.

1.1.1 Photo-Fenton / Fenton-like systems

Photo-Fenton involves a combination of hydrogen peroxide and UV radiation with ferrous iron to produce more hydroxyl radicals in comparison to the conventional Fenton method, which does not add ultraviolet light, or simple photolysis, which does not add the Fenton reagent. The combination of ultraviolet radiation and Fenton's reagent promotes more rapid degradation of organic pollutants by increasing the kinetics of the reaction. The higher production of hydroxyl radical due to the combination of oxidants and metallic catalysts in the presence of UV radiation and the potential applicability of sunlight as the primary UV light resource are some attractive advantages of this system.

The photo-Fenton process forms the Fe(OH)²⁺ complex, which is subsequently oxidized by UV radiation at low pH according to the following reaction sequence:



This has the effect of generating the Fenton catalyst in-situ and enhancing the production of hydroxyl radical through direct photolysis and also by reaction. Kim et al. (1997) used photo-Fenton reactions on municipal landfill leachate that was pre-treated biologically. After pH adjustment to pH < 3.0, the optimum conditions for maximum degradation were: [Fe²⁺] = 1.0 × 10⁻³ M (56 mg/L) and a molar ratio of 1:1 COD:H₂O₂. The starting COD concentration was 1150 mg/L, and after two hours of treatment at 80 mW/cm³, the observed removal was 70%. Morais and Zamora (2005) used the photo-Fenton process to pre-treat raw mature leachate from a sanitary landfill in Brazil. They used a medium-pressure mercury vapor lamp (125 W), an O₂ aeration system (Q = 45 mL/min), and reagent concentrations of 2000 mg H₂O₂/L and 10 mg Fe²⁺/L. The pH was adjusted to 2.8, and after 60 minutes, the initial COD concentration of 5200 mg/L as O₂ was reduced to 2240 mg/L as O₂, which equals a removal of 57%. They also greatly improved the biodegradability of the leachate by increasing the BOD₅/COD ratio from 0.13 to 0.40. This confirms the general opinion that many AOPs enhance the biodegradability of landfill leachate. They proposed to use this process as a pre-treatment of leachate before biological treatment.

Kim et al. (2001) used photo-Fenton treatment to increase the BOD₅/COD ratio of leachate from less than 0.05 to greater than 0.60. Lau et al. (2002) applied photo-Fenton treatment to increase leachate BOD₅/COD from 0.08 to 0.14. Deng and Englehardt (2006) studied the Fenton and

photo-Fenton processes from treatment of landfill leachates using ferrous sulfate and hydrogen peroxide at circumneutral pH. After rapid mixing from 30 seconds to 60 minutes at impeller speeds of 80-400 rpm, they flocculated for 10-30 minutes at 20-80 rpm, followed by sedimentation for periods of from 30 minutes to several days. They found that at optimal pH (2.0-4.5), the removal of COD increased with increasing concentration of iron salt, but removal may be marginal when the concentration of iron salt is high, and the lower pH range inhibited subsequent precipitation and sedimentation. They also optimized the molar ratio of H₂O₂ to Fe²⁺ at 11:1. Using these conditions, they demonstrated 51% COD removal at 80 mW/cm³, but they found no oxidation of ammonia and encountered severe issues with foaming that inhibited mass transfer of hydroxyl radicals to the bulk solution.

Primo et al. (2008) tested a variety of advanced oxidation processes (AOPs), namely photo-Fenton, Fenton-like, Fenton and UV/H₂O₂ for the removal of organic matter and color from landfill leachates. The leachate his team used was characterized by high COD, low biodegradability and an intense dark color. Evaluation of COD removal as a function of the operation variables (H₂O₂, Fe²⁺, UV) led to results that ranged between 30% and 86% removal of COD, and it was observed that the removal efficiencies decreased in the order: photo-Fenton > Fenton-like > Fenton > UV/H₂O₂ > UV by itself. Thus, a detailed experimental analysis was carried out to analyze the effect of hydrogen peroxide and iron concentrations in the photo-Fenton process, observing that: i) the COD removal ranged from 49% to 78% depending on the H₂O₂ dose, ii) the total amount of organic matter removed was increased by adding the reagent in multiple steps (86%), iii) iron concentration corresponding to a Fe²⁺/COD mass ratio = 0.33 was found to be the most favorable and, iv) after a neutralization step, the color and residual concentrations of iron and H₂O₂ were practically negligible in the final leachate solution (Primo et al. 2008). A summary of the COD removal performance for photo-Fenton processes obtained from the scientific literature is presented in Table 5. Ferreira et al. (2008) used the photo-Fenton reaction to treat olive mill wastewater resulting in a color removal of greater than 90% with a hydrogen peroxide dose of 108 g/L and an iron dose of 550 mg/L at pH = 4.2 after a 6-day reaction time. But the photo-Fenton process has not been applied to landfill leachates to our knowledge. However, Fenton's oxidation without UV has been applied for the pretreatment of landfill leachate by Petruzzelli et al. (2007) in which almost 50% COD removal was observed with an initial COD concentration of 10,915 mg/L after 120 min at pH = 3.2.

Table 5. Summary of COD removal performance tests conducted with UV/Fe(II)/ H₂O₂ technologies on landfill leachates.

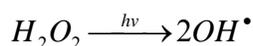
H ₂ O ₂ Dose (g/L)	Fe(II) Dose (mg/L)	UV (W)	COD ₀ (mg/L)	BOD/COD _{before}	BOD/COD _{after}	pH	COD Removal (%)	Reference
1.15	56	500-1000	1150	<0.01	nr	3.0	70	Kim et al. 1997
0.44-1.15	30-70	500-1000	440-1150	0.05	0.60	2.7-3.2	70-78	Kim et al. 2001
0.8	0.3	nr	1910	0.06	0.14	3-4	71	Lau et al. 2002
2.0	10	125	5200	0.13	0.40	2.8	57	Morais and Zamora

200	2316	12	21,000	0.38	nr	3.0	39	2005 Dincer et al. 2008
10	2000	150	3300-4400	0.15-0.24	nr	3.5	86	Primo et al. 2008

Advanced oxidation processes such as conventional Fenton, photo-Fenton and electro-Fenton are powerful advanced oxidation processes that effectively degrade refractory organics and persistent organic pollutants, which are difficult to decompose by other processes such as biological systems. But alone, they appear to be limited and instead must be used as a pretreatment step to facilitate other degradation processes.

1.1.2 Ultraviolet light and hydrogen peroxide (UV/H₂O₂)

Using UV and H₂O₂ without iron or catalyst addition for water treatment results in three modes of treatment: 1) direct photolysis by UV, 2) direct oxidation by H₂O₂, and 3) the indirect generation of hydroxyl radicals. Direct photolysis of hydrogen peroxide also leads to the formation of hydroxyl radicals by the splitting of the oxygen-oxygen bond (Schulte et al. 1995):



The oxidation of combined UV/H₂O₂ processes is more effective at low pH (pH = 2 – 4), which requires pH adjustment and reduction of alkalinity (Steensen 1997). Shu et al. (2006) enhanced the efficiency of their first experiments with H₂O₂ by adding four UV lamps. With this new set-up, they improved the COD removal from 60% with hydrogen peroxide alone to 65%, while reducing the reaction time in half from 600 minutes to 300 minutes. The formation of hydroxyl radical was greatly improved by the addition of UV energy. They also demonstrated the importance of the initial COD concentration on process performance. Indeed, the COD removal increased as the initial COD concentration decreased: 59.2, 61.5 and 88.1% removals were obtained with leachate strengths of 100, 50 and 20%, respectively when keeping the detention time constant at 180 minutes. Morais and Zamora (2005) also performed experiments with the UV/H₂O₂ process and reduced COD by 55% (H₂O₂ = 3000 mg/L). This confirms the initial finding that AOPs can enhance the biodegradability of sanitary landfill leachate.

Shu et al. (2006) designed a thin gap annular photo reactor with 4-UV lamps to decolor and remove chemical oxygen demand (COD) from landfill leachate. They monitored operating parameters such as: UV dosage, hydrogen peroxide concentration, and leachate strength to evaluate their effects on COD and color removal. Using a hydrogen peroxide dosage of 7.9 g/L, they achieved 72% removal of color and 65% removal of COD in 300 minutes. Diluting the leachate to 20% strength, they were able to measure 91% color removal and 87% COD removal within only 120 min. From these experimental results, the UV/H₂O₂ process was an effective pre-treatment or treatment technology for landfill leachate (Shu et al. 2006) contaminated with COD and color, and the process worked much more effectively (87% COD removal) when the leachate was diluted to 20%. Unfortunately no experiments were conducted on ammonia or

heavy metals.

Other experimental results are found in Table 6, where Steensen (1997) shows that removal is relatively independent of lamp power, and Qureshi et al. (2002) shows that increasing the hydrogen peroxide dose, increases the process removal efficiency from 79% COD removal at 5.2 g H₂O₂/L to 96% COD removal at 26 g H₂O₂/L .

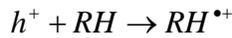
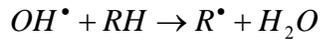
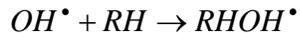
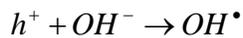
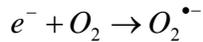
Table 6. Summary of COD removal performance tests conducted with UV/H₂O₂ technologies on landfill leachates.

H ₂ O ₂ Dose (g/L)	UV (W)	COD _o (mg/L)	BOD/COD _{before}	BOD/COD _{after}	pH	Removal (%)	Reference
3.4	150	760	nr	nr	3	99 (without carbonate)	Schulte et al. 1995
0.5	15	1100	<0.01	nr	3-4	90	Steensen 1997
0.5	150	1000	<0.01	nr	3-4	85	Steensen 1997
5.2	1500	26,000	0.11	0.37	3.0	79	Qureshi et al. 2002
13	1500	26,000	0.11	0.40	3.0	91	Qureshi et al. 2002
26	1500	26,000	0.11	0.45	3.0	96	Qureshi et al. 2002
7.9	4x36	3750	0.31	nr	7.8	65	Shu et al. 2006

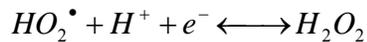
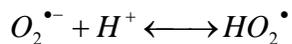
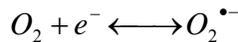
UV/H₂O₂ is another powerful advanced oxidation processes that can effectively degrade refractory organics and persistent organic pollutants, which are difficult to decompose by other processes such as biological systems. But alone, they appear to be limited and instead must be used as a pretreatment step to facilitate other degradation processes because no ammonia, heavy metals, or suspended material are known to be removed.

1.1.3 Photocatalytic oxidation

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. 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. Munter et al. (2001) proposed the following reaction mechanism, where h^+ is a “hole,” e^- is an electron, and R is a generic organic compound:



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 H₂O₂ in the process:



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

Titanium dioxide (TiO₂) also known as titanium (IV) oxide or titania, which is the naturally occurring oxide of titanium, is among the most widely used metal oxides in the industry for photocatalytic applications. Titanium dioxide occurs in nature as the well-known minerals: rutile, anatase and brookite. Approximately 4 million tons of pigmentary TiO₂ are produced annually for consumer products worldwide (corporate.evonik.com), and the cost of a 22 lb bag of titanium dioxide (Figure 1) is around \$600. 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. For acute oral and dermal toxicity, the literature reports LD₅₀ value greater than 10,000 mg/kg for rabbits. The International Agency for Research on Cancer lists titanium dioxide as group 2B (possibly carcinogenic to humans, lack of human evidence). This is due to possible tumor formation in laboratory rats due to overloading inhalation; however, for humans there is no evidence of a carcinogenic effect via the inhalation route, and epidemiological studies have not revealed any evidence to correlate human exposures to titanium dioxide and any diseases of the digestive or respiratory tract. Furthermore, no adverse effects have been measured to fish, daphnia, or bacteria in ecotoxicological studies.

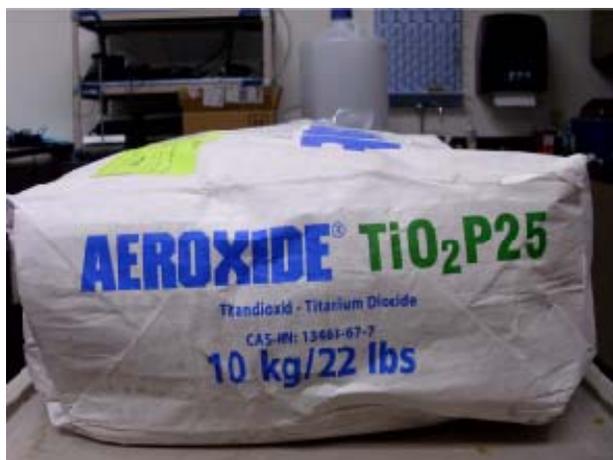


Figure 1. Photograph of 22 lb bag of titanium dioxide P25 photocatalyst.

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).

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.

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). 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.

TiO₂ photocatalysts have generated much attention in environmental waste treatment applications because they generate highly oxidative radicals, which can mineralize a wide variety of aqueous refractory organic contaminants under UV radiation. Hydroxyl radical attack is reported to be the primary mechanism of decomposition. A literature review of photocatalytic alternatives for detoxification and treatment of leachate revealed that several researchers have investigated a wide range of 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 2002), 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).

In terms of reactor design, many successful experiments have used glass plates coated with immobilized catalyst, TiO₂. For instance, Hilmi et al. (1999) used this design in a photocatalytic process 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.

As far as treatment of specific contaminants, Grzechulska and Morawski (2003) used a photocatalytic labyrinth flow reactor with immobilized Degussa P25 (52 m²/g) beds for removal of phenol from water. The photocatalyst was fixed to the bottom of the reactor using polymer glue, and utilized only half of the available surface area. UV lamp power was 140 W. They were able to achieve maximum removal at a starting concentration of 50 mg/L phenol in a reaction time of 5 hours. However at 300 mg/L phenol, the activity of the photocatalyst was noticeably impacted due to near complete coverage of the photoactive surface area with partial decomposition products of phenol. This was confirmed by FTIR (Fourier Transform Infrared Spectroscopy). Another example of studies conducted with immobilized photocatalysts (Kim, Lee, and Shin 2003) found that electrodes coated with TiO₂ prepared by HCl etching and painting with TiCl₃ have low surface resistivity, large surface area, and are capable of treating wastewater containing 50 mg/L of 4-chlorophenol dissolved in 0.2 M NaNO₃. The photocatalytic reaction efficiency was enhanced by 90% by suppressing the recombination of hole-electron pairs.

Yatmaz, Wallis, and Howarth (2001) investigated a novel application of immobilized photocatalysis using a spinning disc reactor with a 400 W UV source rotating at 350 rpm. They also found that the thin film slurries enhanced the transfer of organic constituents to the photocatalytic surface, but it was still less efficient than using particles of Degussa P25. Also at pH 3.1, they found that low pressure lamps ($\lambda_{\text{peak}} = 254 \text{ nm}$) outperformed medium pressure lamps ($\lambda_{\text{peak}} = 365 \text{ nm}$). This finding hints at the possibility of using solar energy to power the process. Zhang, Anderson, and Moo-Young (2000) investigated the use of solar radiation on fixed films of photocatalysts for treatment applications. They immobilized the photocatalyst on both sides of $0.05 \text{ m} \times 0.5 \text{ m}$ corrugated plates and compared effects from solar radiation on one side and UV-A fluorescent lamps on the opposite side of the plate. Capture of reflected photons was shown to depend strongly on the angle of the corrugated plates. It was found that the smaller the angle of the plate ($<30^\circ$), the higher the energy absorption efficiency. Also corrugated plates were found to enhance energy absorption efficiency by more than 100% for solar UV and by 50% for UV-A fluorescent lamps.

Immobilized catalysts are easy to install and reuse but they are limited in the effective surface area available for treatment. Therefore, Kanki et al. (2005) investigated fluidized bed photocatalytic reactors with 0.7 mm diameter ceramic microbeads coated with TiO_2 using the sol-gel method. The reactor volume was 4 liters and used two 9W UV lamps. With a particle concentration of 7-12% volume fraction of the reactor, the bed was fluidized by bottom aeration at 0.5 Lpm to study the degradation of phenolic compounds ($C_o = 10 \text{ mg/L}$). This study found that phenol can be mineralized in 250 minutes, and bisphenol A in 350 minutes. The only intermediates detected were butareoxidized organic acids. Tests were also conducted using ambient solar light, and treatment times were on the order of 4 times longer. Following the same line of investigation, shallow slurry reactors for color removal were investigated by Toor et al. (2006) using 30 nm diameter anatase-based TiO_2 powder ($50 \text{ m}^2/\text{g}$). At an optimum dose of 2 g/L for 3 hours at $25\text{-}50 \text{ W/m}^2$, the removal of yellow dye was maximized at $\text{pH} < 4.5$. In laboratory studies of photocatalysis of landfill leachate, the optimal concentration of TiO_2 photocatalyst typically varies from 1.0 g/L (Kostedt and Mazyck 2006) to 5.0 g/L (Bekbölet et al. 1996).

TiO_2 additives are typically used in one of two forms: 1) immobilized onto a substrate, or 2) suspended in solution in a slurry of fine particles. Using suspended particles is advantageous as it allows maximal utilization of the available specific surface area. Cho, Hong, and Hong (2002) conducted some batch-type experiments on the photochemical oxidation process using Degussa P25 TiO_2 particles with a diameter of 20 nm. Combined with aeration, this process achieved 80% removal of COD ($C_o = 1400 \text{ mg/L}$) but essentially no removal of ammonia when they adjusted to $\text{pH} < 4$ with H_2SO_4 . Conversely, at $\text{pH} > 12$, only 20% COD removal was possible, but the process also achieved 16% removal of ammonia ($C_o = 1525 \text{ mg/L as NH}_3\text{-N}$). Both experiments were run for 12 hours. The influence of pH on degradation of organic compounds and ammonia-nitrogen is such that low pH favors the oxidation of organic matter and high pH enhances the stripping of ammonia. If an optimum pH range can be found, then the two removal mechanisms could occur simultaneously in a small reactor.

This reactor configuration was also used to test the ability of TiO_2 photocatalysis (Degussa P25; 1.0 g/L) to effectively disinfect wastewater using a 12 L coaxial photocatalytic reactor (Rincon

and Pulgarin 2005). Using *E. coli* and *Bacillus* as indicators, the process was found to follow Chick's Law with pH dependence when activated with $\lambda = 364$ nm. Tests conducted without UV energy activation showed no disinfection. It is interesting to note that agitation with oxygen enhanced the process.

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.

To improve the ability to recover photocatalysts, a TiO₂-magnetite process has been proposed. At FAU, a new type of TiO₂ catalyst is coated onto a magnetic substrate, which can be easily separated from aqueous solution using an applied magnetic field. The chemistry of heterogeneous photocatalysis is complex and depends on operating conditions such as pH, temperature, UV intensity, the presence of competing organic or inorganic compounds, mass transfer limitations, and oxygen concentration. Until now, this technology was thought to be too expensive because of the amount of catalyst surface area and the amount of energy required for activation and mixing. However, a new TiO₂-magnetite nanoparticle, developed through a collaboration with Dr. Tsai (FAU-Mechanical Engineering) and Dr. Sun (visiting research professor from Northeastern University, China), uses a novel microemulsion method to coat a magnetic substrate. This technique is cost-effective, since comparatively low-cost inorganic metal salts are used as raw materials instead of expensive metal-alkoxides to achieve uniform particle size/shape and high surface area to volume ratios. In addition, the process proposed for our synthesis of the TiO₂-coated Fe₃O₄ nanopowder produces a byproduct (NH₄Cl), which can be recovered for use as a fertilizer, for example, and thus is not harmful to the environment. The latest version of the TiO₂-Fe₃O₄ nanocomposite particle is characterized by high photoactivity and high surface area to volume ratio, but suffers from reduced magnetic properties. If used in a photocatalytic fluidized spray with agitation by external magnetic field, the contact between the photocatalyst, the light source, and target pollutants will be enhanced, potentially improving reaction kinetics. If the magnetic properties of the core can be worked out, TiO₂-magnetite will enhance process efficiency by permitting precise control of mass transfer and allow the particles to be easily retrieved from the photoreactor for separation and reuse.

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

Water Type	TiO ₂ Dose (g/L)	UV (W)	Reactor	COD _o (mg/L)	pH	Removal (%)	Time (min)	Reference
Grey water	2.0-5.0	nr (TQ 150z1)	Batch	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)	Fixed Bed	62	6.5	86	30	Suri et al. 1999
Simulated wastewater	0.3-1.0	8 W	Batch	10	nr	82	120	Huang et al. 2008

Water Type	TiO ₂ Dose (g/L)	UV (W)	Reactor	COD _o (mg/L)	pH	Removal (%)	Time (min)	Reference
Lagoon wastewater	2.0	Solar radiation	Batch	660	8.0 (315 alk)	42	120	Araña et al. 2002
Industrial wastewater	0.6	6 x 18 W	Batch	3.2	6.0	62	60	Chen et al. 1997
Industrial wastewater	4 plates immobilized	4 x 4 W	Batch	120 (TOC)	9.0	34	30	Nakamura et al. 2008
Industrial wastewater	1.0	415 W	Batch	135	8.0	22 (diluted 1:100 + filtered)	1440	El Hajjouji et al. 2008
Industrial wastewater	0.5	400 W	Batch	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	Thin-film fixed bed	985	5.0	70	480	Bekbölet et al. 1996
Landfill leachate	??	3 x 150 W	??	760	??	15	60	Schulte et al. 1995
Landfill leachate	3.0	8 W (21 W/cm ²)	Batch	1673	8.7	30	720	Cho et al. 2003
Landfill leachate	1.0-2.0	150 W (0.5 mW/cm ²)	Batch	1200	7.5	35-57	60	Poblete et al. 2011

Cho et al. (2003) 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-trichloro-phenoxy 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 7 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 2, 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.

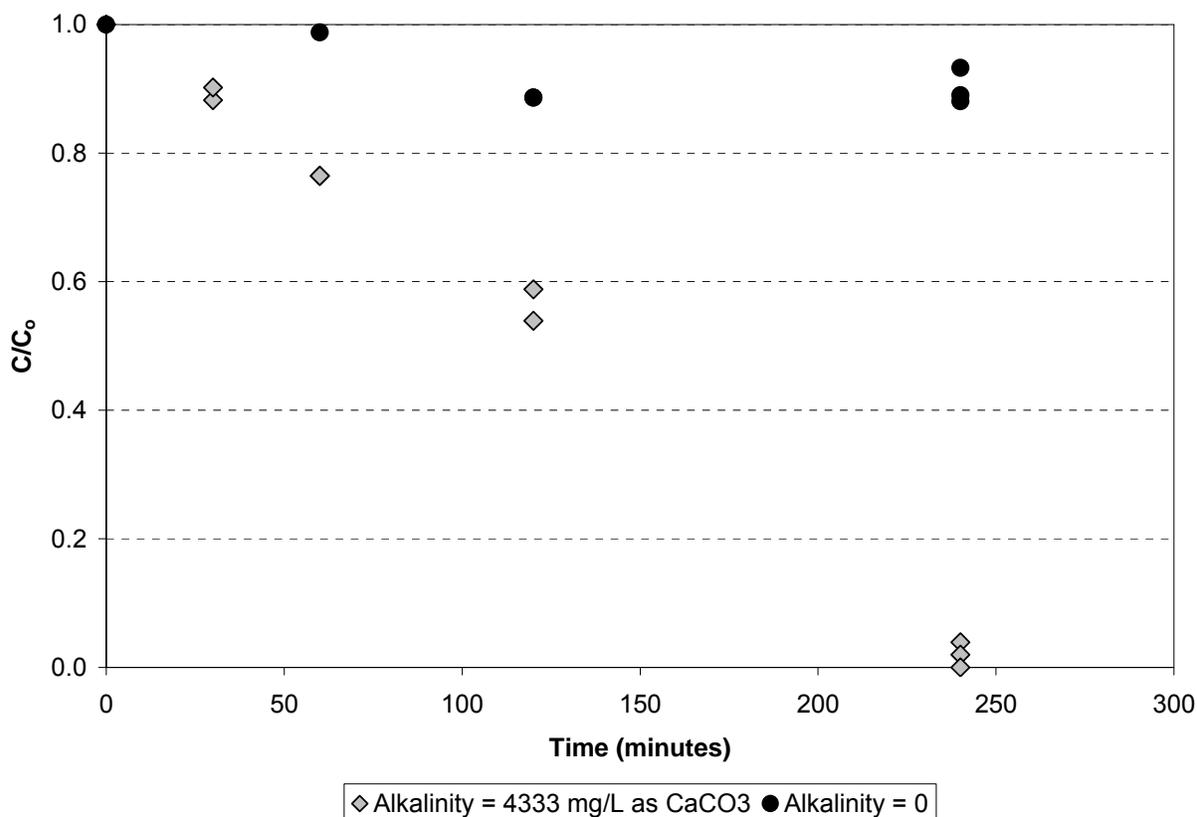


Figure 2. Removal of COD from simulated leachate with and without alkalinity.

1.1.4 Iron-Mediated Aeration (IMA)

Although zero-valent iron (ZVI) has been extensively studied for the reductive dechlorination of organic compounds over the past 20 years (see Tang 2004 for a review), the degradation of organic compounds through iron-mediated oxidation in oxygen-containing water has only recently been reported (Englehardt et al. 2002; Noradoun et al. 2003; Englehardt et al. 2005; Joo

et al. 2004 and 2005; Meeroff et al. 2006; Englehardt et al. 2007). The reaction mechanism of IMA is still not completely known, but evidence suggests that it involves:

- The oxidation of $\text{Fe}_{(s)}$ to Fe^{2+}
- The creation of hydroxyl radical according to the Fenton reaction
- The oxidation action of hydroxyl radical
- The co-precipitation action of ferric precipitates
- The stripping action of the aeration

Both non-ferric iron and aeration were found essential for effective removal of organic compounds. Joo et al. (2004 and 2005) reported oxidative degradation of molinate (a carbothioate herbicide), benzoic acid, aniline, *o*-hydroxybenzoic acid, phenol, and humic acids using nanoscale iron metal. However, they reported that pH was important, in addition to iron metal and air supply. Lower pH resulted in increased degradation of these organic compounds. And, the significant scavenging effect of 1-butanol, a well-known hydroxyl radical scavenger, on Fe(0) oxidation of molinate implied a Fenton mechanism of oxidation. Noradoun et al. (2003) reported complete destruction of separate mixtures of 1.1 mM of 4-chlorophenol and 0.61 mM of pentachlorophenol, in the presence of 0.5 g of iron particles in 10 mL of 0.32 mM ethylenediamine tetraacetic acid (EDTA) under ambient aeration at room temperature. They found that the presence of EDTA greatly improved degradation of these organic compounds, and attributed this observation to the formation of $\text{Fe}^{\text{II}}[\text{EDTA}]$ that might improve the redox cycle between Fe(0) dissolution, the Fenton reaction, and O_2 reduction to H_2O_2 . Three explanations for the oxidative capacity of iron-EDTA-mediated aeration were suggested: 1) heterogeneous activation of O_2 at the Fe(0) surface, 2) homogeneous activation of O_2 by $\text{Fe}^{\text{II}}[\text{EDTA}]$, and 3) heterogeneous activation of O_2 in conjunction with EDTA producing a surface-bound ferryl species (high valent iron).

IMA treatment for landfill leachate was first studied during the FCSHWM-funded project entitled, “*Investigation of options for management of leachate and wastewater,*” directed by Dr. Englehardt (University of Miami) and Dr. Meeroff (Florida Atlantic University) in 2005. They were the first researchers to successfully demonstrate the IMA process for in-situ remediation of organic and metallic contaminants in soil and groundwater at former nuclear weapons facilities managed by the U.S. Department of Energy (2002). Then, they used the process to oxidize organics and co-precipitate inorganics in simulated wastewater (Englehardt et al. 2006; Meeroff et al. 2006; Englehardt et al. 2007). They achieved 99.996% removal of arsenic and 99% removal of EDTA.

Using the IMA process at pH 8.2, Englehardt et al. (2006) reduced the COD of leachate by 56%, and increased the BOD_5/COD mass ratio from 0.1 to 0.28. In addition, the treatment was able to achieve 83% reduction in ammonia and 40% reduction in the effluent electrical conductivity of the leachate. Furthermore, two logs of removal of EDTA, Cd^{2+} , Hg^{2+} , and Pb^{2+} , and an average 63% removal of Ni^{2+} were achieved (Englehardt et al. 2003). At the same time, 1-2 logs of removal of 1.0 mg/L 17- β -estradiol (estrogen) and di-n-butyl phthalate was removed in simulated natural waters at pH 7.5. Deng and Englehardt (2008) were able to increase the efficiency of the IMA process with the addition of hydrogen peroxide reagent. At pH 8.2, COD was reduced by 50%, the BOD/COD ratio was increased from 0.02 to 0.17, 83% ammonia-

nitrogen, and 38% of TDS was also removed with this modification.

In summary, the newly developed IMA process has shown some promising removal capacities in laboratory tests, and Meeroff et al. (2006) demonstrated a preliminary cost projection below \$0.05 per gallon for IMA treatment for scale-up. Laboratory scale testing of IMA has demonstrated that both organics and inorganics can be treated simultaneously. Based on the ranking established during this project, the IMA process may be, at the laboratory scale, one of the most promising AOPs for treatment of all of the constituents found in landfill leachate.

Table 8. Summary of COD removal performance tests conducted with IMA technologies on landfill leachates.

Reactor Type	Fe Dose (g/L)	COD _o (mg/L)	BOD/COD _{before}	BOD/COD _{after}	pH	Removal (%)	Time (min)	Reference
Fibrous fixed bed	40	684	0.10	0.28	8.2	56	1620	Englehardt et al. 2006
Fibrous fixed bed	40	990	0.011	0.011	nr	12	1440	Englehardt et al. 2006
Granular fluidized bed	40	771	0.05	0.05	nr	54	1620	Englehardt et al. 2006

1.1.5 Photochemical Iron-Mediated Aeration (PIMA)

Preliminary studies of the IMA process enhanced with UV radiation were first conducted by Englehardt et al. (2005). This modification was called photochemical iron-mediated aeration (PIMA), which is a new process for oxidizing organics and co-precipitating inorganics in wastewater, currently under development at the University of Miami and Florida Atlantic University. In non-energized laboratory tests, iron-mediated technologies have been shown to oxidize estrogen, EDTA, and phthalate; co-precipitate arsenite, arsenate, mercury, chromate, nickel, lead, cadmium, vanadate, strontium, and nitrate; and inactivate *E. coli*, coliform, and heterotrophic bacteria (Englehardt et al. 2003; Meeroff et al. 2006). Results suggest oxidation via hydroxyl radical and/or ferryl species, implying indiscriminate oxidation of organics.

A particularly surprising result from preliminary laboratory scale tests was that radical scavenging was not observed to terminate the reaction, even with 200 mg/L of bicarbonate and 33% more TOC than raw sewage. Furthermore, the reaction is thought to involve a self-regenerative reactive surface area associated with the soluble Fe(II) phase, which may have a larger effective surface area than proposed new nanocatalysts. The basis for PIMA comes from the fact that under aerobic conditions, some ferric chelates are known to be rapidly photodegraded by solar/UV radiation with a half-life on the order of 2 hours (Frank and Rau 1990; Kari et al. 1995; Lockhart and Blakely 1975). The rate of photodegradation is pH-dependent (optimized at pH<3.1) (Metsärinne et al. 2001). The ferric iron acts as a photosensitizer and may also participate in the formation of oxidants through photo-Fenton chemistry (Meeroff et al. 2006). In the presence of complexed ferric iron, the photoassisted Fenton reaction ($\lambda < 360$ nm) can accelerate the rate of hydroxyl radical formation by two orders of magnitude, while regenerating ferrous iron to propagate a Fenton cycle (Kwan and Chu 2003).

Furthermore, photochemical oxidation with added iron catalysts has been demonstrated for pH 3-8 at millimolar concentrations of organically-bound trace metal contamination (Davis and Green 1999).

Preliminary tests focused on methods to effectively enhance previously demonstrated IMA processes for degradation of EDTA and facilitate the release of bound metal cations, such as Cd, for subsequent removal from solution. The effect of added ultraviolet energy was investigated in comparison to non-energized IMA. Preliminary results indicated that the PIMA process increased the reaction rate for EDTA destruction by a factor of 4 compared to conventional IMA at circumneutral pH (Meeroff et al. 2006). This is an unexpected result since Fenton-like chemical reaction rates are known to be unfavorable at ambient pH (i.e. 6-8). Another surprising result of preliminary testing with EDTA was that identified oxidation byproducts were non-hazardous or readily biodegradable. Furthermore, only about 10% of the original carbon content was accounted for, indicating the possibility of near complete (>90%) mineralization. The implication here is the potential to completely destroy environmentally stable and persistent organic compounds, without pH adjustment or costly chemical addition. Also indications are that PIMA can be more rapid, and perhaps more thorough, than natural biodegradation in terms of eliminating environmental contamination.

Initial laboratory scale experiments with leachate found no significant difference between the PIMA and IMA technique. This result is attributed to the reactor design, the weakness of the UV source, and the steel wool packing density. However, in additional bench-scale experiments, Meeroff et al. (2006) showed a cadmium removal of 29% in a PIMA reactor compared to just 5% in the non-energized control IMA reactor (reaction time was 256 minutes and initial concentration was 0.10 M). The addition of UV seems to improve the removal of cadmium under these conditions. Meeroff et al. (2006), Meeroff, Gasnier, and Tsai (2006 and 2008), and Meeroff (2010) conducted bench scale tests using PIMA at 10 mW/cm² and found that the process removes color and Pb (>90%) very effectively. They also found that COD and BOD₅ were removed at 40%, and the process is capable of removing ammonia with pH adjustment. However, PIMA was unable to address odors or TDS. To our knowledge no other studies have been conducted on the PIMA process, and this technology is still at an immature stage.

Table 9. Summary of COD removal performance tests conducted with IMA technologies on landfill leachates.

Fe Dose (g/L)	UV (W)	COD _o (mg/L)	BOD/COD _{before}	BOD/COD _{after}	pH	Removal (%)	Reference
40	450	990	0.011	0.003	nr	5	Englehardt et al.
40	450	740 simulated	n/a	n/a	7.0	40	Gasnier 2007
10-40	450	4220 real	0.10	0.10	7.5	5	Gasnier 2007
40	450	1050 simulated	nr	nr	7.5	55	Meeroff et al. 2011
40	450	2950 real	nr	nr	7.5	10	Meeroff et al. 2011

1.1.6 Ozone with Ultraviolet Light (O₃/UV)

Hydroxyl radicals can also be generated from the reaction of ozone with ultraviolet radiation. Ozone absorbs UV in the range of 200-300 nm (Langlais et al. 1991). The UV radiation of ozone molecules results in the release of a molecule of diatomic oxygen and a singlet oxygen, which reacts with water to form two hydroxyl radicals as follows:

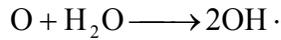
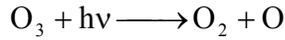


Table 10. Summary of COD removal performance tests conducted with UV/Ozone.

O ₃ Dose (g/h)	UV (W)	COD _o (mg/L)	BOD/COD _{before}	BOD/COD _{after}	pH	Removal (%)	Time (min)	Reference
3.0	100	1280	0.08	0.32	2.0	54	480	Ince 1998
3.0	500	1280	0.08	0.32	2.0	47	480	Ince 1998
3.0-4.2	1500	26,000	0.11	0.35	7.8	63 (TOC)	300	Quereshi et al. 2002
3.0-4.2	1500	26,000	0.11	0.35	7.8	61 (TOC)	300	Quereshi et al. 2002
1.0	15	2300	0.09	0.34	8.0	40	nr	Bigot et al. 1994

1.2 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 deepwells get promulgated, the option of deepwell injection may become cost-prohibitive. Therefore, reliable low cost, low-tech processes are needed for on-site treatment of landfill leachate. This proposal addresses those needs.

1.3 OBJECTIVES

The objective of the proposed research is to pilot test an energized treatment process for the removal of parameters of interest including COD/BOD, ammonia, heavy metals, color, and pathogens using non-biological methods that landfill operators with little training can routinely and reliably employ without spending too much time on the task. The main focus was to validate 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. 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 photochemically-assisted iron-mediated aeration process and 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.

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 Central Disposal Sanitary Landfill because of its close proximity to the FAU Boca Raton campus.

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 11.

Table 11. Historical leachate water quality data for the 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 chlordane	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
Xylenes	55		40		40	µg/L	Yes

Parameter	2009	Flag	2010	Flag	Reporting Limit	Units	Above Reporting Limit
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	µg/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. Samples from different cells of the landfill were analyzed by a National Environmental Laboratory Accreditation Certified (NELAC) laboratory; however, as shown in Table 12, the leachate had fluctuating 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 12: 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

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 Central Disposal 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 REACTOR DESIGN AND CONCEPT TESTING

Using leachate samples collected from various sources (see Section 2.2), testing involved initial screening experiments to determine the magnitude of scale-up parameters such as residual generation, energy consumption, preliminary removal kinetics, etc. using bench scale demonstration units. These performance tests are required to obtain data for scale-up to a pilot unit. A free-standing, laboratory-scale reactor was operated to obtain these parameters.

2.3.1 Laboratory-Scale Reactor Design

The laboratory-scale reactor was an innovative design originally developed by Meeroff et al. (2006) in 2002 at the University of Miami. Since the original prototype, Eli Brossell, François Gasnier, Swapnil Jain, and Hatsuko Hamaguchi later all made modifications to the original design. Figure 3 illustrates the photochemical safety cabinet with all its accessories.

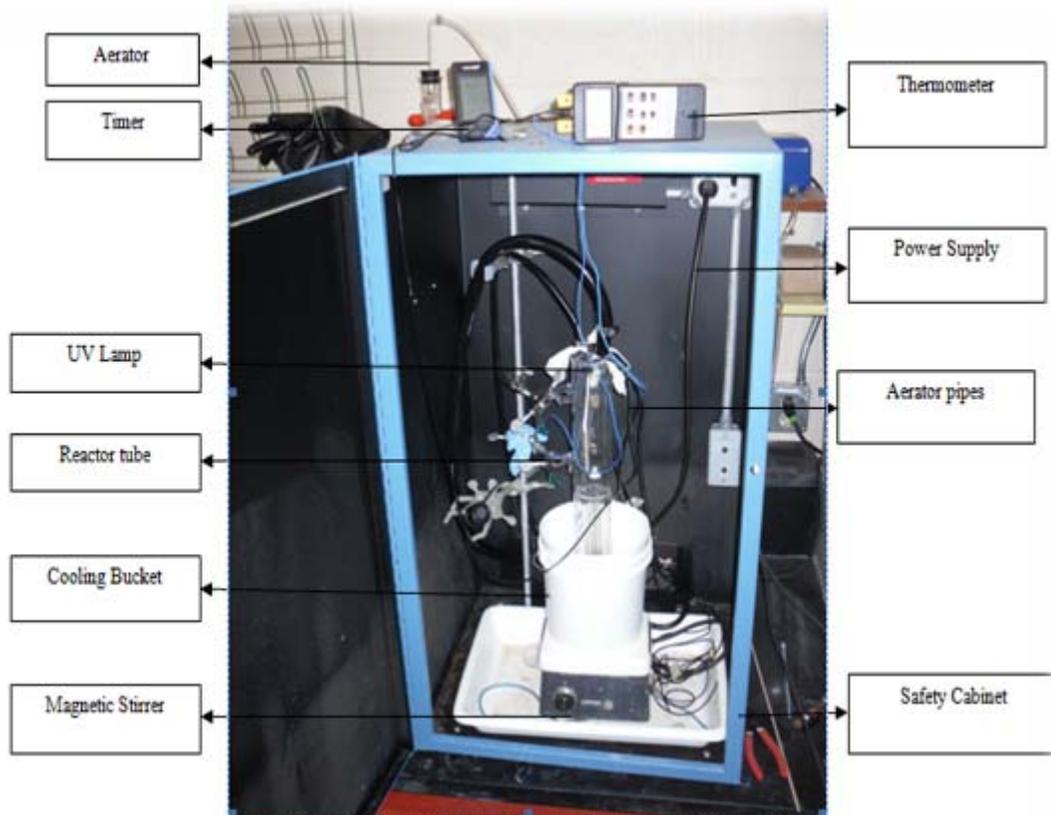


Figure 3. Photograph of the laboratory-scale photocatalytic reactor.

The major components of the laboratory-scale unit are: 1) photochemical safety cabinet; 2) ultraviolet lamp and power supply; 3) photoreactor vessel; and 4) plug flow cooling system

The photochemical safety cabinet (Figure 4) was purchased from Ace Glass Incorporated (Vineland, NJ). The cabinet is constructed of steel and is designed to shield the investigators from the harmful effects of UV radiation. This safety cabinet eliminates the need to construct a special safe area to operate the UV lamps. The cabinet has welded seams and a fully-hinged door with a lip to prevent any ultraviolet light from escaping. Its door has a key lock for secure closure, which engages a safety kill-switch that prevents lamp operation unless the door is fully closed. The cabinet (Figure 4) was modified by drilling a viewing port in the top face of the cabinet to allow the researchers to verify that the lamp is working properly by indirect visual inspection of the blue haze generated by the 450-W medium pressure mercury vapor lamp.



Figure 4. Photochemical Safety Cabinet

The next important component is the ultraviolet light source. A 450-W medium pressure, quartz, mercury-vapor lamp purchased from Ace Glass Incorporated (Vineland, NJ) shown in Figure 5 was used. According to the manufacturer (see Table 13), of the total energy radiated, approximately 40-48 percent is in the ultraviolet portion of the spectrum (from 220 nm to 400 nm), 40-43 percent in the visible, and the balance in the infrared. The typical lamp life is on the

order of 1000 hours. The lamp is attached to a cased open core and coil transformer 450W ultraviolet lamp power supply (Ace Glass Incorporated, Vineland, NJ). The lamp is protected from the test solution in a quartz immersion well purchased from Ace Glass Incorporated (Vineland, NJ) with a built-in plug flow cooling tube (more details below). Some other preliminary experiments used a 15 W penray lamp or a 5.5 W penray lamp from Ace Glass Incorporated (Vineland, NJ). A traceable UV light meter with range of $5 \mu\text{W}/\text{cm}^2 - 19.99 \text{ mW}/\text{cm}^2$ (VWR, Suwanee, GA) was attached to the unit to measure the UV light intensity transmitted ($\lambda = 320 - 390 \text{ nm}$). This is the range at which 16% of the lamp power is radiated (see Table 13)



Figure 5. UV lamp immersion well and quartz jacket

Table 13. Proportion of energy radiated by the 450 W medium pressure ultraviolet lamp

Wave length in nm	Far UV 220 - 280	Middle UV 280 - 320	Near UV 320 - 400	Visible 400 - 600	Infreared 1000 - 1400	Total Radiated Energy
Energy in Watts	27.0	28.7	28.0	75.7	16.4	175.8

Source: Ace Glass Incorporated (Vineland, NJ) catalog

The key component of the laboratory-scale unit is the photoreactor vessel, itself. The ultraviolet

lamp is inserted into a 1000 mL cylindrical reactor tube which has diameter larger than that of the quartz UV lamp immersion well. The space between the tubes is occupied by the solution of TiO₂ particles and leachate. Several different photoreactor vessels were used during photocatalytic oxidation tests. Sample volumes varied between 250 – 375 mL.

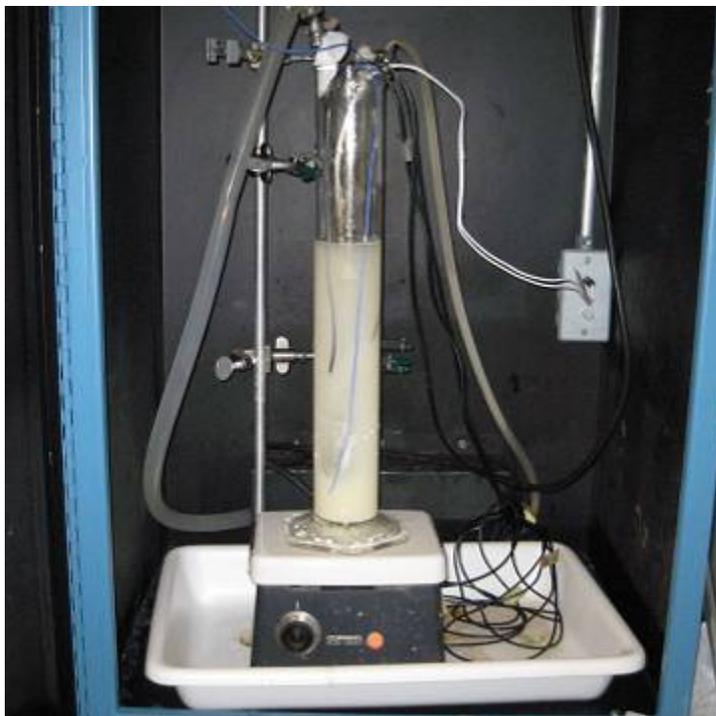


Figure 6. Photoreactor vessel containing TiO₂ particles and real leachate

The final component of the laboratory-scale unit is the plug flow cooling system for the lamp. The cooling system is used to maintain a sensible temperature (<35°C) inside the photoreactor and delay overheating of the UV lamp. The cooling system is also used to maintain a reasonably constant temperature of the leachate during treatment to better simulate field operation in which temperatures would not be expected to increase noticeably. Without this cooling system, the liquid in the photoreactor would have evaporated rapidly because of its small volume. When cooling water was not used, the liquid in the test tubes would boil and completely evaporate after only a short reaction time (less than 0.5 – 2 hours). In some extended experiments, the cooling system needed to be augmented with an ice-water cooling bath. UV-resistant tubing was used to connect to the inlet end of the cooling system to provide cool water from the tap which flows through the quartz jacket of the immersion well to counteract the effects of rising temperature due to the heat output of the lamp. The warm water produced from the heat of the lamp is rejected to a sink after it has circulated once through. The water circulates from the tap into a quartz jacket and the “warm” water is rejected into the sink after one pass through the system.

The photoreactor was placed on top of a magnetic stir plate inside the safety cabinet. A magnetic stirrer was then placed inside the photoreactor just below the quartz immersion well. The photoreactor containing the sample was placed into a plastic bucket with dimensions of 20 cm by height, 17 cm in diameter, and a thickness of 0.3 cm. Once positioned a magnetic egg was placed

into the reactor tube. The thin walls of the bucket allowed the magnetic stir-bar inside the photoreactor to be controlled, while simultaneously allowing the ice water to keep the temperature cold inside the reaction chamber.



Figure 7. Picture of cooling by ice water

An aeration unit was used to: 1) add molecular oxygen, which seems to be a necessary component for the reaction to take place, 2) perform air stripping, which is needed to eliminate ammonia from the liquid, and 3) mix the leachate, which is needed to accomplish homogeneous treatment. The aeration system is comprised of a pump which dispenses air with a maximum pressure of 4.5 psi. The pump was obtained from Aquatic Eco-Systems (Apopka, FL). The air flow is divided into two different lines of flexible tubing. The first line is directly connected to a humidifier flask (Figure 8) and then to a flow splitting valve, which allows the researchers to provide air flow for up to 8 samples simultaneously. For these experiments, only the lines labeled 2, 3, 4 and 7 were used. Flexible pipes are about 8 feet in length. The last segment (approximately 3 feet) is UV resistant: R-3400 UV Resistant Tubing from Tygon (Akron, Ohio). Inserted into this UV resistant pipe is a very thin glass tube (outside diameter = 0.7 - 1.0 mm) from Kimble Glass Inc. (Vineland, NJ). These aeration tubes were then transferred through the back of the cabinet and directed toward the base of the reactor tube as far as the tubing allowed to deliver air directly to the leachate sample near the magnetic stir bar. The second line is connected to a flow control valve that allows the researchers to regulate the flow of air in each of the test tube reactors to avoid sample washout.



Figure 8. Aeration and humidifier system configuration

A digital thermometer from Fisher Scientific was used to monitor the reaction temperatures. The unit was equipped with two channels: 1) for the temperature inside the cabinet to detect any failure of the cooling system, and 2) for the temperature on the outside of the reactor vessel near the bottom of the container. The temperature of the leachate is not directly monitored to avoid contaminating the beaded, fast response Type-K thermocouple. Temperature profiles were recorded using a datalogger (Multi-Function Port Replicator from Kensington Technology Group, Redwood Shores, CA) and specialized software (Traceable[®] Data Acquisition System Version 2.3 from Control Company, Houston, TX). In some instances, the temperatures were recorded manually at 10-minute intervals. Noticeable drops in temperature observed at the sampling points are artifacts that occurs when the temperature monitoring is temporarily paused (and the UV lamp is shut-off to allow access to the contents of the safety cabinet) during the sample collection period. This period of approximately 5-20 minutes does not appear on the temperature profile records.

A sampling device was fashioned out of a 60 mL syringe and a small segment of plastic tubing. The end of the tubing was placed in the bottom of the reaction chamber, and suction was applied to the syringe to obtain samples during experimentation.

2.3.2 Preliminary Concept Testing

The goal of preliminary concept testing was to establish efficacy studies focusing on removal efficiencies for our parameters of interest (i.e. COD/BOD, ammonia, heavy metals, color, and pathogens, as selected in Task 2), and to determine pre-treatment requirements, if necessary. Actual leachate samples were collected from the Solid Waste Authority in Palm Beach, FL, the Waste Management Central Sanitary Landfill in Pompano Beach, FL. The concept testing sought

to optimize the effects of reaction time, dose of catalyst/reactants, UV fluence or intensity, and reactor configuration on the target pollutant removal efficiency.

2.3.2.1 Preparation of Simulated Leachate

Simulated leachates using known materials added to deionized water were created as a representation of real leachate. Simulated leachate samples allowed the researchers to understand the mechanism of each constituent tested prior to applying the treatment process to real leachate. These simulations were also performed in order to determine the optimum dose of TiO₂ photocatalyst and bicarbonate alkalinity for solutions with known composition.

For artificial leachates, reagents were carefully weighed to the nearest hundredth of a milligram on a Mettler Toledo XS204 analytical balance (Columbus, OH) and added to a volumetric flask and filled to the mark with 18.2 MΩ-cm water. To make the buffered matrix for the simulated leachate for preliminary testing, 1.0 liters of distilled water, 0.03 M (2.74 g, 2740 mg/L) of sodium bicarbonate (Carolina Biological Supply Company) were prepared. For COD testing, 0.0041M (0.84 g, 840 mg/L) of 99.95 to 100.05% pure potassium acid phthalate or KHP (Fisher Scientific, Pittsburgh, PA or Cerrilliant Corporation, Round Rock, TX, or EMD Chemicals Inc., Gibbston, NJ), was added to the appropriate amount of matrix water in a 1000 mL volumetric flask. For the composition of other simulated leachates see Table 14. The solution was inverted 20 times and then mixed mechanically overnight. Ammonia-nitrogen was simulated using a solution prepared from NH₄Cl salt dry stock (Fisher Scientific, Pittsburgh, PA). Copper solutions were prepared using a 1000 mg/L primary standard (Hach Company, Loveland, CO).

Table 14. Summary of constituents used to prepare simulated leachates.

Constituent	Model Compound	Concentration	Units	Source
COD	KHP	1000	mg/L	Fisher Scientific (Pittsburgh, PA) Cerrilliant Corp. (Round Rock, TX) EMD Chemicals Inc. (Gibbston, NJ)
BOD	Glucose Glutamic Acid	800	mg/L	Hach Company (Loveland, CO)
Alkalinity	NaHCO ₃	4333	mg/L as CaCO ₃	Carolina Biological Supply Company (Burlington, NC)
Ammonia	NH ₄ Cl	2500	mg/L	Fisher Scientific (Pittsburgh, PA)
Copper	CuCl ₂	3.0	mg/L	Hach Company (Loveland, CO)

TiO₂ samples were obtained from Evonik Industries (Essen, Germany). The appropriate amount of TiO₂ was added and then either 375 mL (for laboratory-scale experiments) or 8000 mL (for pilot scale experiments) of the simulated leachate solution was measured into a graduate cylinder and transferred to the photoreactor. Synthetic leachates provide the substrate for bacteria, but unlike actual leachate, it does not contain a significant microbial population nor does it contain all of the constituents and variable quantities found in the real material. Therefore, actual field samples needed to be tested.

2.3.2.2 Collection of Real Leachate

Leachate was sampled from the Solid Waste Authority (SWA) of Palm Beach County located in West Palm Beach, FL and from the Waste Management Central District Sanitary Landfill (CDSL) in Pompano Beach, FL. The North County Regional Solid Waste Authority Disposal Facility is located near the intersection of S.R. 710 and Jog Road in northern Palm Beach County. Consisting of over 50 million cubic yards of airspace and with a footprint of approximately 330 acres, this landfill opened in 1989 and is currently expected to provide disposal capacity through the year 2021. The Central District Sanitary Landfill is located at the intersection of Powerline Road and Sample Road in Pompano Beach, FL in northern Broward County. The site has a mass-burn facility rated at 2000 tons per day and receives between 10,000 tons (2007 data) to 4000 tons (2010 data) per day. The site has a footprint of 300 acres approximately, of which about 80 acres is being landfilled currently.

The SWA samples were collected from either the wet well or from the collection manhole. The SWA leachate is discharged to a deep injection well.

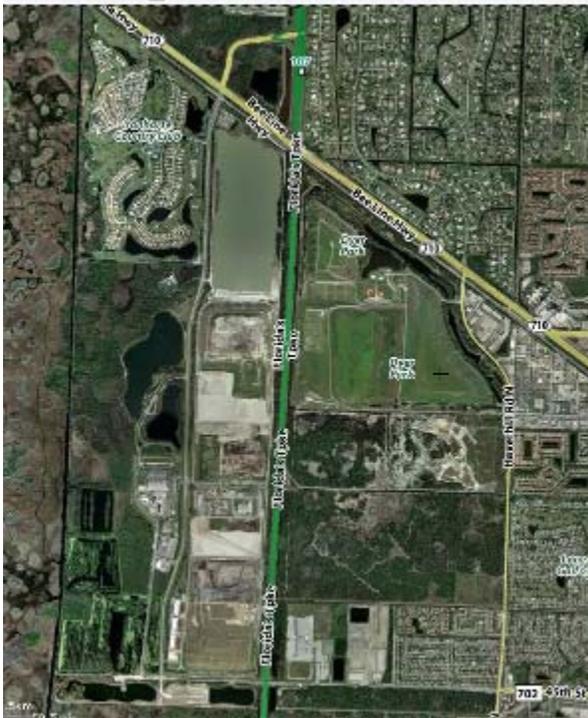


Figure 9. Aerial photograph of the Solid Waste Authority of Palm Beach County.

The CDSL samples were collected from the following sites: the NW corner (old leachate), SW corner (new leachate), SE corner (WTE condensate), or from the wastewater treatment plant sump (combined leachate). The CDSL leachate is discharged to a sanitary sewer collection system and sent directly to the wastewater treatment plant located at the intersection of Powerline Road and Copans Road. Waste Management, who owns the landfill facility, has a 5 year agreement with Broward County's North Regional Wastewater Treatment Plant to accept its leachate provided it meets the industrial pretreatment criteria (see Table 15), but most notably: $TSS < 400 \text{ mg/L}$, $BOD_5 < 400 \text{ mg/L}$, and $COD < 2 \times BOD_5$. According to Jeff Roccapiore (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.



Figure 10. Aerial photograph closeup of the Central Disposal Sanitary Landfill.



Figure 11. Aerial photograph of the Broward County North Regional Wastewater Treatment plant.



Figure 12. Sample location (combined leachate) at the wet well of the deep well injection station at the Solid Waste Authority of Palm Beach County located in West Palm Beach, FL.



Figure 13. Sample location (combined leachate) at the manhole station at the Solid Waste Authority of Palm Beach County located in West Palm Beach, FL.



Figure 14. Research assistant collecting samples from the SW corner (new leachate) sampling location at the Waste Management Central Disposal Sanitary Landfill in Pompano Beach, FL.



Figure 15. Research assistant collecting samples (left) from NW corner (old leachate) at the Waste Management Central Disposal Sanitary Landfill in Pompano Beach, FL, and decontaminating the outside of the sampling container for transport to the lab.



Figure 16. Research assistant collecting samples from the SE corner (WTE condensate) sampling location at the Waste Management Central Disposal Sanitary Landfill in Pompano Beach, FL.



Figure 17. Research assistant collecting samples (left) from the Broward County Wastewater Treatment Facility sump (combined leachate) from the Waste Management Central Disposal Sanitary Landfill in Pompano Beach, FL.

The first leachate samples were collected on 01/15/2010. All real leachate samples were collected in 1-Liter or 5-gallon containers and stored at 4°C until treated in the laboratory. The leachates collected from field sites were not filtered prior to use in the laboratory reactor.

2.3.2.3 Laboratory-Scale Experimental Setup

The laboratory-scale reactor was limited to 375 mL of liquid per run. Prior to initiating any experiment, the volume of the sample for treatment was carefully measured out into a 500 mL graduated cylinder and transferred into the photoreactor tube. The tube was then placed into the ice water bucket and centered on top of the magnetic stir plate. Next, the UV lamp was carefully placed into the quartz immersion well, and then the well was carefully positioned inside the reactor vessel. Once assembly of the reactor was complete, the electrical leads for the UV lamp were connected to the power supply and aeration tubes were then positioned as far down as possible between the immersion well and the photoreactor tube. Then the two thermocouples were positioned so that it would almost touch the glass of the photoreactor tube. The other thermocouple was placed on the inside wall of the safety cabinet. The UV light intensity probe was placed parallel to the photoreactor tube to record a reading based on the light emitted. Then the probe end was connected to the meter. Finally the syringe was then placed on the outside top of the cabinet and its tube positioned towards the base of the photoreactor tube in order to collect sub-samples while the test was in progress. This allowed us to avoid shutting down the reactor for sampling, but also allowed temperatures to climb steadily inside the reactor.

The bucket was then topped off with ice water, and the cabinet was then closed securely. The power supply was engaged to turn on the lamp. To ensure that the 450-W medium pressure mercury vapor lamp was actually on, a small hole was drilled at the top of the safety cabinet. Verification of its operation was confirmed from a blue haze once the lamp was engaged. At this point, the timer was initiated to begin the reaction.

Preliminary laboratory-scale experiments were run for 4 hours. Samples were collected at 0 min, 30 min, 60 min, 120 min and 240 min. For this typical batch reactor experiment, the sample collection procedure was as follows. While photoreactor is still running, 5 mL subsamples were collected via syringe at required times mentioned in experimental conditions. The subsample was

placed in a 15 mL centrifuge tube. The pH was measured and recorded initially and after 4 hours of treatment using a Hach SensIon 3 pH meter with platinum electrode. At the end of the experiment, all centrifuge tubes were centrifuged at 3000 rpm for 5 minutes at 20°C in a refrigerated centrifuge (accuSpin 1R, Fisher Scientific, Pittsburgh, PA). 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.

2.3.2.4 Laboratory Experiments with Lime Addition

For experiments involving pre-treatment with lime addition for the preliminary removal of organics, color, and trace metals, samples were mixed with calcium oxide/lime (supplied from the Glades Road Water Treatment Facility in Boca Raton, FL) in order to remove the color. The lime dose to provide maximum removal of color was performed as follows: 300 mL beakers were filled with 100 mL of leachate; different amounts of lime (0-5 grams) were added to each beaker; each beaker was completely mixed for approximately 30 minutes; after completion of mixing, the solution was allowed to settle for 1 hour.

2.4 PILOT TESTING

The goal of preliminary work was to develop a concept for a flow-through reactor or circulating batch reactor that will better mimic the field operation of a pilot unit. During pilot testing, the primary treatment goal 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 Central Disposal 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

During operation of the pilot unit, periodic (i.e. biweekly or other appropriate time increment) measurements of COD/BOD, ammonia, heavy metals, color, and/or pathogens will be taken to investigate system performance. Troubleshooting and fine-tuning for maximum performance will be investigated, as needed. The operators (and other end users) at the pilot testing facility will be queried as to the performance and feasibility of the system, if scale-up is potentially achievable. The carbon footprint of the process will be calculated and preliminary operating costs will be monitored in terms of electricity consumption, pre-treatment, chemicals, and residuals disposal requirements, as time allows.

Using the data developed in the pilot study, an appropriate level of reactant/catalyst and UV fluence needed to meet the water quality guidelines for general sewer discharge will be determined. An assessment will be conducted to evaluate the associated costs per gallon treated, and the environmental consequences of the proposed full scale unit will be evaluated in context with leachate hauling to offsite wastewater treatment plants

A falling film circulating batch reactor (CE584: Advanced Oxidation Unit, GUNT Hamburg, Germany) is shown in Figure 19. The test rig measures 1510 mm x 790 mm x 1990 mm and weighs approximately 330 lbs. 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 120 W low pressure, ultraviolet lamp with power source (30-35% efficiency). The UV lamp (Strahler NNI 125/84 XL) was purchased from Heraeus Noblelight (Hanau, Germany). The irradiation spectrum (Figure 18) shows that the lamp provides most of its intensity from 250-260 nm in the UVC 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 PMMA XT.

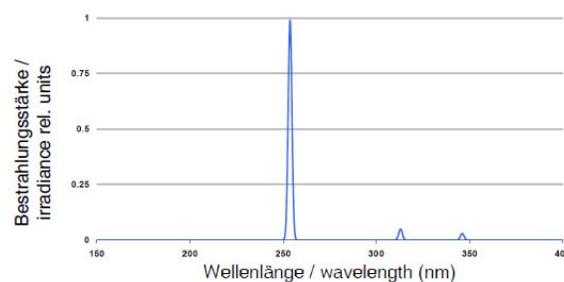


Figure 18. Irradiation spectrum for the Strahler NNI 125/84 XL low pressure UV lamp as provided by the manufacturer.

The leachate sample was aerated for 30 minutes prior to circulation to increase the dissolved oxygen levels and fully mix the sample with the photocatalyst. Aeration was accomplished using a Sweetwater linear air compressor (model SL22, Aquatic Ecosystem, Apopka, FL) with an aeration stone. The air delivery was humidified using a similar set-up as described in laboratory-scale tests.



Figure 19. Photographs of the falling film pilot reactor (left: close up view of the reaction chamber; right: overall view).

In Figure 20, you can see the pilot unit loaded with real leachate, which has a dark coffee color and foul odor. Once the TiO_2 photocatalytic particles are added, the color changes to a light caramel color, as seen in Figure 21 (right). The leachate foams very quickly with the aeration unit at 50% capacity (Figure 21 left). Immediately after foaming is noticed, aeration was stopped to allow the photocatalyst to partially settle before starting the recirculation pumping cycle.

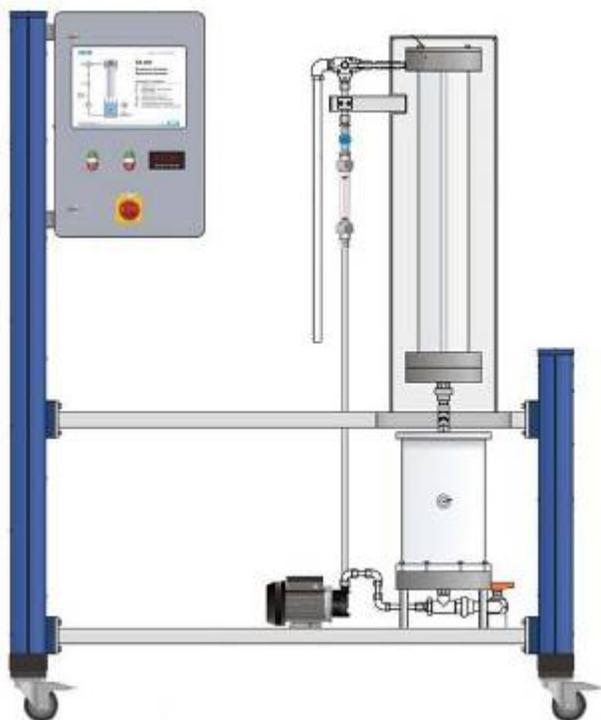


Figure 20. Photograph of the falling film pilot reactor (left: schematic; right: actual rig loaded with real leachate.



Figure 21. 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 .

In Figure 22 (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 22 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 22. 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).

Preliminary pilot-scale experiments were run for up to 6 hours. For these experiment, the sample collection procedure was as follows. Samples were collected from the sampling port using a 50 mL beaker (Figure 23 left). 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.

Ice bags were placed in and around the reservoir to keep the temperature from exceeding 40°C. Volume loss due to evaporation was measured volumetrically. A catalyst recovery device (Figure 23 right) was constructed using a true union three-way ball valve with a 10 μm nylon filter recovery bag. The valve can control the flow to the bag or back into the reservoir. The

collection bag has a nominal 10 μm pore size and the photocatalytic particles have a diameter on the order of 20-25 μm .



Figure 23. Sample being collected from the pilot falling film reactor (left). Closeup photograph of the TiO_2 collection bag and three-way valve (right).

A second configuration for the pilot plant was developed based on ideas set forth by the Technical Advisory Group. A schematic of the proposed design is shown in Figure 24. In this setup, a flow-through reactor design was implemented using a quartz coil and a peristaltic pump to slowly push the fluid through the reaction zone. Figure 25 shows the flow-through coil reactor set-up and operation, and Figure 26 shows a close-up of the custom quartz coil.

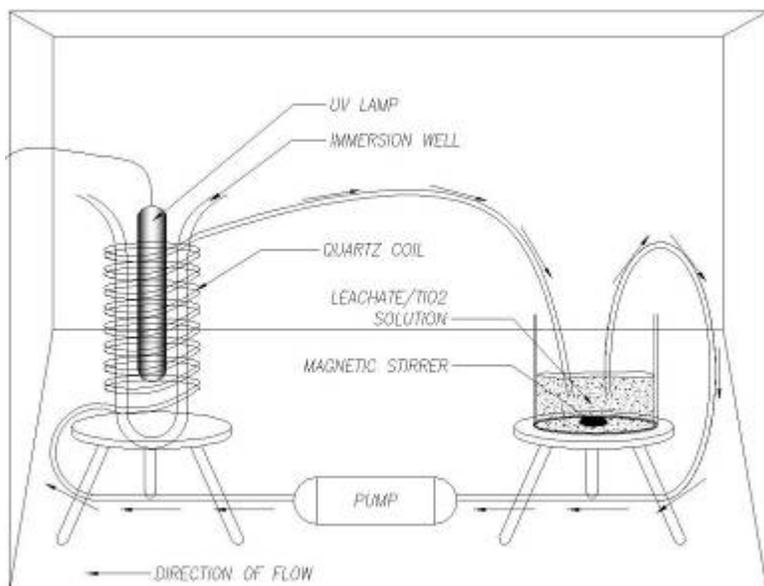


Figure 24. Schematic diagram of proposed flow-through coil reactor.

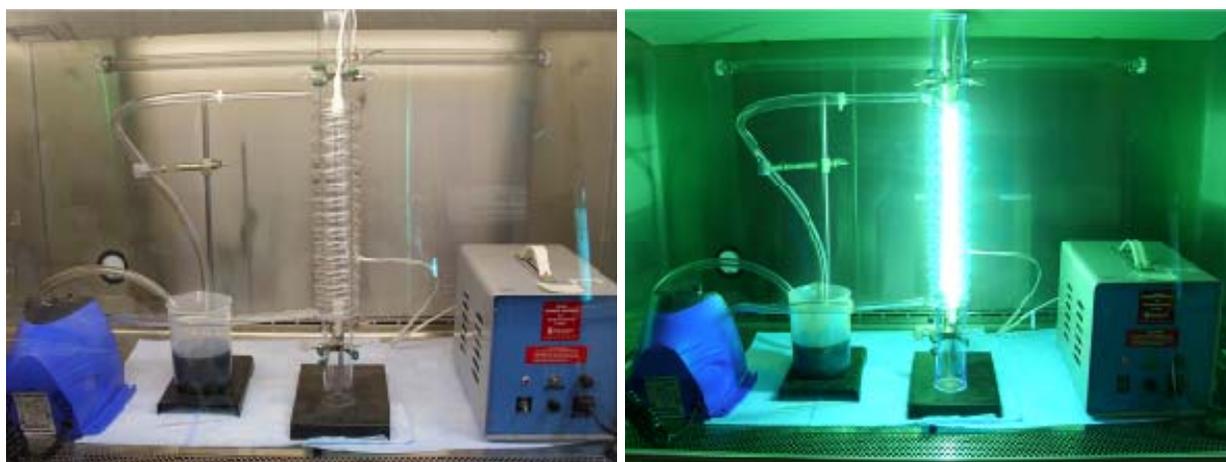


Figure 25. Photograph of the flow-through coil reactor (left: idle; right: in operation).



Figure 26. Custom quartz reactor coil

2.5 ANALYTICAL METHODS FOR PARAMETERS OF INTEREST

The photoreactor was used to test the removal efficiency of the following constituents: COD, BOD₅, copper, arsenic, ammonia, alkalinity, color, and pH.

2.5.1 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 reaction involved in this method is the following:



Consequently two moles of KHP react with 15 moles of dioxygen and the theoretical COD of 1 g of KHP is 1.175 g of dioxygen. After centrifugation sample preparation to separate the photocatalyst particles, samples were diluted to 2.0 mL using 18.2MΩ-cm deionized water. For simulated leachates a dilution factor of 1:4 was used. For real leachates, 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 for 2 hours. Samples were removed from the heating block and allowed to cool for one hour. At this point, samples were wiped clean using a Kim-Wipe paper tissue and analyzed using a Hach DR/4000U UV-Vis spectrophotometer. The COD value in mg/L was recorded. A certified reference material (300 mg/L Hach Company, Loveland, CO) was used to check the instrument calibration. This value varied from 0.6-6.7% error. At least one calibration check standard was analyzed per experiment.

2.5.2 BOD₅

For the 5-day biochemical oxygen demand test (BOD₅) the methodology followed the guidelines as stated in the Standard Methods for the Examination of Water and Wastewater manual (APHA et al. 2005). The biodegradable organics for the simulated leachate experiments were provided by a BOD Standard Solution (10 mL Voluette Ampoule) from Hach (Loveland, CO), which contained 3.00 g/L of glucose and 3.00 g/L of glutamic acid. The ampoule was diluted to obtain the required concentrations.

For raw leachate samples, three dilutions were prepared: 0.5, 1.0 and 2.0 mL of sample (or others as required) to cover a large range of possible BOD₅ values. The standard deviation values were also calculated. Samples were seeded using 1.0 mL of raw wastewater obtained the same day from the Glades Road Wastewater Treatment Facility in Boca Raton, FL. Sterile dilution water was prepared from autoclaved 18.2 MΩ-cm deionized water spiked with 0.3 mL per 300 mL of calcium chloride, magnesium sulfate, ferric iron and phosphate buffer solutions prepared as described in Standard Methods (APHA et al. 2005). All samples were prepared in sterile 300 mL BOD bottles covered in aluminum foil. Duplicates of each sample were analyzed using a YSI 5100 DO meter with YSI 5010 BOD probe (YSI Incorporated, Yellow Springs, OH) or a Hach HqD meter with LDO probe (Hach Company, Loveland, CO).

Table 16. Summary of BOD₅ measurements for real leachate.

Date	Type	BOD ₅ (mg/L)					Flag
		Replicate 1	Replicate 2	Replicate 3	Average	Standard Deviation	
03/28/2010	Raw	702	745	n/a	724	30	a
04/10/2010	Raw	514	547	541	534	18	a
06/08/2010	Raw	723	666	644	678	41	
06/29/2010	Raw	505	534	n/a	520	21	b
07/21/2010	Raw	547	482	n/a	514	46	

Flags:

a	Blank failure ($ DO_0 - DO_5 > 0.2$ mg/L)
b	Probe malfunction
c	Final DO < 1.0 mg/L
d	DO difference < 2.0 mg/L
e	Standard deviation failure

In order to determine the appropriate dilutions for leachate samples after being treated partially with photocatalytic oxidation, a 50% theoretical BOD removal rate was assumed. The the dilution fraction was estimated from the seeded BOD equation. Using this method, the dilutions required sample sizes of 2.0 to 4.0 mL. Therefore three dilutions were prepared: 2.0, 3.0, and 4.0 mL of treated leachate.

During the June 29, 2010 experiment, a problem with the DO probe membrane cap was encountered. The results from this experiment are estimates. For subsequent experiments, LDO probe was used to avoid this problem.

BOD/COD constitutes a good measure of the biodegradability of a wastewater. This wastewater is partially biodegradable according to Chamarro et al. (2001) and Garcia Montano et al. (2006). Contaminants with a ratio of BOD₅/COD ≥ 0.4 are generally accepted as biodegradable, while those with ratios situated among 0.2 and 0.3 units result partially biodegradable (Chamarro et al. 2001; Garcia Montano et al. 2006).

2.5.3 Trace Metals

For copper testing in simulated leachates, the Bicinchoninate Method was used for the DR/4000U spectrophotometer. No pH adjustment was used. For the simulated leachate samples, CuVer 1 powder pillows were used, but due to the hardness and iron levels, the CuVer 2 powder pillows were used for the real leachates. Unfortunately, the copper levels in the real leachate were below the detection limit for the colorimetric method. So for real leachates, the interferences and low method detection limit required a different analytical approach. Therefore, these samples were analyzed for copper and arsenic using a certified laboratory (Xenco Labs, Boca Raton, FL) with an ICP-AES technique (EPA 200.7).

2.5.4 Ammonia-Nitrogen

For ammonia-nitrogen, the EPA Method # 350.2, Detection of ammonia by colorimetry, Nessler spectrophotometric method was used. An ammonia (Medium Range: 0.00 to 9.99 mg/L as NH₃-

N) ion specific meter from Hanna Instruments (Woonsocket, RI) was used. The instrument directly displays concentration in mg/L of ammonia-nitrogen ($\text{NH}_3\text{-N}$) on the liquid crystal display. To convert reading to mg/L of ammonia (NH_3), ammonia-nitrogen values were multiplied by a factor of 1.216. Dilution was necessary to lower the concentrations of known interferences, such as organics, sulfides, color, chloramines, aldehydes, and hardness above 1 g/L as CaCO_3 . Due to the potency of the ammonia in real leachate a 1:1000 dilution was used.

2.5.5 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 1:25, then phenolphthalein indicator was added to the sample. The titrator added titrant until the first 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. 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.

2.5.6 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 1:10 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.

2.5.7 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, or a Hach MP-6 multiparameter unit (Figure 27). Probes were calibrated periodically with standard pH buffers (4, 7, and 10). Sensors were rinsed with deionized water in between sample readings. The pH was adjusted occasionally using a sulfuric acid solution (1.600 N H_2SO_4 , Hach Company, Loveland, CO).

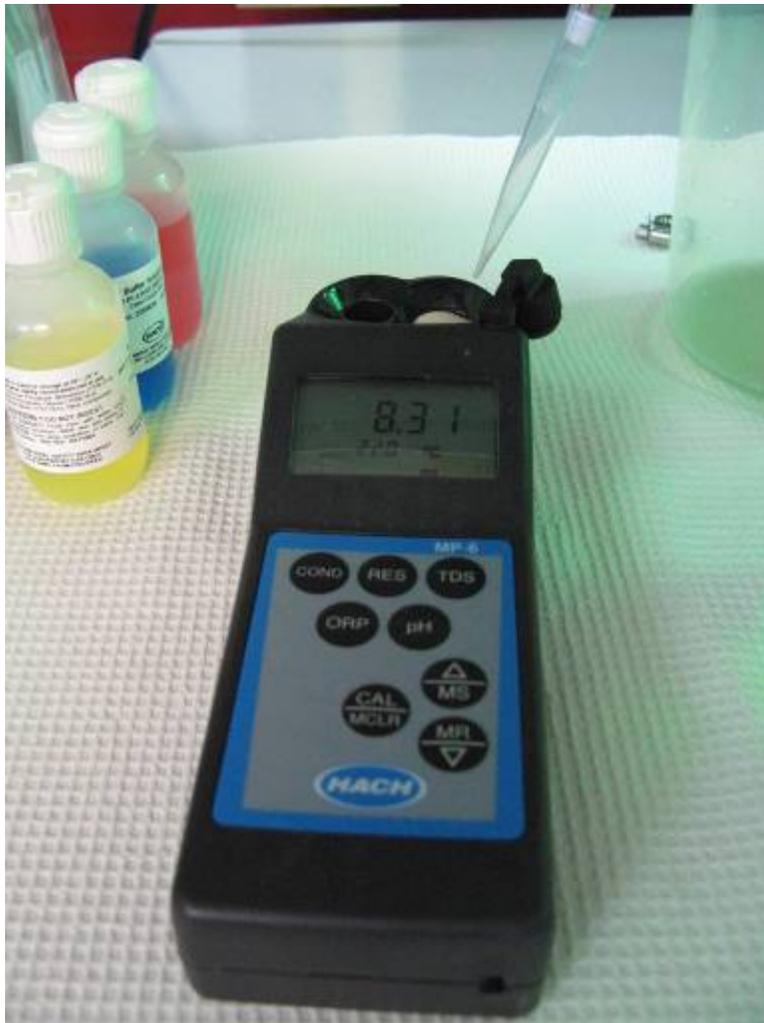


Figure 27. Hach MP-6 multiparameter meter.

3. RESULTS AND DISCUSSION

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

3.1 Laboratory-Scale Experiments of Chemical Oxygen Demand in Simulated Leachate

Before the outcome of the photocatalytic oxidation process can be tested on real leachate, simulated leachate was used as a building block and a means to find the optimum dosage for reactants for scale-up to pilot testing. These scale-up optimization tests were conducted first using chemical oxygen demand removal efficiency with KHP as the model organic compound.

3.1.1 Titanium Dioxide Optimization Results

The raw data for simulated leachate experiments can be viewed in Appendix A. Table 17 shows a summary of the experiments conducted to find the minimum amount of TiO₂ photocatalyst reagent to maximize COD removal in simulated leachates. The initial concentration of these experiments was 1060 mg/L COD. From the data, it can be shown that the optimum amount of photocatalyst occurred between 1.3 – 1.5 grams of TiO₂.

Table 17. Summary of experiments for TiO₂ optimization with simulated leachates, based on COD removal efficiency.

Experiment Number	Date	Max Temp. (°C)	pH		UV Intensity (μW/cm ²)	TiO ₂		NaHCO ₃		% COD Removal (t = 240 min)
			pH ₀	pH _t		(g)	(g/L)	(g)	(g/L)	
1	08/08/2009	75	7.85	9.14	58	0.4	1.07	2.7	7.2	32.4
2	08/23/2009	53	7.86	9.17	70	0.5	1.33	2.7	7.2	41.4
3	08/24/2009	60	7.84	9.13	65	1.0	2.67	2.7	7.2	48.7
4	08/26/2009	60	7.20	9.20	60	1.2	3.20	2.7	7.2	59.4
5	09/07/2009	65	7.16	9.18	63	1.3	3.47	2.7	7.2	75.3
6	09/15/2009	55	7.50	9.17	60	1.5	4.00	2.7	7.2	98.0
7	09/17/2009	56	7.13	9.16	62	1.4	3.73	2.7	7.2	99.0
8	10/06/2009	60	7.16	9.17	45	1.7	4.53	2.7	7.2	90.1
9	10/08/2009	60	7.14	9.18	55	2.0	5.33	2.7	7.2	70.8
12	11/01/2009	60	7.50	9.17	64	1.5	4.00	2.7	7.2	98.7

For example, during experiment 1 the relative concentration (C/C_0) was plotted versus time in Figure 28. It shows a decrease in the C/C_0 values with an S-shaped curve, which implies a complex reaction order. During experiment 1 there was a maximum temperature of 75°C and a UV intensity of 58 μW/cm². The initial pH of the sample was 7.85, and after 240 minutes, the pH increased to 9.14, which was not unexpected. The redox reactions which occur with the TiO₂ photocatalytic particles produce hydroxyl radicals that oxidize most contaminants and as a result increase pH (Rincon and Pulgarin 2005).

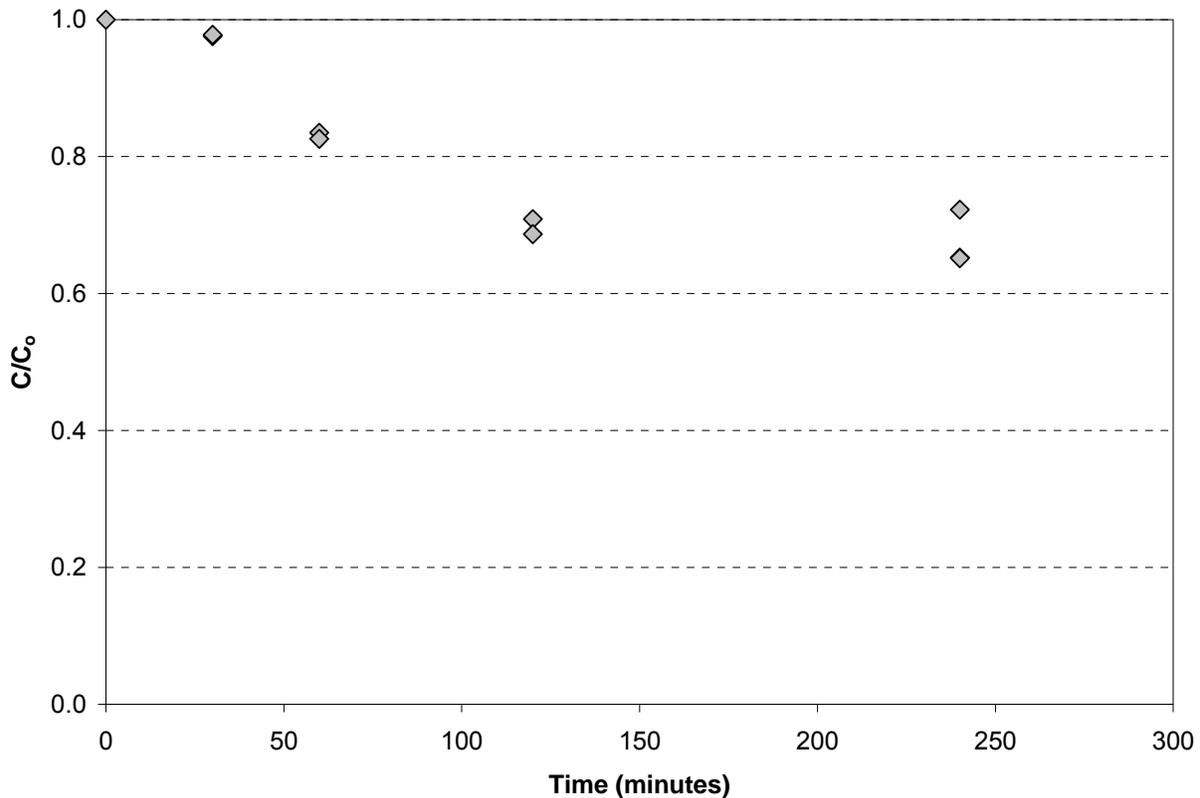


Figure 28. Results of COD removal in experiment #1 with 1.07 g/L TiO₂.

Since the maximum removal was less than 100% mineralization, the dose of photocatalytic particles was increased incrementally, while holding the alkalinity and COD initial starting concentrations constant. For experiment 2, a removal of 41.4% was achieved after 4 hours of treatment. The removal of relative concentration of COD versus time is plotted in Figure 29. The values decreased linearly with an R^2 value of 0.9752. This is a very different shape than observed for the first experiment and is more indicative of a zero-order reaction. However, the correlation is even stronger when the data are plotted for a first order reaction ($R^2 = 0.9857$), and the second order plot ($R^2 = 0.9875$) is also possibly applicable. The reaction order analysis indicates that more time series data is needed to decipher the reaction kinetics. With longer contact times, we might be able to determine the governing reaction mechanism and the rate-limiting step.

The maximum temperature for this experiment reached only 53°C and the UV intensity was measured at 70 $\mu\text{W}/\text{cm}^2$. The lower temperature compared to experiment 1 is thought to have occurred because the thermocouple may have been touching the glass, which was exposed to the ice in the cooling water. Therefore this may have caused the measured irregularities in the actual temperature of the simulated leachate.

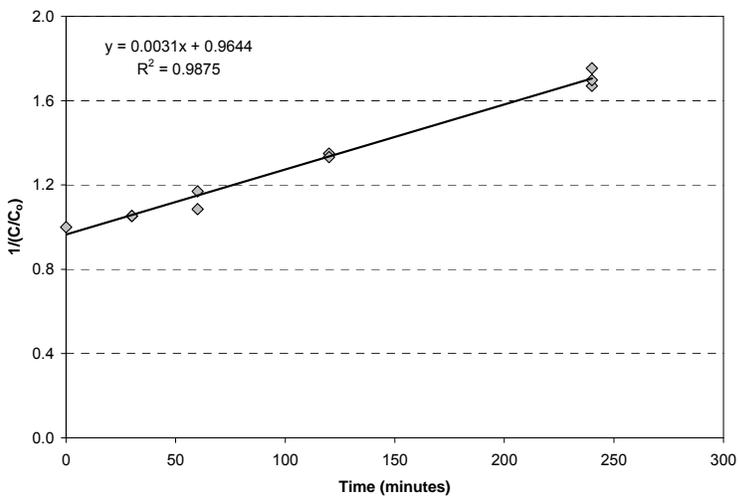
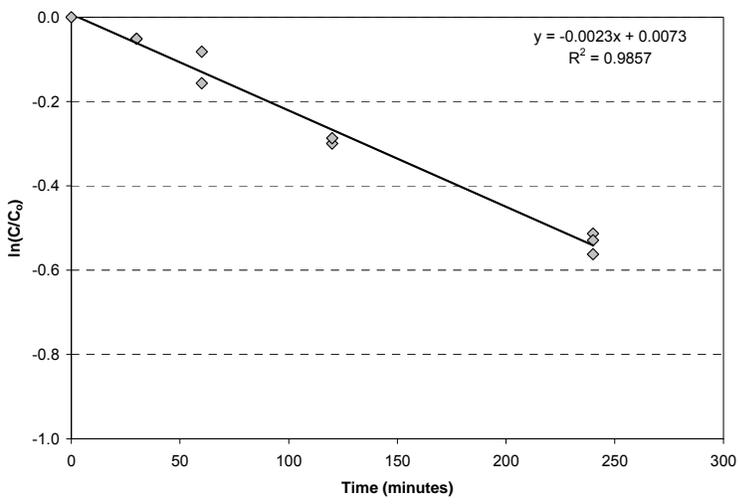
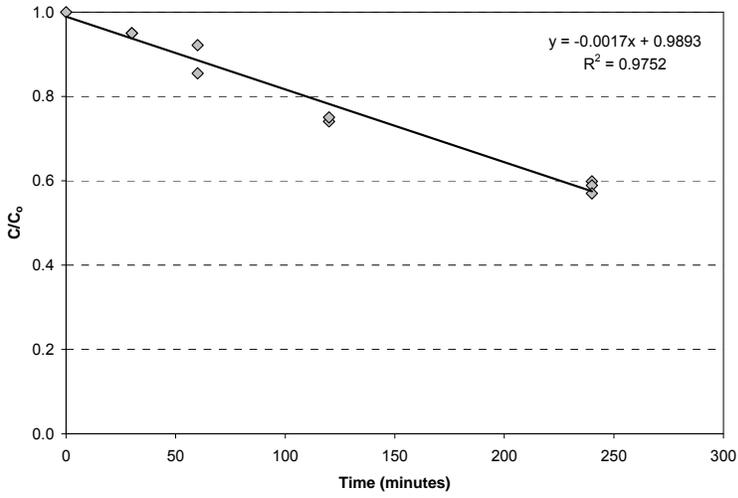


Figure 29. Results of COD removal in experiment #2 with 1.33 g/L TiO₂ (top: zero order plot; middle: first order plot; bottom: second order plot).

Subsequent experiments focused on trying to reach complete mineralization. All conditions were kept constant with the amount of photocatalyst being the only parameter that was changed. Increasing the photocatalyst from 1 g/L to 4 g/L allowed the process to achieve near 100% removal of COD. In experiment 6, the average removal was 98% with one of the samples achieving complete mineralization (Figure 30).

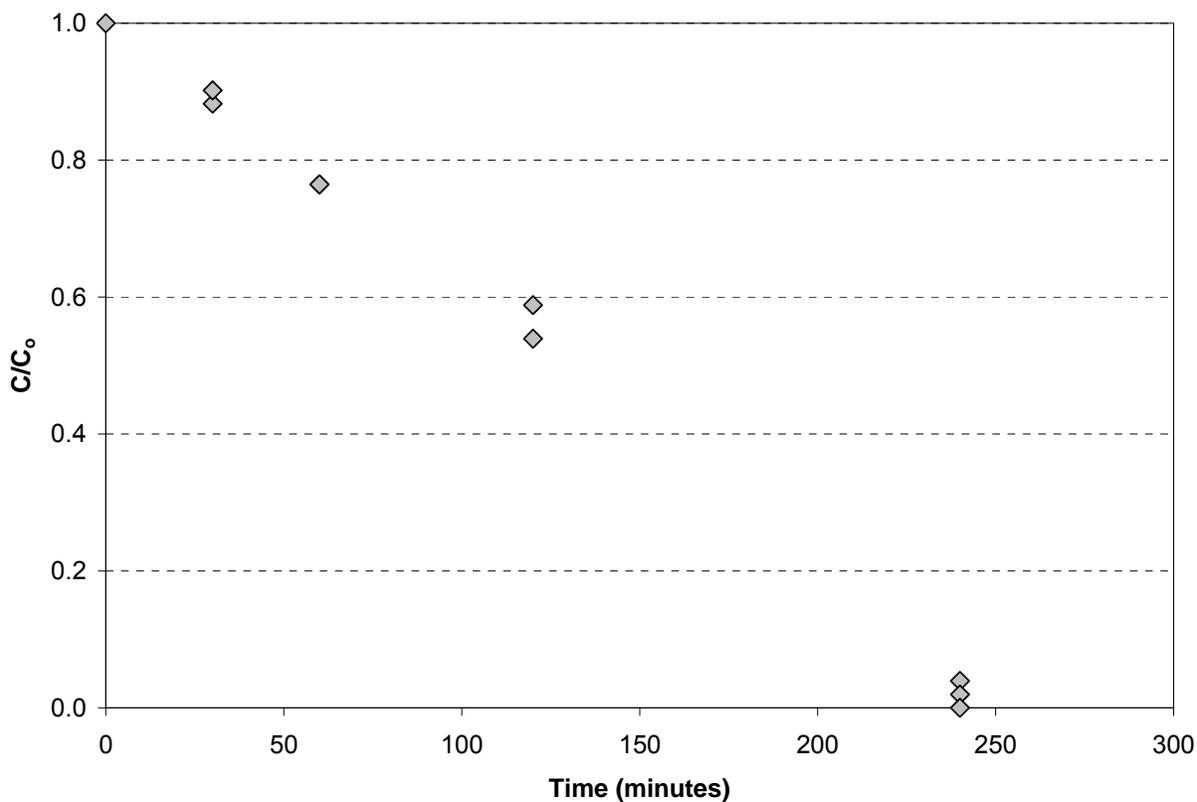


Figure 30. Results of COD removal in experiment #6 with 4.00 g/L TiO₂.

To investigate the reaction kinetics in depth, experiment #6 was plotted in Figure 31. The plot seems to indicate a zero order response ($R^2 = 0.9951$) with $k = -4.1469$ mg/L-min.

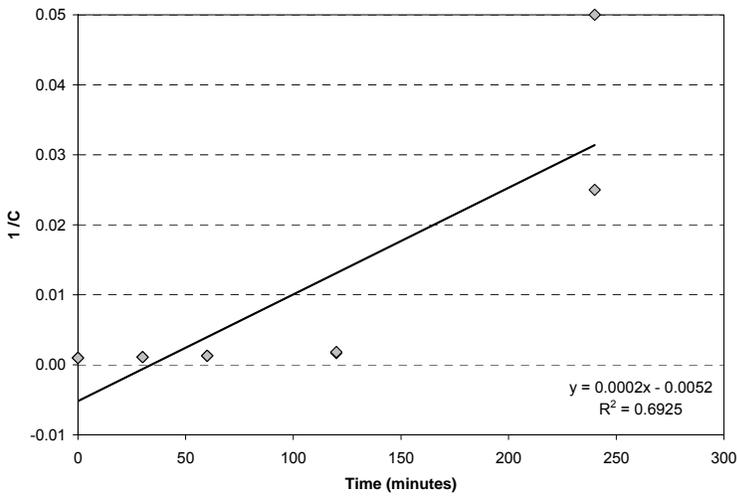
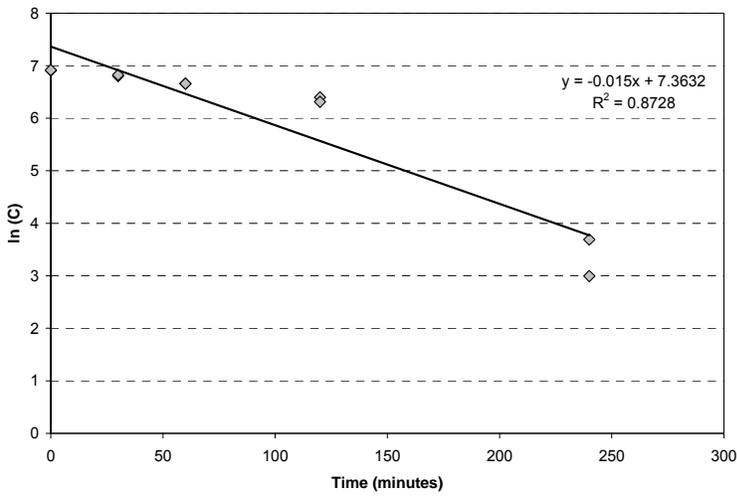
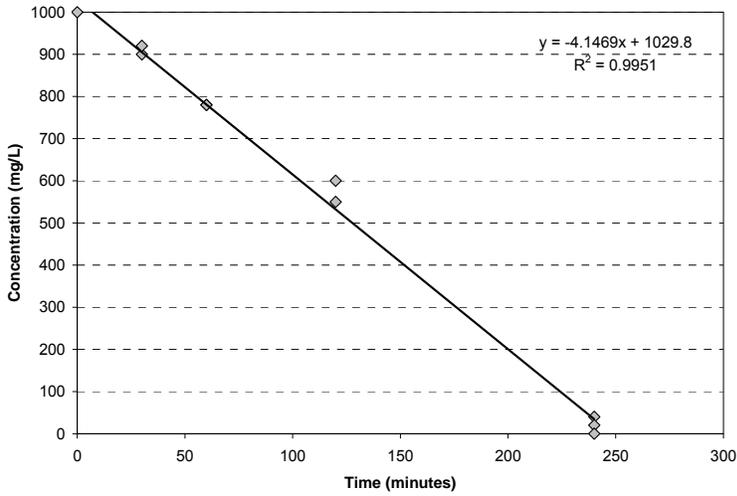


Figure 31. Results of COD removal in experiment #6 with 4.00 g/L TiO₂ (top: zero order plot; middle: first order plot; bottom: second order plot).

Experiment 7 backed the photocatalytic particle addition down from 4 g/L to 3.7 g/L to see if the amount of TiO₂ could be minimized, while still achieving nearly complete mineralization. In Figure 32, the average removal was 99% with one of the samples achieving complete mineralization. This suggests that the optimum amount of photocatalyst lies somewhere in the region between 3.5 to 4.0 g/L at an initial COD concentration on the order of 1 g/L COD. The zero order kinetics were also strongly indicated in this experiment ($R^2 = 0.964$) with $k = -4.170$ mg/L-min).

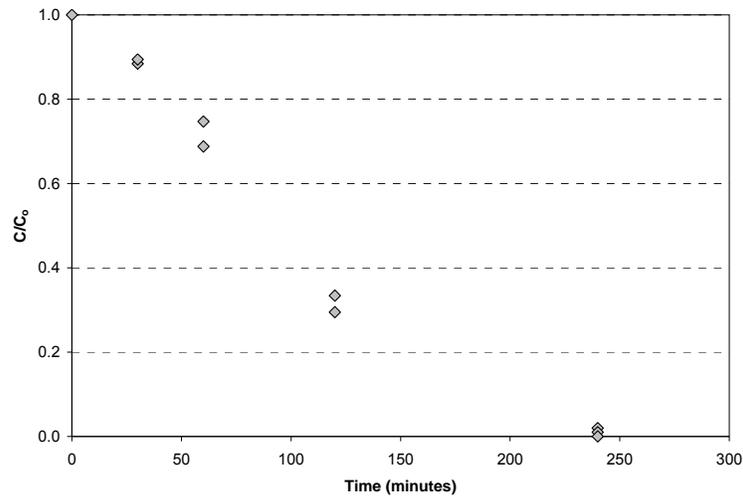


Figure 32. Results of COD removal in experiment #7 with 3.73 g/L TiO₂.

To confirm the optimization, a larger dose was added of more TiO₂ particles. It was expected that there would be a point where the removal efficiency would decrease sharply. The TiO₂ particles are expected to produce electron-hole pairs that can initiate reductive and oxidative reactions on the surface. However, by adding more particles than necessary, its overabundance may randomly prevent the surface reaction from occurring due to auto-destruction of the oxidant or scattering of UV light energy. Plotting the data of percent COD removal at 240 minutes versus TiO₂ to initial COD ratio (data taken from Table 17), the results are illustrated in Figure 33. From the graph, the optimum dosage of photocatalyst is on the order of 3.3 – 3.8 gTiO₂ per gCOD, under these conditions for simulated leachate.

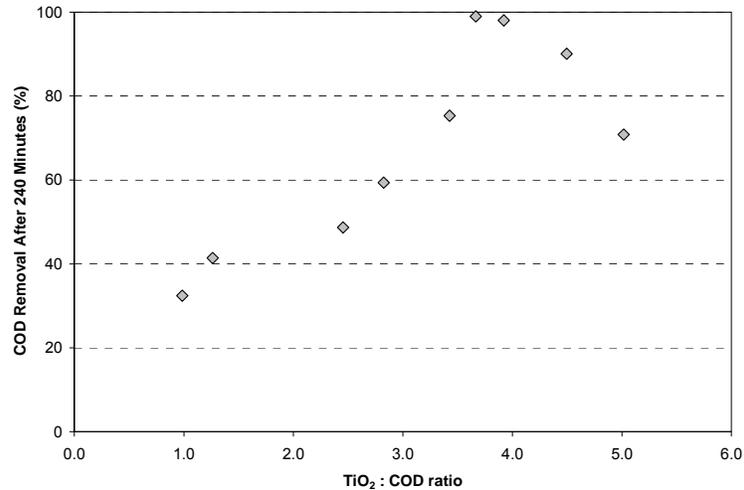


Figure 33. Results of TiO₂ optimization experiments for COD removal on simulated leachates (COD₀ = 1060 mg/L).

3.1.2 Alkalinity Optimization Results

The previous optimization experiments for TiO₂ photocatalyst particles were conducted at a constant alkalinity value (4300 mg/L as CaCO₃). So it was desired to identify the optimum alkalinity level for maximum COD removal efficiency by keeping the photocatalyst dose constant and varying the alkalinity. A summary of the results of these experiments is shown in Table 18.

Table 18. Summary of experiments for alkalinity optimization with simulated leachates, based on COD removal efficiency.

Ex. No.	Date	Initial COD (mg/L)	Max Temp. (°C)	pH		UV Intensity (μW/cm ²)	TiO ₂ : COD	Alkalinity (mg/L as CaCO ₃)	% COD Removal (t = 240 min)
				pH ₀	pH _t				
10	10/27/2009	1063	50	5.71	9.19	55	3.8	3170	63.0
11	10/29/2009	1065	51	6.57	9.15	55	3.8	3650	78.1
12	11/01/2009	1030	60	7.50	9.17	64	3.9	4290	98.7
13	11/02/2009	1029	56	8.21	9.48	56	3.9	4760	93.4
14	11/04/2009	980	58	8.45	9.67	55	4.1	5240	91.1
15	11/06/2009	1090	58	8.34	9.12	50	3.7	5550	82.0
16	02/16/2011	2465	55	8.95	9.87	50	3.2	8690	60.8
17	02/19/2011	6125	67	8.45	9.23	59	4.6	4290	10.5

Taking the data from experiments 10-15, we are able to plot an optimization curve as shown in Figure 34. At these conditions, the optimum occurs between 4100 – 4700 mg/L as CaCO₃.

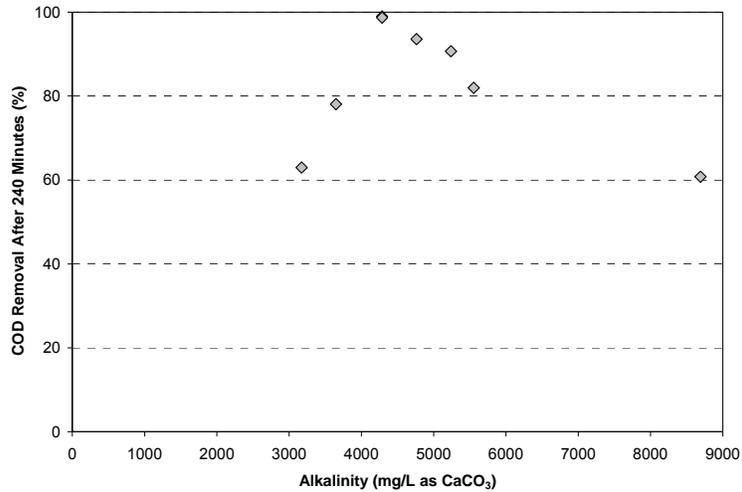


Figure 34. Results of alkalinity optimization experiments for COD removal on simulated leachates (COD₀ = 1040 mg/L and TiO₂ = 4 g/L).

To test if the value is independent of initial COD concentration, another experiment (#17) was conducted in which the alkalinity level was in the optimum range, but the initial COD concentration was 6125 mg/L instead of 1040 mg/L. Under these conditions, the COD removal was only 10.5%, which demonstrates a strong concentration dependence that will likely complicate scale-up without extensive pilot testing. But since the mass of COD is four times higher than the values tested for optimization, the reaction contact time may need to be longer. If the system follows zero order kinetics ($k = -4.15$ mg/L-min from experiment #6), then the extension of treatment to approximately 1475 minutes should yield near 100% mineralization via the retention time equation for zero order reactions in a batch reactor unit ($t = C_0/k$). However, as shown in Figure 35, this is not observed.

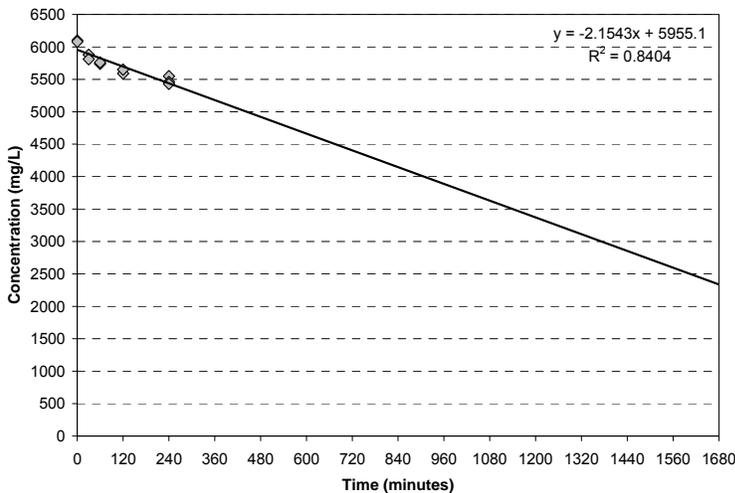


Figure 35. Results of COD removal in experiment #17 with initial COD of 6125 mg/L, alkalinity of 4290 mg/L as CaCO₃ and 4.2 TiO₂ : COD ratio.

It is interesting to note that if the data point collected at 240 minutes (temperature = 67°C) is removed from the analysis, the plot is shown in Figure 36, and the model predicts a reaction time of 1650 minutes, which is much closer to the 1475 minutes predicted by the optimization. It is not clear why the data point collected at 240 minutes has such a strong effect on the reaction kinetics, but it may be more related to the relatively low alkalinity per unit photocatalyst inhibiting photosensitivity of the oxidation reaction or alternatively to the extreme high temperatures at long reaction times which may lead to rapid self-decay of the hydroxyl radical with the bulk solution before it can interact with the pollutants.

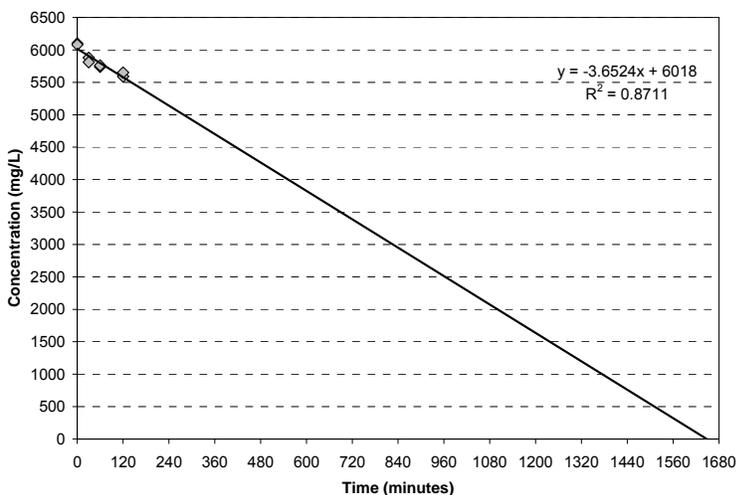


Figure 36. Results of COD removal in experiment #17 with initial COD of 6125 mg/L, alkalinity of 4290 mg/L as CaCO₃ and 4.2 TiO₂ : COD ratio, with the data point at 240 minutes removed.

3.1.3 Scale-Up Testing

The optimization experiments for TiO₂ photocatalyst particles and alkalinity levels on COD removal were tested by creating a simulated leachate with characteristics similar to the real leachate collected from the Waste Management Central Disposal Sanitary Landfill in Pompano Beach, FL. These experiments are summarized in Table 19. The first test was conducted by essentially doubling the previous concentrations from the optimized simulated leachate discussed in 3.1.1 and 3.1.2, with respect to experiment 7. In this case, the removal at 240 minutes dropped from 99% to 61%. This suggests that if the contact time could be extended, it is possible that complete mineralization could be achieved, but it could not be measured because of the temperature effect of running the laboratory scale reactor at times beyond 360 minutes. Furthermore, if the initial concentration was increased 6-fold, but the alkalinity and the photocatalyst concentrations remained constant, the removal dropped to only 11% in 240 minutes.

Table 19. Summary of scale up tests for COD removal in simulated leachates.

Experiment Number	Date	Max Temp. (°C)	pH		UV Intensity (μW/cm ²)	TiO ₂ (g/L)	Alkalinity (mg/L as CaCO ₃)	COD _o (g/L)	% COD Removal (t = 240 min)
			pH _o	pH _t					
7	09/17/2009	56	7.13	9.16	62	3.7	4290	1018	99.0
16	02/16/2011	55	8.95	9.87	50	8.0	8690	2465	60.8
17	02/19/2011	67	8.45	9.23	59	4.0	4290	6125	10.5

3.1.4 Laboratory-Scale Experiments of Chemical Oxygen Demand in Real Leachate

After determining the optimum photocatalyst dose and alkalinity levels, it was desired to test these findings on actual leachate samples collected in the field. Table 20 contains a summary of experiments of COD removal efficiency performed on real leachate.

Table 20. Summary of experiments for alkalinity optimization with real leachates, based on COD removal efficiency.

No.	Date	COD _o (mg/L)	Max Temp. (°C)	pH		UV Intensity (μW/cm ²)	TiO ₂ (g)	TiO ₂ (g/L)	Alkalinity (mg/L as CaCO ₃)	NaHCO ₃ Added (g)	Acid Added (mL)	% COD Removal (t = 240 min)
				pH _o	pH _t							
18	01/27/2010	4550	44	8.02	8.49	3.8	6.67	17.8	8963	7.2	0	16.7
19	01/31/2010	4580	41	8.04	8.58	3.6	6.67	17.8	4630	0	0	21.9
20	02/04/2010	4330	22	8.08	8.51	4.0	6.67	17.8	4630	0	0	24.2
21	02/20/2010	4420	20	6.09	6.76	4.0	6.67	17.8	2970	0	0.115	26.5
22	02/24/2010	4480	23	5.99	6.34	4.0	6.67	17.8	2720	0	0.689	24.2
23	03/07/2010	4530	42	5.84	6.29	45	13.3	35.5	1600	0	0.720	20.8
24	03/11/2010	4660	42	8.13	8.61	65	13.3	35.5	4630	0	0	(19.5)
25	08/05/2010	5240	61	8.13	8.87	65	13.3	35.5	4630	0	0	44.4 @ t= 360 min (31.5)
26	08/18/2010	5100	65	12.37	13.23	79	13.3	35.5	4630	0	0	27.9 @ t= 360 min (39.0)
27	08/23/2010	5070	55	8.12	8.65	30	13.3	35.5	4630	0	0	48.8 @ t= 360 min (12.3)
												20.3 @ t= 360 min

Because the COD removal from real leachate was less than expected, experiments to investigate the effects of color and turbidity were conducted. To this end, lime (calcium oxide, CaO) was added as a coagulation/flocculation/filtration pre-treatment step to aid in clarification of turbidity and co-precipitation of color. The final pre-treatment step of filtration was added to ensure that suspended solids (either initially present or from the coagulation/flocculation treatment) are completely removed prior to photocatalytic oxidation treatment.

It is often suggested that pre-filtration increases the removal efficiency of processes involving UV radiation by reducing the scatter of effective radiation intensity caused by particulates and turbidity. Previous experiments conducted in our laboratory (Meeroff, Gasnier, and Tsai 2008) showed that filtration alone does not impact COD removal efficiency appreciably; however, it is important to note that the real leachate matrix was of very low strength (COD_o = 325 mg/L) in those previous experiments (Figure 37).

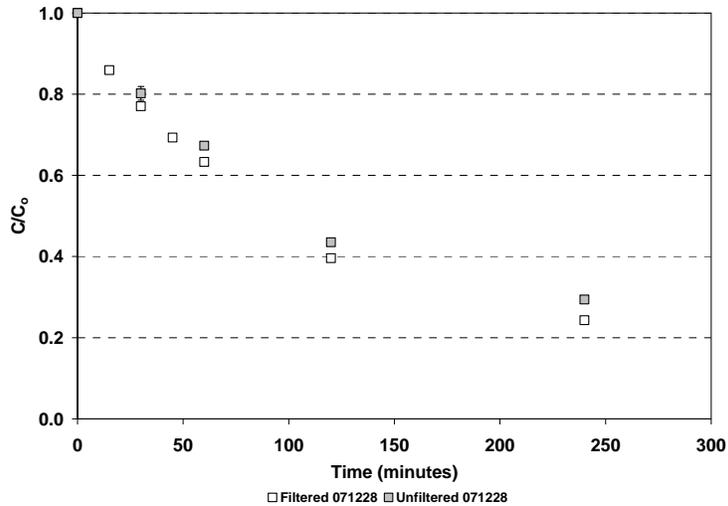


Figure 37. Comparison of recovered photocatalytic particle oxidation with and without filtration using Polk County leachate (sampled August 15, 2004).

One observation from the COD tests of real leachate was that the leachate turbidity was a determining factor that affected the COD removal efficiency. The real leachate proved to be very turbid (44 NTU), which is to be expected especially from its dark brown color. The leachate's turbidity was high because when the water percolated through the landfill, it picked up dissolved materials from the decomposing waste, inorganic materials, heavy metals, and other constituents in the waste. Thus, coagulation/flocculation treatment with lime (CaO) followed by filtration was investigated to reduce the suspended solids content in the leachate prior to photocatalytic oxidation treatment (Hammer and Hammer 2008). The results from the trial and error method of finding the optimum dose of lime are shown photographically in Figure 38 and in tabular form in Table 21.

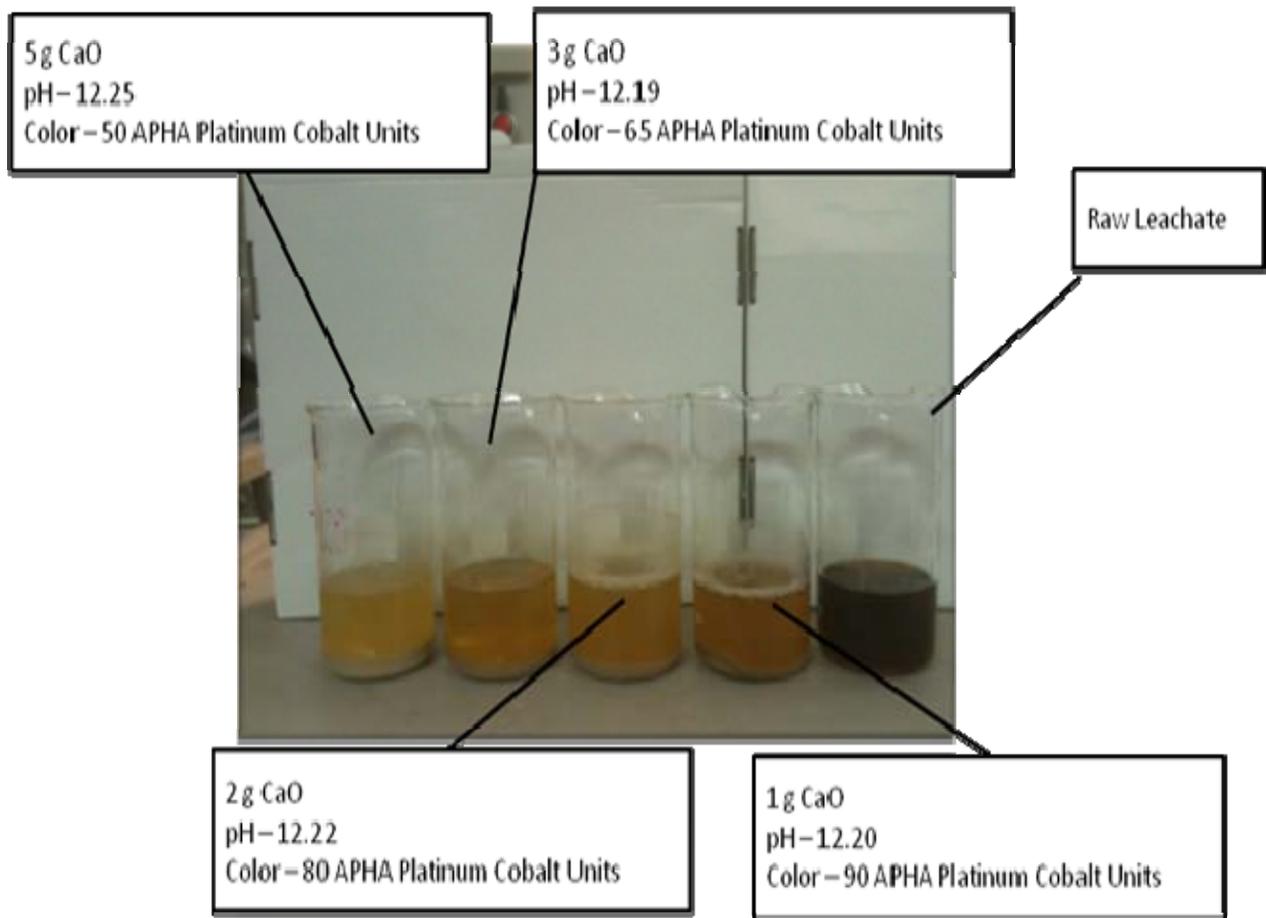


Figure 38. Photograph of lime dosage test results.

Table 21. Experiments to determine the lime dosage for COD and color removal experiments in real leachate.

Experiment No.	CaO (g)	pH	Color (PCU)
1	0	8.32	>500
2	1	12.20	90
3	2	12.19	80
4	3	12.22	65
5	5	12.25	50

The turbidity of real leachate samples were determined to be on the order of 44 NTU, which was expected especially from its dark brown color and fine suspended particulates. The turbidity was high because when water percolates through a landfill, it picks up dissolved materials from the decomposing waste, inorganic materials, and heavy metals. But does this turbidity limit the process removal efficiency?

Three new tests were conducted with real leachate. The first test involved adding lime and filtering the leachate prior to treatment; the pH and color were recorded prior to adding lime, after the addition of lime and after it was treated in the reactor. The second test was done with only filtration, and the third was completed by using neither lime nor filtration. The results of these experiments are summarized in Table 22.

Table 22. Summary of laboratory-scale experiments with coagulation/flocculation and filtration for COD removal in real leachates.

No.	Date	Initial COD (mg/L)	Max Temp. (°C)	pH		UV Intensity ($\mu\text{W}/\text{cm}^2$)	TiO ₂		Lime	Filter	pH adj.	% COD Removal (t = 360 min)	Color PCU
				pH _o	pH _t		(g)	(g/L)					
25	08/05/2010	5240	61	8.13	8.87	65	13.3	35.5	no	yes	no	27.9	nr
26	08/18/2010	5100	65	12.37	13.23	79	13.3	35.5	yes	yes	no	48.8	50
27	08/23/2010	5070	55	8.12	8.65	30	13.3	35.5	no	no	no	20.3	nr
28	03/29/2011	5220	58	7.35	nr	35	13.3	35.5	yes	yes	yes	50.7	nr

Examining experiment 27, which is essentially the optimized control process with no pre-treatment, we can see the reaction kinetics (Figure 39). For the zero order plot, the estimated reaction time for full mineralization is 2100 minutes ($k = -2.31 \text{ mg/L-min}$). Interestingly to note, the first order plot gives a similar result 1915 minutes ($k = -0.00052 \text{ min}^{-1}$). This indicates that more time intervals are needed to work out the kinetics in real leachate. For the simulated leachate with only KHP as the model compound, the reactor followed zero order kinetics. But with the real leachate, less kinetics relationship is less clear. According to Calace et al. (2001), the determination of the molecular weight distribution of the different organics found in real leachate, as well as the different functional groups, explains the complex behavior and reactivity of leachate organic substances.

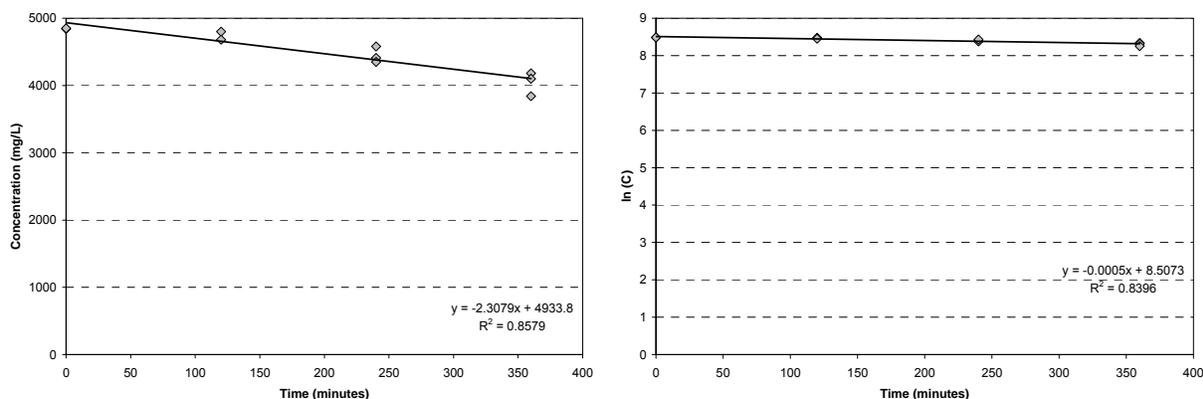


Figure 39. Results of COD removal in experiment #27 with 13.3 g/L TiO₂ and no pre-treatment (left: zero order plot; right: first order plot).

When the same sample is filtered prior to treatment, the kinetics change slightly, as shown in Figure 40, from -2.31 to -3.62 mg/L-min for zero order fit, which reduces the estimated reaction time from 2100 minutes to 1400 minutes.

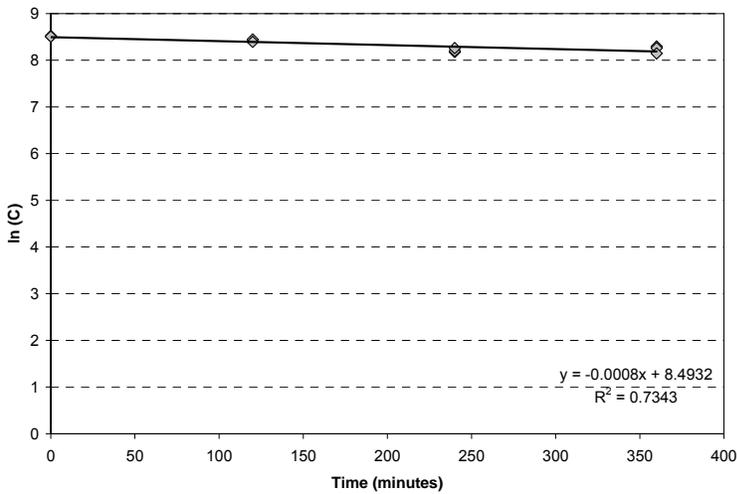
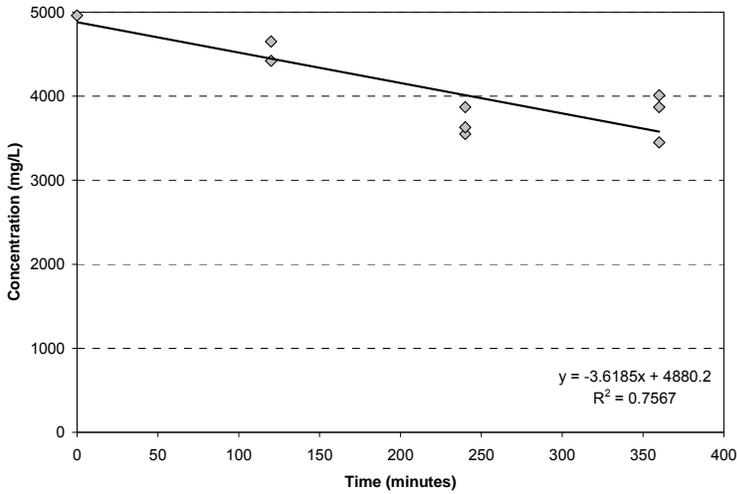


Figure 40. Results of COD removal in experiment #25 with 13.3 g/L TiO₂ and pre-filtration (top: zero order plot; bottom: first order plot).

In light of previous experiments with filtration, we found that adding filtration as a pre-treatment process has no effect on the reaction efficiency. In experiment 25 compared to experiment 27, the reaction time was reduced by about 35% with filtration. Although the data appear to show an effect in Table 22 and Table 23, the lamp intensity fluctuated to about half the level (65 to 30 $\mu\text{W}/\text{cm}^2$) from the filtration test to the unfiltered control test. So this small apparent difference may have had more to do with the lamp power than filtration of particles in the sample.

Table 23. Summary of kinetic coefficients for COD removal of real leachate with various pre-treatment methods.

Exp.	Conditions	Zero order				First order			
		k (mg/L-min)	y-intercept	R ²	Θ (min)	k (min ⁻¹)	y-intercept	R ²	Θ (min)
27	Control	-2.31	4930	0.858	2100	-0.00052	8.51	0.834	1915
25	Pre-filtration	-3.62	4880	0.757	1380	-0.00085	8.49	0.734	1180
26	Lime + Filter	-5.29	4420	0.928	880	-0.00152	8.40	0.951	660
28	Lime + Filter + pH adjustment	-7.68	5215	0.921	660	-0.00209	8.59	0.922	480

The best recorded COD removal (48.8%) in these experiments occurred with pre-treatment using lime and filtration. However, the pH range was very high (12.37 – 13.23), and it is known that the photocatalytic process is favored at lower pH ranges, so it may be likely that the removal could have been even greater if the pH had been readjusted to near neutral values before photocatalytic oxidation. So another experiment was conducted with pH adjustment using concentrated sulfuric acid to pH = 7.35 (experiment 28). The reaction kinetics were improved slightly, but again the lamp intensity fluctuation may have dampened the effect (79 to 35 μW/cm²). It is likely that if the lamp intensity could have been held constant, the pH adjusted sample may have achieved a much higher COD removal efficiency.

3.1.5 Kinetics Testing

Kinetic studies on the photo-mineralization rate of the landfill leachate constituents are useful for process scale-up. Using the COD decomposition experiments, the photo-mineralization kinetics were explored. When determining rate orders, total decomposition should occur in order to elucidate the overall rate of the reaction. When performing the simulated leachate experiments, nearly complete mineralization was achieved. Based on the kinetics analysis, it seems follow a zero order (or a first order) degradation rate. According to Chong et al. (2010), some researchers found that zero order or first order kinetics is sufficient to model the photomineralization of organic compounds. A zero order reaction has the rate law:

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = -k[A]^0 = -k(1) = -k$$

The above rate law can be determined by plotting concentration versus time. The slope of the line is the reaction rate constant, k. When experimenting on real leachate, total decomposition was not achieved; however, the initial stages of removal all illustrate a similar pattern to the decomposition rate of the simulated leachate. Further evidence is needed to verify this.

Assuming complete mixing: $C_t = C_o - kt$. Where C_o is the initial concentration, C_t is the final concentration, t is the time, and k is the zero order reaction rate constant (slope of the line). The value of the initial concentrations, slopes, y-intercepts and R² coefficients were tabulated for simulated as shown in Table 24. For starting COD concentrations on the order of 1000 mg/L, the

zero order reaction rate constant (k) is on the order of -3.19 mg/L-min. It is interesting to note that the rate constant varies if the initial concentration of COD is changed. This is counter-intuitive, but because the alkalinity level plays an important role, we can see why the kinetics decrease for experiment 17 (alkalinity is low) and increase for experiment 16 (alkalinity is high).

Table 24: Summary of zero order kinetics studies on COD removal in simulated leachates.

Experiment number	C_o (mg/L)	k (mg/L-min)	y-intercept	R^2 value
1	1059	-1.40	1032	0.795
2	1050	-1.83	1044	0.980
3	1048	-2.18	1077	0.975
4	1150	-2.84	1139	0.994
5	1000	-3.25	1012	0.983
6	1005	-4.15	1030	0.995
7	980	-4.17	969	0.964
8	1000	-3.87	1029	0.988
9	1060	-3.10	1067	0.983
10	1045	-2.22	909	0.813
11	1120	-3.28	1036	0.921
12	1020	-4.24	1047	0.995
13	974	-3.73	926	0.954
14	1000	-3.65	921	0.954
15	1060	-3.87	1115	0.967
Average	1038	-3.19	1024	0.951
Standard deviation	49.4	0.909	67.6	0.062
16	2450	-5.70	2313	0.973
17	6090	-2.15	5955	0.840

Table 25 shows the value of the initial concentrations, slopes, y-intercepts and R^2 coefficients for the real leachate experiments. It is interesting to note that the only data points with a high correlation coefficient (experiments 26 and 28) showed zero order reaction rate constants of -5.29 and -7.68 mg/L-min, respectively, which is higher than the average rate constant for simulated leachates (-3.19 mg/L-min).

Table 25: Summary of zero order kinetics studies on COD removal in real leachates.

Experiment number	C_o (mg/L)	k (mg/L-min)	y-intercept	R^2 value
18	4500	-1.82	4147	0.413
19	4540	-2.42	4049	0.396
20	4115	-2.32	3735	0.437
21	4270	-2.68	3778	0.433
22	4385	-3.22	4097	0.755
23	4335	-2.82	4219	0.823

Experiment number	C _o (mg/L)	k (mg/L-min)	y-intercept	R ² value
24	4645	-4.48	4309	0.771
25	4985	-3.62	4880	0.757
26	4645	-5.29	4422	0.928
27	4895	-2.42	4968	0.877
Average	4532	-3.11	4260	0.659
Standard deviation	272	1.08	409	0.212
28 (with pH adjustment)	5095	-7.68	5215	0.921

Using the steady state performance equation for ideal batch reactors, the time required to reach the maximum discharge limit for COD for Broward County (800 mg/L), can be calculated from:

$$C_t = C_o + kt$$

$$800 = 4500 + (-3.11 \times t)$$

$$t = 1190 \text{ minutes}$$

Therefore, we would expect the cycle times for real leachate to be on the order of 20 hours for COD removal using a batch reactor.

3.3 Laboratory-Scale Experiments of Biochemical Oxygen Demand in Real Leachate

A summary of the laboratory-scale experiments on biochemical oxygen demand in real leachates is shown in Table 26. These experiments showed that the initial BOD₅ of the real leachate varied from 500 – 725 mg/L. The best removal efficiency was achieved at 360 minutes of contact time (34.4%). For all of these experiments, the conditions were identical, but the sample dilutions and testing conditions combined to fail the test for 4 of the 5 experiments.

Table 26. Summary of laboratory-scale experiments of biochemical oxygen demand in real leachates.

Date	Initial BOD ₅ (mg/L)	Max Temp. (°C)	pH		UV Intensity (μW/cm ²)	TiO ₂		Alkalinity (mg/L as CaCO ₃)	% BOD ₅ Removal (t = 360 min)
			pH _o	pH _t		(g)	(g/L)		
03/28/2010	724	50	8.13	8.61	65	13.3	35.5	4360	n/a
04/10/2010	534	55	8.02	8.75	63	13.3	35.5	4330	n/a
06/08/2010	678	61	8.11	8.45	60	13.3	35.5	4630	n/a
06/29/2010	520	48	8.04	8.33	54	13.3	35.5	4630	7.0
07/21/2010	514	61	8.13	8.87	65	13.3	35.5	4630	34.4

Using the data from the 07/21/2010 experiment, we can investigate the reaction kinetics for BOD removal. As shown in Figure 41, similar to the COD in real leachate, the BOD₅ process kinetics can fit either zero or first order (Table 27). Comparing the zero order reaction rate constant to the COD in real leachate, the value is about 5 times less, but comparing the first order reaction rate constant to the COD in real leachate shows a doubling in the reaction rate constant. With longer time series data, we may be able to work out the kinetic coefficients and determine more precisely, the estimated reaction times. Using zero order kinetics, we estimate complete removal

of BOD in about 1160 minutes and with first order kinetics, the value is on the order of 950 minutes.

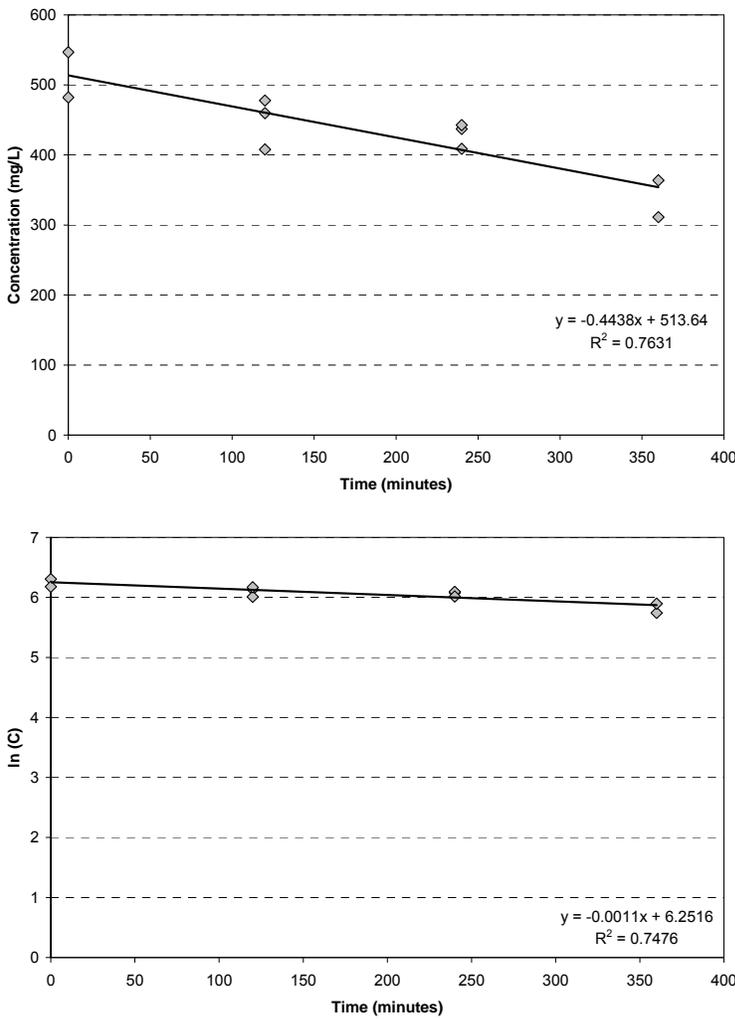


Figure 41. Results of BOD₅ removal with 13.3 g/L TiO₂ (top: zero order plot; bottom: first order plot).

Table 27. Summary of kinetic coefficients for BOD₅ removal of real leachate.

Date	Zero order				First order			
	k (mg/L-min)	y-intercept	R ²	Θ (min)	k (min ⁻¹)	y-intercept	R ²	Θ (min)
07/21/2010	-0.44	510	0.763	1160	-0.0011	6.25	0.746	950

3.4 Laboratory-Scale Experiments of Ammonia-Nitrogen

As seen in Table 28, experiments with real leachate revealed relatively high (70.8 – 74.2%) removal of ammonia-nitrogen compared to COD removal.

Table 28. Summary of laboratory-scale experiments of ammonia-nitrogen.

Date	Type	Initial NH ₃ (mg/L)	Max Temp. (°C)	pH		UV Intensity (μW/cm ²)	TiO ₂		Alkalinity (mg/L as CaCO ₃)	% NH ₃ Removal (t = 360 min)
				pH _o	pH _t		(g)	(g/L)		
07/20/2010	Real	2420	51	7.64	7.86	45	13.3	35.5	4630	74.2
07/28/2010	Real	2150	53	7.91	8.15	56	13.3	35.5	4630	70.8
02/19/2011	Simulated	2550	67	8.45	9.23	59	4.0	10.67	4290	20.3

@ 240 min

In the experiment dated 07/28/2010, a time series of data points were collected to investigate the removal of ammonia over time in the laboratory-scale reactor with real leachate. The results are shown in Figure 42. The removal appears to be fairly linear ($R^2 = 0.9801$) with respect to time over the interval from 0 to 6 hours.

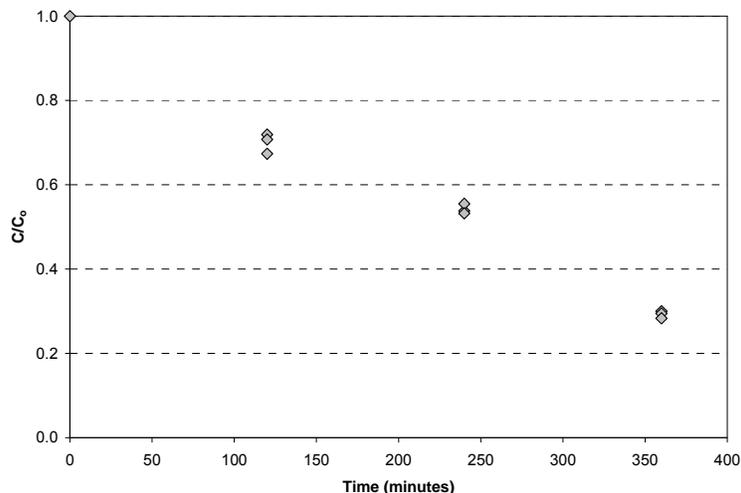


Figure 42. Results of ammonia-nitrogen removal in laboratory-scale experiments with real leachate.

When we investigate the reaction kinetics, as plotted in Figure 43, again we cannot distinguish between zero and first order. However, the first order coefficients predict complete ammonia removal in 300 minutes, but the experiment was conducted up to 360 minutes with only 70.8% removal. Therefore, it seems more reasonable that the zero order kinetics fit better for the ammonia removal mechanism.

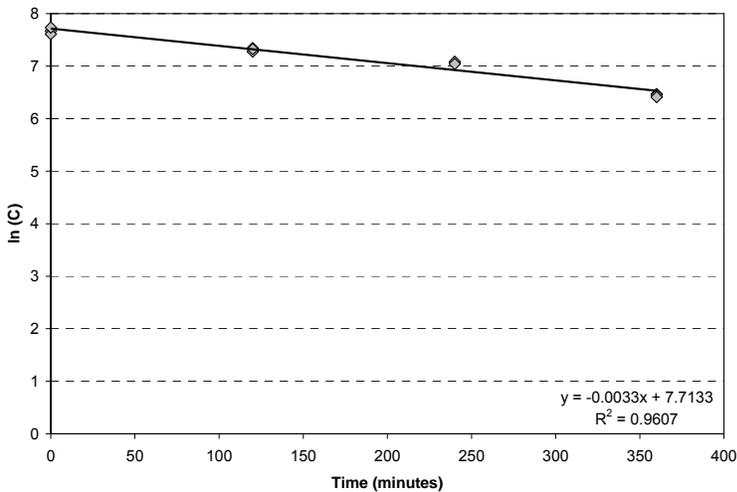
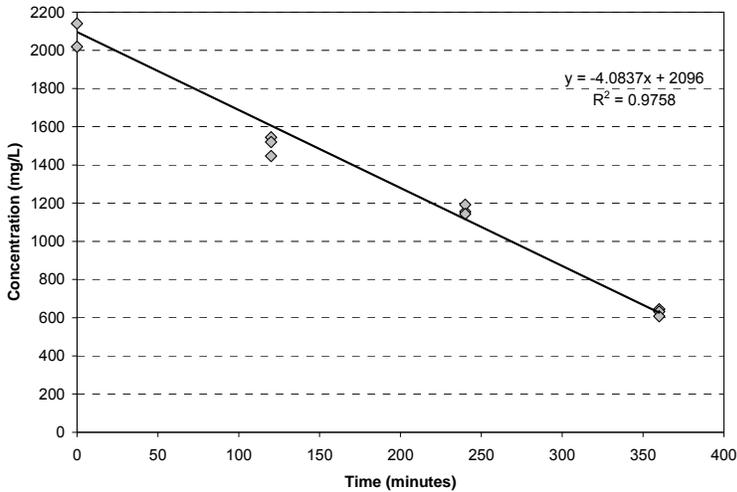


Figure 43. Results of ammonia-nitrogen removal in laboratory-scale experiments with real leachate on 07/28/2010 (top: zero order plot; bottom: first order plot).

Table 29. Summary of kinetic coefficients for ammonia-nitrogen removal of real leachate.

Date	Zero order				First order			
	k (mg/L-min)	y-intercept	R ²	Θ (min)	k (min ⁻¹)	y-intercept	R ²	Θ (min)
07/28/2010	-4.08	2100	0.976	530	-0.0033	7.71	0.961	305

Ammonia is a soluble gas with a small Henry’s law constant (59 M/atm), which means that ammonia is readily soluble in water and vice versa. Ammonia is rapidly converted to ammonium at ambient pH, ($K_a = 5.6 \times 10^{-10}$), which means that unless the pH is high enough (>9.3), the ammonia will remain in solution as the ionized ammonium cation. This concept may provide additional insight as to why the ammonia removal rates are so high. The pH is generally above 8.3, which favors some conversion of ammonium to aqueous ammonia. And because air is also being blown into the reactor, it works as an air stripping mechanism to aid in the ammonia removal process. Quan et al. (2009) illustrated that there is a critical value for the air flow rate over which stripping efficiency and the mass transfer coefficient increases rapidly. An efficient

air stripping of ammonia should be conducted at a higher ambient temperature ($>25^{\circ}\text{C}$), and a higher air flow rate (>1.4 Lps) (Quan et al. 2009). The temperatures during experimentation were in excess of 25°C , which would favor ammonia stripping; however, air flowrates were less than 0.47 Lps.

3.5 Laboratory-Scale Experiments of Trace Metals

The consensus removal mechanism for trace metals in photocatalytic reactions involves metal plating on the catalyst surface when metals interact with holes. It is thought that the copper that is able to dissociate in solution may also bind with the hydroxyl group (from water), which acts as an electron donor to produce the hydroxyl radicals. The electrons react with dissolved oxygen in water acting as an electron acceptor to yield super oxide radicals. Some of the generated electron-hole pairs, which do not participate in the redox reaction with water or oxygen, disappear as heat through the recombination of holes and electrons, such that the free copper and the complexed copper, which was liberated by the hydroxyl radical mechanism (and is now free) can combine with free hydroxides and precipitate out of solution. Another important removal mechanism could be co-precipitation, when metals interact with co-constituents in solution, elevated pH, and oxidizing conditions in the reactor to precipitate target metals.

A summary of laboratory-scale experiments is found in Table 30.

Table 30. Summary of laboratory-scale experiments of trace metals.

Leachate Type	Date	Initial Conc. (mg/L)	Max Temp. ($^{\circ}\text{C}$)	pH		UV Intensity ($\mu\text{W}/\text{cm}^2$)	TiO ₂ (g/L)	Alk (g/L as CaCO ₃)	% Removal (t = 240 min)
				pH _o	pH _t				
Simulated	05/07/2010	Cu = 0.33	60	7.65	8.21	56	4.0	4.3	78.6
Simulated	05/09/2010	Cu = 0.43	54	7.42	8.13	53	4.0	4.3	84.9
Real	08/25/2010	Cu < 0.17	56	8.18	8.75	56	35.5	4.6	nr
Real	08/25/2010	As = 0.70	56	8.18	8.75	56	35.5	4.6	40.7

The time series for simulated copper removal is shown in Figure 44. The observed removal is similar for the two experiments, in which the only difference is the starting concentration of copper. From the plot, it seems clear that the reaction is not zero order, and from the shape of the curve, there is evidence of a concentration dependence. No chemical precipitates were noted in the simulated leachate experiments, but the concentrations were very low to begin with.

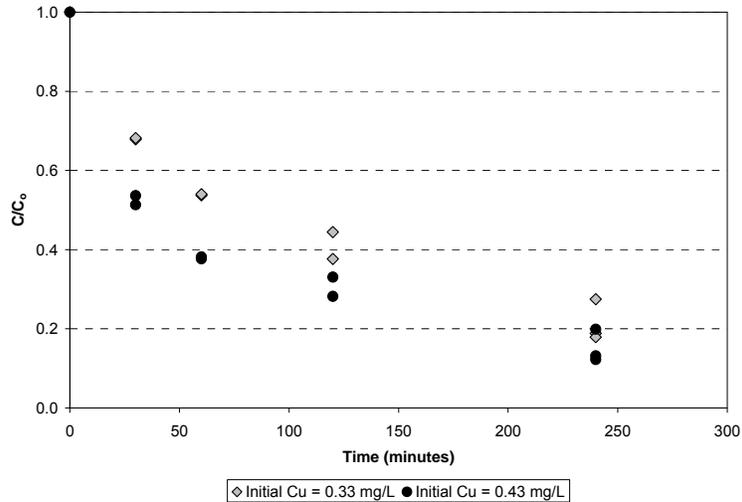


Figure 44. Results of copper removal in laboratory-scale experiments with simulated leachate.

However, when we analyze the data for zero or first order reaction kinetics, the results are inconclusive, as shown in Figure 45. In fact, second order kinetics also potentially fit as well, but the predicted reaction times are not realistic (21-32 minutes). Not enough information is known to decipher the governing kinetics, and even the reaction mechanism for metals removal is unclear. In Table 31, the set of first order coefficients predict complete copper removal in less than 160 minutes, but the experiments were conducted up to 240 minutes with only 78.6-84.9% removal. Therefore, it seems more reasonable that the zero order kinetics fit better for the copper removal mechanism.

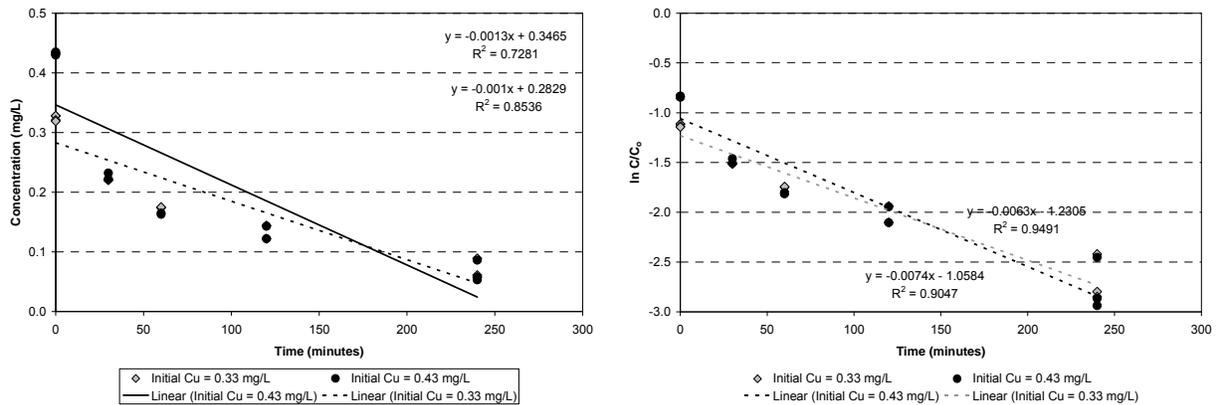


Figure 45. Results of kinetics analysis for copper in simulated leachate (left: zero order; right: first order).

Table 31. Summary of kinetic coefficients for copper removal in simulated leachate.

Date	Zero order				First order			
	k (mg/L-min)	y-intercept	R ²	Θ (min)	k (min ⁻¹)	y-intercept	R ²	Θ (min)
05/07/2010	-0.0010	0.283	0.854	330	-0.0063	-1.23	0.949	160
05/09/2010	-0.0013	0.346	0.728	320	-0.0074	-1.05	0.905	140

In real leachate experiments, the initial copper levels were below detection, so the reaction process efficiency could not be investigated. Copper concentrations in real leachate are usually low, and copper is not generally considered a health hazard to humans although more than 1.0 mg/L can impart a bitter taste and cause vomiting which may eventually lead to liver damage. Copper salts, such as copper sulfate (CuSO_4), are used to control algae; however, they may also be toxic to fish and other wildlife.

CuCl is known to be insoluble in water but readily dissolves in aqueous solutions containing halogens and ammonia, which are in high concentrations in leachate. Furthermore, copper would generally be found as the oxidized cupric form (Cu^{2+}) under the conditions of photocatalytic treatment. According to Babbit et al. (1983) cupric chloride (CuCl_2) is sometimes difficult to dissociate completely, but copper in the cupric form is known to be insoluble in combination with arsenate ($K_{\text{sp}} = 7.6 \times 10^{-36}$), sulfide ($K_{\text{sp}} = 8.7 \times 10^{-36}$), hydroxide ($K_{\text{sp}} = 1.6 \times 10^{-19}$), and carbonate ($K_{\text{sp}} = 2.5 \times 10^{-10}$), all of which may be found in elevated concentrations in leachate. So, it is possible that one mechanism of removal could be precipitation.

The standard copper solution which was used as a calibration check showed an unexplained high percent error, roughly half of the expected value. It is recommended to obtain a second calibration check standard to determine the source of this problem. As a temporary solution, all subsequent tests were sent to a NELAC-certified laboratory (Xenco Laboratories, Boca Raton, FL) for independent verification of the results by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) method. Unfortunately, the real leachate samples had very low copper concentrations below the instrument detection limits (0.170 mg/L), so the results were inconclusive. It is recommended to run trace metal analysis with lower detection limits in the future.

For the arsenic tests, there was an initial decrease of about 40% as shown in Figure 46 during the first 120 minutes. But this removal efficiency was essentially constant over the entire 360 minutes of the reaction. Arsenic is a redox-sensitive element, and it is generally found in an oxyanionic form in aqueous solution. Arsenite (AsO_2^-) predominates in reducing conditions, like those that would be expected in landfill leachate. The arsenate (AsO_4^{3-}) is favored during oxidizing conditions. It is entirely possible that the removal that is observed is related to arsenite being converted to arsenate under oxidizing conditions, or from differential adsorption due to the pH regime and the presence of iron oxides, aluminum oxides, and clay particles.

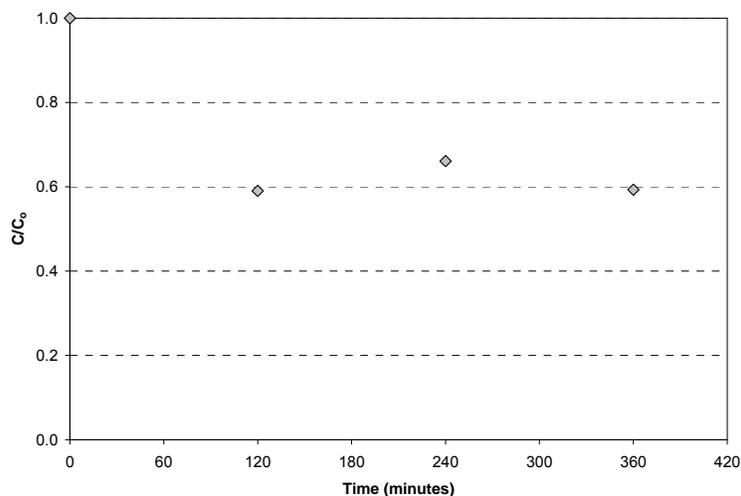
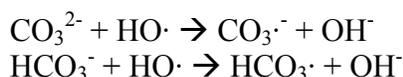


Figure 46. Summary of results of arsenic removal in real leachate.

3.6 Laboratory-Scale Experiments to Determine Alkalinity Effects

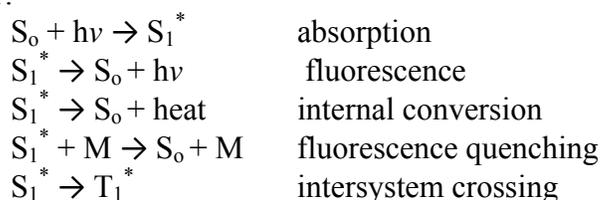
The effect of ions such as sulfate, nitrate, chlorate, chloride, etc. on the photocatalytic oxidation process has been studied by many investigators. In trying to understand the effect of alkalinity, attention was focused on the bicarbonate/carbonate system of ions. These ions, which form the basis for natural alkalinity, are known to interact with hydroxyl radicals in a quenching reaction as a radical scavenger, as follows:



The downside is that the carbonate radical anion is a very weak oxidizing agent that hardly reacts with other constituents (Haarstrick et al. 1996; Bhatkhande et al. 2001). Thus, they act more like radical scavengers. It seems that if the target compound is strongly adsorbing, the effect of bicarbonate/carbonate can be significant. For instance, at concentrations of 1 mM bicarbonate (3050 mg/L as CaCO₃), the photodegradation rate was reduced by 50% (Haarstrick et al. 1996).

In our work, we also found that bicarbonate seemed to be necessary to initiate the reaction, similar to the action of a photosensitizer, which is a species capable of transferring the energy of absorbed light. The latest understanding of the mechanism of photosensitization is as follows:

Type 1:

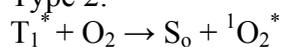


Once light of the appropriate wavelength is absorbed, the sensitizer is converted from a stable electron structure (S_0) to an excited state known as the singlet state (S_1^*), which is short-lived and may undergo conversion to a longer-lived excited state known as the triplet state (T_1^*),

which is the photoactive state responsible for the photochemical generation of cytotoxic species. The lifetime of the singlet state is generally less than 1 μs, and the main role of this state in the photosensitization mechanism is to act as a precursor of the metastable triplet state. However, its involvement cannot be overlooked because if the fluorescence is quenched through the binding of the sensitizer to a particular substrate (fluorescence quenching), the overall excitation efficiency from the ground state to the triplet state is correspondingly reduced. A type I process can involve hydrogen abstraction from the sensitizer to produce free radicals or electron transfer resulting in ion formation (Dougherty 1989).

The type II mechanism, in contrast, exclusively involves interaction between molecular oxygen and the triplet state to form an electronically excited state of O₂ known as singlet oxygen (¹O₂^{*}), which is highly reactive in biological systems (Dougherty 1989).

Type 2:



The near-resonant energy transfer from the triplet state to O₂ can be highly efficient: the singlet oxygen yield may approach the triplet state yield (Dougherty 1989).

3.7 Laboratory-Scale Experiments to Determine pH Effects

The rate of reaction for many compounds differs under acidic and alkaline conditions. Changes in pH may also affect the properties of the photocatalyst. For different types of wastewaters, different pH conditions will result in the formation of different reaction products. So the effect of pH is likely variable depending upon catalyst, target compound, and matrix properties. In the literature, for experiments with synthetic solutions, TiO₂ catalyst and aniline, *p*-toluidene, and 2,4-xylene have been tested (Kabra et al. 2004). The catalyst was found to be more effective in acidic and slightly alkaline media. A similar study was carried out for the purification of groundwater from an abandoned military base (Preis et al. 1997). A pH of 3.5 was suggested as the optimal value for the degradation of phenol using anatase (Okamoto et al. 1985), but another study concluded that alkaline conditions are necessary for the elimination of COD (Chen et al. 1997).

Under acidic or alkaline conditions the surface of titanium photocatalysts can be protonated or deprotonated. Thus, the photocatalytic surface will remain positively charged under acidic conditions (pH < 6.9) and negatively charged under basic conditions (pH > 7.1). Titanium dioxide is reported to have higher oxidizing activity at lower pH but excess H⁺ at very low pH can decrease the reaction rate (Sun et al. 2006). Change in pH can result in enhancement of process efficiency for the removal of organic pollutants without affecting the rate equation (Shourong et al. 1997). At optimized conditions better degradation has been reported (Mansilla 2006; Gaya and Abdullah 2008).

Cho et al. (2002) monitored the effects of varying the pH from 2 – 12 with 3 g/L TiO₂ on the removal efficiency of COD and found that the degradation rate was significantly higher in acidic solution compared to neutral or alkaline pH. The reason cited was that a Nernstian shift of the

band edges of the semiconductor to a more negative value with increasing pH. Furthermore, at pH <4, the reaction mechanism is postulated to be a direct hole oxidation, while above this pH level, it shifts progressively to a hydroxyl radical-like reaction following a rate-limiting hole oxidation of surface radicals.

Table 32: Summary of pH effects on COD removal.

Date	TiO ₂		UV Intensity ($\mu\text{W}/\text{cm}^2$)	COD ₀ (mg/L)	Max Temp. (°C)	pH		Alkalinity (mg/L as CaCO ₃)	Acid Added (mL)	% COD Removal (t = 240 min)
	(g)	(g/L)				pH ₀	pH _t			
02/20/2010	6.67	17.8	4.0	4420	20	6.09	6.76	2970	0.12	26.5
02/24/2010	6.67	17.8	4.0	4480	23	5.99	6.34	2720	0.69	24.2
03/07/2010	13.3	35.5	45	4530	42	5.84	6.29	1600	0.72	20.8
03/11/2010	13.3	35.5	65	4660	42	8.13	8.61	4630	0.00	(19.5) 44.4 @ 360 min

The affect of the titanium dioxide mechanism on various pH levels also can play a major role in the efficiency of the process. In several of the experiments, the pH was adjusted using concentrated sulfuric acid to measure the effects on the COD removal. The results of this experiment are summarized in Table 33, which shows that a more efficient COD removal was attained when the samples were closer to a neutral pH.

Table 33: Effect of pH on COD removal.

Initial pH	COD ₀ mg/L	TiO ₂ g/L	TiO ₂ : COD	COD removal (%) t = 240 min
5.80	1600	17.8	11.1	25
6.00	2720	17.8	6.5	23
6.10	2970	17.8	6.0	29
7.43	313	2.8	8.9	76
8.13	4630	35.5	7.7	20

The pH is one of the most important operating parameters that affect the charge on the photocatalyst particles. Based on the initial and final pH values of the batch reactor test, any variation of the pH between 7 and 9 provides a steady removal of the constituents of concern including COD in the landfill leachate. It was clear that decreasing the pH had an effect on the COD removal efficiency. The photocatalyst particles seem to be at least partially dependent on the operating pH. A more rigorous control experiment should be conducted to elucidate the impacts of pH, similar to the optimization of alkalinity in this manuscript.

3.8 Summary of Laboratory Scale Findings

In the batch reactor system, the overall photocatalysis reaction rate still remains unclear. Laboratory experiments to determine the rate and reaction order were inconclusive due to the inability to control the reaction temperature and extend the reaction times. It has been stated (Gaya and Abdullah 2008) that an increase in photocatalytic reaction temperature (>80°C) promotes the recombination of charge carriers and limits the adsorption of organic compounds onto the TiO₂ surface. When the COD efficiency was at its greatest removal, the maximum

temperature was 65°C. But since, field scale implementation of the reaction should be at 20-30°C, the reaction rate may be over-inflated. Without more knowledge of the reaction kinetics and the activation energy for the Arrhenius equation, we cannot determine the impact of temperature on the reaction rate coefficient. However, nearly tripling the temperature from 20°C to 65°C, could artificially increase the kinetic coefficient by 7-8 times ($\theta = 1.047$).

An optimum TiO₂ dose and alkalinity level was achieved for simulated leachate COD removal. When the amount of TiO₂ increases above a saturation level, the light photon absorption coefficient usually decreases noticeably. The excess TiO₂ particles can create a light screening effect that reduces the effective surface area of TiO₂ exposure to light illumination which reduces the photocatalytic efficiency. The optimized photocatalyst dose was tested by scaling-up the concentrations of COD and other constituents, and this seemed to follow similar effectiveness, only requiring longer reaction times. This finding holds true until the reaction is attempted on real leachate, when the mechanism becomes even less clear due to the wide variety of pollutants, concentrations, functional groups, chemical properties, and competing constituents. Nevertheless, for most of the parameters tested in real leachate, by extending the reaction times, it seems possible that high levels of removal can be achieved. According to Chong et al. (2010), the geometry and operating conditions of the reactor where the photocatalytic reaction is initiated upon light photon absorption plays an important role. Therefore, pilot tests were initiated with a larger scale recirculating batch reactor and a plug-flow reactor.

The long term management problem of landfill leachate is that the quantity and quality of the leachate constantly varies. And when performing experiments, the initial concentrations of the constituents were randomly distributed. Owing to the photonic nature of the photocatalysis reaction, excessively high concentrations of organic substrates are known to simultaneously saturate the TiO₂ surface and reduce the photonic efficiency leading to photocatalyst deactivation (Saqib et al. 2003). The results obtained from laboratory scale tests agree with this assertion. Particular with regards to the COD experiments, a noticeable variation was observed when the initial COD concentration increased from approximately 4000 to 5000 mg/L, resulting in a possible concentration dependence but likely more related to insufficient reaction time and lack of temperature control.

The overall photocatalytic oxidation reaction can be divided into five independent steps according to Herrman (1999) and Fogler (1999). Initially mass transfer of organic contaminants onto the TiO₂ surface is followed by adsorption of the organic contaminants onto the photo-activated TiO₂. The photocatalysis reaction for the adsorbed phase then occurs, which leads to desorption and finally the mass transfer of the intermediate back to the bulk of the fluid. This outlines the importance of possibly trying to monitor the molecular adsorption or surface contact with the catalyst during the photocatalytic degradation. If the mass transfer steps are rate limiting, a change in the aeration or liquid flow conditions may alter the overall photocatalytic reaction rate. Again, this can be effectively investigated with extended reaction times and temperature control.

3.9 Pilot-Scale Experiments for COD Removal

UV radiation causes the water to heat up, such that part of the original sample could theoretically evaporate. In experiments at extended contact times, the target compounds for removal may

actually become artificially concentrated due to this evaporative volume loss. At high recirculation rates, this could exacerbate the volume loss. In this case, the measured concentrations must be corrected for the evaporative losses. At low levels of evaporation (<2%), this effect can be largely ignored. But at higher levels, it can be significant. So, the amount of evaporative losses was measured using 8 L of deionized water under the same conditions as the pilot tests. During the experiment, the water temperature rose from 19.3°C to 44.2°C. The results are shown in Figure 47. From the data, it can be shown that the expected evaporation rate is on the order of 11.5 mL/hr, and the overall volume loss for the 6 hour period is only 70 mL or only 0.9%, which is less than 2%. Thus, the evaporative losses may be ignored.

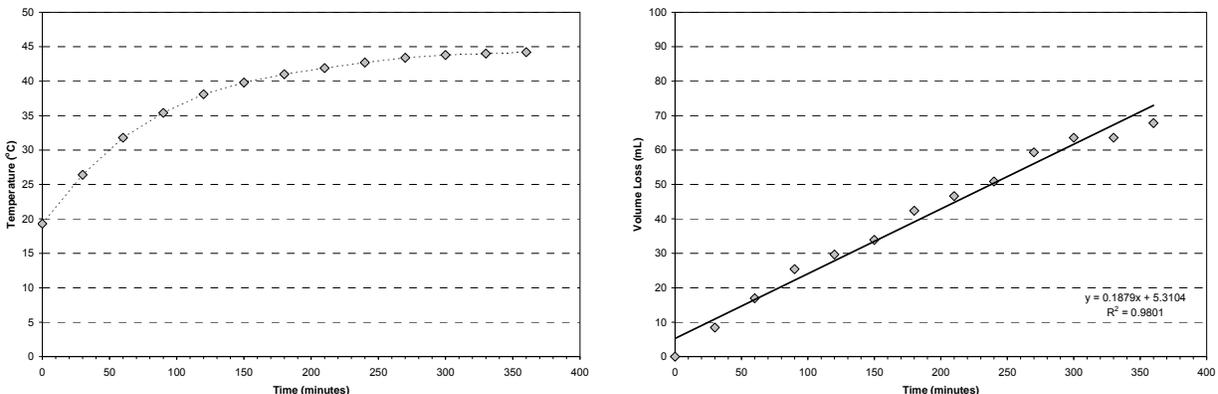


Figure 47. Temperature curve for the falling film pilot reactor (flowrate = 30 Lph) using UV and Aeration (left). Falling film pilot reactor volume loss due to evaporation using UV and aeration with 8 L deionized water (right).

The first experiment was conducted using real leachate collected from the CDSL SE corner sample site. The dark reaction was tested. No changes in pH were noted, and no COD removal was recorded after 6 hours reaction time with 36.7 g/L TiO₂ (ratio of TiO₂:COD = 10.1)

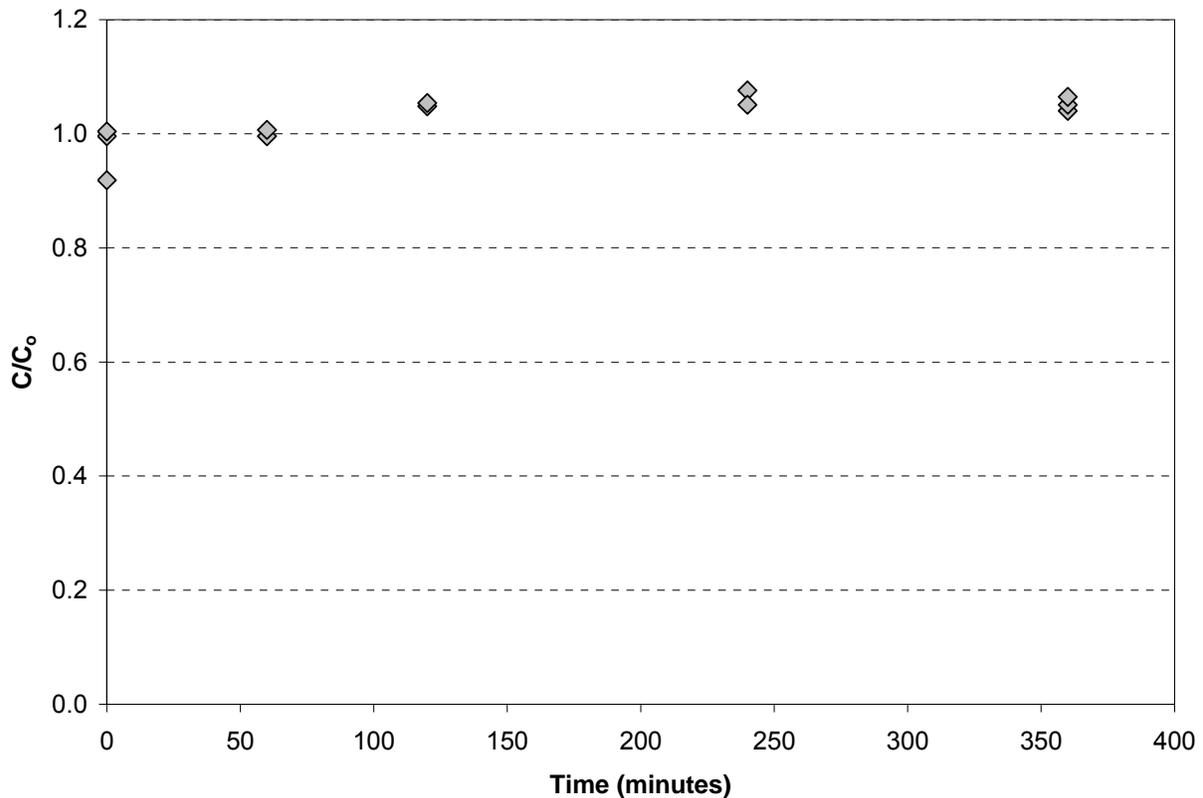


Figure 48. Results of the pilot test dark reaction.

In the next experiment, a ratio of TiO_2/COD of 7.7 was used. The pH changed from 7.92 to 8.63 after 6 hours of treatment. The volume loss due to evaporation of 130 mL (1.6%) was recorded. The COD removal was measured at 19% for this experiment ($11 \mu\text{W}/\text{cm}^2$). When the TiO_2/COD was increased to 10.4, the COD removal ceased. The initial alkalinity in these samples was on the order of 4000 mg/L as CaCO_3 and decreased to 2750 after 3 hours of treatment and remained unchanged at 2750 after 12 hours of treatment.

Future experiments:

- Optimize Catalyst Dosage
- Optimize Flow Rate
- Understand Alkalinity Dependence
- Reaction Order Kinetics
- Concentration Dependence
- Temperature Regulation
- Vary UV Dosages
- BOD Testing
- Catalyst Recovery
- Plug Flow Model Experiments

4. CONCLUSIONS AND RECOMMENDATIONS

4.1 Summary of Findings

Leachate generation is a major drawback associated with sanitary landfills. This material must be managed appropriately before it can be safely discharged back to the environment. From review of the state-of-the-art in leachate management, several issues have been identified. These include biological, chemical, and physical constituents of leachate, such as ammonia, COD, BOD, heavy metals, TSS, and TDS. In addition to specific water quality concerns, leachate is a highly variable waste stream because the volumes and constituents are dependent upon a great many factors that cannot be easily controlled, such as precipitation, waste composition, age, etc. Conventional leachate management approaches simply are not equipped to deal with all of these issues effectively, necessitating alternative methods.

Advanced oxidation technologies that utilize the strong oxidizing power of the hydroxyl radical, are becoming more popular as research demonstrates encouraging performance at laboratory and pilot scale. Photocatalysis using titanium dioxide is among these emerging technologies. The process is capable of detoxifying complex waste streams by dealing with ammonia, organics, color, heavy metals, and even common inorganic anions, simultaneously, as discussed in detail in Chapter 1. Furthermore, it can potentially be operated at ambient temperature and pH with just the power of the sun and sufficient photocatalyst, a material that does not get used up in the reaction.

From laboratory-scale testing, 100% mineralization of simulated leachates was demonstrated in 4 hours of treatment. In addition, removal of 79% copper and 50% ammonia was also achieved. The optimum dose of TiO_2 particles at pH 7.1 – 9.2 was found to be 4.0 g/L for initial COD concentrations of 1000 mg/L with an initial alkalinity of 4333 mg/L as CaCO_3 . It was determined that alkalinity potentially acts as a photosensitizer or facilitates adsorption to the photoactive sites on the catalyst surface, but it also is a known radical scavenger, which inhibits the reaction at elevated alkalinity levels.

Based on anticipated constituent levels in the real leachate, the COD concentration in the simulated leachate was increased from 1040 mg/L to 2550 mg/L to see if 100% mineralization of COD could be achieved using the optimal conditions developed in the initial lab tests at lower starting concentrations. The reaction exhibited a concentration dependence because only 62% removal of COD was achieved using the scale-up conditions from the complete mineralization tests. This concentration dependence proved to be a factor, and further experiments are required to investigate why complete mineralization was not achieved from linear extrapolation of the optimum conditions at lower concentrations. Plots of relative concentration versus time demonstrated that not enough sample times were collected to determine the reaction order with any degree of certainty. The reaction must be conducted for longer contact times beyond 360 minutes; however, until the temperature can be maintained constant, the lab-scale reactor cannot be operated for longer than 240-360 minutes. Furthermore, the kinetic coefficients are affected by temperature. So until the temperature issue can be resolved, the concentration dependence and the kinetics of the governing reaction remain unclear.

Until this point, all samples of simulated leachate were tested as individual components, but real leachate contains a wide variety of constituents mixed together. So to more accurately mimic the real leachate, a simulated mixture with BOD, COD and ammonia was made using the actual concentrations found in the real leachate. For this combined mixture, a maximum COD removal of 15% and ammonia removal of 50% were achieved after 240 minutes of contact time. The BOD₅ experiment failed due to the inability to distinguish between the model compounds for COD (KHP) and BOD₅ (glucose/glutamic acid). It proved difficult to duplicate a biodegradable sample within the simulated leachate.

Using real leachates at the laboratory-scale, 53% mineralization of COD, 74% ammonia, 34% BOD₅, 52% arsenic removal was demonstrated after 360 minutes of contact time using the optimal conditions developed for the simulated leachate. The BOD/COD ratio began at 0.12, which is considered difficult to biodegrade, and after treatment was converted to 0.21, which is considered partially biodegradable. Scale-up has been complicated due to an observed concentration dependence and our inability to run the reaction longer than 360 minutes. We estimate that using zero order reaction kinetics, the appropriate reaction time is on the order of 20 hours.

4.2 Preliminary Cost Analysis

The Central District Disposal Landfill currently pays disposal fees based on million gallons per year. The first 12 million gallons per year are free of charge, but this landfill is averaging 42-96 million gallons per year of leachate discharged to the sewer. In addition to this, exceedance fees of \$350,000 per year in FY 2010 were added because of high constituent concentration (i.e. COD > 800 mg/L). If the new photocatalytic oxidation of TiO₂ for leachate treatment process can achieve a lower operating cost, it would be cost effective to install the process. 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 costs between \$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 20 hours, the reactor volume would need to be on the order of 96,000 – 220,000 gallons. Currently a 22 lb bag of TiO₂ cost \$600. The batch reactor optimization was on the order of 13.3 g/L of TiO₂. Therefore the amount of TiO₂ needed would be on the order 4800 – 11,000 kg. Without factoring in the economies of scale, the total cost of photocatalyst is \$290,000 - \$662,000. Remember this is essentially a one-time cost because the catalyst is reusable.

Further estimates are needed regarding the reservoir size, UV lamps and pumps in order to establish a capital cost. Assuming that a reservoir is needed to treat the amount of leachate generated per day. The daily tank volume should be on the order of 300,000 gallons to account for the worst case scenario. Currently the UV lamp in the batch system produces 450 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 estimate.

Costs	42 MG/year	96 MG/year
TiO ₂ chemical costs (one time only)	\$289,630	\$662,010
2 x 0.2 MG tanks	\$30,000	
2 x 0.3 MG tanks		\$60,000
UV lamps/ballast/power supply	\$40,000	\$60,000
Pumps/blowers/plumbing/etc.	\$10,000	\$15,000
Total capital cost	\$369,630	\$797,010
Annualized (6%, 20 years)	\$32,232	\$69,500
O&M costs (est. 10% of capital)	\$36,963	\$79,701
Total annual costs	\$69,195	\$149,201
Cost per 1000 gallons	\$1.65	\$1.55

In the current development of the photocatalytic oxidation landfill leachate treatment process, the possible application for the industry is still being investigated at batch and pilot plant scale. The first pilot plants have been established by FAU to obtain feasibility data, such as the treatment efficiency, site area requirements for targeted volume, electrical energy consumption, process emissions and chemical costs. The next step is to collect field data from pilot scale treatment units to devise more reliable cost data.

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. 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 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.
- 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).

- Conduct experiments to investigate concentration dependence on COD removal efficiency.
- Successfully simulate the contents of real leachate and optimize the process for the simulated leachate at the expected level of the real leachate.
- Investigate the reuse of photocatalytic particles.
- Investigate the photoinhibitory effect of alkalinity and pH so as to determine the optimum values for maximum decomposition.
- Investigate the ecotoxicity of treated effluents and spent catalysts.
- Instead of using KHP, phenol, or isobutanol for the model COD compound, something that is not as photosensitive should be tested to see if the photocatalyst can perform against truly recalcitrant model compounds. In other references, *p*-cresol has been used, but a set of standard humic acids would also be helpful in investigating COD and color removal simultaneously.
- In addition to COD, optimization studies should be conducted on ammonia, BOD₅, color, 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.
- In this study, the effects of color were investigated by pre-treating with lime, but the pH of the solution after lime addition was not adjusted and should be reduced (pH<8) to see if this may aid the COD removal process, based on pH effects studied here.
- Lifetime of the photocatalyst has not been determined. It is critical to develop methods to capture the photocatalyst after batch processing for reuse in the next batch. Furthermore, the number of times the photocatalyst can be reused before it is fouled, denatured, or otherwise in need of replacement must be determined.
- Future pilot tests are needed to be performed in order to address the question of the hereto unanswered concentration dependence. Because the composition of landfill leachate is expected to vary with time, and from site to site. Additional field tests are necessary to interpret the concentration dependence on COD efficiency. Without these tests, it is not possible at this time to develop cost estimates, process footprint, pre-treatment requirements, and operation and maintenance issues.

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