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**INVESTIGATION OF ENERGIZED OPTIONS FOR LEACHATE  
MANAGEMENT:  
Year Two Tests of Advanced Oxidation Processes  
for Treatment of Landfill Leachate**

January 2008

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## LIST OF ABBREVIATIONS AND NOTATIONS

AOP: *Advanced Oxidation Process*

BDL: *Below Detection Limits*

BOD<sub>5</sub>: *Biological Oxygen Demand in g/L*

COD: *Chemical Oxygen Demand in g/L*

EP: *Energized Process*

FDEP: *Florida Department of Environmental protection*

HRT: *Hydraulic Retention Time*

IMA: *Iron Mediated Aeration*

KHP: *Potassium Hydrogen Phthalate or Potassium Acid Phthalate*

MSW: *Municipal Solid Waste*

PIMA: *Photochemical Iron-Mediated Aeration*

SC: *Specific Conductivity in S/m*

TDS: *Total Dissolved Solids in g/L*

TSS: *Total Suspended Solids in g/L*

USEPA: *United State Environmental Protection Agency*

VOCs: *Volatile Organic Compounds*

## **FINAL REPORT**

August 2006 – February 2008

**PROJECT TITLE:** Photochemical iron-mediated aeration treatment of landfill leachate

**PRINCIPAL INVESTIGATOR(S):** Dr. Daniel Meeroff and Dr. C.T. Tsai

**AFFILIATION:** Florida Atlantic University

**COMPLETION DATE:** February 2008      **PHONE NUMBER:** (561) 297-2658

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

### **ABSTRACT**

Municipal landfill leachate is a high strength wastewater containing high levels of COD, TDS, ammonia and eventually high BOD<sub>5</sub> and other toxics. Treatment of leachate is becoming more of an issue as regulations tighten and wastewater treatment plants reduce their acceptance of leachate. Several treatment techniques are currently available. The first objective is to establish an outline of these techniques and rank the alternatives according to efficiency, cost and environmental sustainability. This list should not be limited to current practice. Relatively uncommon approaches, i.e. advanced oxidation processes and energized processes seem to show the most promising results in the literature. Thus photochemical iron-mediated aeration (an energized process) will also be tested, first on simulated leachate and then on real leachate from the Solid Waste Authority of Palm Beach County. A laboratory scale Photochemical Iron Mediated Aeration (PIMA) reactor was designed and tested for five components (COD, BOD<sub>5</sub>, ammonia, TDS and conductivity). Results are encouraging but are expected to be improved during subsequent testing with real leachate.

## **EXECUTIVE SUMMARY**

August 2006 – February 2008

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**PRINCIPAL INVESTIGATOR(S):** Dr. Daniel Meeroff and Dr. C.T. Tsai

**AFFILIATION:** Florida Atlantic University

**COMPLETION DATE:** February 2008

This report describes the results of the first year of a proposed two-year study of energized options for leachate management.

### **OBJECTIVES**

The objective of the proposed two-year study was to develop two new energized processes for leachate treatment and assess their sustainability (performance, risk, and cost) comparatively to the currently available treatment alternatives. Specifically, objective one was to examine the literature on energized alternatives for detoxification and treatment of leachate; collect leachate quality data; identify issues/trends associated with long-term leachate management; and prepare a list of energized alternatives ranked according to environmental sustainability, efficiency, risk, and economic factors. During this first year, leachate has been characterized, treatment techniques are under study. Objective two of the proposed study was to design and test laboratory reactors for leachate treatment using energized options such as the photochemical iron-mediated aeration technology (PIMA) and TiO<sub>2</sub>-magnetite photocatalytic processes. During the first year of this project, only the PIMA process has been investigated. Objective 3 was to prepare preliminary cost analyses and risk assessments on selected technologies to provide a Florida-specific matrix of engineering alternatives that are innovative, economical, and environmentally sound to aid solid waste management personnel in decision-making.

### **RATIONALE**

Municipal landfill leachate is a high strength wastewater characterized by high concentrations of recalcitrant organic compounds, ammonia and, metals. As such, leachate is difficult to treat biologically or chemically. Additionally, because of widely varying practices in solid waste management across the state of Florida, an understanding of emerging issues and an inclusive solution to long-term management of landfill leachate is currently not available. Currently, leachate is mainly discharge to the sewer system. But stricter regulations and more and more reluctant wastewater treatment plant are forcing to find other solutions. This research will address these needs and produce a valuable decision-making tool for solid waste managers. The research will also generate performance data to develop unit treatment costs for scale-

up and address current barriers to the use of futuristic technologies for reducing toxic loads in water, wastewater, and soils in addition to leachate.

## **METHODS**

This study was divided into four distinct but overlapping tasks. The first task was to establish the list of the existing technologies and examine their respective efficiencies and costs. During this process, leachate was also characterized in quality as well as in quantity. Resources such as the FAU S.E. Wimberley Library services (Electronic databases such as FirstSearch or WorldCat and Electronic journals), Internet (reliable sources such as government or universities web sites: [www.epa.gov](http://www.epa.gov), [www.dep.state.fl.us](http://www.dep.state.fl.us)), record review at the FDEP of Palm Beach were used. Also, the Technical Advisory Group was very helpful to specifically center this task on Florida.

Task two was dedicated to the design of the PIMA and TiO<sub>2</sub>-magnetite photocatalysis reactors. The Photochemical Iron-Mediated Aeration process reactor design is based on the development made by Meeroff et al. (2006). The TiO<sub>2</sub>-magnetite photocatalysis reactor is under development at this time.

The testing of the process was executed in task three. Components tested are: ammonia, BOD<sub>5</sub>, COD, dissolved solids, conductivity and heavy metals. This step was divided into three subtasks. In the first one, the influent leachate was made up using a solution of a unique component. In the second subtask, the influent was a made up mixture of these components. And finally, the processes were tested on real leachate, collected from the Solid Waste Authority of Palm Beach County. At this time, lead is the only component that has not been studied on the first subtask of the PIMA process.

The final task was to compare the PIMA and TiO<sub>2</sub>-magnetite catalysis processes with other viable technologies. During the development of the process, the most efficient parameters will be found. Based on these pilot scale reactors and results from real leachate, a capital and an operational and maintenance cost will be estimated for the two processes. A ranking of the technologies will be established as a function of removal efficiency, cost per gallon of treated leachate and environmental risk. This task is currently not started.

## **CONCLUSIONS**

Based on the literature review conducted, it appears that many different options are available to treat leachate. These options are municipal sewer discharge without pretreatment, natural evaporation pond, deep well injection, hauling off-site, leachate recirculation or bioreactor, on-site treatment which can be biological processes such as activated sludge systems, waste equalization ponds, aerated lagoons, trickling filters, rotating biological contactors, or anaerobic digesters or physical and chemical processes such as coagulation, flocculation, precipitation and sedimentation, carbon adsorption, ion exchange, air stripping, filtration. Of these alternatives, none is

showing good treatment efficiency without producing more dangerous residuals. Another area of treatment method is the advanced oxidation processes and energized processes. Such processes are hydrogen peroxide, Fenton ( $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ), ozone, ozone and hydrogen peroxide, ultraviolet light, Photo-Fenton / Fenton-like systems, ultraviolet light and hydrogen peroxide, ultraviolet light and ozone, ultraviolet light, ozone and hydrogen peroxide, photocatalytic oxidation such as the Iron-Mediated Aeration (IMA), the PIMA and the UV/ $\text{TiO}_2$  catalysis. This second category seems to achieve a better treatment while producing less harmful residuals. The literature review also permitted to establish the composition of a typical leachate. The main parameters are ammonia,  $\text{BOD}_5$ , COD, conductivity, TDS and heavy metals.

At this time, scoping tests concerning ammonia,  $\text{BOD}_5$ , COD, conductivity and TDS have been performed using the PIMA process. The results obtained conform to the expectations. Ammonia is not removed by the air stripping because of the acidic pH. Concerning conductivity and TDS, the removal is counter balanced by the dissolution of iron in solution. But concerning COD and  $\text{BOD}_5$ , the PIMA process showed better removal results than the IMA and UV control processes. But these results are expected to improve when using real leachate.

# 1. INTRODUCTION AND LITERATURE REVIEW

## 1.1 MUNICIPAL SOLID WASTE MANAGEMENT

### 1.1.1 Generation and disposal

Signed the 21st of October 1976, the Resource Conservation and Recovery Act (RCRA) defines solid waste as: “Any garbage, or refuse, sludge from a wastewater treatment plant, water supply treatment plant, or air pollution control facility and other discarded material, including solid, liquid, semi-solid, or contained gaseous material resulting from industrial, commercial, mining, and agricultural operations, and from community activities.” Municipal solid waste (MSW) is comprised of household waste, commercial solid waste, non hazardous sludge, conditionally exempt small quantity hazardous waste (such as alkaline batteries), and industrial solid waste. Basic rules of hygiene and public health protection require that this waste be collected and properly disposed of. After collection, not all wastes are handled in the same manner. A recent trend is to recycle and compost as much as possible, but for materials that are not recycled and those for which recycling are not possible, combustion (incineration) or landfilling is the solution.

In 2003, according to the USEPA, 236 million tons of municipal solid waste was generated in the United States. Figure 1 presents the distribution of these  $236 \times 10^6$  tons. It is important to know the waste composition to have a better understanding of the composition of the leachate that is generated from this material (this will be discussed in detail later).

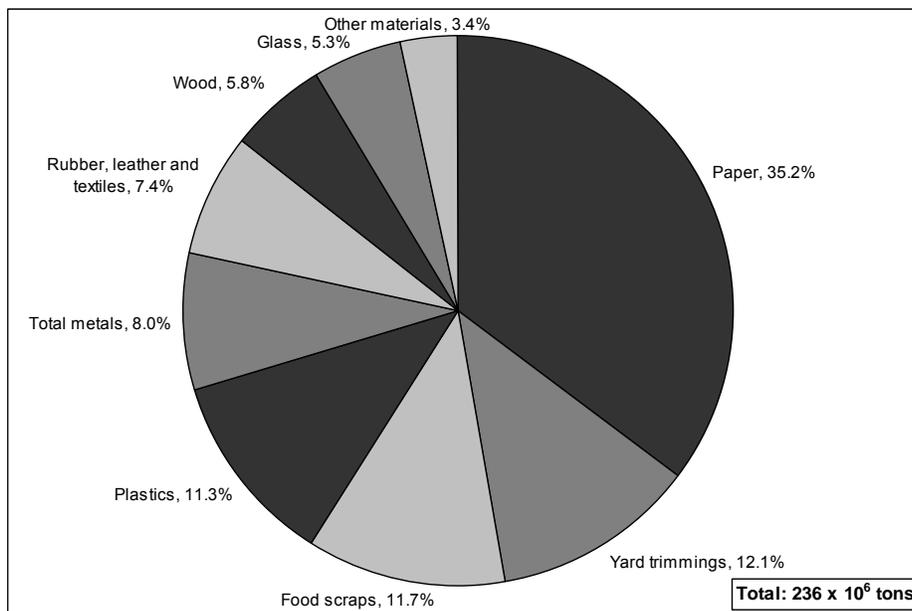


Figure 1. Municipal solid waste composition before recovery in 2003 (USEPA 2005)

Figure 2 shows the evolution of municipal solid waste generation since 1960. It clearly appears that a vast effort is underway to decrease the amount of waste disposed of in landfills. But this effort is hindered by the exponential growth of the US population and the increasing per capita generation rate. This rate was 2.68 lb/capita/day in 1960 and gained 66 percent to reach 4.45 lb/capita/day in 2002, the highest rate worldwide (Tchobanoglous and Kreith 2002).

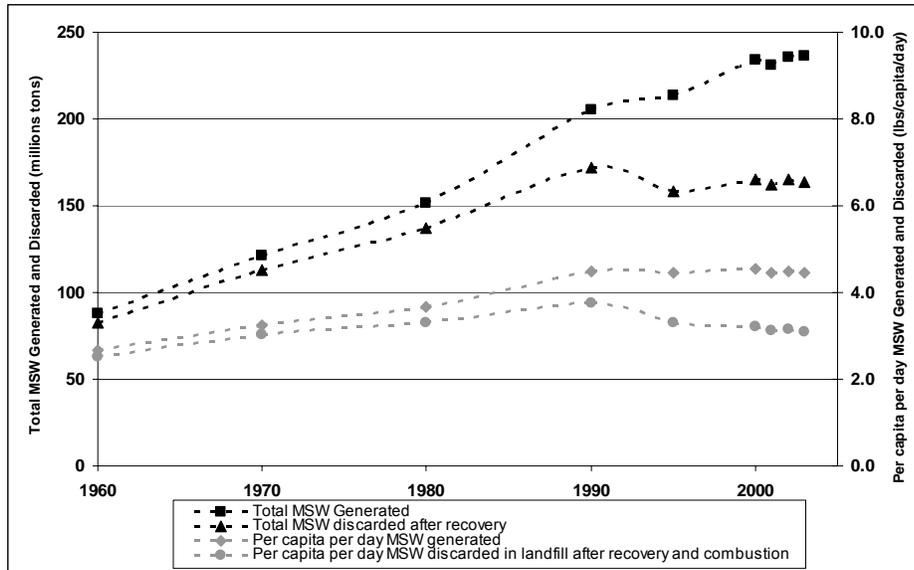


Figure 2. Municipal solid waste rates from 1960 to 2003 (USEPA 2005).

As for the State of Florida, the Florida Department of Environmental Protection (FDEP) reported that 25 million tons of MSW were generated statewide in 2000 (FDEP 2002). With a total population of approximately 16.5 million (and neglecting the tourist population), this number corresponds to a rate of 8.8 lb/capita/day.

In terms of municipal solid waste management, the priority is to reduce the amount of waste landfilled or more generally to reduce the amount of waste generated. To do so, waste should be managed in the following order of preference:

1. Source reduction
2. Reuse
3. Recycling and composting
4. Energy recovery
5. Treatment
6. Containment
7. Disposal in landfills

Besides waste reduction at the source, recycling, combustion, and landfilling are the conventional solid waste management solutions. Incineration is one of the most

popular alternatives for in Europe for example, but in the US, landfilling is the most common option. In his book *American Alchemy – The History of Solid Waste Management in the United States* (2003), H. Lanier Hickman Jr. gives several explanations for this, such as the opposition of environmental groups and of the public in general, the non-interest of the USEPA, the end of tax credits, and the strict air emissions regulations. Even if incineration presents important advantages such as: considerable reduction in waste volume, production of energy and reduction of oil dependency, and production of ash used in the construction field, for instance, incineration is still underdeveloped in the US. In 2000, about 15 percent (3.8 million tons) of MSW was incinerated, 27 percent (7.0 million tons) was recycled, and 58 percent (14.9 million tons) was disposed of in landfills in the State of Florida (FDEP 2002). The goal of recycling 30 percent of the MSW generated before 1994 has not been achieved, and landfills are still the most common method of final waste disposal.

### 1.1.2 Landfills

A landfill is a method of solid waste disposal in which refuse is buried or accumulated between layers of soil. Divided into cells, they are carefully designed structures built into or on top of the ground in which waste is isolated from the surrounding environment by a barrier system. Three construction methods are typically utilized:

1. **Excavated cell/trench method.** Soil is excavated and used as daily and final cover. Wastes are placed in the trench or cell and when they are full, a new cell is constructed.
2. **Area method.** Where the terrain is not suitable for excavation (ground water table very high like in many parts of coastal Florida), the soil is not excavated and waste is piled above the ground on top of a soil liner. The waste is piled to a prescribed height, and when that level is reached, a new cell is constructed.
3. **Canyon/depression method.** For this method, canyons, ravines, dry pits, and quarries are filled with wastes.

Figure 3 is an illustration of the cross-section of a typical sanitary landfill.

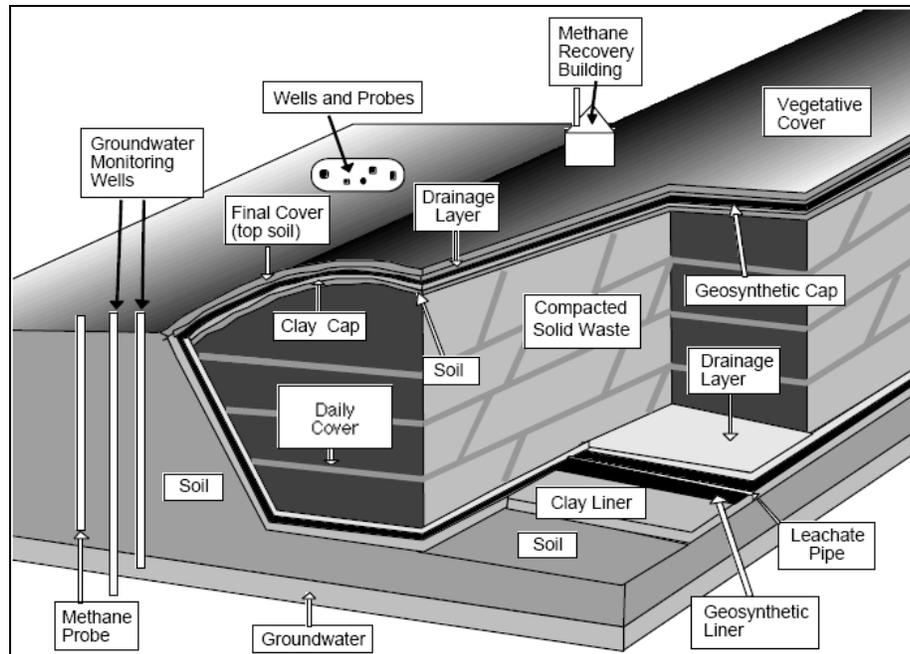


Figure 3. Schematic of a Typical MSW Landfill (O'Leary and P. Walsh 1995).

Federal and state regulations govern where a modern sanitary landfill can be sited and how it should be constructed and operated to protect human health and the environment. Sanitary landfills are required to be constructed with a number of safeguards, including liners, leachate collection systems, odor control systems, gas monitoring equipment, as well as methane recovery systems, ground water monitoring systems, and other equipment depending on the type of waste being managed. For instance, the FDEP began requiring liners for Class I and II landfills (the classification of landfills is given in the next paragraph) in 1985. Today, Rule 3 of Section 62-701.400 - Landfill Construction Requirements of the Florida Administrative Code, requires that sanitary landfills shall be constructed with composite or double liners and a leachate collection and removal system without distinguishing the class of the landfill. Nevertheless, the FDEP shall exempt Class III landfills from some or all of the requirements for liners, leachate controls, and water quality monitoring if the applicant demonstrates that no significant threat to the environment will result from the exemption based upon the types of waste received, methods for controlling the types of waste disposed of, and the results of mandated hydrogeological and geotechnical investigations.

Once a landfill reaches its permitted capacity, it may be expanded if a new permit can be obtained or it is closed and capped. Closed landfills are then monitored to be sure that the aging process and long term performance are managed properly. Research is ongoing in this field to better define the necessary timeframe of long term monitoring (in years). Even after closure, contamination of soil and ground water is still a potential issue. When no potential hazard is detectable from ground water monitoring programs, a sanitary landfill can eventually become a new resource for the community (i.e. golf courses or recreation parks).

The USEPA classifies landfills into two different types according to the kind of wastes they contain:

1. **Solid Waste Landfills:** These include municipal solid waste, industrial waste, construction and demolition (C&D) debris, and bioreactors. Typically, MSW consists of food and garden wastes, paper products, plastics and rubber, textiles, wood, ash (in the case of a co-disposal landfill), and the soils used as daily cover material.
2. **Hazardous Waste Land Disposal Units:** These include surface impoundments, waste piles, injection wells, and other geologic repositories specifically designed to handle hazardous materials that are corrosive, reactive, toxic, or flammable.

Rule 62-701.340(3) of the Florida Administrative Code adds another classification of MSW landfills (FDEP 2002):

1. **Class I landfills**, which receive an average of 20 tons or more of solid waste (non-hazardous household, commercial, industrial and agricultural wastes) per day.
2. **Class II landfills**, which receive an average of less than 20 tons of solid waste (non-hazardous household, commercial, industrial and agricultural wastes) per day.
3. **Class III landfills**, which receive only wastes designated as Class III. They contain only yard trash, construction and demolition debris, processed tires, asbestos, carpet, cardboard, paper, glass, plastic, furniture other than appliances, or other materials approved by the FDEP, which are not expected to produce leachate but pose a threat to public health or to the environment. These wastes do not contain putrescible household solid waste.
4. **Ash monofills**, which receive exclusively ash from waste-to-energy facilities.

In 2002, the State of Florida had 60 Class I landfills, no Class II landfills, 34 Class III landfills, and 11 ash monofills.

For all types of sanitary landfills, complying with the regulations, whether designing a new unit or monitoring an old facility requires several equally important steps. The *Decision Maker's Guide to Solid Waste Management – Vol. II* (O'Leary et al. 1995) reports a set of nine critical steps for proper management of solid waste:

1. Establish a leachate management plan
2. Institute a groundwater monitoring program
3. Set up a gas management plan

4. Prepare landfill final cover specifications
5. Obtain closure plan approval
6. Establish financial assurance for closure and post-closure care
7. Operate and construct the landfill
8. Close the landfill
9. Provide long term post-closure care

Regulations are regularly updated according to new science, which enhances our understanding of the long term impacts of solid waste management and the introduction of new technologies, which allow greater control of long term management.

## 1.2 LEACHATE

### 1.2.1 Definitions

Leachate is the liquid that percolates through the landfill and is captured by the leachate collection system in the case of modern sanitary landfills or directly transmitted to the ground beneath the bottom of a landfill in the case of older landfills and dumps. Even if no distinction is made in this document, according to O'Leary et al. (1995), leachate can be divided into two different types:

1. **Primary leachate**, which is part of the liquid content of the waste placed in the landfill that percolates through the waste by the force of gravity.
2. **Secondary leachate**, which is formed when water from precipitation percolates through the landfill and becomes contaminated via contact with the waste component of the landfill's contents. This type of leachate occurs only when the landfill is in operation and only for those portions of the landfill that are not capped.

These definitions omit a third type of leachate production, referring to the metabolic water created by the aerobic and anaerobic degradation of waste materials over the active life of the landfill. Figure 4 presents a simplified water budget of a sanitary landfill before and after closure.

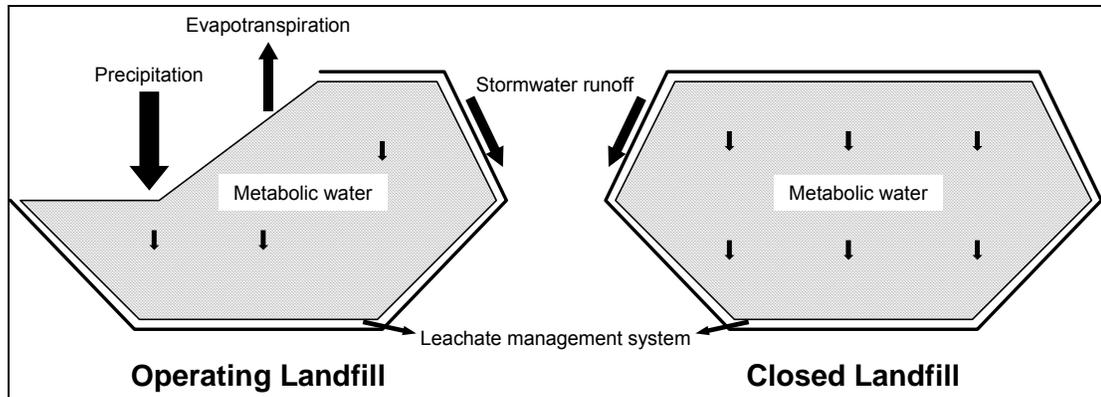


Figure 4. Landfill water balance (adapted from Reinhart and Townsend 1998)

Regardless of the source of the water, the liquid extracts particles and dissolves contaminants from the waste. Due to simultaneous and interrelated physical, chemical and microbial reactions in the decomposing MSW layers, the leachate will contain dissolved and suspended materials (organic or inorganic compounds, such as heavy metals, ammonia, dissolved and suspended solids, COD and BOD, etc). More details of the composition of leachate will be described later.

The volume of leachate generated is directly linked to the type of landfill construction (degree of compaction), its age (degree of decomposition), size (physical area), waste composition (type of waste disposed), and climatic conditions (rainfall, humidity, temperature, evaporation, evapotranspiration) (Lema et al. 1988, Méndez-Novelo et al. 2005). For example, a large operating landfill site will produce a greater amount of leachate than a small closed site. The South Dade landfill in Miami-Dade County, with a current area of 142 acres (of which 46 acres are closed, 46 acres are at final elevation and are undergoing closure, and 50 acres are actively receiving solid waste), generates up to 1.0 million gallons per day (MGD) of leachate during extraordinary rain events. More typically, during the dry season, the average flow is approximately 25,000 gpd with a range of 0 to 40,000 gpd; whereas during the wet season, the average flow is approximately 150,000 gpd per day with a range of 75,000 to 320,000 gpd. The Class I landfill of the Solid Waste Authority of Palm Beach County has a surface area of approximately 2260 acres. During the period from October 2004 to August 2005, the average volume of leachate produce per day was 214,500 gallons. It varied from 130,900 gpd in December 2004, up to 323,000 gpd in July 2005. However, for the period from October 2006 to April 2007, the average volume of leachate produced per day was only 179,500 gallons with a variation from 89,500 gpd in January 2007, up to 244,300 gpd in October 2006. A landfill in Brazil (Gramacho Municipal Landfill in Duque de Caxias, a city in the Rio de Janeiro state) located in a tropical climate region similar to South Florida reportedly produces 800 m<sup>3</sup> (210,000 gallons) of leachate per day (Bila et al. 2005). As a result, leachate quantity is difficult to predict, and volumes are highly variable (Méndez-Novelo et al. 2005).

Leachate generation data is generally not routinely recorded (Winthelser

1998); therefore, quantity data are extremely difficult to collect. As a result, leachate quantity is difficult to predict. The major issue with leachate management is the contamination of both ground water and eventually surface water (contamination of surface water is less likely to occur because the main flow direction of leachate is vertical and South Florida has very little elevation difference). With new landfills, risks of contamination are limited by multiple engineered liners (clay and/or geosynthetic liners are commonly used). But historically, most landfills (or open dumps) were built without liners or leachate collection systems, and leachate still continues to be discharged directly into the ground from those older facilities.

The liner system is an important part of the leachate collection system. The role of the collection system is to collect and remove the leachate from the base of the landfill. It should also prevent the contamination of the surrounding environment. Figure 5 is a cross section of a typical leachate collection system. Holding and treatment facilities are also an important part of the leachate collection system. Great care must be taken to connect these elements to an enclosed system to prevent any seepage from contaminating the ground water or soil beneath the liner.

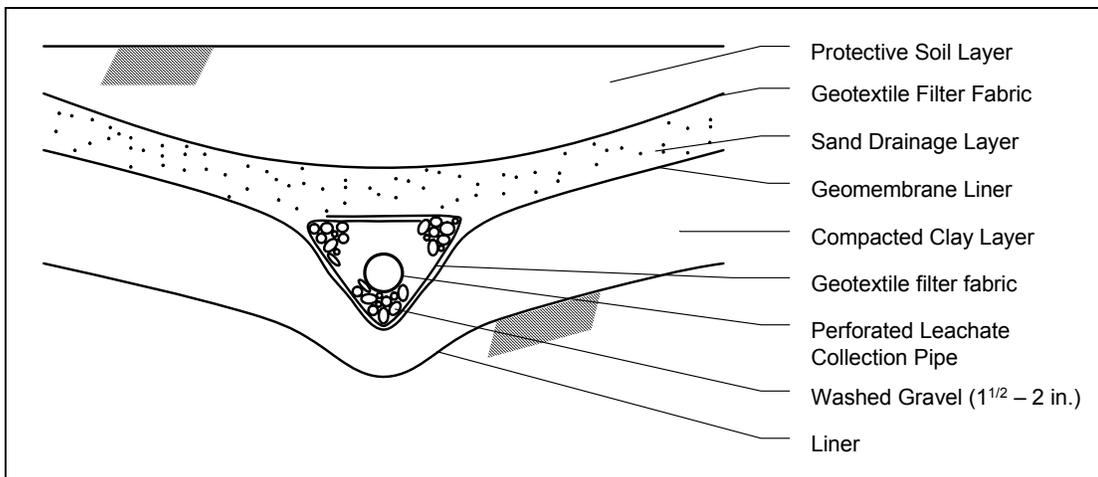


Figure 5. Typical leachate collection pipe (adapted from Tchobanoglous and Kreith 2002).

If leachate reaches a water body, impacts can range from rapid oxygen depletion, changes in the fauna and flora, and aquifer or soil strata contamination with potential migration of the pollutant plume offsite (Bruner et al. 2002). A portion of the contaminants may remain in the soils because of their physical-chemical properties. Eventually, leachate leaks can also be responsible for the generation of landfill gas outside of the perimeter of the landfill (Robinson et al. 1992). Clearly, leachate management is dependent upon the nature and concentration of specific constituents.

### 1.2.2 Typical leachate composition

While in operation, a landfill is constructed during several decades in a series of

cells. Consequently, it contains wastes of completely different ages and different stages of decomposition. Landfill maturity can be classified into different phases. Pohland and Harper (1986) divided the life cycle of a landfill into five successive stages:

- I. **Initial adjustment phase.** During this phase, which takes place just after the placement of the refuse in the landfill, the aerobic biodegradation of organic compounds occurs. The daily soil cover is the main provider of the organisms responsible for this decomposition.
- II. **Transition phase.** The air trapped inside the landfill is depleted and anaerobic conditions develop rapidly. If leachate is produced, the pH decreases due to the production of organic acids and  $\text{CO}_2$  within the decomposing waste, as a result of anaerobic microbial activity.
- III. **Acid phase.** This phase is the continuation of the previous transition phase along with the production of organic acids. As a result, the pH is rapidly reduced,  $\text{H}_2$  gas is generated, and both biochemical and chemical oxygen demand (BOD and COD) increase during this phase. The low pH also dissolves inorganic constituents such as metals, which increases the conductivity and total dissolved solids (TDS).
- IV. **Methane fermentation phase.** During this phase, certain microorganisms convert the organic acids into  $\text{CH}_4$  and  $\text{CO}_2$ . As the organic acids are consumed, the pH rises to a more neutral value, and BOD, COD, conductivity, and metals content decreases.
- V. **Maturation phase.** This phase begins when all the available biodegradable materials have been converted into  $\text{CH}_4$  and  $\text{CO}_2$ . The leachate produced is weaker in terms of contaminant concentrations, and the  $\text{BOD}_5/\text{COD}$  ratio is very low.

Figure 6 shows the typical composition of leachate according to the different phases. The duration of the phases described above varies because of the construction process of the landfill. For example, a new cell can be placed on top of one which is already in the third phase. The resulting leachate will be a mixture of the characteristics of the two phases.

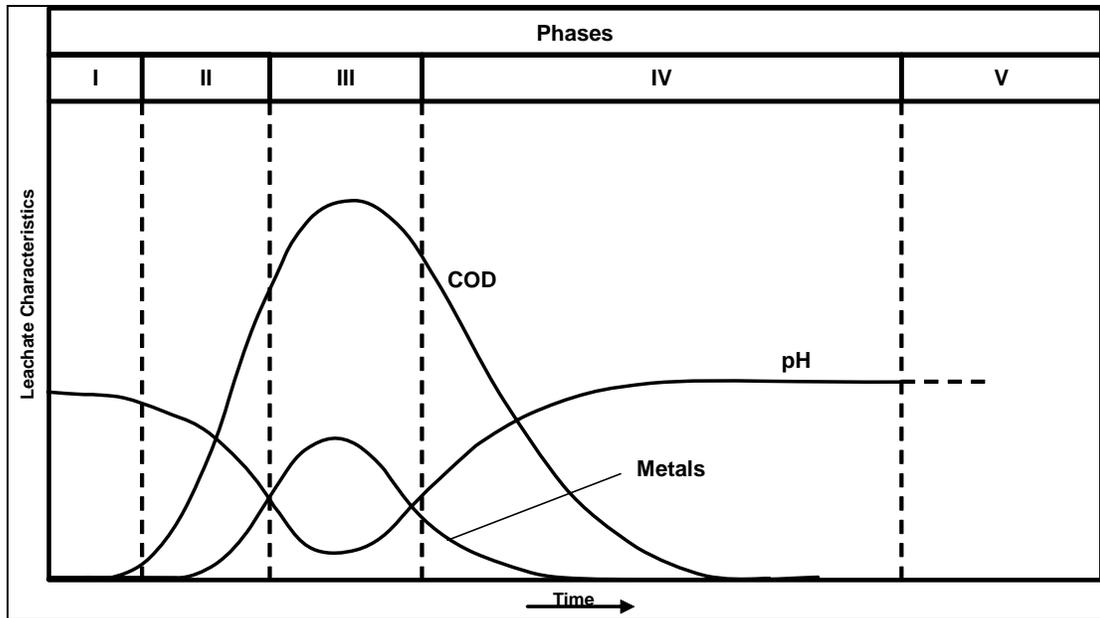


Figure 6. Role of phases in the leachate composition (adapted from Tchobanoglous and Kreith 2002)

Basically landfill leachate is a high strength wastewater characterized by high levels of organic constituents and ammonia. This waste stream also potentially contains toxic contaminants such as arsenic or lead. A typical young leachate may have COD levels that are 30-40 times higher than raw sewage, whereas mature leachate may be equal in COD to raw sewage but will typically contain much more recalcitrant organic constituents compared to domestic sewage. Untreated leachates can permeate into the ground water or mix with surface waters and contribute to the pollution of soil, ground water, and surface water. Additionally, leachate may be malodorous.

The composition of municipal landfill leachate exhibits noticeable temporal and site-specific variation in chemical and microbiological characteristics, attributable to a combination of factors including landfill age, type of waste, moisture availability, temperature, pH, depth of fill, and compaction (USEPA 1995; Viraraghavan and Singh 1997). As a result, reported concentrations of leachate contaminants range extensively, and often vary by several orders of magnitude. The internal biological and chemical transformations within landfills occurring as wastes decompose have a strong relationship with leachate characteristics.

Another classification has been proposed by Amokrane et al. (1997). They compared three types of landfills according their age and maturity. This classification is worth mentioning because they also specified the efficiency of different treatment techniques according the types of landfill in their study. Table 1 summarizes their findings.

**Table 1. Leachate classification, adapted from Amokrane et al. (1997)**

| <b>Characteristic</b>       | <b>Young Landfill</b> | <b>Medium Landfill</b> | <b>Old Landfill</b> |
|-----------------------------|-----------------------|------------------------|---------------------|
| Landfill age (years)        | < 5 yrs               | 5 – 10 yrs             | >10 yrs             |
| Landfill type               | Biodegradable         | Intermediate           | Stabilized          |
| pH                          | < 6.5                 | 6.5 – 7.5              | > 7.5               |
| COD (mg/L)                  | >10,000               | 5000 – 10,000          | < 5000              |
| BOD <sub>5</sub> /COD ratio | > 0.5                 | 0.1 – 0.5              | < 0.1               |

Several reviews have been conducted with the goal of collecting information regarding 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. 2003, 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). Basically, the available leachate quality data sets lead to the same conclusion: the composition of leachate is highly variable and site specific. Differences can be as high as several orders of magnitude. Typically, the most environmentally significant parameters of leachate quality are ammonia, BOD<sub>5</sub>, COD, TDS, and heavy metals concentration:

1. **Ammonia** (NH<sub>3</sub>) is a gas at standard temperature and pressure. It is mainly used to produce fertilizer and is generated during the anaerobic digestion of organic material. As it has a high solubility in water, ammonia gas readily transfers to leachate and forms soluble ionized ammonium (NH<sub>4</sub><sup>+</sup>). According to the USEPA (1986), levels of ammonia in the environment as low as 0.0017 mg/L are acutely toxic to freshwater fish. Ammonia-nitrogen in leachate may be present in concentrations up to 2000 mg/L (Englehardt et al. 2006). These ammonia levels, released from nitrogen-containing wastes mainly by decomposition of protein, may be lethal to microorganisms. And, ammonia concentrations may persist in the leachate with time, so that ammonia has been regarded as one of the most problematic constituents in leachate over the long term (Kjeldsen et al. 2002).
2. **Biochemical Oxygen Demand** (BOD<sub>5</sub>) is a test used to measure the concentration of biodegradable organic matter present in a sample of water. It is the amount of oxygen that would be consumed if all the biodegradable organics were oxidized by microorganisms.
3. **Chemical Oxygen Demand** (COD) is a test used to indirectly measure the amount of organic compounds (both recalcitrant and biodegradable). It is the amount of oxygen that would be consumed if all the organics were oxidized

by a strong chemical oxidant such as dichromate ( $\text{Cr}_2\text{O}_7^{2-}$ ). Specific organics such as phthalate esters, volatile aromatics, aromatic sulphonates, chlorinated volatile hydrocarbons, phenols, cresols, and numerous other organic pollutants have been identified in various concentrations in landfill leachate (Jimenez et al. 2002).

4. **Total Dissolved Solids** (TDS) are the total amount of charged ions, including minerals, salts, or metals dissolved in water. TDS is directly related to the purity of water and its electrical conductivity. Excess dissolved solids are objectionable in drinking water because of possible physiological effects, unpalatable mineral tastes, and higher costs because of corrosion or the necessity for additional treatment.
5. **Heavy metals** include some of the trace metals such as cobalt, copper, manganese, vanadium, or zinc, which are required as micronutrients to sustain microbial populations, but excessive levels can be detrimental. Other heavy metals such as mercury, lead, or cadmium have no known vital or beneficial effect on microorganisms, and their accumulation over time are biotoxic and can cause serious illness in human populations. Heavy metals can be a significant concern in leachate, although Kjeldsen et al. (2002) reported that metals in leachate were found at concentrations at or below drinking water standards due to adsorption, precipitation and complexation processes occurring in the landfill. For example, chemically treated wood makes up about 6% of the wood waste stream in Florida, and this fraction is projected to increase to 25-30% by 2020 due to disposal of aging structures (Englehardt et al. 2006). Ash from the combustion of a wood solid waste containing as little as 6% CCA treated wood will fail the toxicity characteristic leaching procedure test (TCLP) according to Hinkley (2003), indicating that ash monofill leachate contains copper, chromium, and arsenic (CCA), and this material will also generate arsenic-contaminated leachate. Another source of toxic metals is electronic waste, potentially contributing lead, nickel, cadmium, and others to the leachate.

Table 2 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 2. Extreme values for the composition of leachate**

| Parameters                                 | Concentration |               |               |        |
|--|---------------|---------------|---------------|--------|
|  | Lowest Value  | Highest Value | Average Value | Median |
| COD in mg/L as O <sub>2</sub>              | 0.4           | 152,000       | 10,300        | 4,200  |
| Conductivity in µS/cm                      | 5.2           | 95,000        | 13,100        | 8,600  |
| TDS in mg/L                                | 0.0           | 88,000        | 11,000        | 7,600  |
| BOD <sub>5</sub> in mg/L as O <sub>2</sub> | BDL*          | 80,800        | 4,000         | 190    |
| Ammonia in mg/L as NH <sub>3</sub> -N      | BDL*          | 8,750         | 830           | 750    |
| Lead in mg/L                               | BDL*          | 5.0           | 0.1           | 0.1    |
| TSS in mg/L                                | 10.0          | 45,000        | 840           | 950    |
| pH   | 2.0           | 11.3          | 7.5           | 7.5    |

\* BDL = Below Detection Limits

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 et 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).

For comparison purposes, Table 3 shows the concentrations of the same constituents in a typical medium-strength untreated domestic wastewater and average concentrations of leachate.

**Table 3. Comparison of the composition of untreated domestic wastewater and leachate (Adapted from Metcalf and Eddy 2003)**

| Parameters                                 | Concentration   |               |
|--|-----------------|---------------|
|  | Wastewater      | Leachate      |
|  | Medium strength | Average Value |
| COD in mg/L as O <sub>2</sub>              | 430             | 10,300        |
| Conductivity in µS/cm                      | n/a             | 13,100        |
| TDS in mg/L                                | 500             | 11,000        |
| Ammonia in mg/L as NH <sub>3</sub> -N      | 25              | 830           |
| BOD <sub>5</sub> in mg/L as O <sub>2</sub> | 190             | 4,000         |
| Lead in mg/L                               | n/a             | 0.1           |
| TSS in mg/L                                | 210             | 840           |
| pH   | n/a             | 7.5           |

It is clear that leachate is a highly concentrated waste stream. In general, leachates contain the same constituents at 1-2 orders of magnitude higher than medium strength domestic wastewater. The average TDS and TSS concentrations in

leachate are respectively 22 and 4 times larger than medium strength wastewater, ammonia is 33 times more concentrated in leachate, and BOD<sub>5</sub> and COD are about 24 and 21 times larger in leachate than in the medium strength wastewater.

As this research will address leachate specifically from Florida, the literature review was particularly focused on collecting data from Florida landfills. Previous research conducted by Ward et al. (2002) and Statom et al. (2004) among others were considered. In addition, data have been collected from the Solid Waste Authority of Palm Beach County (leachate samples from 2004 to 2005). Also a record review was conducted with Andrell Maxie at the FDEP Regional Office in West Palm Beach, FL. Several reports were made available to FAU to extract laboratory results of leachate composition from landfills in St. Lucie, Okeechobee, Broward, and Miami-Dade counties. The complete table can be found in APPENDIX A, and Table 4 below contains a summary of this analysis.

**Table 4. Typical composition of leachate in Florida landfills**

| Parameters                            | Concentrations |         |
|---------------------------------------|----------------|---------|
|                                       | Range          | Average |
| COD in mg/L as O <sub>2</sub>         | 55 - 14,000    | 3,000   |
| Conductivity in μS/cm                 | 1,000 - 95,000 | 11,600  |
| TDS in mg/L                           | 900 - 88,000   | 9,300   |
| BOD <sub>5</sub> in mg/L              | BDL - 445      | 150     |
| Ammonia in mg/L as NH <sub>3</sub> -N | BDL - 1,350    | 500     |
| Lead in mg/L                          | BDL - 0.1      | 0.03    |
| TSS in mg/L                           | *              | *       |
| pH                                    | 2.0 - 11.3     | 7.5     |

\* No data were available.

All of the data collected emphasize the site specificity and the wide variability of leachate composition already outlined. This simple comparison demonstrates the obvious necessity of leachate treatment, when compared to raw sewage. It is clear that long term management of leachate will require treatment prior to discharge back to the environment. However due to the elevated concentrations of certain constituents, the efficiency of the currently available treatment processes may not be sufficient to achieve the regulated (or target) effluent quality. The variability in both quality and quantity and the continual generation of leachate over a long period of time are the main issues in determining an effective management approach that includes adequate treatment.

The next paragraph will present a review of the existing treatment processes for management of leachate. A brief description is followed by performance data on efficiency, as well as advantages and disadvantages are presented.

## 1.3 TREATMENT OPTIONS

This section will present a review of the existing treatment processes currently employed for management of leachate. A brief description is followed by performance data on process efficiency, as well as advantages and disadvantages in terms of applicability to long term management of leachate.

### 1.3.1 Municipal sewer discharge without pretreatment

The most common option for leachate treatment is discharge directly to municipal sewer systems, such as in Miami-Dade County. However, this option has major issues. Boyle and Ham (1974), stated that high strength leachate with COD exceeding 10,000 mg/L can be treated at a level of 5 percent by volume without seriously impairing the treatment process or the effluent quality of an activated sludge municipal wastewater treatment plant (cited by Qasim and Chiang 1994 and Lema et al. 1988).

Beyond the 5 percent level, leachate addition results in substantial solids production (from increased waste activated sludge), increased oxygen uptake rates, and poorer settling of biomass. Leachate should be diluted prior to discharge and the detention time in the activated sludge process train must be increased for leachates. It is also suggested that the presence of heavy metals, ammonia, other toxins, and extremely high organic loading in leachate may cause severe upsets in the biological treatment systems due to biotoxicity. Cited by Qasim and Chiang (1994), Chian and DeWalle (1977) are also reported to have found that leachate greater than 5 percent by volume reduced the treatment plant efficiency. But, Raina and Mavinic (1985) have successfully treated laboratory-scale combinations of 20 to 40 percent leachate by volume with municipal wastewater in aerobic batch (fill and draw) reactors with sludge residence times of 5, 10, and 20 days.

Zachopoulos et al. (1990) studied co-disposal of leachate in Publicly Owned Treatment Works (POTWs) and concluded that leachate can be treated without any adverse effect plant performance (no details on leachate composition or treatment conditions were reported). Pohland and Harper (1985) also reported success treating combined leachate in conventional wastewater treatment plants. In their investigation, BOD<sub>5</sub> and COD removal efficiency (over 90 percent) and complete nitrification (over 80 percent) was obtained with 10-day sludge residence times.

The literature reports many uncertainties about treatment efficiency and volume percentage. Although BOD<sub>5</sub>, COD, and also heavy metals removal have been demonstrated, the results are highly variable and not reproducible. A case-by-case is needed in order to determine the most cost effective and efficient treatment. Poorly clarified effluent, sludge bulking, corrosion of plant equipment and increases in effluent COD are potential operational issues at conventional domestic wastewater treatment facilities that accept landfill leachate. Co-treatment of domestic sewage

with landfill leachate is certainly feasible although careful operation is required and the approach may be problematic for small treatment plants.

### **1.3.2 Evaporation**

Natural pond systems are used to concentrate the constituents of the leachate, while reducing the liquid volume through evaporation. The process occurs in lined impervious basins and is highly dependent on climate conditions conducive to promoting rapid evaporation. Temperature, precipitation, wind, and humidity will affect the rate of evaporation. If these conditions are optimal, the process may be a viable solution for separating the water from the leachate contaminants, but it presents several inconveniences. First, the residues have to be properly disposed of afterwards and secondly, natural evaporation ponds can not be easily applied in Florida due to the tropical weather. Ultimately, the leachate pollutants are in higher concentration (Di Palma et al. 2002) or in a solid form, but they are not treated: post treatment is required. Evaporation can also be executed in a reactor, but similar problems would be encountered. Nevertheless, in laboratory testing, distillates containing 99 percent less COD and 85 percent less ammonia, along with complete removal of heavy metals can be achieved (Di Palma et al. 2002). In return, the concentrations of the same constituents were much higher in the residue. For instance, COD and Pb were 4 times higher in the evaporation residue than in the initial leachate. Little information is found in the literature on leachate evaporation assisted by using heat from landfill-generated methane burners. Historically in Florida, leachate evaporation has not been widely implemented due to operational problems related to gas collection, odor, and process operation and maintenance (Reinhart 2005).

### **1.3.3 Deep well injection**

Underground Injection Control (UIC) is an inexpensive and popular way (Saripalli et al. 2000) to rapidly dispose of a waste stream without treatment and without further surface and human contact, if the appropriate geology is present. No treatment is generally performed on leachate disposed of in this manner, and the pollution problem is not truly addressed. Constituents of leachate are transferred to the host soil formation and diluted in the surrounding ground water. This may become an issue if this receiving ground water reaches an aquifer used as a potential drinking water source. Surface water is equally at risk in the case of a spill during the transport or delivery of the waste. Also, the same authors (Saripalli et al. 2000) demonstrated that the injection well performance is subject to a rapid decline if the TSS content is greater than 50 mg/L. This is very often the case for leachate. In the near future, this option may no longer be acceptable as the regulations are becoming more stringent with regards to securing permits. According to the Groundwater Protection Council (2005), in 2004, there were “approximately 190,000 injection wells in the United States that store or dispose of fluids in underground rock

formations, keeping the fluids away from underground sources of drinking water.” The number of active deep injection wells for industrial applications have already started to diminish: 819 deep well injection installations (including industrial, municipal and nuclear sectors) were counted in 1986 in the US, but only 485 were still in operation in 1991.

At the Solid Waste Authority of Palm Beach County, the leachate is generated from three landfills: 1) closed Class I, 2) operating Class I, and 3) operating Class III. All three leachates are mixed together and sent underground to the boulder zone, below all sources of drinking water (the Biscayne aquifer and the upper Floridian aquifer).

### **1.3.4 Hauling off-site**

Off-site hauling does not directly address the pollution problem either. The leachate is just moved to another location. The option presents a high transportation risk and is an expensive solution. 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 the leachate. After a phone conversation with the Solid Waste Division of Polk County, it appears that an experimental bioreactor landfill is currently being tested under the supervision of T. G. Townsend of the University of Florida, in order to reduce the amount of hauled leachate.

### **1.3.5 Leachate Recirculation: Bioreactor Landfills**

Leachate recirculation was pioneered in the 1970s. Since then, laboratory, pilot, and full scale studies have been conducted with the goal of converting the landfill into an aerobic bioreactor. Such leachate recirculation has the potential to decrease the stabilization time of landfill leachate from several decades to 2 –3 years, increase methane gas production rates, accelerate landfill settlement before final closure, partially treat the leachate, and reduce leachate volumes by evaporation or adsorption in refuse (Diamadopolous 1994; Reinhart and Al-Yousfi 1996). This innovative option consists of the re-injection of the collected leachate back into the landfill so that it percolates again through the waste. By recycling the leachate, the organic load may be reduced by the microorganisms present in the waste. Morris et al. (2003) reported that with the exception of ammonia, it was found that the concentrations of the BOD, heavy metals, chlorinated VOCs, and benzene, toluene, ethylbenzene, and total xylenes (BTEX) were reduced to below drinking water standards after 5 years of closure and following 7 years of leachate recirculation in a MSW landfill facility (located at the Central Solid Waste Management Center in Sandtown, Delaware). Conductivity was reduced from 12,000 to 8,400  $\mu\text{Sm}/\text{cm}^2$ , ammonia was reduced from 600 to 400 mg/L as N, and BOD was reduced by 99 percent from an initial value of 40,000 mg/L. Pohland et al. (1990) found that when leachate was continuously collected and reapplied to an experimental landfill column, the organic

loading decreased to a small fraction of its peak value (i.e. from 20,000 mg/L of COD to less than 1,000 mg/L) in a period of just over a year (cited by Qasim and Chiang 1994). This reduction in leachate strength and quantity has the advantage of lowering the cost of post-treatment. Leachate recirculation also presents the advantages of enhancing the gas generation and improving the rate of landfill stabilization by enhancing the biodegradation of the refuse; thereby; increasing the landfill life time and reducing the operating costs. Recycling leachate is one of the least expensive options (Lema et al. 1988). However, these advantages cannot hide the fact that recirculation system represents a substantial investment, and depending on the local requirements post-treatment of leachate may still be necessary if the recirculated leachate does not reach the allowable discharges limits (Lema et al. 1988, Winthelser 1998). Also as long as the bioreactor is in operation, the volume of leachate contained inside the landfill is not likely reduced as, some active cells are still open (not yet capped) and additional precipitation will percolate through those layers of refuse. Furthermore, leachate ponding and surface seeps have been operational challenges, and insufficient liquid availability limits applicability in dry areas. Most importantly, recirculation alone does not provide sufficient attenuation of leachate constituents to allow, in many cases, direct discharge of leachate to municipal wastewater treatment facilities within short recirculation times (Wintheiser 1998).

### **1.3.6 Spray Irrigation**

The irrigation of landfill leachate by spray or pipe flow systems onto grasslands, woodlands, or peat slopes has been employed in areas where high rainfall leads to the production of large volumes of dilute leachate and where there are appropriate lands suitable for irrigation. The practice has been regarded as an appropriate technology for dilute, high volume leachate, and for the polishing of pre-treated leachate. However, applicability is limited by the availability of large vegetated areas near the landfill, generation of aerosols and subsequent exposure of workers and others to hazardous constituents, and by other negative impacts such as leaf damage, premature leaf senescence, and plant attrition (Mensar et al. 1983; Ettala 1988; Wong and Leung 1989; Cureton et al. 1991; Gray et al. 2005). Furthermore, spray irrigation has limited capacity for the removal of recalcitrant organics, relying on a combination of physicochemical and biological processes to provide polishing of biodegradable organics, ammonia, and heavy metals (Maehlum 1995; Martin and Johnson 1995).

### **1.3.7 On-site treatment**

On-site systems used to attenuate constituent concentrations in leachate can be designed using many different unit processes. They are deployed as pretreatment steps prior to discharging the effluent to a wastewater treatment facility, or to the environment if it meets the permit requirements. On-site treatment systems can be separated into two categories: biological and physicochemical processes. Laboratory studies of biological and chemical leachate treatment processes have been reported

since the early 1970s (Boyle and Ham 1974; Ho et al. 1974), and some specific examples are reported in the following sections.

### 1.3.6.1 Biological processes

Biological processes are based on the action of a mixed culture of microorganisms in an aerobic or anaerobic environment. Treatment can be accomplished via activated sludge systems, waste equalization ponds, aerated lagoons, trickling filters, rotating biological contactors, or anaerobic digesters. These methods are equivalent to discharging to an off-site wastewater treatment plant and as a result have the same disadvantages, namely: 1) they do not address bio-toxic constituents, and 2) their efficiency is highly dependent on the effluent composition and strength. Since, landfill leachate has been demonstrated to have volumes and concentrations that are highly variable. Therefore, these processes may have a limited impact of leachate quality and should be considered as a first step of a more comprehensive process (for instance: the pretreatment of leachate prior to discharge into the sewer system). Aerobic processes transform the organic matter to CO<sub>2</sub> and biomass; anaerobic treatment processes mainly transform the organic matter to CO<sub>2</sub>, CH<sub>4</sub> and a minor part in biomass (Lema et al. 1988). Sludge production may be an issue as aerobic treatment produces appreciable amounts of biomass residuals resulting in a subsequent problem of disposal (residual presence of heavy metals) as well as odor generation.

Biological processes can be effective for young leachate with a high BOD<sub>5</sub>/COD ratio (Ehrig and Stegmann, 1992). Using acclimated sludge, Anagiotou et al. (1993) removed 97 percent of ammonia of 93 percent of BOD<sub>5</sub>, and 45 percent of COD in 14 days with initial concentrations of 920 mg N/L, 6765 mg/L, and 3300 mg/L, respectively. The removal percentage is considerable for ammonia and BOD<sub>5</sub>, but for recalcitrant COD, in particular, the removal is generally inadequate when relying solely on microbiological degradation. In practice, the required residence time will take up large amounts of available space, which is extremely valuable at a sanitary landfill site. Thus a large footprint would represent an effective loss of capacity for the landfill area of the facility. For example, if this technique was applied at the South Dade Landfill in Miami-Dade County, the aeration basins would have a volume of 280,000 ft<sup>3</sup> if designed to handle the average wet season flow. For the aeration basins alone this represents an area of 14,300 ft<sup>2</sup> (0.33 acre, resulting in a reduction of the effective available surface area for landfilling purposes by 0.23 percent) at a depth of 20 ft.

Lema et al. (1988) reported results using a variety of detention times, temperatures, and nutrient ratios. Processes are not always efficient, but more importantly, the major issue reported here is that the efficiency is not always reproducible. Leachate quality and quantity are too variable to maintain a constant and predictable effluent quality. Thus specific treatment conditions are necessary for each type of leachate (young or old, highly diluted or concentrated). Similar

conclusions can equally be drawn concerning anaerobic biological processes. Calli et al. (2005) used anaerobic reactors to treat young landfill leachate. With a detention time of 3 days, they achieved 90 percent removal of COD ( $C_o = 20,700$  mg/L). But excessive ammonia loading (greater than 3250 mg/L) can considerably reduce the performance of biological unit processes.

Even though, biological treatments (either aerobic or anaerobic) can be cost effective (Morais and Zamora 2005), due to the variation in composition of leachate, they may not be a very efficient method and may suffer from frequent drops in treatment performance (Fang et al. 2005). Therefore, alternative techniques are still the subject of ongoing research.

### 1.3.6.2 Physical and chemical processes

Since biological processes may not effectively treat leachate with a low BOD<sub>5</sub>/COD ratio or with high concentrations of toxic constituents, physical-chemical processes may be more useful in these cases. Physical and chemical processes utilize the addition of chemical or mechanical means to ensure treatment. They are often used with in conjunction with a biological process (Lema et al. 1988). Physical/chemical treatment processes are often required for treatment of mature and recalcitrant leachates. The common chemical processes include: coagulation-flocculation-precipitation (Amokrane et al. 1997; Tatsi et al. 2003), activated carbon adsorption (Copa and Meidl 1986), membrane filtration (Ushikoshi et al. 2002), and chemical oxidation (Ince 1998; Qureshi et al. 2002; Lopez et al. 2004) and are described in more detail below:

1. **Coagulation, flocculation, chemical precipitation and sedimentation.** They are fully developed processes used in the removal of substances capable of forming solid precipitates, such as soluble heavy metals, dissolved organics and colloidal particles suspended in the leachate. While they are independent mechanisms, they are interrelated and often used in conjunction of one another. More details will be given with the physical processes of flocculation and sedimentation, below.
2. **Carbon adsorption.** Activated carbon is used in water treatment due to its high adsorptive surface area. Using biologically pretreated leachate, Morawe et al. (1995) reported COD and BOD<sub>5</sub> removal of 91 and 65 percent, respectively. But their initial BOD<sub>5</sub> was very low ( $< 3.0$  mg/L) and their initial COD was on the order of 900 mg/L. Using granular activated carbon media, Abdel-Halim et al. (2003) reached an uptake of 89 percent on lead contained in industrial or synthetic wastewater. The initial lead concentration was 4.0 mg/L. This value is on the high range of the expected concentrations found in typical leachate. In a second experiment, the initial concentration was 10 mg/L and the removal efficiency was nearly the same at 86.4 percent. Other experiments conducted by Copa and Meidl (1986) demonstrated the

benefits of combining aerobic treatment with the granular activated carbon technology. With a detention time of 12 days, they achieved complete removal of BOD<sub>5</sub> ( $C_o = 30$  mg/L). They also achieved 77 percent removal of COD ( $C_o = 920$  mg/L), 98 percent removal of ammonia-nitrogen ( $C_o = 210$  mg N/L), and 46 percent removal of suspended solids (210 mg/L). In a second step, they implemented their treatment process with sand filters and a second polishing stage of granular activated carbon treatment. This modification increased the removal of COD and suspended solids to 90 and 99 percent, respectively. The activated carbon technology is a particularly efficient technique for removing non-biodegradable compounds. Also, low molecular weight compounds are preferentially adsorbed (Morawe et al. 1995). But this is considered to be an expensive solution due to the necessity of frequent media regeneration in a column reactor or the cost of the large quantities of carbon powder required (Lema et al. 1988). In leachate treatment, this is also typically the case as carbon has to be regenerated more often due to the high concentrations of impurities, suspended solids in particular. Pretreatment may be necessary to reduce the solid contents and limit bacterial growth.

3. **Ion exchange.** Ion exchange involves the interchange of ions between an aqueous solution and a solid material: the ion exchange resin. The main use of this process is water softening to reduce concentrations of magnesium and calcium hardness using sodium ions. In wastewater treatment, it is used for the removal of nitrogen ( $\text{NH}_4^+$  and  $\text{NO}_3^-$ ), heavy metals, and TDS. Zeolites are natural ion exchange materials, and synthetic materials such as: aluminosilicates, resins, or phenolic polymers can also be used. Street et al. (2002) reported that a novel polyacrylate-based ion-exchange material removed modest amounts of lead in the high-ppm concentration range and reduce the effluent lead concentration to the low-parts per billion range. Likewise, Papadopoulos et al. (1996) successfully used clinoptilolite (microporous mineral from the zeolites group) in a sodium form in an ion exchange reactor. A maximum removal of 83 percent of ammonia was achieved with a starting concentration of 2700 mg N/L. They also achieved 15 percent removal of BOD<sub>5</sub>, with a starting concentration of 8500 mg/L. Contradicting Bishkin (1998), unfortunately, Escobar et al. (2006) report that the ion exchange technology requires costly resin regeneration (producing additional liquid wastes) or inevitable resin replacement because of fouling. The presence of competing ions such as sulfate, the excessive suspended solid content, and organic fouling due to the presence of oil and grease are the major operational issues. Also, to be competitively efficient as compared to other less expensive technologies, this process requires preliminary treatment such as filtration and pH control to reduce concentrations prior to the ion exchanger. Those are the two main explanations why this technology is not more widespread in water treatment operations.

The common physical processes are:

1. **Air stripping.** This technology is used to remove ammonia and volatile organic compounds (VOCs) (American Water Works Association 1999). The mechanism involved in air stripping is the transfer of a gas from the liquid phase to the gaseous phase. This is accomplished by contacting the liquid containing the gas with another gas (usually air) that does not contain the target gas initially. This creates a concentration gradient, which is the driving force to remove the substance from the water into the gaseous phase. However, air stripping does not address the other constituents, such as BOD<sub>5</sub>, COD or metals, which are not volatile. Consequently, it cannot be used on its own. Furthermore, air stripping of ammonia typically requires a pH adjustment to a value near 11, which is usually accomplished using lime addition (Lema et al. 1988). For instance, after 96 hours, Silva et al. (2003) achieved a removal of 99.4 percent of ammonia with an initial concentration of 880 mg/L as N. It should be noted that during the same experiments, ammonia was not removed by coagulation/flocculation or membrane fractionation. Calli et al. (2005) also demonstrated considerable removal (94 percent) with an initial concentration on the order of 2330 mg/L as N from raw young leachate using conventional air stripping treatment.
2. **Flocculation and sedimentation.** Coagulation, precipitation, flocculation, and sedimentation are fully-developed technologies and have long been used in water treatment applications. They are generally practical, effective, and relatively low-cost for water softening, inorganic phosphorus and heavy metal removal, removal of suspended particles, color and turbidity but limited removal of COD. Information concerning the removal of other constituents is very rare. Common coagulants include metallic salts such as aluminum sulfate (Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>), aluminum chloride (AlCl<sub>3</sub>), ferric sulfate (Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>), ferric chloride (FeCl<sub>3</sub>), or lime (CaO). But selecting the most effective combination of these is not an easy task as results depend on the initial composition of the waste (Méndez-Novelo et al. 2005). These processes can also be used as an efficient pretreatment step prior to biological or membrane treatment, or alternatively as an effective post-treatment step for the leachate (Amokrane et al. 1997; Tatsi et al. 2003). However, coagulation/precipitation is generally not appropriate for full treatment of leachate, due to its limited efficiency for removal of organic content. Reported leachate COD removal efficiencies depend primarily on coagulant species, coagulant dose, pH and leachate characteristics, ranging widely from 10 to 80 percent. Several investigators reported that coagulation favored removal of high molecular organic compounds in leachate (Chian and DeWalle 1977; Slater et al. 1985; Yoon et al. 1998). Silva et al. (2003) reported 25 percent removal of COD, but no removal of ammonia using coagulation and flocculation with aluminum sulfate. Ferric chloride appeared to be more efficient than alum in removing organic constituents in leachate, particularly at pH values above 9.0. Wu et al. (2004) reported a removal of 60 percent of COD using ferric chloride as the

coagulant. As a traditional coagulant, lime can achieve up to 90 percent removal of heavy metals such as Fe, Cd and Cr. However, lime increases pH and hardness, provides poor COD removal (20 – 40 percent), and generates excessive sludge at high dosages (Amokrane et al. 1997). Amokrane et al. (1997) also attempted coagulation with ferric chloride, flocculation, and sedimentation but were only able to achieve 54 percent removal of COD. Méndez-Novelo et al. (2005) tried different coagulants at different doses but could not achieve a removal of COD greater than 47 percent. Of the 864 jar tests they conducted, the average removal was only 4 percent. They attribute their successful results to the action of sweep floc or enhanced coagulation, which requires excess addition of coagulant. The literature reported here on these processes shown that they are mostly used prior to additional treatment such as ozonation or advanced oxidation processes.

- 3. Filtration.** Filtration is a solid/liquid separation technique. It is also generally employed before advanced treatment processes to remove excess suspended solids. Slow and rapid sand gravity filtration technologies are variations of the depth filtration process, which are effective for removal of suspended and colloidal solids and insoluble metal precipitates. For removing even smaller materials, membrane filtration such as: microfiltration, ultrafiltration, nanofiltration and reverse osmosis (RO) can be used. In that order, they produce an effluent with a higher and higher quality; and are effective on a multitude of compounds, dissolved matter in particular, but the brine, which contains concentrated constituents, must be handled separately. Membrane processes usually constitute the last stage of a treatment train that may consist of particle filtration, biological pretreatment, pH adjustment, and disinfection prior to introduction of the wastewater to the membrane filter. Slater et al. (1983) reported after initial treatment (oil/grease separation, coagulation by lime, recarbonation, and pH adjustment), they were able to achieve 98 percent removal of TDS ( $C_o = 16,400$  mg/L), 68 percent removal of COD ( $C_o = 26,400$  mg/L), and 59 percent removal of TOC ( $C_o = 8500$  mg/L) using a reverse osmosis unit with a permeate flux of 4.4 gpd/ft<sup>2</sup> (cited by Qasim and Chiang 1994). Removals of up to 90 percent of ammonia-nitrogen, 91 percent of BOD<sub>5</sub>, 98 percent of COD, and 99 percent of the conductivity have been reported also using a reverse osmosis system (Ushikoshi et al. 2002). Other research (Linde et al. 1995) showed similar removal efficiencies. Mohammad et al. (2004) studied the nanofiltration process on sanitary landfill leachate from a landfill in Malaysia. After pre-filtration, they achieved 90 percent removal of COD ( $C_o = 5600$  mg/L), 30 percent removal of ammonia ( $C_o = 5900$  mg N/L), 97 percent removal of conductivity ( $C_o = 16,450$   $\mu$ S/cm), 87 percent removal of lead ( $C_o = 0.355$  mg/L), and complete removal of TSS ( $C_o = 240$  mg/L). They concluded that nanofiltration could be a relatively low-energy method but should be combined with a biological process for increased performance. However, disposal of filtration processes concentrates is a serious problem (Perters 1998). High salt concentration in the leachate may induce rapid membrane fouling resulting in low membrane flux (due to

suspended solids, oil and grease, microbial growth, manganese and iron precipitation, and scale formation due to calcium carbonate and magnesium hydroxide). Thus pretreatment is generally required. And although membrane filtration processes can generate high quality filtrates, they also have extensive operating and maintenance requirements, such as pretreatment, chemical addition, membrane cleaning (also generating liquid wastes), and energy consumption (Escobar et al. 2006, contradicting the conclusion drawn by Mohammad et al. 2004).

In conclusion, physical and chemical processes present the advantages of being immediately functional, relatively easy to operate, and insensitive to temperature variations. However, they typically generate large quantities of residuals (sludge, concentrates, and filter backwash water) and may require daily chemical addition and process maintenance, adding significant costs to the operation (Lema et al. 1988).

Reviewing all these traditional methods to treat landfill leachate leads to the eventual conclusion that individually none of them is efficient from the perspective of long-term management of landfill leachate. Each has advantages and limitations, but none can achieve consistent removal of the major constituents of concern while generating an environmentally-acceptable effluent and residuals. Thus formulating a global recommendation for leachate treatment using conventional wastewater unit processes is not possible at this time. A combination of several methods can be used, but the cost will then increase, possibly becoming prohibitive because to improve the effluent and residuals quality, the treatment must be more extensive (driving the costs up). Consequently, an all inclusive solution is currently not available for long-term leachate management. Thus, new technologies must be considered and further studies conducted. One of the potential solutions may involve advanced oxidation processes (AOPs) or energized processes (EPs).

### **1.3.8 Alternative treatment methods (AOPs and EPs)**

Chemical oxidation is based on oxidation-reduction (redox) reactions tailored for the destruction of organics and precipitation of metals. 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 5 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 easily biodegradable and less toxic to common microorganisms found in a wastewater treatment plant for instance (Schulte et al. 1995; Morais and Zamora 2005).

**Table 5. Relative oxidation power of selected oxidizing species (Munter et al. 2001).**

| Oxidation Species   | Relative Oxidation Power |
|---|--------------------------|
| Chlorine  | 1.00                     |
| Hypochlorous Acid   | 1.10                     |
| Perrnanganate   | 1.24                     |
| Hydrogen peroxide   | 1.31                     |
| Ozone   | 1.52                     |
| Atomic oxygen   | 1.78                     |
| Hydroxyl radical  | 2.05                     |
| Positively charged hole on titanium dioxide, TiO <sub>2</sub> | 2.35                     |

An energized process (EP) is based on the same mechanisms with the additional action of ultraviolet (UV) 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 without activation by iron salt or UV radiations, the oxidation power is far less than with this activation. The use of iron or photo-energy improves this oxidation power by accelerating the formation of hydroxyl radicals. Staehelin and Hoigné (1983) pointed out however, that “radical scavengers,” such as: carbonates species ( $\text{CO}_3^{2-} / \text{HCO}_3^-$ ) 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 this type 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). If they are used as a pre-treatment step before a biological treatment, it has been demonstrated that oxidation processes reduced the detention time required (the removal percentage is not indicated in the publication) for that biological treatment (reported by 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.

AOPs and EPs are known to handle are known to handle many of the constituents typically found in leachate:

1. **Elevated ammonia:** EPs convert ammonia to nitrate through aeration and promote stripping of  $\text{NH}_3(\text{g})$  at suitable pH (American Water Works Association 1999).
2. **High COD/BOD ratios:** EPs convert refractory COD into readily

biodegradable BOD (Suty et al. 2004). BOD<sub>5</sub> is then mineralized by oxidation to simple products such as H<sub>2</sub>O, CO<sub>2</sub>, 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.
4. **pH toxicity:** EPs minimize pH impacts as a byproduct of aeration treatment.
5. **Volatile organic compounds:** EPs can destroy recalcitrant organics and, because of their volatility, promote the stripping of VOCs during aeration, provided the appropriate conditions (American Water Works Association 1999, Suty et al. 2004).

As stated earlier, advanced oxidation processes can occur both with and without the addition of energy. In the following brief list of specific process mechanisms, the first three are non-photochemical reactions (AOPs), and the others are photochemically energized reactions (EPs).

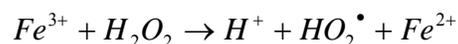
#### 1.3.7.1 Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>)

One of the simplest methods to generate hydroxyl radicals in aqueous waste streams is through the addition of hydrogen peroxide. Hydrogen peroxide is a strong oxidant and is also a widely used disinfection agent. H<sub>2</sub>O<sub>2</sub> is produced by the electrolysis of ammonium bisulfate and the oxidation of alkyhydroanthraquinones.

Amokrane et al. (1997), used hydrogen peroxide as a pre-treatment step before coagulation-flocculation phase. They demonstrated that H<sub>2</sub>O<sub>2</sub> had a minor influence on the overall process. The COD removal percent was increased only slightly from 54 to 57 percent by using 1.94 g/L of H<sub>2</sub>O<sub>2</sub>. Similarly, other experiments showed hydrogen peroxide's comparatively low removal efficiency. Loizidou et al. (1993) treated leachate from a stabilized landfill near Athens for a period of 24 hours using a dose of 100 mL H<sub>2</sub>O<sub>2</sub>/L of waste (880 mM). The initial COD concentration was 7000 mg/L, and the final measured concentration was about 5900 mg/L. This represents the removal of 1100 mg/L of COD, but only 16 percent removal. Shu et al. (2006) experimented with hydrogen peroxide on leachate from a landfill in Taiwan. After 600 min of reaction ([H<sub>2</sub>O<sub>2</sub>] = 232.7 mM), they removed 60 percent of the COD (C<sub>0</sub> = 4000 mg/L). Information concerning the removal of other significant parameters (ammonia, suspended solid, BOD<sub>5</sub> or lead) typically encountered in leachate are very restricted. Although, hydrogen peroxide seems to have a wide range of action due to the effect of the hydroxyl radical, this method can be enhanced as demonstrated by Steensen (1997). The benefits of combining the catalytic effect of ferrous ions to hydrogen peroxide are detailed in the next section.

### 1.3.7.2 Fenton ( $H_2O_2/Fe^{2+}$ )

The Fenton reaction is probably the oldest AOP agent used in wastewater treatment. The Fenton process for the oxidation of maleic acid was reported by Fenton well over a hundred years ago (Fenton and Jones 1900). Reagents used are generally hydrogen peroxide and ferrous iron. The process is the result of the catalytic action of ferrous ions ( $Fe^{2+}$ ) with hydrogen peroxide according to the following system:



An increase in the hydrogen peroxide to substrate ratio results in more extensive degradation, while a higher concentration of iron leads to increased yield (Lopez et al. 2004). The Fenton process is known to degrade organics that can be found in typical leachate (Zhang et al. 2005), and the process can also improve biodegradability and remove odor and color. Most importantly, the Fenton process can significantly remove recalcitrant and toxic organic compounds. The reaction is fast at low pH (ideal pH is between 3 and 5), often requiring an initial pH adjustment. Because of the use of iron, sludge residuals, mainly from ferric precipitates, can be generated in large quantities. An additional step such as sedimentation is generally required after the Fenton process to deal with these residuals.

Fenton processes can be roughly grouped into four categories: 1) direct Fenton treatment, 2) Fenton pretreatment prior to biological treatment, 3) Fenton treatment preceded by physical/chemical treatment, and/or occasionally followed by biological treatment, and 4) Fenton treatment preceded by biological treatment, and/or occasionally followed by physical/chemical or biological treatment. The difference between direct Fenton treatment and Fenton pretreatment for a biological process is that the former focuses on COD removal, while the latter focuses on increasing the  $BOD_5/COD$  ratio. The first category is more appropriate for mature leachate, because biodegradable organics in young leachate can be readily removed by biological processes. The second category is also appropriate for mature leachate because the Fenton pretreatment decomposes the recalcitrant organics to less complex intermediates, which are then more readily biodegradable. Lopez et al. (2004) found that dosages of Fenton reagents required to achieve sufficient improvement in organic biodegradability are significantly lower than those required to achieve a target COD level in a typical mature raw leachate. The third category frequently involves coagulation as pretreatment. This is done to reduce organic loading on the Fenton process. Since the 1970s, lime, alum, and ferric salts have been extensively investigated for full treatment and pretreatment of landfill leachate (Thornton and Blanc 1973; Cook and Foree 1974; Ho et al. 1974; Millot et al. 1987; Amokrane et al. 1997; Forgie 1988; Kim et al. 2001; Trebouet et al. 2001; Wang et al. 2002a; Wang et al. 2002b; Tatsi et al. 2003; Monje-Ramirez and de Velasquez 2004; Pala and Erden 2004; Silva et al. 2004; Wu et al. 2004). COD removal efficiencies reported for coagulation depend primarily on the coagulant species, coagulant dose, pH and

leachate characteristics, ranging widely from 10% to 80%. Several authors reported that coagulation favored removal of high molecular organic compounds in leachate (Chian and DeWalle 1976; Slater et al. 1985; Yoon et al. 1998). A modification of coagulation using ferric salts combined with the Fenton treatment involves the recycling of Fenton sludge. In this scheme, a portion of the Fenton sludge is returned to the coagulation tank to increase COD removal efficiency, and reduce coagulant consumption and sludge disposal cost (Yoo et al. 2001). Finally, if effluent from the Fenton unit contains COD above the discharge standard, post-treatment must be employed (Lin and Chang 2000). The fourth category involves biological pretreatment utilizing aerobic or anaerobic processes to eliminate biodegradable organics or ammonia at a low operating cost (Gau and Chang 1996; Bae et al. 1997; Yoon et al. 1998; Wang et al. 2000a; Lau et al. 2001; Gulsen and Turan 2004). Gau and Chang (1996) used activated carbon adsorption as an effective post-treatment to decrease COD from 320 mg/L to 150 mg/L. The reason for this efficiency may be that the effluent from Fenton treatment will likely contain an important fraction of low molecular organics (Yoon et al. 1998), which may be more efficiently removed by activated carbon adsorption (Chiang et al. 2001). Another option for removal of COD in Fenton-treated leachate is by using activated sludge post-treatment (Bae et al. 1997). In addition, a two-stage Fenton process, comprised of two successive Fenton processes in series, can be used in place of a single Fenton process. Gau and Chang (1996) reported that the second Fenton step could further reduce COD in leachate, though dosages of Fenton reagents in the second stage were much higher than those in the first step.

Lopez et al. (2004) utilized the conventional Fenton reaction to increase the BOD<sub>5</sub>/COD ratio above 0.5, to treat a raw leachate with an original BOD<sub>5</sub>/COD ratio equal to 0.22. Kim and Huh (1997) performed testing to raise the BOD<sub>20</sub>/COD ratio in leachate from 0.10 to 0.58 by using the conventional Fenton process. Kim et al. (2001) used photo-Fenton treatment to increase the BOD<sub>5</sub>/COD ratio of leachate from less than 0.05 to greater than 60. Loizidou et al. (1993) also treated leachate from a stabilized landfill near Athens, Greece, for a period of 24 hours using 40 mg/L of FeSO<sub>4</sub> and 100 mL H<sub>2</sub>O<sub>2</sub>/L of waste. The initial COD concentration was 7000 mg/L, and the final measured concentration was about 4550 mg/L. This represents 35 percent of removal. For BOD<sub>5</sub>, the removal was 18 percent (C<sub>0</sub> = 3400 mg/L), but the final treated effluent concentration was 2800 mg/L. Lopez et al. (2004) also treated raw leachate with the Fenton process. After adjusting the pH to 3.0, adding 10,000 mg/L of H<sub>2</sub>O<sub>2</sub>, and 830 mg/L of Fe<sup>2+</sup>, they demonstrated a maximum removal of 60 percent with a detention time of 2 hours (C<sub>0</sub> = 10,540 mg/L). Englehardt et al. (2005) also used the Fenton process on pre-filtered and pH-adjusted leachate and achieved 61 percent removal of COD and 14 percent removal of ammonia. Zhang et al. (2005) demonstrated that the Fenton process is more efficient at low pH. An optimal pH of 2.5 was found, and experiments adjusted pH using 1.0 M sulfuric acid. A decrease in the removal percentage was also found as the initial COD concentration increased, even though the amount of COD removed increased. Regarding ammonia, Lin and Chang (2000) reduced the concentration by 16 percent (C<sub>0</sub> = 33 mg/L) using an electro-Fenton process and a dosage of 750 mg H<sub>2</sub>O<sub>2</sub>/L in less than 30 minutes.

They also obtained a colorless effluent. Calli et al. (2005) used the Fenton process on pretreated leachate. With a 60 second rapid mix of 1000 mg FeSO<sub>4</sub>/L and 2000 mg H<sub>2</sub>O<sub>2</sub>/L, and a sedimentation period of 30 min, removal of 85 percent of the 1875 mg/L initial COD was recorded at pH < 4.0.

As mentioned earlier, although Fenton treatment can potentially increase the biodegradability of organic compounds, the increase may not be adequate to support subsequent biological treatment. For example, Kim et al. (2001) raised leachate BOD<sub>5</sub>/COD from 0.14 to 0.22 and 0.27 by Fenton and Fenton-like methods, respectively. Lau et al. (2002) applied photo-Fenton treatment to increase leachate BOD<sub>5</sub>/COD from 0.08 to 0.14. And, Lin and Chang (2000) obtained a BOD<sub>5</sub>/COD ratio of 0.30 by electro-Fenton treatment of a leachate (original BOD<sub>5</sub>/COD = 0.10). Information on the removal of other common leachate constituents (e.g., TDS, metal ions) using the Fenton treatment is scarce.

Deng and Englehardt (2006) studied the Fenton process from treatment of landfill leachates using ferrous sulfate and hydrogen peroxide at circumneutral pH. After rapid mixing from 30 seconds to 60 minutes at impellor 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 increment may be marginal when concentration of iron salt is high, and the lower pH range inhibited subsequent precipitation and sedimentation. They also optimized the molar ratio of H<sub>2</sub>O<sub>2</sub> to Fe<sup>2+</sup> at 11:1. Using these conditions, they demonstrated 51 percent COD removal at 80 kW/m<sup>3</sup>, they found no oxidation of ammonia and encountered severe issues with foaming that inhibited mass transfer of hydroxyl radicals to the bulk solution.

### 1.3.7.3 Ozone (O<sub>3</sub>)

Glaze et al. (1987) stated that ozone has been used as a chemical reagent, an industrial chemical, and an oxidant for water treatment for over a century. Ozone is known to be a powerful oxidant and disinfectant, with a thermodynamic oxidation potential that is the highest of the common oxidants (refer to Table 5). The action of ozone itself is difficult to evaluate as ozone is very unstable in water ( $t_{1/2} < 30$  minutes in distilled water), it rapidly decomposes to the hydroxyl radical, and it reacts immediately with a number of constituents.

In principle, ozone should be able to oxidize inorganic substances to their highest stable oxidation states and be able to oxidize organic compounds to carbon dioxide and water to achieve complete mineralization. In practice however, ozone is known selectivity with respect to oxidation affinity. In water treatment, ozone has been most successful for removing taste and odors in water, for aiding coagulation and filtration processes, and as a first barrier to microorganisms. Ozonation also significantly improves the biodegradability of organic residues, and converts refractory COD to

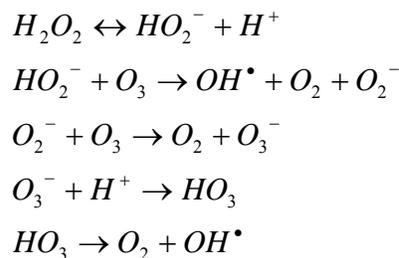
methane and biomass (Fang et al. 2005).

Geenens et al. (2000) achieved a maximum COD removal of 30 percent with a specific ozone consumption of 1.5 g O<sub>3</sub> per g COD (C<sub>0</sub> = 895 mg/L as O<sub>2</sub>). Imai et al. (1998) obtained better results using leachate with a starting concentration of 126 mg/L as O<sub>2</sub>. They reported 35 percent removal of COD with 10 minutes of contact time. Then, they further treated the effluent in two biological activated carbon fluidized bed reactors in series (anaerobic and aerobic with a 24 hour detention time) and improved the treatment to 63.5 percent removal of COD. This modification demonstrated 75 percent removal of BOD<sub>5</sub> as well. Calli et al. (2005) used ozone on pre-treated leachate with an ozone dose of 2.8 g/L/h and a reaction time of 30 minutes. Under these conditions, they achieved 85 percent removal at pH = 9.0 (C<sub>0</sub> = 1875 mg/L).

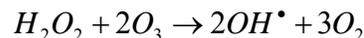
Despite its strong oxidation power, ozone should be used with caution, as formation of toxic disinfection byproducts may occur. Economically, ozone is regarded as energy-intensive because it must be generated on-site due to its instability, and therefore the process is more expensive (Geenens et al. 2000). Even if ozone has a theoretical oxidizing potential which is sufficient to directly convert many organic substances to mineral end products, oxidation can be further enhanced with the combined action of another radical reaction (Steensen 1997). Thus, ozone has been successfully combined with other oxidation processes, some of which are described further below.

#### 1.3.7.4 Ozone and hydrogen peroxide (O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>)

The combination of hydrogen peroxide with ozone offers an alternative way of generating the hydroxyl radical. The multi-step reaction mechanism is the following:



The overall equation of the formation of the hydroxyl radical is:



The use of ozone and hydrogen peroxide has the double effect of generating hydroxyl radicals and also directly oxidizing the contaminants. This combination is notably employed for wastes that are relatively impermeable to UV and for large flow volumes (Schulte et al. 1995).

Schulte et al. (1995) established a comparison between the ozone process, the hydrogen peroxide process, and the combined ozone/hydrogen peroxide ( $O_3/H_2O_2$ ) process by monitoring the degradation of COD. They did not give any details about the origin of their samples, but they first confirmed that  $H_2O_2$  itself is not very efficient, since the observed removal of COD was not greater than 6 percent. Using only ozone, they achieved a removal of 38 percent. By mixing the two reagents with a 1:1 ratio, they degraded 97 percent of the initial COD ( $C_0 = 760$  mg/L). On the other hand, Wang et al. (2004) used a combination of 8 g  $O_3$  and 0.63 g  $H_2O_2$  per liter of raw aged leachate to achieve 63 percent removal of 1100 mg/L of COD. Simultaneously, they degraded 40 percent of ammonia-nitrogen ( $C_0 = 455$  mg/L). Compared to the results they obtained using only ozone, they concluded that the effect of  $H_2O_2$  is relatively insignificant and did not justify the additional cost.

The literature reported on the combined ozone and hydrogen peroxide process shows a wide range of treatment efficiencies. Using different leachates with low COD and different ratios of reagent, the removal achieved varies. As a result, this process seems difficult to apply at full scale as leachate quantity also greatly fluctuates.

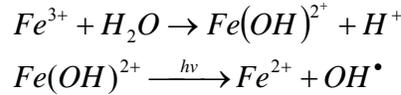
#### **1.3.7.5 Ultraviolet light (UV)**

Ultraviolet light is commonly used for disinfection applications. The process involved is the photolysis of bacterial DNA. UV is also known to enhance the production of the hydroxyl radical (Schulte et al. 1995) by direct photolysis of water, but this is not its only action in water treatment. Indeed, the same authors explained that because of UV-light absorbing properties, many molecules are destroyed directly by photolysis or are activated by photosensitivity, thus making them more easily oxidizable. Using three 150-W lamps and a 60-minute reaction time, Schulte et al. (1995) removed approximately 15 percent of COD from a sanitary landfill leachate with an initial concentration of 760 mg/L. Dobrović et al. (2007) also used the UV process to reduce the natural organic matter in lake water. They used mercury lamps with a total ultraviolet output of 13.8 W. The COD removal was nearly noticeable in just over 12 minutes of treatment. They estimated the reaction to be first order with a reaction rate constant of  $6.8 \times 10^{-3} \text{ min}^{-1}$ . They also estimated the organic matter half life to be on the order of 41.1 minutes.

In general, UV by itself does not appear to be a very efficient treatment process for applications involving leachate. Metals are not affected by UV, which explains why UV is typically combined with other reagents to achieve better removal efficiencies.

### 1.3.7.6 Photo-Fenton / Fenton-like systems

The photo-Fenton process consists of the addition of UV energy to the Fenton reaction. At low pH, the  $Fe(OH)^{2+}$  complex is formed and is subsequently oxidized by UV radiation according to the following reaction sequence:

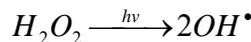


This has the effect of generating the Fenton catalyst in-situ and enhancing the production of hydroxyl radical through direct photolysis and also by reaction.

Kim et al. (1997) used this process on municipal landfill leachate that was pre-treated biologically. After pH adjustment to  $pH < 3.0$ , the optimum conditions for maximum degradation were:  $[Fe^{2+}] = 1.0 \times 10^{-3} M$  (56 mg/L) and a molar ratio of 1:1 COD:H<sub>2</sub>O<sub>2</sub>. The starting COD concentration was 1150 mg/L, and after two hours of treatment at 80 kW/m<sup>3</sup>, the observed removal was 70 percent. 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 O<sub>2</sub> aeration system (Q = 45 mL/min), and reagent concentrations of 2000 mg H<sub>2</sub>O<sub>2</sub>/L and 10 mg Fe<sup>2+</sup>/L. The pH was adjusted to 2.8, and after 60 minutes, the initial COD concentration of 5200 mg/L as O<sub>2</sub> was reduced to 2240 mg/L as O<sub>2</sub>, which equals a removal of 57 percent. They also greatly improved the biodegradability of the leachate by increasing the BOD<sub>5</sub>/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.

### 1.3.7.7 Ultraviolet light and hydrogen peroxide (UV/H<sub>2</sub>O<sub>2</sub>)

Using UV and H<sub>2</sub>O<sub>2</sub> without iron for water treatment results in three modes of treatment: 1) direct photolysis by UV, 2) direct oxidation by H<sub>2</sub>O<sub>2</sub>, and 3) the indirect generation of OH<sup>•</sup> radicals. Direct photolysis of hydrogen peroxide also leads to the formation of OH<sup>•</sup> radicals by the splitting the oxygen-oxygen bond (Schulte et al. 1995):

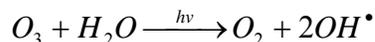


The oxidation of combined UV/H<sub>2</sub>O<sub>2</sub> processes is more effective at low pH ( $pH = 2 - 4$ ), which requires pH adjustment and reduction of alkalinity (Steensen, 1997). Shu et al. (2006) enhanced the efficiency of their first experiments with H<sub>2</sub>O<sub>2</sub> (described earlier) by adding four UV lamps. With this new set-up, they improved the COD removal from 60 percent with hydrogen peroxide alone to 65 percent, 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 percent removal was obtained with leachate strengths of 100, 50 and 20 percent, respectively when keeping the detention time constant at 180 minutes. Morais and Zamora (2005) also performed experiments with the UV/H<sub>2</sub>O<sub>2</sub> process and reduced COD by 55 percent (H<sub>2</sub>O<sub>2</sub> = 3000 mg/L). This confirms the initial finding that AOPs can enhance the biodegradability of sanitary landfill leachate.

### 1.3.7.8 Ultraviolet light and ozone (UV/O<sub>3</sub>)

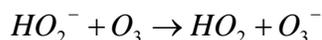
Ozone readily absorbs UV radiation to form H<sub>2</sub>O<sub>2</sub>, which will itself decompose into hydroxyl radicals by the following mechanism:



Prengle and co-workers at the Houston Research Inc. were the first to see the commercial potential of the O<sub>3</sub>/UV system (cited from Glaze et al. 1987). They showed that activating O<sub>3</sub> with UV energy enhances the oxidation of COD and BOD and also complexed cyanides, chlorinated solvents, and pesticides as well. Ince (1998) used this combination on pretreated leachate from a municipal landfill. He applied 3.0 g H<sub>2</sub>O<sub>2</sub>/L and compared the influence of: 1) wide band UV wavelengths from 200 to 470 nm from a high pressure mercury lamp and 2) the monochromatic germicidal wavelength ( $\lambda = 253.7$  nm) from a low pressure mercury lamp ( $t_d = 8$  hrs). With the first lamp, the removal percentage was 47 percent, and the second lamp achieved 54 percent removal of COD ( $C_0 = 1290$  mg/L). This demonstrates the importance of the UV wavelength or delivery mechanism in the overall process efficiency. The O<sub>3</sub>/UV process can also be upgraded by adding hydrogen peroxide as a third oxidant as discussed below.

### 1.3.7.9 Ultraviolet light, ozone and hydrogen peroxide (UV/O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>)

The addition of H<sub>2</sub>O<sub>2</sub> to the O<sub>3</sub>/UV process accelerates the decomposition of ozone, resulting in an increased rate of hydroxyl radical production. The conjugate base of H<sub>2</sub>O<sub>2</sub>, HO<sub>2</sub><sup>-</sup> has been shown to initiate this mechanism (Kidman and Tsuji 1992, Munter et al. 2001):



This step initiates the decomposition of ozone resulting in the production of additional hydroxyl radicals.

Ince (1998) achieved 89 percent removal of COD with an initial concentration of 1290 mg/L, while using these three oxidants together. Reactor conditions were: 3 g

O<sub>3</sub>/L, 2.1 g H<sub>2</sub>O<sub>2</sub>/L, a low pressure mercury lamp, and contact time of eight hours. In the absence of O<sub>3</sub>, the system removed 59 percent of the COD, and in the absence of H<sub>2</sub>O<sub>2</sub>, the system removed only 54 percent of the COD. The combination however enhanced the performance of the system to removal of 89 percent. This energized process can be compared to the experiments conducted by Loizidou et al. (1993) who were using only H<sub>2</sub>O<sub>2</sub>. Percentages of removal are not equal, but the actual quantities of COD removed were very similar. This observation demonstrates that the combination of UV, O<sub>3</sub>, and H<sub>2</sub>O<sub>2</sub> is still not capable of improving the quality of leachate to the level sufficient for discharge to the environment.

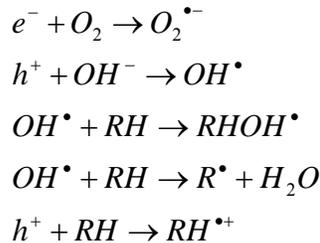
#### **1.3.7.10 Electrochemical oxidation**

Electrochemical oxidation uses the process of electrolysis to effect treatment. A typical electrolytic system includes a direct current (DC) power supply, a cathode, an anode, and the electrolyte, which is the medium that permits ion transport between the anode and the cathode. Metal cations are removed at the cathode via reduction, and other constituents, most notably non-biodegradable organics, can be oxidized at the anode. Additionally, an oxidation reaction may occur in the bulk solution by secondary oxidants generated by partial oxidation at the electrodes. Electrochemical oxidation has been investigated as an efficient means of controlling pollution in water and wastewater treatment applications (Comninellis and Pulgarin 1991; Rao et al. 2001; Canizares et al. 2005), and recently Deng and Englehardt (2007) have studied its potential for landfill leachate treatment. They demonstrated COD removal of 70 to 90 percent after pretreatment with a sequencing batch reactor, which reduced the energy requirements by 31 percent compared to direct electrochemical oxidation. They also investigated pretreatment with chemical coagulation and activated carbon adsorption, which achieved 90 percent COD removal but increased the overall energy consumption by 20 percent. Byproducts were not investigated.

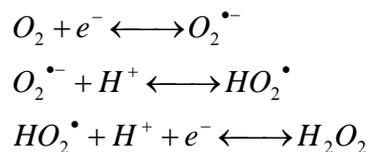
Electrochemical oxidation can reduce concentrations of organic contaminants, ammonia, and color in leachate (Comninellis and Pulgarin 1991; Rao et al. 2001; Deng and Englehardt 2007). Pretreatment methods, anode materials, pH, current density, chloride concentration, and competing electrolytes can considerably influence performance, although high energy consumption and the formation of organochlorine byproducts may limit its application.

#### **1.3.7.11 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. Munter et al. (2001) proposed the following possible 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  $H_2O_2$  in the process:



Titanium dioxide ( $TiO_2$ ) is one of the most widely used metal oxides in the industry for photocatalytic applications.  $TiO_2$  particles generate strong oxidizing power when illuminated with UV light at wavelengths less than 400 nm. Irradiation of  $TiO_2$  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 ( $HO^{\bullet}$ ) and superoxide radical ( $O_2^{\bullet -}$ ). For photocatalysis to occur, electron “holes” must migrate to the surface of the  $TiO_2$  crystal. The “holes” primarily react with hydroxide ( $OH^{-}$ ) from water acting as electron donors to produce hydroxyl radicals. The electrons primarily react with  $O_{2(aq)}$  (dissolved oxygen) in water acting as electron acceptors to yield the superoxide radical. Some of the electron-hole pairs, which do not participate in the redox reaction with water or oxygen, disappear as heat losses via the recombination of holes and electrons. Utilizing the combined oxidation power of holes and hydroxyl radicals generated in the valence band (VB), and electrons and superoxide radicals generated in the conduction band (CB), illuminated  $TiO_2$  photocatalysts can decompose organic compounds by participating in a series of mineralization reactions (Rincon and Pulgarin 2005).

$TiO_2$  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).

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 (i.e. Pb) by TiO<sub>2</sub> particles can occur.

In terms of reactor design, many successful experiments have used glass plates coated with immobilized TiO<sub>2</sub>. 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.

As far as treatment of specific contaminants, Grzechulska and Morawski (2003) used a photocatalytic labyrinth flow reactor with immobilized Degussa P25 (52 m<sup>2</sup>/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 relatively low 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 TiO<sub>2</sub> prepared by HCl etching and painting with TiCl<sub>3</sub> 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 NaNO<sub>3</sub>. 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 m × 0.5 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  $\text{TiO}_2$  using the sol-gel method. The reactor volume was 4 liters and used two 9W UV lamps. With a particle concentration of 7-12 percent volume fraction of the reactor, the bed was fluidized by bottom aeration at 0.5 Lpm to study the degradation of phenolic compounds ( $C_0 = 10 \text{ mg/L}$ ). This study found that phenol can be mineralized in 250 minutes, and bisphenol A in 350 minutes. The only intermediates detected were butareoxidized tooranic 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  $\text{TiO}_2$  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  $\text{pH} < 4.5$ .

The  $\text{TiO}_2$  is 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 et al. (2002) conducted some batch-type experiments on the photochemical oxidation process using Degussa P25  $\text{TiO}_2$  particles with a diameter of 20 nm. Combined with aeration, this process achieved 80 percent removal of COD ( $C_0 = 1400 \text{ mg/L}$ ) but essentially no removal of ammonia when they adjusted to  $\text{pH} < 4$  with  $\text{H}_2\text{SO}_4$ . Conversely, at  $\text{pH} > 12$ , only 20 percent COD removal was possible, but the process also achieved 16 percent removal of ammonia ( $C_0 = 1525 \text{ mg/L}$  as  $\text{NH}_3\text{-N}$ ). 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  $\text{TiO}_2$  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  $\lambda = 364 \text{ nm}$ . 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 TiO<sub>2</sub> 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 TiO<sub>2</sub> catalysts enjoy free contact with UV irradiation in an aqueous photoreactor, they would certainly be expected to achieve higher levels of efficiency compared to immobilized TiO<sub>2</sub> 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 and re-use the catalyst.

To improve the ability to recover photocatalysts, a TiO<sub>2</sub>-magnetite process has been proposed. In this study, a new type of TiO<sub>2</sub> 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 TiO<sub>2</sub>-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. The new TiO<sub>2</sub>-Fe<sub>3</sub>O<sub>4</sub> nanocomposite particle is characterized by high photoactivity, high surface area to volume ratio, and excellent magnetic properties, which will enhance process efficiency and allow the particles to be easily retrieved from the photoreactor for separation and reuse. The magnetite core of the experimental catalyst permits precise control of mass transfer as well as selective separation from mixtures. 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. In addition, the process proposed for our synthesis of the TiO<sub>2</sub>-coated Fe<sub>3</sub>O<sub>4</sub> nanopowder produces a byproduct (NH<sub>4</sub>Cl), which can be recovered for use as a fertilizer, for example, and thus is not harmful to the environment.

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. A review of the literature with respect to the application of photocatalysis of leachate was conducted. Bekbölet et al. (1996) performed experiments with leachate but were not very successful using a thin film fixed bed reactor. They achieved only 3 percent TOC reduction with 5 g/L Degussa P25, but at  $\text{pH} < 3-5$ , they increased removal to 43 percent. 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.

In studies of photocatalysis of leachate, the concentration of  $\text{TiO}_2$  photocatalyst varied from 1.0 g/L (Kostedt and Mazyck 2006) to 5.0 g/L (Bekbölet et al. 1996). With initial pH of 6.5,  $\text{TiO}_2$  photocatalytic processes demonstrated 99% removal efficiency of phenol in 160 minutes with irradiation of 254 nm (Ilisz et al. 2002). In a case study of the end point of photocatalytic degradation of landfill leachate containing refractory matter (Cho, Hong, and Hong 2002), the researchers reported 52 percent COD removal and 79 percent TOC removal after 5 hours, and 56 percent COD removal and 88 percent TOC removal after 10 hours, with an initial pH of 3.1.

Cho, Hong, and Hong (2002) also investigated photocatalytic degradation of landfill leachate. In these tests, suspended Degussa P25 (70% anatase) was used (DIA = 20 nm). Photodegradation of refractory and nitrogen-containing substances was favored under acidic conditions ( $\text{pH}_{\text{optimal}} = 4.0$ ). 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  $103^\circ\text{C}$  and by filtration with a GF/C filter. The same researchers (Cho, Hong, and Hong 2004) continued this work and reported 52 percent COD removal and 79 percent TOC removal after 5 hours at  $\text{pH} = 4.0$  with a photocatalyst dose of 3.0 g/L in a continuously stirred aerated quartz tube reactor at  $\lambda = 254 \text{ nm}$ . Under these conditions, 20 percent 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 percent for COD and 88 percent for TOC.

Deng and Englehardt (2007) reported that UV alone has been used for treatment of leachate with reported COD removal efficiencies of up to 31%. When UV/ $\text{TiO}_2$  was used for treatment of leachate with  $\text{BOD}_5/\text{COD} < 0.05$ , 80% removal of COD was achieved. 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 be able to oxidize the color, if it is organic in origin.

### 1.3.7.11 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 (Tang, 2004), the degradation of organic compounds through iron-mediated oxidation in oxygen-containing water has only recently been reported (Englehardt et al. 2002; and 2005; Joo et al. 2004 and 2005).

The reaction mechanism of IMA is still not completely known, but evidence suggests that it involves:

- The oxidation of  $\text{Fe}_{(s)}$  to  $\text{Fe}^{2+}$
- 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 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  $\text{O}_2$  reduction to  $\text{H}_2\text{O}_2$ . Three explanations for the oxidative capacity of iron-EDTA-mediated aeration were suggested: 1) heterogeneous activation of  $\text{O}_2$  at the Fe(0) surface, 2) homogeneous activation of  $\text{O}_2$  by  $\text{Fe}^{\text{II}}[\text{EDTA}]$ , and 3) heterogeneous activation of  $\text{O}_2$  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 wastewater (Englehardt et al. 2005; Meeroff et al. 2006). They achieved 99.996 percent removal of arsenic and 99 percent

removal of ethylenediamine tetraacetic acid (EDTA).

Using the IMA process at circumneutral pH, Englehardt et al. (2005) reduced the COD of leachate by 56 percent, and increased the BOD<sub>5</sub>/COD mass ratio from 0.1 to 0.28. In addition, the treatment was able to achieve 83 percent reduction in ammonia and 40 percent reduction in the effluent electrical conductivity of the leachate. Furthermore, two logs of removal of EDTA, Cd<sup>2+</sup>, Hg<sup>2+</sup>, and Pb<sup>2+</sup>, and an average 63 percent removal of Ni<sup>2+</sup> were achieved by Englehardt et al. (2003). Englehardt et al. (2003) also achieved 1-2 logs of removal of 1.0 mg/L 17-β-estradiol (estrogen) and di-n-butyl phthalate in simulated natural waters at pH 7.5. The newly developed IMA process has shown some promising removal capacities in laboratory tests. Organics and inorganics are both affected by its action, and Meeroff et al. (2006) demonstrated a preliminary cost projection below \$0.05 per gallon for IMA treatment for scale-up.

Based on the ranking established during this project and explained at the conclusion of this introduction, the IMA may be, at the laboratory scale, the best performing AOP presently available.

#### **1.3.7.12 Photochemical Iron-Mediated Aeration (PIMA)**

Preliminary studies on the IMA process enhanced with UV process were first conducted by Englehardt et al. (2005). This modification was called photochemical iron mediated aeration (PIMA). PIMA is a new photochemically-assisted iron-mediated aeration process for oxidizing organics and co-precipitating inorganics in wastewater, which is 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 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. 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 to propagate a Fenton cycle (Kwan and Chu 2003). Furthermore,

photochemical oxidation with added 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 ethylenediamine tetraacetic acid (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 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 percent) 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 percent in a PIMA reactor compared to just 5 percent 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. To our knowledge no other studies have been conducted on the PIMA process, and this technology is still at an immature stage.

### **1.3.9 Ranking of treatment options**

The technical literature reviewed for different engineering alternatives for leachate treatment generally considers COD or specific organic pollutants. Regarding the traditional options, some are capable of producing a high quality liquid effluent (such as membrane filtration, for instance), but the pollutants are merely transferred to another media, which in turn must be managed properly. Other conventional options are not efficient enough or have too many binding requirements (such as weather issues or surface area constraints, for example) to be used effectively for leachate applications. Consequently, traditional wastewater treatment solutions are not suitable for long term management of leachate. On the other hand, advanced oxidation processes have shown promising results with difficult-to-treat waste streams because they oxidize and/or reduce a broad spectrum of pollutants.

Furthermore, the addition of UV has been demonstrated to enhance the reaction of simple advanced oxidation processes. Therefore, AOPs and other energized processes like photocatalytic oxidation and the IMA and PIMA processes should be the center of attention precisely because there is presently no one solution that is, over the lifetime of a landfill, efficient enough to lower initial pollutant concentrations to the required levels for safe discharge to a municipal sewer system (see Table 6 for more details on these limits). As a consequence, it is urgent to find an environmentally-friendly and viable solution for leachate management on a long term basis.

**Table 6. Allowable public sewer discharge concentrations for the City of Boca Raton, FL**

| Parameter                                     | Units                      | Maximum Allowable Value over any 24-hr Period |
|---|----------------------------|---|
| Lead  | mg/L                       | 0.37  |
| Total dissolved solids                        | mg/L                       | 2000  |
| Total suspended solids                        | mg/L                       | 400   |
| Chemical oxygen demand (COD)                  | mg/L                       | 800   |
| Biochemical oxygen demand (BOD <sub>5</sub> ) | mg/L                       | 400   |
| pH  | mg/L                       | 6.0-8.5                                       |
| Iron  | mg/L                       | 21  |
| Ammonia                                       | mg/L as NH <sub>3</sub> -N | Not listed                                    |
| Conductivity                                  | µS/cm                      | Not listed                                    |

Source: Environmental Health and Safety, Florida Atlantic University, (2004). "Chemical Hygiene Plan", <http://www.fau.edu> (accessed: February 24, 2006).

Leachate management in the future must have the following characteristics:

1. Must be sustainable
2. Must be site-specific
3. Must be capable of adaptation to evolving regulations, climate change, population growth, and leachate variability

The most likely approach that will be able to achieve these objectives is some form of on-site pretreatment, to reduce the toxicity of the leachate, followed by discharge to the sanitary sewer network for eventual treatment in a wastewater treatment facility and safe discharge to the environment.

The advantages and disadvantages of the engineering alternatives discussed in the previous sections are summarized in Table 7.

**Table 7. Summary of advantages and disadvantages of selected leachate management strategies**

| <b>Technology</b>                               | <b>Type</b> | <b>Advantages</b>   | <b>Disadvantages</b>  |
|---|-------------|---|---|
| Municipal Sewer Discharge without Pre-Treatment | Off-site    | <ul style="list-style-type: none"> <li>• No on-site treatment required</li> <li>• No footprint required</li> <li>• Efficient for BOD<sub>5</sub></li> </ul>   | <ul style="list-style-type: none"> <li>• High COD and ammonia toxicity can disrupt WWTP if Q &gt; 2-5%. Impacts include: longer detention times, poorer settling properties, and increased sludge production.</li> <li>• Does not address bio-toxics</li> <li>• Results are highly variable and not reproducible</li> <li>• Odor generation</li> </ul>  |
| Evaporation                                     | On-site     | <ul style="list-style-type: none"> <li>• Efficient on COD</li> <li>• Efficient on ammonia</li> <li>• Efficient on inorganics</li> </ul>   | <ul style="list-style-type: none"> <li>• Dependent on climate conditions</li> <li>• Post treatment required for residuals</li> <li>• Large footprint required</li> </ul>  |
| Deep Well Injection (Natural Attenuation)       | On-site     | <ul style="list-style-type: none"> <li>• No or minimal on-site treatment required</li> <li>• Small footprint</li> </ul>   | <ul style="list-style-type: none"> <li>• No treatment performed</li> <li>• Environmental treat to ground water and soil</li> <li>• Difficult to permit</li> </ul>   |
| Hauling Off-Site                                | Off-site    | <ul style="list-style-type: none"> <li>• No or minimal on-site treatment required</li> <li>• Small footprint</li> </ul>   | <ul style="list-style-type: none"> <li>• No treatment performed</li> <li>• High transportation risk</li> <li>• Dependent upon finding an entity that will accept the leachate</li> </ul>  |
| Leachate Recirculation Bioreactor               | On-site     | <ul style="list-style-type: none"> <li>• Efficient on COD</li> <li>• Efficient for BOD<sub>5</sub></li> <li>• Efficient on ammonia</li> <li>• Efficient on inorganics</li> <li>• Small footprint</li> </ul> | <ul style="list-style-type: none"> <li>• Treatment efficiency is dependent on the initial leachate quality and waste composition</li> <li>• Treatment performance is highly variable and not reproducible</li> <li>• Duration of treatment is not known</li> <li>• Post treatment may be required</li> </ul>  |
| Aerobic and Anaerobic Biological Processes      | On-site     | <ul style="list-style-type: none"> <li>• Efficient for BOD<sub>5</sub></li> <li>• Proven technology</li> </ul>  | <ul style="list-style-type: none"> <li>• Treatment efficiency is dependent on the initial leachate quality and waste composition</li> <li>• Treatment performance is highly variable and not reproducible</li> <li>• Does not address bio-toxics</li> <li>• Potentially large sludge production</li> <li>• Potential for odor generation</li> <li>• Large footprint</li> <li>• Potentially large energy requirements</li> <li>• Does not address TDS or conductivity</li> </ul> |
| Carbon Adsorption                               | On-site     | <ul style="list-style-type: none"> <li>• Efficient on COD</li> <li>• Efficient for BOD<sub>5</sub></li> <li>• Efficient on ammonia</li> <li>• Efficient on inorganics</li> <li>• Small footprint</li> </ul> | <ul style="list-style-type: none"> <li>• Treatment efficiency is dependent on the initial leachate quality and waste composition</li> <li>• Treatment performance is highly variable and not reproducible</li> <li>• Pre-treatment required (pH adjustment, filtration)</li> <li>• Does not address TDS or conductivity</li> </ul>  |

| <b>Technology</b>  | <b>Type</b> | <b>Advantages</b>   | <b>Disadvantages</b>   |
|--|-------------|---|--|
| Ion Exchange   | On-site     | <ul style="list-style-type: none"> <li>• Efficient on ammonia</li> <li>• Efficient on inorganics</li> <li>• Efficient on TDS and conductivity</li> <li>• Small footprint</li> </ul> | <ul style="list-style-type: none"> <li>• Treatment efficiency is dependent on the initial leachate quality and waste composition</li> <li>• Treatment performance is highly variable and not reproducible</li> <li>• Inefficient for BOD<sub>5</sub> and COD</li> <li>• Pre-treatment required (pH adjustment, filtration)</li> </ul>  |
| Air Stripping  | On-site     | <ul style="list-style-type: none"> <li>• Efficient on ammonia, at elevated pH</li> <li>• Efficient for VOCs</li> <li>• Small footprint</li> </ul>                                   | <ul style="list-style-type: none"> <li>• Treatment efficiency is dependent on the initial leachate quality and waste composition</li> <li>• Treatment performance is highly variable and not reproducible</li> <li>• pH adjustment required</li> <li>• Inefficient for COD</li> <li>• Inefficient for BOD<sub>5</sub></li> <li>• Inefficient for inorganics</li> <li>• Does not address TDS or conductivity</li> <li>• Potential odor generation</li> <li>• Potential air toxics risks</li> </ul>    |
| Physical/Chemical Processes<br>(Coagulation, Flocculation, Precipitation, Sedimentation) | On-site     | <ul style="list-style-type: none"> <li>• Efficient on COD</li> <li>• Efficient on inorganics</li> <li>• Efficient on TSS</li> <li>• Some disinfection action</li> </ul>             | <ul style="list-style-type: none"> <li>• Treatment efficiency is dependent on the initial leachate quality and waste composition</li> <li>• Treatment performance is highly variable and not reproducible</li> <li>• Limited effectiveness for ammonia</li> <li>• Unknown effectiveness for TDS and conductivity</li> <li>• Potential odor generation</li> <li>• Large footprint</li> <li>• Chemical addition</li> <li>• Potential chemical storage risks</li> <li>• Sludge disposal</li> </ul>      |
| Membrane Filtration  | On-site     | <ul style="list-style-type: none"> <li>• Efficient for TSS</li> <li>• Efficient for particulate organics (pBOD<sub>5</sub>, pCOD)</li> <li>• Some disinfectant action</li> </ul>    | <ul style="list-style-type: none"> <li>• Treatment efficiency is dependent on the initial leachate quality and waste composition</li> <li>• Treatment performance is highly variable and not reproducible</li> <li>• Pre-treatment required (pH adjustment, anti-scalant, cartridge filtration)</li> <li>• Post-treatment required (degasifier, membrane cleaning, backwash)</li> <li>• Brine disposal issues</li> <li>• Potentially large energy requirements</li> <li>• Large footprint</li> </ul> |

| <b>Technology</b> | <b>Type</b> | <b>Advantages</b>   | <b>Disadvantages</b>  |
|-------------------|-------------|---|---|
| Hydrogen Peroxide | On-site AOP | <ul style="list-style-type: none"> <li>• Improves biodegradability</li> <li>• Strong disinfectant action</li> <li>• Efficient on COD</li> <li>• Medium footprint</li> </ul>   | <ul style="list-style-type: none"> <li>• Treatment efficiency is dependent on the initial leachate quality and waste composition</li> <li>• Treatment performance is highly variable and not reproducible</li> <li>• Not efficient by itself</li> <li>• Limited effectiveness on ammonia</li> <li>• Limited effectiveness on inorganics</li> <li>• Limited effectiveness on BOD<sub>5</sub></li> <li>• Does not address TDS and conductivity</li> <li>• Long detention times or storage requirements</li> <li>• Chemical addition</li> <li>• Potential chemical storage risks</li> </ul>  |
| Fenton Process    | On-site AOP | <ul style="list-style-type: none"> <li>• Improves biodegradability</li> <li>• Removes odor and color</li> <li>• Efficient on COD</li> <li>• Medium footprint</li> </ul>   | <ul style="list-style-type: none"> <li>• Treatment efficiency is dependent on the initial leachate quality and waste composition</li> <li>• Treatment performance is highly variable and not reproducible</li> <li>• Limited effectiveness on ammonia</li> <li>• Limited effectiveness on inorganics</li> <li>• Limited effectiveness on BOD<sub>5</sub></li> <li>• Does not address TDS and conductivity</li> <li>• Pre-treatment required (pH adjustment)</li> <li>• Post-treatment required (pH adjustment and filtration)</li> <li>• Long detention times or storage requirements</li> <li>• Chemical addition</li> <li>• Potential chemical storage risks</li> </ul> |
| Ozone             | On-site AOP | <ul style="list-style-type: none"> <li>• Improves biodegradability</li> <li>• Strong disinfectant action</li> <li>• Efficient on COD</li> <li>• Efficient on BOD<sub>5</sub></li> <li>• Increases dissolved oxygen levels</li> <li>• Short detention time</li> <li>• Small footprint</li> </ul> | <ul style="list-style-type: none"> <li>• Treatment efficiency is dependent on the initial leachate quality and waste composition</li> <li>• Treatment performance is highly variable and not reproducible</li> <li>• Formation of byproducts may occur (aldehydes, acids, ketones)</li> <li>• Ozone must be generated on-site</li> <li>• Potentially large energy requirements</li> <li>• Unknown effectiveness on ammonia</li> <li>• Limited effectiveness on inorganics</li> <li>• Does not address TDS and conductivity</li> <li>• Post-treatment often required</li> </ul>  |

| <b>Technology</b>           | <b>Type</b> | <b>Advantages</b>   | <b>Disadvantages</b>   |
|-----------------------------|-------------|---|--|
| Ozone and Hydrogen Peroxide | On-site AOP | <ul style="list-style-type: none"> <li>• Improves biodegradability</li> <li>• Strong disinfectant action</li> <li>• Efficient on COD</li> <li>• Efficient on BOD<sub>5</sub></li> <li>• Increases dissolved oxygen levels</li> <li>• Short detention time</li> <li>• Small footprint</li> </ul> | <ul style="list-style-type: none"> <li>• Treatment efficiency is dependent on the initial leachate quality and waste composition</li> <li>• Treatment performance is highly variable and not reproducible</li> <li>• Formation of byproducts may occur (aldehydes, acids, ketones)</li> <li>• Ozone must be generated on-site</li> <li>• Potentially large energy requirements</li> <li>• Unknown effectiveness on ammonia</li> <li>• Limited effectiveness on inorganics</li> <li>• Does not address TDS and conductivity</li> <li>• Post-treatment often required</li> <li>• Chemical addition</li> <li>• Potential chemical storage risks</li> </ul>    |
| Iron-Mediated Aeration      | On-site AOP | <ul style="list-style-type: none"> <li>• Efficient on metals</li> <li>• Efficient on COD</li> <li>• Efficient on ammonia, with pH adjustment</li> <li>• Improves biodegradability</li> <li>• Disinfectant action</li> <li>• Broad spectrum applicability for organics and inorganics</li> </ul> | <ul style="list-style-type: none"> <li>• Treatment efficiency is dependent on the initial leachate quality and waste composition</li> <li>• Treatment performance is highly variable and not reproducible</li> <li>• Limited effectiveness on TDS and conductivity</li> <li>• Requires metallic iron reagent, partially recoverable</li> <li>• Not catalytic</li> <li>• Can generate important quantities of iron sludge residuals</li> <li>• Longer detention times</li> <li>• Requires filtration post-treatment</li> <li>• Requires pH adjustment for ammonia stripping</li> <li>• Potentially large energy requirements for aeration mixing</li> </ul> |
| Ultraviolet Processes       | EP          | <ul style="list-style-type: none"> <li>• Improves biodegradability</li> <li>• Strong disinfectant action</li> <li>• Efficient on photosensitive COD</li> <li>• Efficient on photosensitive BOD<sub>5</sub></li> <li>• Short detention time</li> <li>• Small footprint</li> </ul>                | <ul style="list-style-type: none"> <li>• Treatment efficiency is dependent on the initial leachate quality and waste composition</li> <li>• Treatment performance is highly variable and not reproducible</li> <li>• Not very efficient by itself</li> <li>• Pre-filtration required for the UV to work efficiently</li> <li>• Does not address ammonia</li> <li>• Does not address inorganics</li> <li>• Does not address TDS and conductivity</li> <li>• Potentially large energy requirements</li> </ul>  |

| <b>Technology</b>        | <b>Type</b> | <b>Advantages</b>  | <b>Disadvantages</b>  |
|--------------------------|-------------|--|---|
| UV and Hydrogen Peroxide | EP          | <ul style="list-style-type: none"> <li>• Improves biodegradability</li> <li>• Strong disinfectant action</li> <li>• Efficient on COD</li> <li>• Lower detention times compared to the H<sub>2</sub>O<sub>2</sub> process</li> <li>• Small footprint</li> </ul>   | <ul style="list-style-type: none"> <li>• Treatment efficiency is dependent on the initial leachate quality and waste composition</li> <li>• Treatment performance is highly variable and not reproducible</li> <li>• Pre-filtration required for the UV to work efficiently</li> <li>• Does not address ammonia</li> <li>• Does not address inorganics</li> <li>• Does not address TDS and conductivity</li> <li>• Potentially large energy requirements</li> <li>• Chemical addition</li> <li>• Potential chemical storage risks</li> </ul>  |
| Photo-Fenton Processes   | EP          | <ul style="list-style-type: none"> <li>• Improves biodegradability</li> <li>• Some disinfectant action</li> <li>• Efficient on COD</li> <li>• Small footprint</li> </ul>   | <ul style="list-style-type: none"> <li>• Treatment efficiency is dependent on the initial leachate quality and waste composition</li> <li>• Treatment performance is highly variable and not reproducible</li> <li>• Pre-filtration necessary for the UV to work more efficiently</li> <li>• Limited effectiveness for ammonia</li> <li>• Limited effectiveness for inorganics</li> <li>• Limited effectiveness for TDS and conductivity</li> <li>• Potentially large energy requirements</li> <li>• Chemical addition</li> <li>• Potential chemical storage risks</li> <li>• Post-treatment often required</li> </ul>                                |
| UV and Ozone             | EP          | <ul style="list-style-type: none"> <li>• Improves biodegradability</li> <li>• Strong disinfectant action</li> <li>• Efficient on COD</li> <li>• Efficient on BOD<sub>5</sub></li> <li>• Increases dissolved oxygen levels</li> <li>• Short detention time (increased hydroxyl radical generation rate)</li> <li>• Small footprint</li> </ul> | <ul style="list-style-type: none"> <li>• Treatment efficiency is dependent on the initial leachate quality and waste composition</li> <li>• Treatment performance is highly variable and not reproducible</li> <li>• Pre-filtration required for the UV to work efficiently</li> <li>• Limited effectiveness for ammonia</li> <li>• Limited effectiveness for inorganics</li> <li>• Limited effectiveness for TDS and conductivity</li> <li>• Potentially large energy requirements</li> <li>• Formation of byproducts may occur (aldehydes, acids, ketones)</li> <li>• Ozone must be generated on-site</li> <li>• Post-treatment required</li> </ul> |

| Technology                           | Type | Advantages   | Disadvantages  |
|--------------------------------------|------|--|--|
| UV and Ozone and Hydrogen Peroxide   | EP   | <ul style="list-style-type: none"> <li>Improves biodegradability</li> <li>Strong disinfectant action</li> <li>Efficient on COD</li> <li>Efficient on BOD<sub>5</sub></li> <li>Increases dissolved oxygen levels</li> <li>Short detention time (increased hydroxyl radical generation rate)</li> <li>Small footprint</li> </ul>   | <ul style="list-style-type: none"> <li>Treatment efficiency is dependent on the initial leachate quality and waste composition</li> <li>Treatment performance is highly variable and not reproducible</li> <li>Pre-filtration required for the UV to work efficiently</li> <li>Limited effectiveness for ammonia</li> <li>Limited effectiveness for inorganics</li> <li>Limited effectiveness for TDS and conductivity</li> <li>Potentially large energy requirements</li> <li>Formation of byproducts may occur (aldehydes, acids, ketones)</li> <li>Ozone must be generated on-site</li> <li>Post-treatment required</li> <li>Chemical addition</li> <li>Potential chemical storage risks</li> <li>Complex process to operate</li> </ul> |
| Photochemical Iron Mediated Aeration | EP   | <ul style="list-style-type: none"> <li>Efficient on metals</li> <li>Efficient on COD</li> <li>Efficient on BOD<sub>5</sub></li> <li>Efficient on ammonia, with pH adjustment</li> <li>Improves biodegradability</li> <li>Strong disinfectant action</li> <li>Broad spectrum applicability for organics and inorganics</li> <li>No pre-treatment required</li> <li>Short detention time</li> <li>Small footprint</li> </ul> | <ul style="list-style-type: none"> <li>Treatment efficiency is dependent on the initial leachate quality and waste composition</li> <li>Treatment performance is highly variable and not reproducible</li> <li>Limited effectiveness on TDS and conductivity</li> <li>Requires metallic iron reagent, partially recoverable</li> <li>Not catalytic</li> <li>Can generate important quantities of iron sludge residuals</li> <li>Requires filtration post-treatment</li> <li>Requires pH adjustment for ammonia stripping</li> <li>Potentially large energy requirements for aeration mixing and ultraviolet energy</li> </ul>  |
| Photocatalytic Oxidation             | EP   | <ul style="list-style-type: none"> <li>Efficient on COD</li> <li>Efficient on BOD<sub>5</sub></li> <li>Efficient on ammonia</li> <li>Catalytic process</li> <li>Improves biodegradability</li> <li>Broad spectrum applicability for organics and inorganics</li> <li>No pre-treatment required</li> <li>Strong disinfectant action</li> <li>Short detention time</li> <li>Small footprint</li> </ul>                       | <ul style="list-style-type: none"> <li>Treatment efficiency is dependent on the initial leachate quality and waste composition</li> <li>Treatment performance is highly variable and not reproducible</li> <li>Limited effectiveness on TDS and conductivity</li> <li>Requires recoverable photocatalyst</li> <li>Potentially large energy requirements for aeration mixing and ultraviolet energy</li> </ul>  |

For the purpose of comparison, a preliminary ranking of these alternatives is based on the following five criteria:

1. **Efficiency of Treatment.** This criterion focuses on pollutant removal performance for the major contaminants of interest in leachate.

2. **Preliminary Costs.** This criterion focuses on the capital and operation and maintenance costs for the proposed treatment process. However, with only pilot-scale and no full-scale demonstration testing results, the determination of capital and operating costs for each of the selected landfill leachate treatment alternatives is preliminary at this stage.
3. **Residuals.** This criterion focuses on solid or liquid by-products generated during treatment or as a consequence of treatment.
4. **Footprint.** This criterion focuses on the physical size requirements of the proposed treatment process.
5. **Others Parameters.** This catch-all criterion includes environmental impacts, odor generation, dependency on climate conditions, etc.

Each treatment process analyzed was assigned a score from 0 to 5 for each of these five criteria. To sort them by importance, a weight was also assigned to each criterion as follows:

- **Efficiency of Treatment**, weight coefficient of 5.
- **Preliminary Costs**, weight coefficient of 3.
- **Residuals**, weight coefficient of 2.
- **Footprint**, weight coefficient of 1.
- **Others Parameters**, weight coefficient of 4.

If an alternative scores 5 on each criterion, then the highest total weighted score is therefore 75. Since costs developed in this report are only preliminary, the ranking presented here is only based on four criteria: efficiency, residuals, footprint, and other parameters, for a total maximum weighted score of 60. The best way to illustrate this ranking system approach is to perform an example. In this case, we will select municipal sewer discharge without pretreatment as an example. Details of how the scores were determined are based on the information collected during the literature review. This example is summarized in Table 8.

**Table 8. Example of alternative analysis selection matrix**

| Criterion         | Weight | Score         | Weighted Score | Reasons  |
|-------------------|--------|---------------|----------------|--|
| Efficiency        | 5      | 2             | 10             | Efficient for BOD but not for COD, Ammonia, or toxic metals                        |
| Preliminary Costs | 3      | Not available | --             |  |
| Residuals         | 2      | 4             | 8              | Tends to increase sludge production and odors at the wastewater treatment facility |
| Footprint         | 1      | 5             | 5              | No on-site treatment means zero footprint  |
| Other Parameters  | 4      | 3             | 12             | Odor generation, impacts on wastewater treatment facility                          |
| Total             |        |               | 35 (out of 60) |  |

The same analysis was repeated for all of the engineering alternatives evaluated

in this report. The results are presented in Table 9 in descending order. The on-site treatment options assume municipal sanitary sewer discharge for disposal. During the course of this study, data will be collected that will allow refinement of the scores, particularly for the PIMA and photocatalytic oxidation processes.

**Table 9. Summary of alternative analysis comparison results**

| Technology  | Efficiency | Residuals | Footprint | Other | Total Weighted Score |
|---|------------|-----------|-----------|-------|----------------------|
| <b>On-Site Management Options</b>   |            |           |           |       |                      |
| Municipal Sewer Discharge without Pre-Treatment                                       | 2          | 4         | 5         | 4     | 39                   |
| Leachate Recirculation Bioreactor   | 4          | 2         | 3         | 3     | 39                   |
| Evaporation   | 2          | 2         | 1         | 3     | 27                   |
| Hauling Off-Site  | 0          | 5         | 5         | 0     | 15                   |
| Deep Well Injection (Natural Attenuation)   | 0          | 5         | 3         | 0     | 13                   |
| <b>On-Site Treatment Options</b>  |            |           |           |       |                      |
| Photocatalytic Oxidation  | 4          | 4         | 3         | 4     | 47                   |
| Membrane Filtration   | 5          | 1         | 3         | 2     | 38                   |
| Iron-Mediated Aeration  | 4          | 1         | 3         | 3     | 37                   |
| Photochemical Iron Mediated Aeration  | 4          | 1         | 2         | 3     | 36                   |
| Hydrogen Peroxide   | 3          | 3         | 2         | 3     | 35                   |
| Ion Exchange  | 3          | 2         | 3         | 3     | 34                   |
| Physical/Chemical Processes (Coagulation, Flocculation, Precipitation, Sedimentation) | 3          | 2         | 2         | 3     | 33                   |
| Fenton Process  | 3          | 1         | 2         | 3     | 31                   |
| UV and Hydrogen Peroxide  | 3          | 3         | 2         | 2     | 31                   |
| Photo-Fenton Processes  | 3          | 1         | 2         | 3     | 31                   |
| Carbon Adsorption   | 3          | 2         | 3         | 2     | 30                   |
| Ultraviolet Processes   | 2          | 4         | 3         | 2     | 29                   |
| UV and Ozone and Hydrogen Peroxide  | 3          | 2         | 2         | 2     | 29                   |
| UV and Ozone  | 3          | 2         | 2         | 2     | 29                   |
| Ozone   | 2          | 2         | 3         | 2     | 25                   |
| Aerobic and Anaerobic Biological Processes  | 2          | 2         | 2         | 2     | 24                   |
| Ozone and Hydrogen Peroxide   | 2          | 2         | 2         | 2     | 24                   |
| Air Stripping   | 1          | 3         | 3         | 2     | 22                   |

In terms of on-site management systems, the bioreactor landfill approach and the direct municipal sewer discharge option are heavily favored. If pre-treatment prior to sewer discharge is desired, then the most advantageous options include the energized processes. The average score obtained for the energized processes is 33.1 compared to 30.2 for the conventional treatment techniques and 30.4 for the advanced oxidation processes. This demonstrates the benefits of AOPs, and especially EPs, which showed the highest average scores. Their main strength is in broad spectrum applicability, higher performance efficiency, and low environmental impacts. However, some improvements can still be accomplished as the highest individual score from the EPs category is still below 50 points (47 out of 60). Furthermore, costs have not been factored, which may be significant.

## 1.4 PROBLEM STATEMENT

Over the past century, environmental engineers have made great strides in improving the quality of our water resources through technology. While many pathogens and acutely toxic contaminants can be virtually eliminated from our drinking water supplies, emerging contaminants continue to plague our precious groundwater resources and our aquatic ecosystems. As we plan for the future and given the fact that a state like Florida has about 800 new residents each day, our current methods of solid waste management begin to come under scrutiny as a possible threat to the protection of our water resources. Over 100 sanitary landfills currently exist in Florida. Of those, 64 have liners and leachate collection systems (2002 data) to prevent leachate migration into drinking water supplies, and this number is expected to continue to grow.

A current survey of 34 Class I landfills in Florida (FDEP 2002) found that approximately 10.5 million gallons per year of variable quality high strength wastewater is generated. From work collected in this study, that number seems to be an underestimate. 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 and ammonia, incinerator ash leachate contains important concentrations of organochlorine compounds and heavy metals (i.e. Pb, Hg, and Cd), which must be removed before safe discharge to the environment.

A major limitation to management of landfill leachate has been the lack of effective methods to guarantee safe long-term disposal. 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 makes matters worse. Many times, hazardous pollutants are not known to be problematic until ecological damage, often irreversible, has been done. The solid waste industry must be proactive in addressing these issues.

Current leachate management options as discussed in the introduction section, include: on-site treatment, municipal sewer discharge, natural attenuation (including deep well injection), or a combination approach. Limited studies have indicated that leachate recirculation may also be viable (Reinhart 1996). A common approach is discharge to a municipal sewage treatment plant. However, studies have shown that hydraulic loading rates greater than 2% will disrupt plant operations (Booth et al. 1996; Çeçen and Çakıroğlu 2001) due to high BOD and ammonia content. Regardless of the disposal option, the nature of the leachate waste stream is such that some form of aerobic treatment is required to reduce leachate strength prior to discharge. However, biological treatment 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, such as activated carbon filtration, membrane processing, air stripping, or reed beds may be indicated. Unfortunately, activated carbon adsorption and certain advanced treatment processes (i.e. O<sub>3</sub>) do not adequately address inorganics, and membrane methods or air stripping merely transfer organics to another phase (i.e. membrane concentrate or the atmosphere).

Because of widely varying practices in solid waste management, an understanding of emerging issues and an all-inclusive solution to long-term management of landfill leachate is currently not available. This research will address these needs in an effort to assist in development of a valuable decision-making tool for solid waste managers.

In summary, long-term management of landfill leachate continues to be a complex issue. One of the reasons is due to the absence of leachate collection in many older landfills. Some are continuously releasing contaminants directly into the environment. A second reason is related to the available treatment technologies, which are not completely satisfactory. There is currently no technology that addresses all the constituents of leachate and produces a safe, dischargeable effluent, without generating dangerous residuals. Some processes can lower the concentration of several constituents, but they either do not treat some others (such as air stripping or aerobic treatment) or produce an even more concentrated residual (such as aerated lagoons or membrane filtration). Newer technologies such as advanced oxidation (AOPs) and energized processes (EPs) show encouraging capabilities for dealing with high strength wastewaters. Among them, the photocatalytic oxidation and IMA technologies and their variations, developed at laboratory scale, seem to be the most capable of producing a safe dischargeable effluent, at a reasonable cost. These technologies are currently under development and have only been the subject of limited research thus far. Greater efforts are necessary in order to have a better understanding of the mechanisms, which will allow for optimization of process efficiency and eventually lowering of costs. Also, several studies cited here (Shu et al. 2006, Meeroff et al. 2006 for instance) demonstrated the multiple benefits of implementing an advanced oxidation process in combination with UV radiation. If the IMA process can be significantly enhanced by ultraviolet radiation in terms of reaction time and removal efficiency by this upgrade, then it should be implemented in this configuration in treatment applications. The only results reported using UV and IMA processes applied to leachate are those conducted by Englehardt et al. (2005) and Meeroff et al. (2006). They concluded that due to technical issues, such as reactor design and insufficient UV power, the IMA and PIMA processes were similar in performance. This research was very limited, and with an improved reactor design and adequate UV intensity, the oxidation power of the PIMA process may be significantly improved compare to the existing IMA process. The development of engineering performance data for the PIMA process and photocatalytic oxidation processes for the treatment of leachate is the subject of this report.

## 1.5 OBJECTIVES

The primary objective is to develop a laboratory scale reactor for the Photochemical Iron-Mediated Aeration and TiO<sub>2</sub>-magnetite photocatalytic oxidation processes. The original designs were based on the developments made by Meeroff et al. (2006), and a schematic of the process is shown in Figure 7 below.

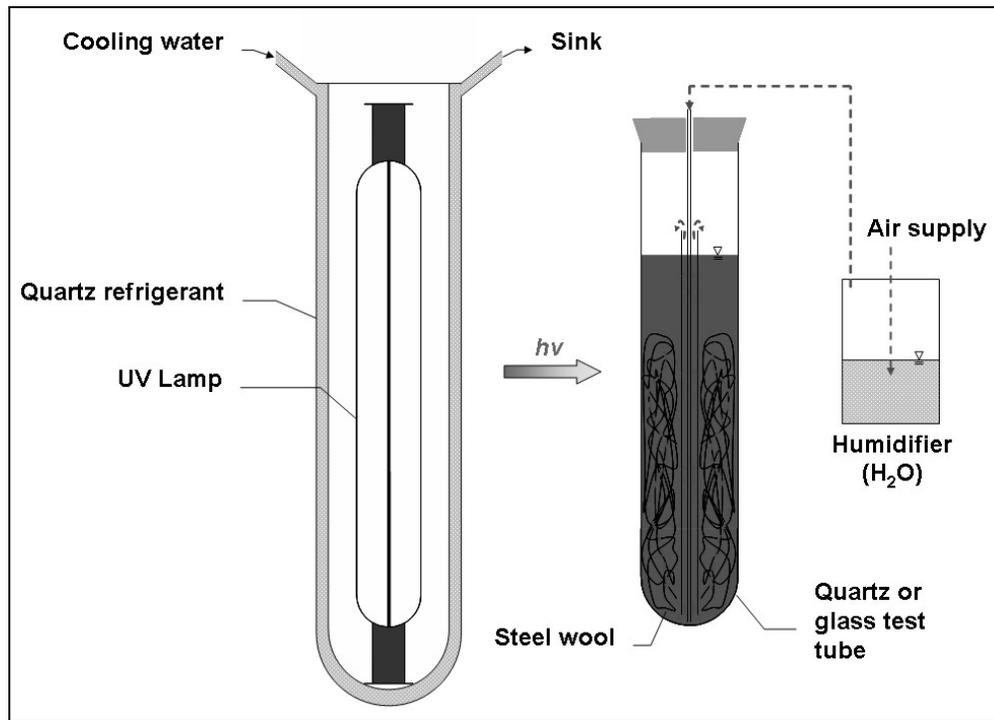


Figure 7. Schematic diagram illustrating the PIMA principle

The PIMA process is an on-site treatment option. It was initially designed to be inserted into a municipal landfill leachate collection and treatment system. Nevertheless, during this experimental approach, the laboratory-scale reactor was designed to allow the researchers to conduct multiple experiments simultaneously (absence or presence of iron, for instance).

The second objective is to evaluate the treatment efficiency of the PIMA process. Research, literature review, and laboratory experimentation were performed, and performance data were generated. Preliminary results of the literature review showed that the most environmentally-relevant components of typical leachate are: ammonia, BOD<sub>5</sub>, COD, dissolved solids, conductivity, and certain heavy metals. The targeted goal was to achieve the allowable concentrations for municipal sewer discharge to consider the effluent as a typical wastewater that will not disrupt the operation of a typical domestic wastewater treatment plant. As the experiments were made in the Civil Engineering Department at the Florida Atlantic University in Boca Raton, FL, the allowable discharge concentrations selected were for the City of Boca Raton

Sewer Use Policy Limits Regulated Pollutants. Those limits were presented in Table 6.

The final step was to compare the experimental results with the other alternative leachate treatment options and to draw up a comparative statement regarding the removal efficiency, the anticipated cost per gallon of treated leachate, and the environmental risks associated with longterm leachate management.

## 2. METHODOLOGY

### 2.1 REACTOR DESIGN AND CONSTRUCTION

#### 2.1.1 PIMA Reactor

The PIMA reactor was designed according to the development made by Meeroff et al. (2006). It was constructed by Eli Brossell, Courtney Skinner and François Gasnier and is comprised of the following components:

1. **Photochemical safety cabinet.** Purchased from Ace Glass Incorporated (Vineland, NJ), the safety cabinet is designed to shield the investigators from the harmful effects of UV radiation. The cabinet 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. The photochemical safety cabinet is shown in Figure 8.



Figure 8. Photochemical Safety Cabinet

- Sample holding rack chamber.** The custom designed rack can accommodate space for up to 32 test tube reactors and the UV lamp in its center. The test tube reactors can be configured at three different distances from the lamp: 6.3 cm, 10.2 cm and 15.2 cm. Note that the distance is measured from the center of the lamp to the center of the test tube. The rack is composed of two stages. The bottom one receives the round end of the test tubes, and the top one aligns the reactors in the upright vertical position. The two stages are linked by four shanks with adjustable thumb screws. Figure 9 is a view from above of this arrangement.

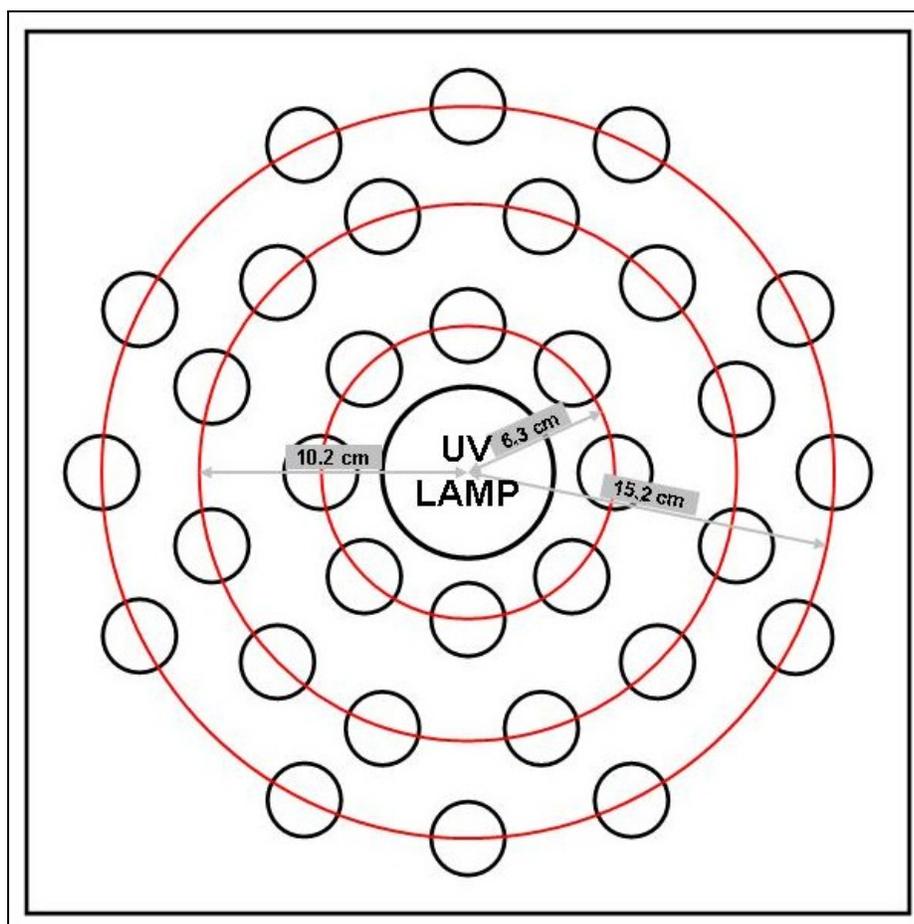


Figure 9. PIMA sample holding rack chamber configuration

- Ultraviolet lamp.** A medium pressure, quartz, mercury-vapor lamp of 450 W from Ace Glass Incorporated (Vineland, NJ) shown in Figure 10 was used for PIMA experiments. According to the manufacturer (see Table 10), 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.



Figure 10. UV lamp immersion well and quartz jacket

Table 10. Proportion of energy radiated by the 450 W medium pressure ultraviolet lamp

| Wave length in nm | Far UV<br>220 - 280 | Middle UV<br>280 - 320 | Near UV<br>320 - 400 | Visible<br>400 - 600 | Infreared<br>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

- Plug flow cooling system for the lamp.** The cooling system is used to maintain a sensible temperature inside the cabinet and delay overheating of the UV lamp. The cooling system is also used to maintain a reasonable and constant temperature of the leachate during treatment to better simulate field operation in which temperatures would not be expected to increase noticeably. If such a technique 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). 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. A calculation was performed to compare the cost of the water wasted with the cost of purchasing

and operating a recirculating chiller. The reactor should be run 24 hours a day for about 9,000 days in order for the cost of the cooling water system to equal the price of an economically-priced recirculating chiller unit.

5. **Aeration system.** This aeration system shown in Figure 11 has three different goals: 1) addition of molecular oxygen, which seems to be a necessary component for the reaction to take place, 2) air stripping, which is needed to eliminate ammonia from the liquid, and 3) mixing of the leachate, which is needed to accomplish homogeneous treatment. The system is comprised of a pump which dispenses the air with a maximum pressure of 4.5 psi from Aquatic Eco-Systems (Apopka, FL). The air flow is divided into two different pipes. The first line is directly connected to a humidifier flask and then to a flow splitting valve, which allows the researchers to provide air flow for up to 8 samples simultaneously whereas 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 11 is a picture of the humidifier set-up. 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). This tube is slipped into a larger quartz tube and both together produce the mixing of the liquid by elevating the bottom liquid to the top of the test tube in a recirculating pattern.



Figure 11. Aeration and humidifier system configuration

6. **Digital thermometer.** Monitoring of temperatures is accomplished using a digital thermometer from Fisher Scientific, which is used to monitor the temperature inside the cabinet and detect any failure of the cooling system. The temperature of the leachate is not directly monitored. However, starting with experiment No. 13, a temperature monitoring tube was used to estimate the leachate temperature. Temperature profiles were recorded using a datalogger (Multi-Function Port Replicator from Kensington Technology Group, Redwood Shores, CA) and specialized software (Traceable<sup>®</sup> Data Acquisition System Version 2.3 from Control Company, Houston, TX). The instantaneous drop of temperature observed at the sampling points is an artifact 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 30 minute does not appear on the temperature profiles reported here.

Simulated and actual leachate samples were placed into the test tube reactors. The tubes have an external diameter of 3.2 cm and an internal diameter of 2.8 cm, their height is 20 cm; as a result, they have a volume of approximately 123 mL. Since UV radiation will be shielded by borosilicate glass, quartz tubes, which allow the passage of UV light, were used for PIMA experiments. During scoping tests, the impact of UV on the process was studied with a borosilicate glass tube (to simulate the IMA process). One quartz tube did not contain iron wool in order to observe the influence of iron on the process (UV process). The reactor was first set up to host 6 test tubes. It was adapted to accept 8 test tubes according to the configuration shown in Figure 12 below. With this configuration, the reactor can hold six PIMA process tests (two at 6.3 cm, two at 10.2 cm and two at 15.2 cm), one IMA control at 10.2 cm and one UV control at 10.2 cm. After conducting the first experiments with simulated leachate, it was determined that the effects of IMA and PIMA were very similar. It was determined that a portion of the light emitted by the mercury lamp may be passing through the borosilicate glass test tube and causing confounding effects. Thus, the reactor was improved by incorporating a thin shield placed between the lamp and the IMA control test tube to insure that no radiation, UV or visible, is received by the IMA control test tube during testing.

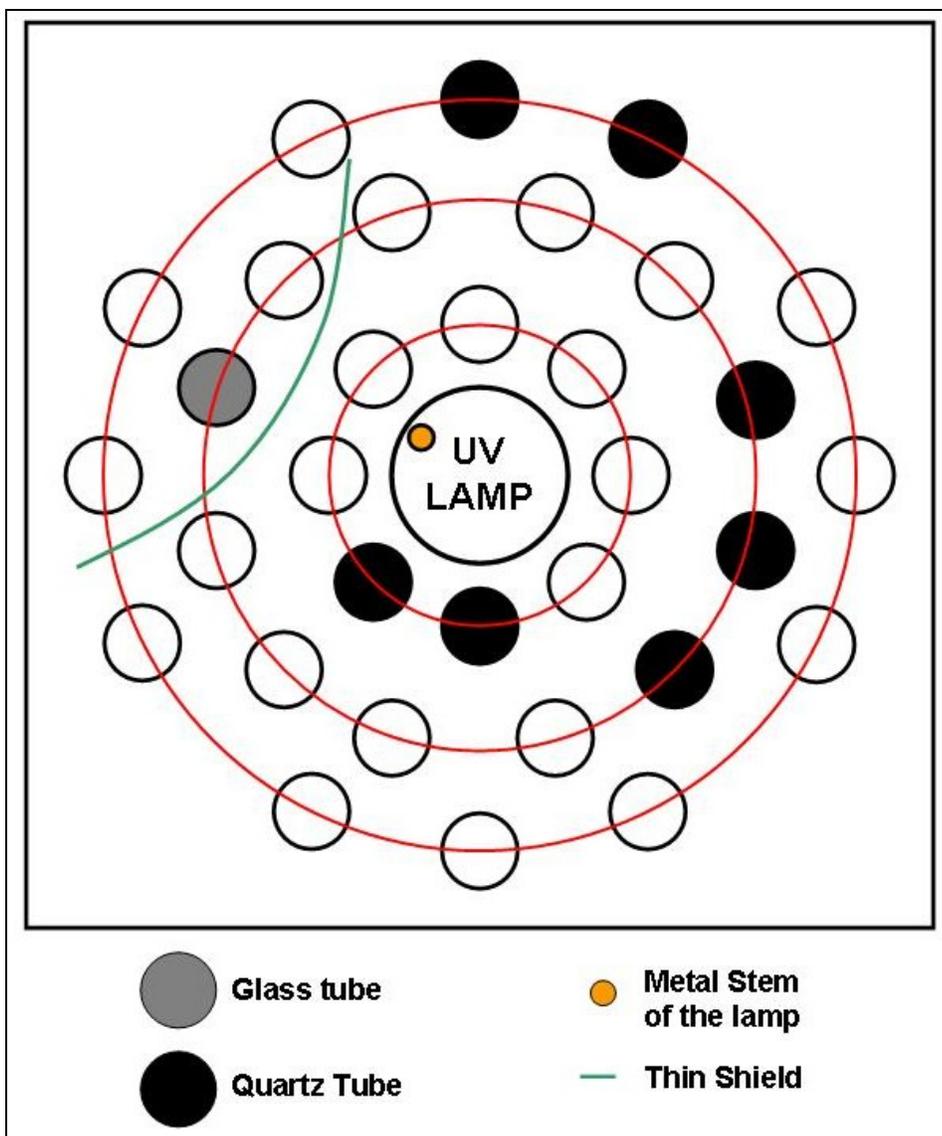
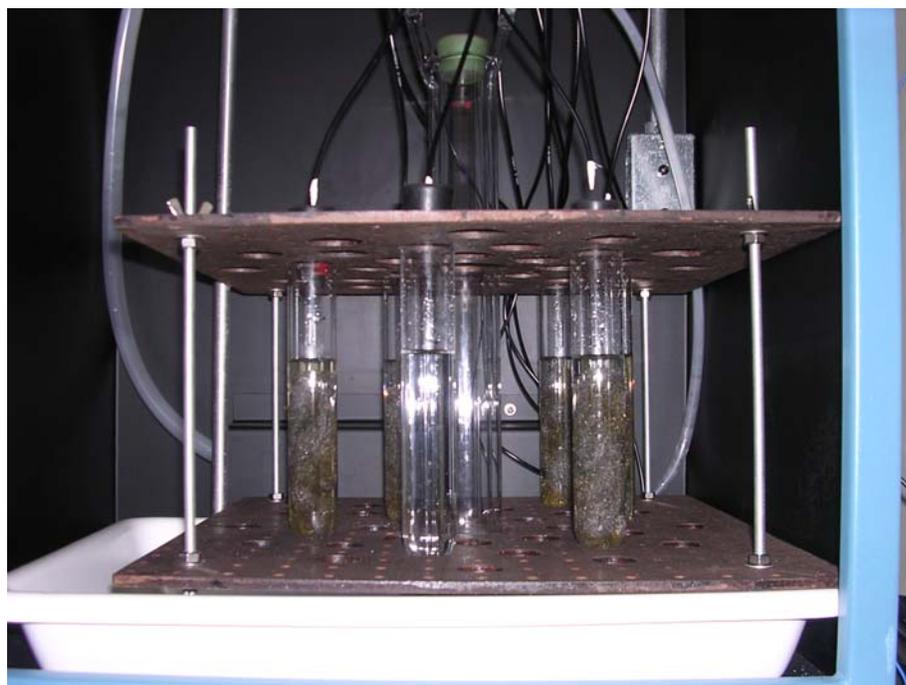


Figure 12. Reactor configuration with test tubes placement

The following photographs illustrate the laboratory scale reactor set-up:



**Figure 13. View of the inside of the safety cabinet and aeration piping**



**Figure 14. Reactor set up prior to an experiment**

### 2.1.2 Photocatalytic Reactor

The photocatalytic reactors were designed according to the development made by Meeroff et al. (2006). They were constructed by Swapnil Jain and Hatsuko Hamaguchi and are comprised of the following components:

1. **Photochemical safety cabinet.** Purchased from Ace Glass Incorporated (Vineland, NJ), the safety cabinet is designed to shield the investigators from the harmful effects of UV radiation. The cabinet 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. This is the same cabinet used for PIMA experiments.
2. **Ultraviolet lamp.** A medium pressure, quartz, mercury-vapor lamp of 450 W from Ace Glass Incorporated (Vineland, NJ) shown in Figure 10 was used for certain experiments. According to the manufacturer (see Table 10), 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. Some other preliminary experiments used a 15 W penray lamp or a 5.5 W penray lamp from Ace Glass Incorporated (Vineland, NJ).
3. **Photoreactor vessel.** The ultraviolet lamp is inserted in a 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 TiO<sub>2</sub> particles and leachate. Several different photoreactor vessels were used during photocatalytic oxidation tests. Sample volumes varied between 250 – 375 mL.

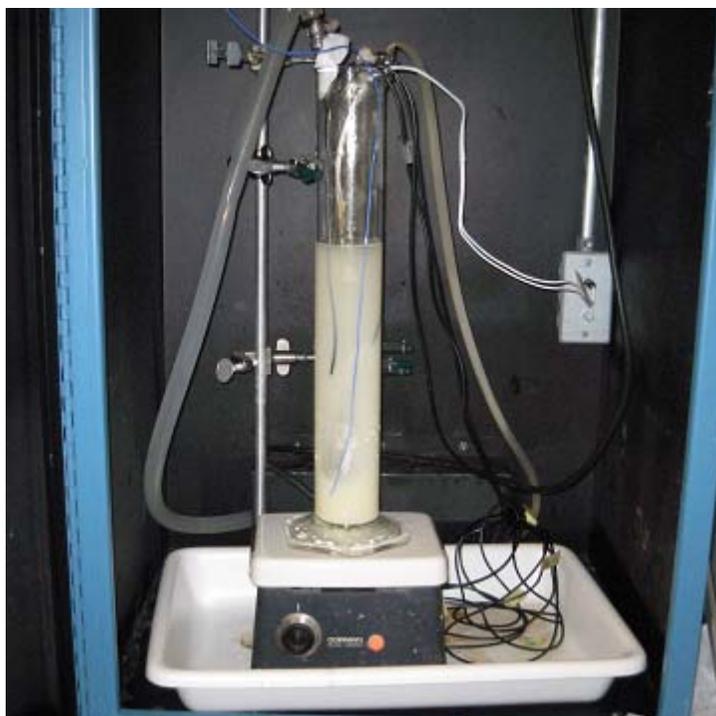


Figure 15. Photoreactor vessel containing  $\text{TiO}_2$  particles and real leachate

4. **Plug flow cooling system for the lamp.** The cooling system is used to maintain a sensible temperature ( $<35^\circ\text{C}$ ) inside the cabinet and delay overheating of the UV lamp. The cooling system is also used to maintain a reasonable and constant temperature of the leachate during treatment to better simulate field operation in which temperatures would not be expected to increase noticeably. If such a technique 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). 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. This is the same cooling system used for PIMA experiments. For some experiments, an ice water bath was also used to support the cooling system as shown in Figure 16.



Figure 16. Picture of cooling by ice water

5. **Aeration system.** This aeration system (Figure 17) is basically the same system used for PIMA experiments shown in Figure 11. The purpose of aeration has three different goals: 1) addition of molecular oxygen, 2) air stripping, which is needed to eliminate ammonia from the leachate, and 3) mixing of the leachate, which is needed to accomplish homogeneous treatment. The system is comprised of a pump which dispenses the air with a maximum pressure of 4.5 psi from Aquatic Eco-Systems (Apopka, FL). The air flow is divided into two different pipes. The first hose is directly connected to a humidifier flask and then to a flow splitting valve, which allows the researchers to provide air flow for up to 8 sample lines simultaneously whereas the second hose is connected to a flow control valve that allows the researchers to regulate the flow of air to avoid sample washout. Figure 11 is a picture of the humidifier set-up. 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).



**Figure 17. Picture of aeration and humidifier systems**

6. **Magnetic stirring.** A stir plate and magnetic stir egg were used to suspend the photocatalytic particles in the solution for the reaction to occur. The magnetic stir egg was placed in the photoreactor vessel below the quartz immersion well, so as not to damage the UV lamp. The whole system was then placed over a magnetic stirrer. When the system was switched on, the stir egg inside the reactor rotated and lifted the photocatalytic particles and together with the addition of the air supply, allowed the researchers to completely mix the solution.
7. **Digital thermometer.** Monitoring of temperatures is accomplished using a digital thermometer from Fisher Scientific, which is used to monitor the temperature inside the cabinet and detect any failure of the cooling system. The temperature of the leachate is not directly monitored. However, starting with experiment No. 13, a temperature monitoring tube was used to estimate the leachate temperature. Temperature profiles were recorded using a datalogger (Multi-Function Port Replicator from Kensington Technology Group, Redwood Shores, CA) and specialized software (Traceable<sup>®</sup> Data Acquisition System Version 2.3 from Control Company, Houston, TX) as shown in Figure 18. The instantaneous drop of temperature observed at the sampling points is an artifact 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 30 minute does not appear on the temperature profiles reported here. The temperature of the leachate and the outside room temperature were directly monitored for some experiments.

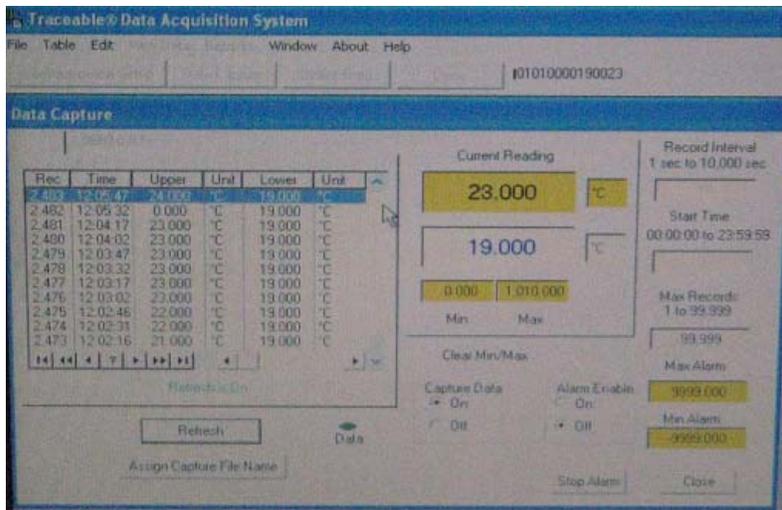


Figure 18. Picture of display of digital thermometer

## 2.2 EXPERIMENTAL PROTOCOLS

Collection of PIMA process performance data was conducted in two different phases. The first set of experiments was conducted with simulated leachate, and the next phase was conducted with actual samples from the Solid Waste Authority of Palm Beach County, FL. All dilutions, standard preparations, and rinsing were conducted using deionized water (18.2 MΩ). A similar approach was used for photocatalytic oxidation experiments with titanium dioxide.

### 2.2.1 Simulated leachate

The utilization of simulated leachate will give individual removal efficiencies for each pollutant (ammonia, BOD<sub>5</sub>, COD, dissolved solids, conductivity, and lead). The first step was the testing of the PIMA process on one pollutant at a time and then on a mixture of pollutants. These first experiments on simulated leachate were used to develop preliminary testing conditions: UV intensity, reaction times and pH but also to determine the magnitude of residual generation and oxidation. To a lesser extent, air requirements and mass of catalyst/reactant were also investigated.

Three experiments at different concentration levels (low, medium and high) were conducted for each constituent. These levels were determined according to the leachate quality data collected from various sources in the State of Florida (refer to Table 4). This allowed the researchers to gain experience with the testing procedures

and analyses and also to make adjustments to the reactor design. The procedures to measure concentrations in the influent and effluent are described later in this section of the report (see Section 2.2.4).

For each experiment, the simulated leachate was prepared by adding the appropriate amount of the contaminant of concern to 1.0 L of reagent water. Samples were mixed vigorously overnight prior to use. Simulated leachate mixtures were prepared similarly.

### **2.2.2 Real leachate**

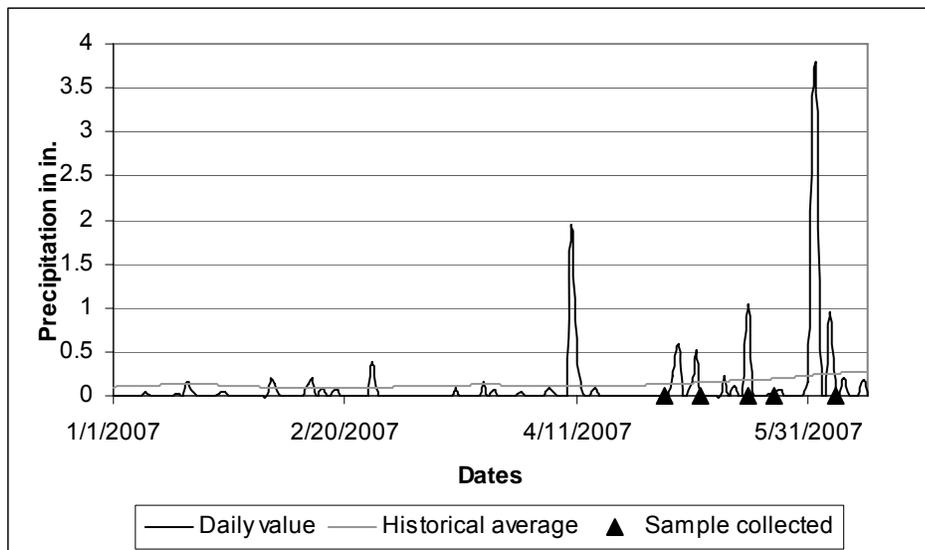
Synthetic leachate provides the substrate for bacteria, but unlike actual leachate, it does not contain a significant microbial population. Therefore, actual field samples need to be tested. Several landfills offered to provide actual leachate samples. Samples were obtained from Polk County, Broward County, and Palm Beach County.

Leachate samples from the Solid Waste Authority of Palm Beach County located in West Palm Beach, FL were collected on the 30<sup>th</sup> of April 2007 in 1.0 L plastic bottles and stored at 4°C. Samples from Polk and Broward were collected similarly. For samples collected at the Solid Waste Authority of Palm Beach County, two bottles were filled with leachate from the Class I landfill. This landfill receives municipal solid waste and incinerator ash. The facility also collects leachate from a Class III landfill and a closed Class I landfill. However, it was chosen to use leachate from the operating Class I landfill as this is the most common type of landfill. Every sample collected afterwards was stored in a one gallon plastic jar. Figure 19 is a photograph of the leachate collection site. Weather conditions were generally dry, so leachates were not diluted by rain water: South Florida is currently under a severe drought. Figure 20 is showing the deficit of precipitation at the Palm Beach International Airport (7 miles away from the landfill) since the beginning of the year 2007. As of the 14<sup>th</sup> of June, 2007, it is showing a current total amount 16.23 inches of rain since the 1<sup>st</sup> of January 2007 when the historical average at that time of the year should be 22.21 inches (data recorded from the web site <http://www.wunderground.com/>). More accurately, the web site of the Solid Waste Authority (<http://www.swa.org>) indicates a deficit of 7.23 inches from the beginning of the year 2007 to the 14<sup>th</sup> of June 2007.

The first experiment with real leachate was conducted on the 2<sup>nd</sup> of May 2007. Leachates were not filtered prior to treatment, unless otherwise noted. The methods used to determine the quality of leachate before, during and after treatment were the same as those used for the simulated leachate and were detailed in the previous section. However, due to technical difficulties, minor adjustments were eventually made as needed. More details are given in the results section.



**Figure 19. Leachate collection site**



**Figure 20. Precipitation at the Palm Beach International Airport (06.14.07)**

A bacterial analysis was performed during experiment No. 22. Two sterile swabs were respectively used to collect samples from the raw leachate and the PIMA treated leachate, at 16 hours. The analysis was made by MICRIM LABS Inc. (Fort Lauderdale, FL). Samples were collected using the aseptic technique.

### 2.2.3 Sample Collection Procedure

For typical PIMA bench scale experiments, the sample collection procedure after treatment was accomplished as follows:

1. Reactor is shut down: UV lamp, aeration system, and thermometer are turned off.
2. The appropriate test tube reactor is taken out of the photochemical safety cabinet, and weighed in order to monitor any losses in mass (and adjust the aeration system as needed).
3. 0.6 mL of sample is collected and filtered with a syringe-less filter.
4. pH is measured and recorded.
5. The test tube reactor is then placed back inside the photochemical safety cabinet.
6. Steps 2 through 5 are repeated for all appropriate test tubes.
7. Once the tube reactors are returned to their places in the rack, the system is then restarted (digital thermometer is turned on, aeration system is turned on, UV lamp is turned on, and the timer is restarted).

All samples were analyzed immediately or preserved overnight at 4°C.

For typical photocatalytic bench scale experiments, the sample collection procedure after treatment was accomplished as follows:

1. Reactor is shut down: UV lamp, aeration system and magnetic stirrer are turned off.
2. The appropriate reactor is taken out of the photochemical safety cabinet and about 6.0 mL of sample solution is transferred to a 14 mL centrifuge tube.
3. The sample is centrifuged at 4000 rpm for 25 minutes at 20°C in a refrigerated centrifuge.
4. pH is measured and recorded.
5. The reactor is then placed back inside the photochemical safety cabinet.
6. The reactor is then restarted (magnetic stirrer is turned on, digital thermometer is turned on, aeration system is turned on, UV lamp is turned on, and the timer is restarted).
7. For photocatalytic reactions, it was desired to recover and reuse the particles after each experiment. After all reaction times in the experiment have been sampled, the remaining solution is centrifuged (4000 rpm, 25 min, 20°C) and washed 3 times by deionized water. The rinsate is transferred to porcelain dishes and kept at 70°C in a drying oven overnight or until completely dry. After the recovery process, the reusable material is weighed and recorded. Approximately 80 percent of TiO<sub>2</sub> was recoverable using this method. For example, in one experiment, 0.8207g of the original 1.0138g of TiO<sub>2</sub> was recoverable (81 percent).

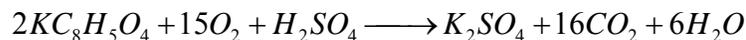
All samples were analyzed immediately or preserved overnight at 4°C.

## 2.2.4 Analytical Methods

The procedures to measure concentrations in the influent and effluent were as follows:

- **Ammonia** (EPA Method # 350.2, Detection of Ammonia by Colorimetry, Nessler Method). An Ammonia (Medium Range: 0.00 to 9.99 mg/L as NH<sub>3</sub>-N) Ion Specific Meter from Hanna Instruments (Woonsocket, RI) was used. The first experiment on ammonia (“High” concentration of 1.00 g/L) was conducted using a solution prepared with a Nitrogen Standard Solution (1.0 mg/mL ± 0.01 mg/mL as N) from VWR International (West Chester, PA). For subsequent experiments, ammonia was simulated using a solution prepared from NH<sub>4</sub>Cl salt. No pre-treatment was executed on the solution. Dilution was necessary to lower the conductivity concentration to the admissible range of the tester. For the first two experiments conducted on real leachate, ammonia was analyzed by an external certified laboratory (see the Heavy Metals section below for details on the laboratory). The method used was the EPA Method # 350.1 (Colorimetric, Automated Phenate). The MDL of this method is 3.00 mg/ L as NH<sub>3</sub>-N.
- **BOD<sub>5</sub>** (standard 5-day BOD test). The methodology followed the guidelines given in the Standard Methods for the Examination of Water and Wastewater manual (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. No pre-treatment was executed on the solution. Due to measurement constraints, experiments were run for 16 straight hours with only 2 samples: one for the PIMA process at middle-distance and the second for the IMA or UV control process, also at middle-distance. Then, three dilutions were prepared: 50, 10 and 5 mL of sample (or others as required), and the BOD<sub>5</sub> measured. Samples were seeded using 2.0 mL of raw wastewater obtained the same day from the South Central Regional Wastewater Treatment Facility in Boynton Beach, FL. Laboratory analytical capacity was expanded before the mixture scoping tests were run, so that additional samples could be tested simultaneously, in subsequent tests.
- **COD** (Reactor Digestion Method DR4000 Procedure from Hach, Loveland, CO). Two types of COD digestion vials were used: 1) High Range (20 to 1,500 mg/L as O<sub>2</sub>) and 2) High Range Plus (200 to 15,000 mg/L as O<sub>2</sub>). For the first experiment, the solution was prepared using a solution of Potassium Acid Phthalate (2000 ± 62 mg/L as C) at 99 percent purity from Cerrilliant Corporation (Round Rock, TX). Subsequent experiments were performed using Potassium Hydrogen Phthalate crystals (KC<sub>8</sub>H<sub>5</sub>O<sub>4</sub> or KHP) at 99.95 to

100.05 percent purity from EMD Chemicals Inc. (Gibbston, NJ), an affiliate of Merck KGaG, Darmstadt, Germany. 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. No pre-treatment was executed on the solution.

- **Conductivity.** Conductivity was tested with a Pocket Pal Conductivity tester (10 to 1,990  $\mu$ S/cm  $\pm$  2 percent at 25°C) from Hach (Loveland, CO). According to Snoeyink and Jenkins (1980), the conductivity (or specific conductivity, SC) of a solution can be estimated using the following formulas:

$$\mu = 2.5 * 10^{-5} * TDS$$

$$\mu = 1.6 * 10^{-5} * SC$$

$$TDS = \frac{1.6}{2.5} * SC$$

For the simulated leachate experiments, dissolved solids were added as sodium chloride salt (NaCl, 99.9 percent purity). Since the Snoeyink and Jenkins equations are empirical, the measured conductivity was not necessarily equal to the estimated value, but this is not considered as an issue as the range of conductivity in real leachate is extremely variable. More information is detailed on this subject later. Dilution was necessary to lower the conductivity concentration to the admissible range of the tester.

- **TDS.** Total dissolved solids were tested using a Pocket Pal TDS tester (10 to 1,990 mg/L  $\pm$  2 percent at 25°C) from Hach (Loveland, CO). Total dissolved solids and conductivity were measured during the same experiments and simulated by the sodium chloride salt. Dilution was necessary to lower the TDS concentration to the admissible range of the tester. No pre-treatment was executed on the solution.
- **Heavy Metals.** Lead was selected as the model contaminant for heavy metals. After trying two different methods (colorimetric and atomic absorption spectroscopy) to measure the lead concentration, the decision was made to analyze the samples using Inductively Coupled Plasma – Mass Spectroscopy (ICP-MS). The presence of a number of interferents in the sample matrix, most notably iron is the primary reason for this choice. This analysis was conducted by a certified laboratory: USBiosystems (Boca Raton, FL). Depending on the settings used, the Minimum Detection Limit (MDL) of this method is on the order of 0.000088 mg/L in the case of EPA method #200.8 or 0.023 mg/L in the case of EPA method #3010/6010B (value

detailed for each experiment). Lead pollutant concentrations were simulated using a Lead Standard Solution of  $100 \pm 1$  mg/L as  $\text{Pb}^{2+}$  from Hach (Loveland, CO) and performing an appropriate dilution. No pre-treatment was executed on the solution.

### **2.2.5 Synthesis of photocatalytic particles**

For certain photocatalytic oxidation experiments, the  $\text{TiO}_2$  particles were synthesized in the FAU Nanoparticle Applications Laboratory. The basic process to synthesize approximately 5-6 grams of photocatalytic material is outlined as follows:

1. Reagent 1: Exactly 5.0 mL of Titanium isopropoxide (TTIP) was added to 25 mL of ethanol.
2. Reagent 2: Exactly 0.5 mL of reagent water and 0.5 mL of 0.10 M HCl were added to 25 mL of ethanol, and stirred vigorously in an ice bath for about 10 minutes.
3. Reagent 1 was added to Reagent 2 dropwise with constant stirring in an ice bath.
4. After the mixture has been completely added, it is removed from the ice bath and stirred vigorously for 1 hour.
5. The ethanol in the mixture is evaporated overnight in the fume hood.
6. The next day, the mixture is calcined at  $450^\circ\text{C}$  in the muffle furnace and cooled down to room temperature slowly.
7. The calcined mixture is then washed with one volume of ethanol and then two volumes of water, with centrifugation separation in between.

## **2.3 PARAMETERS**

### **2.3.1 Hydraulic retention time (HRT)**

Hydraulic retention time (HRT) is one of the most important engineering parameters of the process design. To keep the cost of treatment low, the HRT must also be low because it directly impacts the size of the reactor. Consequently, concentrations were measured at different times of the process. For the PIMA experiments, concentration measurements that could be performed with a small sample (ammonia, COD, conductivity and TDS) were made after zero, two, six, sixteen and twenty four hours of treatment. Preliminary experiments conducted showed a measurable removal after sixteen hours, but no significant improvement after eight additional hours. For the  $\text{BOD}_5$  and lead experiments, the treatment was run for sixteen hours and only one measurement was performed. Monitoring the concentrations at different times was necessary to develop an understanding of the kinetics of the PIMA process.

Similarly, the photocatalytic oxidation experiments were monitored at various

time intervals to determine information regarding the kinetics and removal efficiencies of the process. The exact time intervals are listed for each experiment in the results section.

### 2.3.2 Distance (UV radiation intensity)

The UV energy is provided by a 450-W medium pressure mercury vapor lamp from ACE Glass Inc. (Vineland, NJ), or in some experiments by a 15 W or 5.5 W pen-ray lamp. Approximately 40-48 percent of the radiated energy is in the ultraviolet spectrum (from 220 nm to 400 nm). For PIMA experiments, test tubes were placed in the reactor at different distances from the UV source so that the dose of radiation received by individual samples could be controlled.

The irradiance of the lamp was first measured on March 21, 2006, with a UV light meter from Fisher Scientific (range from 0 to 19.99 mW/cm<sup>2</sup> ± 2 percent). The intensity was calculated according to the inverse square law, which states that the intensity per unit area varies in inversely proportion to the square of the distance between the source and the surface receiving the radiation. If the light intensity (in mW) is I, the distance (in cm) is d, and the irradiance (in mW/cm<sup>2</sup>) is E, then:

$$E = \frac{I}{d^2}$$
$$\frac{E_2}{E_1} = \left( \frac{d_1}{d_2} \right)^2$$

The results of UV irradiance measurements are presented in Table 11 below. These data, which illustrate the difference in the radiation received by the samples at the three distances, will be used in the discussion of the process results. Since the intensity of the lamp is expected to decrease over time, a second set of measurements was repeated April 9, 2007. Fifteen experiments were conducted between the two dates. Results are presented in Table 12 below. The fifteen experiments run between the two measurements correspond to a utilization of the UV lamp of approximately 284 hours. The intensity of the lamp declined by 27 percent during this time.

**Table 11. UV energy measurements and calculations (March 21, 2006)**

| Parameters                       | Distance |        |        |
|----------------------------------|----------|--------|--------|
|                                  | Close    | Middle | Far    |
| Distance from the lamp in cm     | 6.3      | 10.2   | 15.2   |
| Irradiance in mW/cm <sup>2</sup> | 56.7     | 21.6   | 9.7    |
| Intensity in mW                  | 2251.5   | 2251.5 | 2251.5 |

**Table 12. UV energy measurements and calculations (April 9, 2007)**

| Parameters                       | Distance |        |        |
|----------------------------------|----------|--------|--------|
|                                  | Close    | Middle | Far    |
| Distance from the lamp in cm     | 6.3      | 10.2   | 15.2   |
| Irradiance in mW/cm <sup>2</sup> | 41.3     | 15.8   | 7.1    |
| Intensity in mW                  | 1641.2   | 1641.2 | 1641.2 |

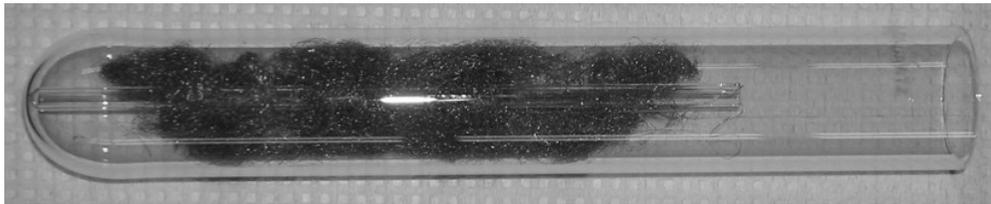
For photocatalytic oxidation experiments, the leachate solutions were placed directly in the photoreactor vessel containing the UV lamp immersion well. Ultraviolet energy was varied by using different lamps including: 5.5 W, 15W, and 450W.

### 2.3.3 Iron fibers

For PIMA experiments, two options were available for providing the iron reagent for the reaction: 1) iron fibers or 2) iron filings. Iron filings have been previously used by Dr. Meeroff in preliminary experiments, and he demonstrated that this form of iron was not effective (data not published). However significant removal was achieved while using iron fibers (Meeroff et al. 2006; Englehardt et al. 2003,; Englehardt et al. 2005). This is the main reason why iron fibers were also chosen for this study. The iron used during all experiments came from Soap-Free Steel Wool manufactured by Brillo (New York, NY). Steel usually contains between 0.2 to 2.0 percent of carbon, the remaining portion is iron. Steel wool fibers were chosen in lieu of iron fibers in order to minimize costs in laboratory scale. Before conducting the experiments, the fibers were stretched and pulled apart into a thin flat sheet and cleaned. To do so, they were plunged into a bath of hexane (minimum 85 percent purity) from VWR International (West Chester, PA). After drying, they were plunged into a second bath of 0.10 M hydrochloric acid prepared from a stronger acid solution (36.5 - 38.0 percent purity) from VWR International (West Chester, PA) and completely dried using a heat gun to remove impurities and surface oils still present from the manufacturing process. They were stored in a sealed bag to prevent

oxidation prior to initiating the experiment. After the completion of the experiment, the remaining material was discarded, and new steel wool was used for each new experiment.

For all simulated leachate scoping tests, two grams of steel wool were wrapped loosely around the aeration tube and plunged into the sample test tubes as demonstrated in Figure 21. For the real leachate experiments, the first two experiments were conducted using two grams of steel wool per sample. Then, for the three following experiments, the amount of steel wool was varied in order to estimate the impact of initial dose of steel wool on the process performance. Samples containing 0.5 g, 1.0 g, and 2.0 g of steel wool were tested.



**Figure 21. Steel wool wrapped loosely around the aeration tube**

The amount of steel wool used was recorded for every experiment before filling the reactors with influent. In addition, after experiment No. 13, the remaining steel wool was cleaned under deionized water to remove the excess particles, dried in the oven at 105°C, and weighed to estimate the maximum dissolved iron concentration in the reactor, gravimetrically. Additional measurements were performed using a titrimetric method to estimate the dissolved iron concentration in the sample. Table 13 presents the results of these calculations and demonstrates that UV enhances the dissolution and subsequent precipitation of iron to ferric precipitates.

**Table 13. Iron fiber consumption during experiment No. 13**

| Process           | Initial mass of steel wool in g<br>(1) | Remaining mass of steel wool after 24 hours in g<br>(2) | Percentage of steel wool remaining<br>(3) | Estimate of the maximum iron concentration in the effluent in g/L*<br>(4) = [(1) - (2)] / 0.075 |
|-------------------|--|---|---|---|
| IMA, x = 10.2 cm  | 2.00                                   | 1.84  | 92%                                       | 2.13  |
| PIMA, x = 6.3 cm  | 1.89                                   | 1.40  | 74%                                       | 6.53  |
| PIMA, x = 6.3 cm  | 2.10                                   | 1.62  | 77%                                       | 6.40  |
| PIMA, x = 10.2 cm | 2.00                                   | 1.65  | 83%                                       | 4.67  |
| PIMA, x = 10.2 cm | 2.02                                   | 1.75  | 87%                                       | 3.60  |
| PIMA, x = 15.2 cm | 2.00                                   | 1.81  | 91%                                       | 2.53  |

\* Estimation made using 75 mL of sample.

In addition to these calculations, USBiosystems certified laboratory was contracted to measure the concentration of soluble iron in the effluent after treatment in experiment No. 14. Results are presented in Table 14. At first, the results obtained for experiment No. 14 appeared to be unusually low compared to measurements conducted in the laboratory with a digital titration method (measurements made using TitraVer Titration Cartridge, method 8214 from Hach, Loveland, CO), and USBiosystems was asked to re-run their analysis. The results came back unchanged. This means that during the sixteen hours of the process, only a small quantity of iron actually dissolved into the effluent; the major part remained in the steel wool form or fell to the bottom sludge as ferric precipitates, readily separated by filtration. This explains the loss of mass pointed out in the previous paragraph. This is a very interesting result as the iron concentration levels are in fact lower than the limit authorized by the City of Boca Raton (21 mg/L). However, subsequent experiments demonstrated a wider range of concentration (0.13 to 110 mg/L). Differences in mixing regime and aeration rate may explain the variability and the large amount of dissolved iron in the IMA sample of experiment No. 15 or the very low amount in one of the PIMA samples of experiment No.16. Iron concentration was also evaluated during a real leachate experiment (experiment No. 21). Table 15 summarizes the results. In raw leachate, iron was measured at a higher concentration level than in the effluent; such levels were all below the limits for direct sewer discharge. This table also demonstrates that soluble iron did not correlate with the initial reactant dose. This may signify that the dose of iron can be lowered even more without altering process performance. However, this finding requires further study for optimization.

**Table 14. Iron concentration in the effluent of the simulated leachate experiments**

| Process           | Experiment 14, Lead Medium                                      |               | Experiment 15, mixture Medium                                     | Experiment 16, Lead Medium                                       | Experiment 17, mixture Low  |
|-------------------|---|---------------|---|--|---|
|                   | Soluble iron concentration in the effluent after 16 hrs in mg/L |               | Soluble iron concentration in the effluent after 16 hours in mg/L | Soluble iron concentration in the effluent after 4 hours in mg/L | Soluble iron concentration in the effluent after 16 hours in mg/L |
|                   | Measurement 1   | Measurement 2 |   |  |   |
| IMA, x = 10.2 cm  | U   | U             | 110.00  | 16.00  | -   |
| PIMA, x = 6.3 cm  | U   | U             | -   | -  | -   |
| PIMA, x = 6.3 cm  | U   | U             | -   | -  | -   |
| PIMA, x = 10.2 cm | 4.40  | 3.70          | 20.00   | 67.00  | 4.50  |
| PIMA, x = 10.2 cm | 4.50  | 6.80          | 58.00   | 0.15   | 6.30  |
| PIMA, x = 10.2 cm | -   | -             | 52.00   | -  | 6.90  |
| PIMA, x = 10.2 cm | -   | -             | -   | -  | 8.10  |
| PIMA, x = 15.2 cm | 7.50  | 6.30          | -   | -  | -   |
| PIMA, x = 15.2 cm | 0.15  | 0.13          | -   | -  | -   |

U The concentration was measured below the MDL of = 0.075 mg/L  
 - The iron was not measured for these samples

**Table 15. Iron concentration in the influent and effluent of real leachate experiment No. 21**

| Process           | Experiment 21, Real leachate |   |
|-------------------|------------------------------|---|
|                   | Dose of stell wool in g      | Soluble iron concentration in the effluent after 16 |
| Raw Leachate      |                              | 10.30   |
| PIMA, x = 10.2 cm | 2.1                          | 2.05  |
| PIMA, x = 10.2 cm | 1.0                          | 6.70  |
| PIMA, x = 10.2 cm | 0.5                          | 2.45  |

These results demonstrate that the part of the steel wool iron fibers that do not remain in this form, are not particularly soluble and rapidly fall to the bottom as ferric iron sludge. Using the limited data available, a range of 2.4 g to 6.5 g of iron sludge is generated per liter of leachate treated.

#### **2.3.4 Mixing and aeration conditions**

Mixing of the samples was executed jointly with the air stripping. As described earlier, this was accomplished by a combination of a thin glass pipe inserted inside a slightly larger diameter quartz tube. A schematic of this principle is shown in Figure 3. Figure 11 is an illustration of the actual mechanism, and Figure 22 shows a quartz test tube reactor with and without the aeration system working with the “tube-in-tube” recirculation mixing approach.

The air flow was measured using a Humonics Veri\_Flow Electronic Flowmeter (model 650, operating range: 5.0 - 5,000 mL/min  $\pm$  2 percent) from Agilent Technologies Co. (Shanghai, P.R. China). Table 16 below shows the results of selected measurements conducted from May 2006 to June 2007 with all eight tube reactors in operation simultaneously. This represents the most conservative estimates of air flow delivery to the reactors. Complementary measurements were made during the entire study. They showed that the variability of air flow delivery ranged from 0.06 to 0.668 L/min (nearly one order of magnitude). However, the ability to adjust the air flow reproducibly was limited because the air cannot be equally divided into the eight flow paths (nearly every experiment was conducted with eight test tube reactors). If the flow was too strong, it would blow the liquid out of the tube. This was especially true for the real leachate samples, which had a tendency to generate foam. However if the setting was too low, the air flow was not powerful enough to completely mix the samples. A compromise was found in order to limit both negative actions.



Figure 22. Aeration System Off (left) and On (right)

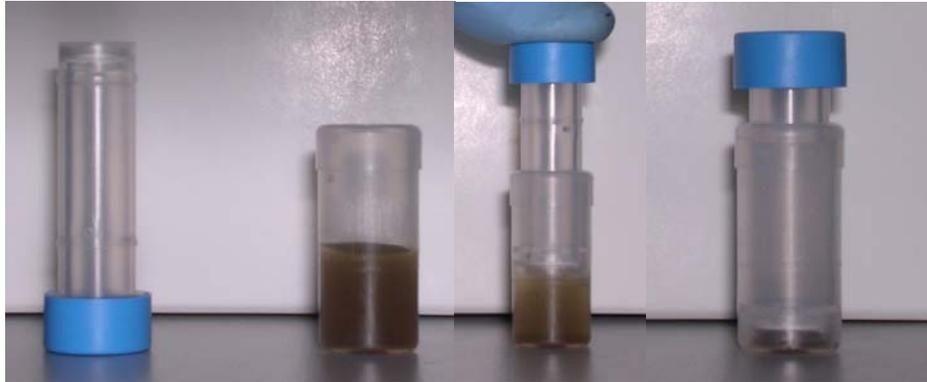
Table 16. Summary of air flow measurements in L/min for selected PIMA experiments

| Flow path              | Date of measurement |          |          |          |
|------------------------|---------------------|----------|----------|----------|
|                        | 05/03/06            | 05/04/06 | 02/19/07 | 06/12/07 |
| 1, IMA control process | 0.138               | 0.130    | 0.084    | 0.105    |
| 2, UV control process  | 0.101               | 0.110    | 0.064    | 0.068    |
| 3, PIMA process        | 0.093               | 0.109    | 0.175    | 0.185    |
| 4, PIMA process        | 0.054               | 0.067    | 0.090    | 0.100    |
| 5, PIMA process        | 0.152               | 0.196    | 0.045    | 0.368    |
| 6, PIMA process        | 0.202               | 0.338    | 0.490    | 0.668    |
| 7, PIMA process        | 0.206               | 0.435    | 0.500    | 0.630    |
| 8, PIMA process        | 0.080               | 0.089    | 0.155    | 0.190    |

### 2.3.5 Filtration

Since the influent was not pre-filtered, filtration was necessary to eliminate suspended solids such as iron particles in simulated and real leachate after treatment. This process simulated sedimentation or filtration in the field. Before composition analysis, all samples were filtered using either syringe-less filters (see Figure 23) or

vacuum filtration (see Figure 24). In both cases, the filter pore size was  $0.45\mu\text{m}$ . The syringe-less filters were manufactured by Whatman Inc. (Clifton, NJ) and glass microfiber filters used with the vacuum filtration process were from Pall Corporation (Ann Arbor, MI). The syringe-less filters were used for the intermediate and final monitoring experiments for PIMA tests, where only a small quantity (0.2 to 0.4 mL) of samples was necessary to conduct the measurements. Vacuum filtration was used at the end of the treatment, for the BOD<sub>5</sub> and lead experiments, where only one measurement was performed and a larger volume of sample was required for analysis.



**Figure 23. Syringe-less filter operation**



**Figure 24. Vacuum filtration apparatus**

For some experiments involving real leachates, the influent was filtered by gravity using Whatman #4 filter paper (20 cm circles) and a glass funnel as pictured in Figure 25.



**Figure 25. Photograph of gravity filtration procedure used with real leachates tested by photocatalytic oxidation**

### 2.3.6 pH

pH is an important parameter in water related sciences. Except for experiments No. 02 and 03, pH was recorded during every experiment using pH Indicator Strips from Whatman Inc. (Clifton, NJ). However, pH was never adjusted, unless noted otherwise. This choice was made in order to limit the cost impact of chemicals required to lower (or increase) the pH before treatment and then higher (or lower) it after in order to respect the discharge limits (6.0 - 8.5 in Boca Raton). For some readings a Hach Sension 4 pH meter calibrated daily with 4.0, 7.0, and 10.0 buffers was also used.

### 3. RESULTS AND DISCUSSION

The following section describes the results from PIMA experiments using simulated leachates and real leachate under various conditions. Then experiments involving photocatalysis with TiO<sub>2</sub> are described and discussed.

#### 3.1 PIMA INDIVIDUAL SCOPING TESTS: SIMULATED LEACHATE

Table 17 summarizes the order of individual scoping tests on simulated leachate experiments.

**Table 17. Order of execution of the PIMA simulated leachate experiments**

| Experiment Number | Component tested                   | Level  | Date      | Shield used? |
|-------------------|------------------------------------|--------|-----------|--------------|
| 01                | Conductivity                       | Test   | 2-Feb-06  | No           |
| 02                | COD                                | Low    | 7-Feb-06  | No           |
| 03                | Ammonia                            | High   | 2-Mar-06  | No           |
| 04                | COD                                | High   | 29-Mar-06 | No           |
| 05                | Conductivity & TDS                 | Medium | 15-Aug-06 | No           |
| 06                | COD                                | Medium | 23-Aug-06 | No           |
| 07                | BOD <sub>5</sub>                   | Medium | 12-Sep-06 | No           |
| 08                | Ammonia                            | Medium | 20-Sep-06 | No           |
| 09                | Ammonia                            | Low    | 28-Sep-06 | No           |
| 10                | BOD <sub>5</sub>                   | High   | 3-Oct-06  | No           |
| 11                | BOD <sub>5</sub>                   | Low    | 11-Oct-06 | No           |
| 12                | Conductivity & TDS                 | High   | 18-Oct-06 | No           |
| 13                | Conductivity & TDS                 | Low    | 2-Nov-06  | Yes          |
| 14                | Lead                               | Medium | 8-Jan-07  | Yes          |
| 16                | Lead & BOD <sub>5</sub> separately | Medium | 21-Feb-07 | Yes          |

Beginning with COD, this section presents the results obtained during this first phase of scoping experiments. Table 18 below summarizes the starting concentration of every component tested during this phase. Deviations were made from the typical concentration values compiled for the State of Florida (Table 4) in order to generate relevant performance data; it concerns especially the components that have a lower limit of zero and lead.

**Table 18. Initial concentrations of individual simulated leachate tests using PIMA**

|  |              | <b>Level</b> |        |        |
|--|--------------|--------------|--------|--------|
|  |              | Low          | Medium | High   |
| <b>COD, in g/L as O<sub>2</sub></b>              | Theoretical  | 0.05         | 3.00   | 14.00  |
|  | Experimental | 1.05         | 3.30   | 10.90  |
| <b>Conductivity in μS/cm</b>                     | Theoretical  | 1,000        | 11,600 | 95,000 |
|  | Experimental | 2,750        | 16,250 | 81,625 |
| <b>TDS in g/L</b>                                | Theoretical  | 0.90         | 9.30   | 88.00  |
|  | Experimental | 0.83         | 8.12   | 40.00  |
| <b>BOD<sub>5</sub>, in mg/L as O<sub>2</sub></b> | Theoretical  | 0            | 150    | 445    |
|  | Experimental | 55           | 120    | 425    |
| <b>Ammonia, in mg/L as NH<sub>3</sub>-N</b>      | Theoretical  | 0            | 500    | 1,350  |
|  | Experimental | 110          | 540    | 930    |
| <b>Lead, in mg/L</b>                             | Theoretical  | 0.00         | 0.03   | 0.10   |
|  | Experimental | n/a          | 0.30   | n/a    |

### 3.1.1 Chemical Oxygen Demand (COD)

Experiments on chemical oxygen demand were the first to be fully completed. Three scoping tests for COD have been performed. The initial concentrations were respectively 1.05, 3.30 and 10.90 g/L as O<sub>2</sub> for the low, medium and high concentration levels.

#### 3.1.1.1 Low COD concentration level

The first experiment (experiment No. 02), performed on the low concentration level (initial concentration measured at 1.05 g/L as O<sub>2</sub>, influent prepared with 100 mL of the 2,000 mg/L as C using KHP Standard Solution diluted in a 500 mL flask), was monitored after zero, two, four and twenty-four hours of treatment. Table 19 presents the results of this experiment. It showed a best removal of 54 percent for the PIMA process at close-distance (6.3 cm), the concentration was reduced to 0.58 g/L as O<sub>2</sub> after 24 hours. The IMA process, at mid-distance achieved a removal of 21 percent and reduced the COD concentration to 0.83 g/L as O<sub>2</sub> after 24 hours. The UV process control at mid-distance achieved a removal of 13 percent after 4 hours, in which the COD concentration was reduced to 0.91 g/L as O<sub>2</sub>. The dose of iron was 2.0 g per sample, and the air flow was not changed during the whole experiment. After twenty-four hours of experiment, one PIMA sample (at close distance, 6.3 cm) was empty. This was due to sample overflow from uneven air mixing: the air flow on this particular test tube was strong enough to blow the liquid completely out of the tube. And, with evaporation helping, it emptied the tube. The action taken to remedy this undesired outcome has been to take more care of the air flow set up after each

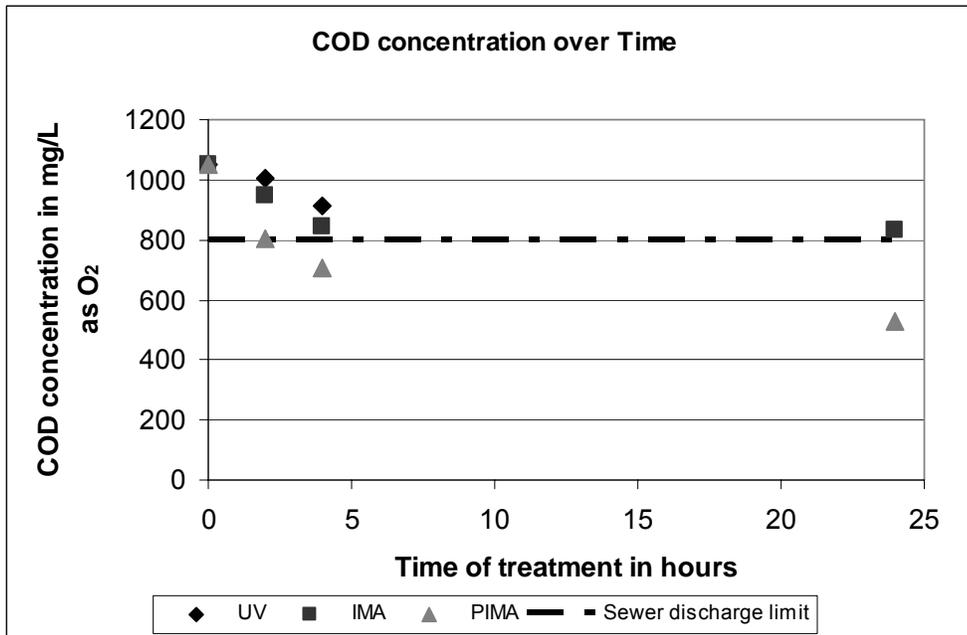
sampling and to monitor the mass of test tubes and record any losses.

**Table 19. Summary of simulated COD experimental results for the individual PIMA medium concentration level (1.05 g/L as O<sub>2</sub>) scoping tests**

| Process           | C / C <sub>0</sub> |
|-------------------|--------------------|--------------------|--------------------|--------------------|
|                   | 0 hr               | 2 hrs              | 4 hrs              | 24 hrs             |
| IMA, x = 10.2 cm  | 1                  | 0.90               | 0.80               | 0.79               |
| UV, x = 10.2 cm   | 1                  | 0.96               | 0.87               | 0.04               |
| PIMA, x = 6.3 cm  | 1                  | 0.72               | 0.64               | 0.46               |
| PIMA, x = 6.3 cm  | 1                  | 0.74               | 0.69               | tube empty         |
| PIMA, x = 10.2 cm | 1                  | 0.75               | 0.65               | 0.49               |
| PIMA, x = 15.2 cm | 1                  | 0.85               | 0.71               | 0.56               |

*Note: The extremely low value obtained after 24 hours with the UV process is certainly due to a handling error during the measurement protocol.*

The level of removal achieved during this experiment was acceptable since the effluent meets the allowable discharge criteria for the public sewer network of Boca Raton. Figure 26 shows the COD concentration over treatment. The dashed line represents the discharge limit (800 mg/L as O<sub>2</sub>). After two hours, the PIMA effluent could have already been authorized.



**Figure 26. COD concentration throughout the individual simulated low level test**

### 3.1.1.2 Medium COD concentration level

The second experiment (experiment No. 06), performed on the medium concentration level (initial concentration measured at 3.30 g/L as O<sub>2</sub>, influent prepared by adding 2.6 g of KHP to 1.0 L of deionized water), was monitored after zero, two, six, sixteen, and twenty-four hours of treatment. Table 20 presents the results of this experiment. The dose of iron was 2.0 g per sample, and the air flow was not changed during the whole experiment. The temperature was recorded and the profile is shown below in Figure 27. After 24 hours, it showed a best average removal of 44.5 percent for the PIMA process at mid-distance (10.2 cm). The two removals recorded under these conditions were 47 and 42 percent, and the effluent COD concentration was reduced to an average value of 1.8 g/L as O<sub>2</sub>. Similarly to the first experiment, the mid-distance PIMA process showed the highest removal. However, the difference with the IMA process is not as important. Indeed, the IMA process, also at mid-distance achieved a removal of 46 percent and lowered the concentration to 1.78 g/L as O<sub>2</sub> after 24 hours of treatment. However, the UV control only achieved 8 percent removal, and after 24 hours the concentration was 3.03 g/L as O<sub>2</sub>.

**Table 20. Summary of simulated COD experimental results for the individual PIMA medium concentration level (3.30 g/L as O<sub>2</sub>) scoping tests**

| Process           | C / C <sub>0</sub> |
|-------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
|                   | 0 hrs              | 2 hrs              | 6 hrs              | 16 hrs             | 24 hrs             |
| IMA, x = 10.2 cm  | 1                  | 0.83               | 0.66               | 0.47               | 0.54               |
| UV, x = 10.2 cm   | 1                  | 1.05               | 1.01               | 0.89               | 0.92               |
| PIMA, x = 6.3 cm  | 1                  | 0.96               | 0.68               | 0.53               | 0.64               |
| PIMA, x = 6.3 cm  | 1                  | 0.84               | 0.69               | 0.63               | 0.81               |
| PIMA, x = 10.2 cm | 1                  | 0.97               | 0.67               | 0.50               | 0.53               |
| PIMA, x = 10.2 cm | 1                  | 0.93               | 0.65               | 0.52               | 0.58               |
| PIMA, x = 15.2 cm | 1                  | 0.96               | 0.72               | 0.49               | 0.57               |
| PIMA, x = 15.2 cm | 1                  | 1.00               | 0.65               | 0.48               | 0.59               |

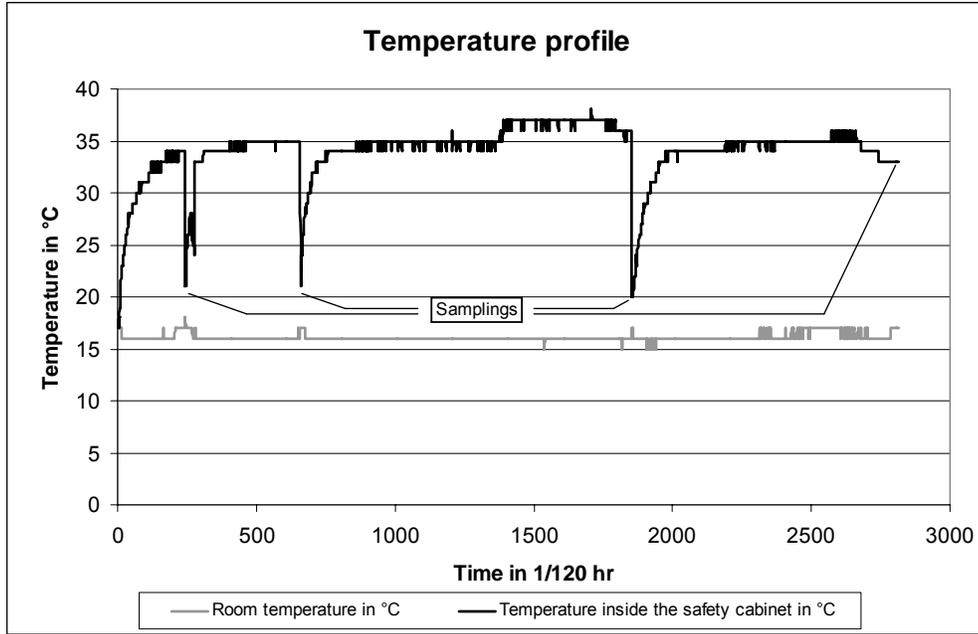


Figure 27. Temperature profile of experiment No. 06

The level of removal achieved during this experiment was not acceptable, since the effluent did not meet the allowable discharge criteria for the public sewer network of Boca Raton. Table 20 and Figure 28 show the COD concentration over treatment time. The dashed line represents the discharge limit. Even after twenty four hours, the PIMA effluent does not meet the criteria for discharge.

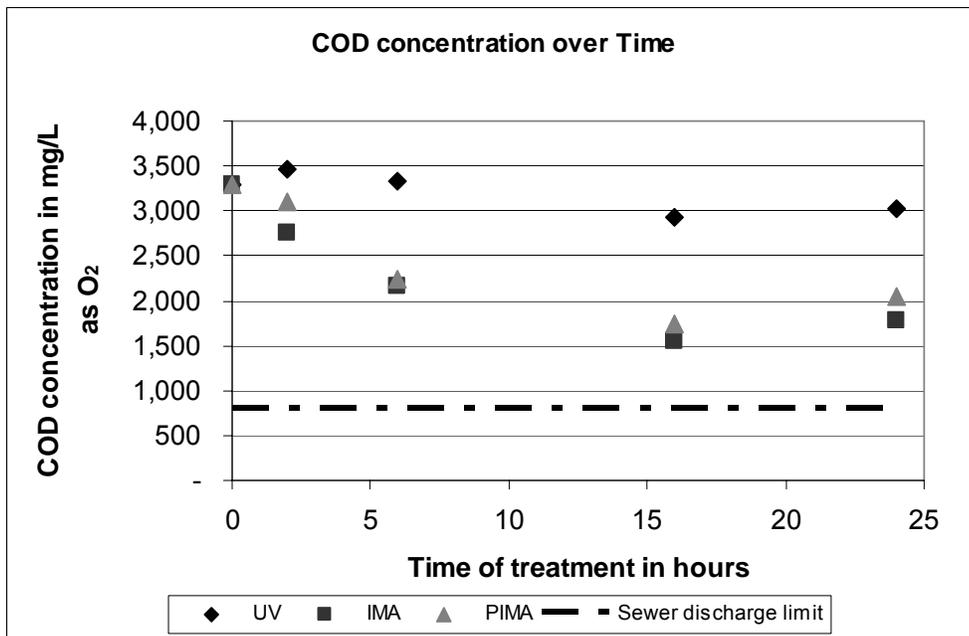


Figure 28. COD concentration throughout the individual simulated medium level experiment using PIMA

### 3.1.1.3 High COD concentration level

The third experiment (experiment No. 04), performed on the high concentration level (initial concentration measured at 10.90 g/L as O<sub>2</sub>, influent prepared by adding 5.9 g of KHP to 700 mL of deionized water), was monitored after zero, two, four, eight, sixteen, and twenty-four hours of treatment. Table 21 presents the results of this experiment. The dose of iron was 2.0 g per sample, and the air flow was kept constant during the whole experiment. Temperature was also monitored.

The best removal was observed with the PIMA process, independently of the distance from the UV source. After 24 hours, the removal was about 40 percent, which represents a drop of 4.36 g/L as O<sub>2</sub> in the COD concentration. As encountered during the medium level experiment, the UV control process achieved essentially no removal, and the concentration went down approximately 0.3 g/L only (2 percent removal). Also confirming what occurred during the first two experiments, the IMA process gave similar results compared to the PIMA. Compared to the removal efficiency at 8 and 24 hours, the value registered at 16 hours for the first PIMA process at mid-distance is probably a manipulation error, such as an excessive amount of sample added in the COD vial.

**Table 21. Summary of simulated COD experimental results for the individual PIMA high concentration level (10.90 g/L as O<sub>2</sub>) scoping tests**

| Process           | C / C <sub>0</sub> |
|-------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
|                   | 0 hr               | 2 hrs              | 4 hrs              | 8 hrs              | 16 hrs             | 24 hrs             |
| IMA, x = 10.2 cm  | 1                  | 1.03               | 0.87               | 0.74               | 0.61               | 0.58               |
| UV, x = 10.2 cm   | 1                  | 0.97               | 1.05               | 0.99               | 0.97               | 0.98               |
| PIMA, x = 6.3 cm  | 1                  | 0.92               | 0.86               | 0.76               | 0.65               | 0.60               |
| PIMA, x = 6.3 cm  | 1                  | 0.98               | 0.85               | 0.73               | 0.99               | 0.64               |
| PIMA, x = 10.2 cm | 1                  | 0.93               | 0.83               | 0.75               | 0.63               | 0.59               |
| PIMA, x = 10.2 cm | 1                  | 0.95               | 0.91               | 0.79               | 0.81               | 0.97               |
| PIMA, x = 15.2 cm | 1                  | 0.99               | 0.85               | 0.73               | 0.80               | 0.62               |
| PIMA, x = 15.2 cm | 1                  | 0.98               | 0.87               | 0.69               | 0.57               | 0.58               |

The level of removal achieved during this experiment was not acceptable since the effluent did not meet the allowable discharge criteria for the public sewer network of Boca Raton.

### 3.1.1.4 Summary of COD experiments with PIMA

The results of these three experiments are illustrated in Figure 29, which shows the average removal percentages for COD at different times without distinction of initial concentration. It is clearly demonstrated that UV is far less efficient than IMA

or PIMA. This fact is even more evident as the initial starting concentration increases. However, no major differences were noticed between the IMA process and the PIMA process. A portion of the light emitted by the UV lamp is suspected to pass through the glass test tube used to shield the IMA control reactor from the light to better simulate an IMA process. The reactor was improved by installing a thin shield between the lamp and the IMA control test tube to prevent any visible radiation from irradiating the leachate in the IMA control.

These three experiments showed that there is no benefit to extending the reaction time beyond 16 hours. Nevertheless, for all simulated leachate experiment, the process was evaluated up to twenty-four hours. No pH adjustment was made, but it was recorded at each sampling time and stayed at an average of 5.5, independently of the KHP concentration. The temperature inside the cabinet was recorded and stayed stable over time. No conclusions were drawn on the influence of temperature on the process.

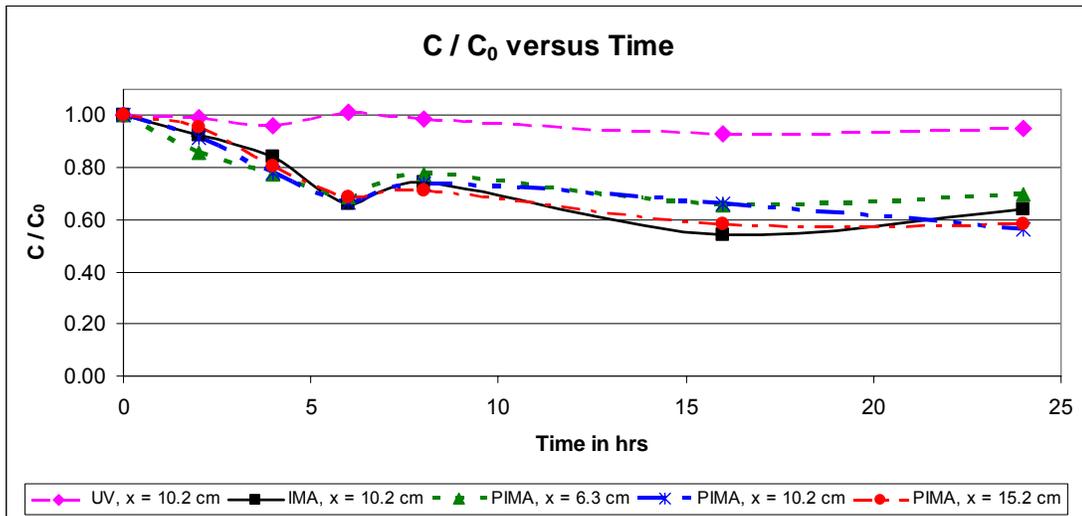


Figure 29. Summary of simulated COD experimental results using PIMA

### 3.1.2 Conductivity and Total Dissolved Solids (TDS)

The very first experiment (experiment No. 01) conducted with PIMA in this study was performed on conductivity. This was a preliminary test, and the results were only measured after 2 hours of treatment. Running this experiment was very useful to learn about the reactor and how to conduct future experiments.

A full experimental run (experiment No. 05) on conductivity and TDS was also completed. The initial values were 16,250  $\mu\text{S}/\text{cm}$  and 8.12 g/L respectively. This corresponds to the medium concentration level. The next two experiments were executed on the high (experiment No. 12) concentration level with initial values of 81,625  $\mu\text{S}/\text{cm}$  and 40.0 g/L and the low (experiment No. 13) concentration level with initial values of 2,750  $\mu\text{S}/\text{cm}$  and 0.83 g/L.

### 3.1.2.1 Low conductivity and TDS concentration level

Experiment (No.13) performed on the low concentration level, was monitored after zero, two, six, sixteen, and twenty-four hours of treatment. The influent was prepared by adding 1,000 mg of NaCl in 1.0 L of deionized water. Initial concentrations were measured at the values of 2,750  $\mu\text{S}/\text{cm}$  for conductivity and 830 mg/L for TDS. During this experiment, the steel wool was weighed before and after the treatment. Results were shown earlier in Table 13. According to the loss in weight, the maximum average iron concentration that can be encountered in the filtered effluent after 24 hours of treatment is approximately 4.3 g/L. However, this concentration may never be reached because part of the lost iron is not dissolved in the effluent but remains in the sludge at the bottom of the test tube. Figure 30 shows the bottom sludge five minutes after removing the steel wool from the test tube. The volume of sludge is estimated from the figure at 8.0 mL. As a result, the treatment of 1.0 L of leachate treated would generate approximately 100 mL (10 percent) of sludge containing iron and compound precipitates. This volume would likely have been reduced with a longer settling time. This is the principal explanation for the lack of conductivity removal for the PIMA and IMA control processes: the decrease of conductivity due to the initial addition of salt might be compensated for by the increase in conductivity due to the dissolving iron. What is more surprising is that the same trend is also observed in the absence of iron (UV control process). This is probably due to the nature of the component used to simulate TDS and conductivity. The evaporation of sample water may also explain this result.

Table 22 summarizes the conductivity results of this experiment. The dose of iron was 2.0 g per sample, and the air flow was constant during the whole experiment. No pH adjustment was made, but pH readings were recorded at each sampling time and for the most part remained at an average value of 6.0. For this experiment, the temperature was recorded using an additional test tube at mid-distance filled with water. Over time, it indicated a maximum temperature of 35°C. This value is more representative of the leachate temperature than the previous setup, which only monitored the air temperature in the photochemical safety cabinet. But, as temperature was simply monitored, no conclusion can be drawn on its influence on the process. A temperature profile equivalent to the one obtained during this experiment is shown in Figure 43 (Experiment No. 15). Experiment No. 13 was the first experiment where a shield was used to prevent visible light from striking the IMA control test tube. Its impact cannot be evaluated on this experiment alone.



**Figure 30. Iron sludge residuals generated after 24 hours of experiment**

**Table 22. Summary of simulated conductivity experimental results for the individual low concentration level (2,750  $\mu\text{S}/\text{cm}$ ) using PIMA**

| Process           | $C / C_0$ |
|-------------------|-----------|-----------|-----------|-----------|-----------|
|                   | 0 hr      | 2 hrs     | 6 hrs     | 16 hrs    | 24 hrs    |
| IMA, x = 10.2 cm  | 1.00      | 1.27      | 1.00      | 1.03      | 1.06      |
| UV, x = 10.2 cm   | 1.00      | 1.03      | 0.97      | 0.97      | 1.03      |
| PIMA, x = 6.3 cm  | 1.00      | 1.00      | 1.06      | 1.30      | 1.42      |
| PIMA, x = 6.3 cm  | 1.00      | 1.06      | 1.06      | 1.21      | 1.30      |
| PIMA, x = 10.2 cm | 1.00      | 1.06      | 1.06      | 1.18      | 1.15      |
| PIMA, x = 10.2 cm | 1.00      | 1.03      | 1.00      | 1.06      | 1.12      |
| PIMA, x = 15.2 cm | 1.00      | 1.06      | 0.97      | 0.94      | 1.03      |

Table 23 presents the results of this experiment concerning TDS. Due to the sensitivity of the Pocket Pal TDS tester and to the required dilution factor, TDS concentration readings vary only from 10 to 20 mg/L. This is the reason why the results presented for  $C/C_0$  range just from 0 to 2. Compared to conductivity, similar conclusions were drawn for TDS, as expected because of the correlation between conductivity and TDS seen in Section 2.2.1.

**Table 23. Summary of simulated TDS experimental results for the individual low concentration level (830 mg/L) using PIMA**

| Process           | $C / C_0$ |
|-------------------|-----------|-----------|-----------|-----------|-----------|
|                   | 0 hr      | 2 hrs     | 6 hrs     | 16 hrs    | 24 hrs    |
| IMA, x = 10.2 cm  | 1.0       | 2.4       | 1.0       | 1.0       | 1.0       |
| UV, x = 10.2 cm   | 1.0       | 1.0       | 1.0       | 1.0       | 1.0       |
| PIMA, x = 6.3 cm  | 1.0       | *         | 1.0       | 2.0       | 2.0       |
| PIMA, x = 6.3 cm  | 1.0       | 2.0       | 1.0       | 2.0       | 2.0       |
| PIMA, x = 10.2 cm | 1.0       | 1.5       | 1.0       | 2.0       | 2.0       |
| PIMA, x = 10.2 cm | 1.0       | 1.5       | 1.0       | 2.0       | 2.0       |
| PIMA, x = 15.2 cm | 1.0       | 2.0       | 1.0       | 1.0       | 2.0       |

\* Sample was lost during the measurement.

### 3.1.2.2 Medium conductivity and TDS concentration level

The second experiment (No. 05), performed on the medium concentration level, was monitored after zero, two, four, eight, sixteen, and twenty-four hours of treatment. The influent was prepared by adding 7.7 g of NaCl in 1.0 L of deionized water. Initial concentrations were measured at the values of 16,250  $\mu\text{S}/\text{cm}$  for conductivity and 8.12 g/L for TDS.

At the medium concentration level, no removal is observed. The results of the experiment using the low concentration level are confirmed here. As treatment occurs, conductivity tends to increase slightly. This is probably due to the increase of dissolved iron. This explains the gain of up to 38 percent of conductivity for the IMA and PIMA processes. Concerning the UV control process, the same conclusion is drawn as during the low concentration level experiment.

Table 24 presents the results of this experiment. The dose of iron was 2.0 g per sample, and the air flow was constant during the whole experiment. No pH adjustment was made, but pH levels were recorded at each sampling time and remained at an average of 6.0. The temperature inside the cabinet was recorded and stayed stable over time at a value near 36°C. As it was simply monitored, no conclusion can be drawn on its influence on the process.

**Table 24. Summary of simulated conductivity experimental results for the individual medium concentration level (16,250  $\mu\text{S}/\text{cm}$ ) using PIMA**

| Process           | $C/C_0$ | $C/C_0$ | $C/C_0$ | $C/C_0$ | $C/C_0$ | $C/C_0$ |
|-------------------|---------|---------|---------|---------|---------|---------|
|                   | 0 hr    | 2 hrs   | 4 hrs   | 8 hrs   | 16 hrs  | 24 hrs  |
| IMA, x = 10.2 cm  | 1.00    | 0.98    | 0.85    | 0.95    | 1.14    | 1.38    |
| UV, x = 10.2 cm   | 1.00    | 0.98    | 0.78    | 0.95    | 1.19    | 1.33    |
| PIMA, x = 6.3 cm  | 1.00    | 1.00    | 0.93    | 0.93    | 1.14    | 1.23    |
| PIMA, x = 6.3 cm  | 1.00    | 0.99    | 1.05    | 0.67    | 1.18    | 1.43    |
| PIMA, x = 10.2 cm | 1.00    | 0.99    | 0.95    | 1.11    | 1.16    | 1.28    |
| PIMA, x = 10.2 cm | 1.00    | 1.00    | 1.03    | 0.96    | 1.12    | 1.46    |
| PIMA, x = 15.2 cm | 1.00    | 1.00    | 0.99    | 0.95    | 1.09    | 1.25    |
| PIMA, x = 15.2 cm | 1.00    | 0.99    | 1.05    | 1.13    | 1.14    | 1.28    |

Table 25 presents the results of this experiment concerning TDS. The same conclusions can be formulated regarding TDS. As was mentioned previously, this is correlated to the relationship between conductivity and TDS seen in Section 2.2.1.

**Table 25. Summary of simulated TDS experimental results for the individual medium concentration level (8.12 g/L) using PIMA**

| Process           | $C/C_0$ | $C/C_0$ | $C/C_0$ | $C/C_0$ | $C/C_0$ | $C/C_0$ |
|-------------------|---------|---------|---------|---------|---------|---------|
|                   | 0 hr    | 2 hrs   | 4 hrs   | 8 hrs   | 16 hrs  | 24 hrs  |
| IMA, x = 10.2 cm  | 1.00    | 0.92    | 0.85    | 0.92    | 1.03    | 1.33    |
| UV, x = 10.2 cm   | 1.00    | 0.92    | 0.85    | 0.92    | 0.92    | 1.33    |
| PIMA, x = 6.3 cm  | 1.00    | 0.92    | 0.88    | 0.85    | 0.62    | 1.23    |
| PIMA, x = 6.3 cm  | 1.00    | 0.92    | 1.00    | 0.62    | 0.62    | 1.33    |
| PIMA, x = 10.2 cm | 1.00    | 0.92    | 0.92    | 1.08    | 0.72    | 1.23    |
| PIMA, x = 10.2 cm | 1.00    | 0.92    | 0.85    | 0.92    | 1.03    | 1.44    |
| PIMA, x = 15.2 cm | 1.00    | 0.92    | 0.92    | 0.92    | 1.03    | 1.23    |
| PIMA, x = 15.2 cm | 1.00    | 0.92    | 1.00    | 1.03    | 1.13    | 1.23    |

This second experiment was the opportunity to verify the relationship between conductivity and TDS. Using the 45 measurements of conductivity and TDS made during the experiment, an average factor of 2.23 was found between conductivity and TDS. This is slightly greater than the 1.54 factor commonly used in analytical chemistry at 20°C (personal communication with YSI 2006). This confirms the existence of a relationship between the two factors, but does not entirely validate the experimental relationship proposed by Snoeyink and Jenkins (1980). However, verifying the accuracy of these equations is beyond the scope of the current study. The temperature of the sample, which was not accounted for, and the nature of the ions may be responsible for this deviation. However, results are presented with the ratio of  $C/C_0$ , which essentially eliminates this issue.

### 3.1.2.3 High conductivity and TDS concentration level

Experiment (No. 12) performed on the high concentration level, was monitored after zero, two, six, sixteen, and twenty-four hours of treatment. The influent was prepared by adding 30.0 g of NaCl in 1.0 L of deionized water. Initial concentrations were measured at the values of 81,625  $\mu\text{S}/\text{cm}$  for conductivity and 40.0 g/L for TDS.

Table 26 presents the results of this experiment. The dose of iron was also 2.0 g per sample, and the air flow was constant during the whole experiment. Conductivity values remained stable throughout the whole experiment. Thus no consequential removal of conductivity was observed. This also confirms the results of the first two experiments, on the medium and low concentration level. After the first six hours of treatment, the PIMA process achieved an average of 7 percent removal. This removal is equal to a decrease of 5,700  $\mu\text{S}/\text{cm}$ . As the experiment continued, conductivity started to increase again. Contrary to the medium level experiment, where conductivity increase was significant, here the initial concentration of this high level experiment was too high to observe the same range of increase. Concerning the UV control process, as seen in the two previous experiments, conductivity remained stable during the 24 hours of treatment. No pH adjustment was made, but it was recorded at each sampling time and stayed at an average of 6.0. The temperature inside the cabinet was recorded and stayed stable over time at a value near 36°C. As it was simply monitored, no conclusion can be drawn on its influence on the process.

**Table 26. Summary of simulated conductivity experimental results for the individual high concentration level (81,625  $\mu\text{S}/\text{cm}$ ) using PIMA**

| Process           | $C / C_0$ |
|-------------------|-----------|-----------|-----------|-----------|-----------|
|                   | 0 hrs     | 2 hrs     | 6 hrs     | 16 hrs    | 24 hrs    |
| IMA, x = 10.2 cm  | 1.00      | 0.94      | 1.02      | 1.02      | 0.92      |
| UV, x = 10.2 cm   | 1.00      | 0.92      | 1.00      | 0.93      | 0.89      |
| PIMA, x = 6.3 cm  | 1.00      | 0.99      | 0.76      | 1.13      | 0.87      |
| PIMA, x = 6.3 cm  | 1.00      | 1.00      | 0.98      | 1.05      | 1.02      |
| PIMA, x = 10.2 cm | 1.00      | 0.97      | 0.94      | 0.99      | 1.06      |
| PIMA, x = 10.2 cm | 1.00      | 0.96      | 1.03      | *         | 1.01      |
| PIMA, x = 15.2 cm | 1.00      | 0.93      | 0.90      | 1.03      | 1.08      |
| PIMA, x = 15.2 cm | 1.00      | 0.91      | 0.97      | 1.04      | 1.06      |

\* Sample was lost during the measurement.

Table 27 presents the results of the high level experiment concerning TDS. Once again, the same conclusions for conductivity were formulated concerning TDS. As was mentioned previously, this is correlated to the relationship between conductivity and TDS seen in Section 2.2.1.

**Table 27. Summary of simulated TDS experimental results for the individual low concentration level (40.00 g/L) using PIMA**

| Process           | C / C <sub>0</sub> |
|-------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
|                   | 0 hrs              | 2 hrs              | 6 hrs              | 16 hrs             | 24 hrs             |
| IMA, x = 10.2 cm  | 1.00               | 1.00               | 1.00               | 1.00               | 0.97               |
| UV, x = 10.2 cm   | 1.00               | 0.94               | 1.00               | 0.94               | 1.03               |
| PIMA, x = 6.3 cm  | 1.00               | 0.97               | 0.88               | 1.13               | 1.13               |
| PIMA, x = 6.3 cm  | 1.00               | 1.00               | 0.97               | 1.03               | 0.97               |
| PIMA, x = 10.2 cm | 1.00               | 0.97               | 0.94               | 0.97               | 1.06               |
| PIMA, x = 10.2 cm | 1.00               | 0.97               | 1.00               | *                  | 1.00               |
| PIMA, x = 15.2 cm | 1.00               | 0.94               | 0.88               | 1.03               | 1.06               |
| PIMA, x = 15.2 cm | 1.00               | 0.91               | 0.97               | 1.00               | 1.03               |

\* Sample was lost during the measurement.

### 3.1.2.4 Summary of conductivity and TDS experiments with PIMA

The results of these three experiments conducted on conductivity and TDS are summarized in Figure 31 for conductivity and Figure 32 for TDS. These two graphs represent the average removal percentages of conductivity and TDS at the different times without regard to the initial concentration. The conclusion drawn from these three experiments is that the limited removal action of the two processes using iron (IMA and PIMA) is canceled out by the dissolution of iron and by the evaporation of liquid. If the starting concentrations are low enough, an increase in conductivity and TDS can even be noticed. The evaporation of water and the nature of the component used to simulate TDS and conductivity appear to influence these results. These three experiments also confirmed that there is no benefit to extending the reaction time beyond 16 hours. No pH adjustment was made, but it was recorded at each sampling time and generally stayed at an overall average of 6.0, independent of the initial concentration. The temperature of the atmosphere inside the cabinet was recorded during experiments No. 5 and No. 12 and stayed stable over time. The equilibrium temperature from the monitoring data is close to 30°C. As well, it was simply monitored and no conclusion can be drawn on its influence on the process. During experiment No. 13 the temperature was monitored using an additional test tube filled with water in order to have a more realistic idea of the temperature of the liquid itself. In this case, the equilibrium temperature is close to 35°C. After this upgrade, the temperature profile is similar to the one described in Figure 43. But also, as no temperature adjustment can be executed on the leachate during the experiment, no conclusion can be drawn on its influence on the process. In addition, the impact of the shielding cannot be noticed on this set of experiments only.

Concerning TDS, for these three experiments, the minimum acceptable level of treatment (refer to Table 6) was never achieved. Without dilution, none of the effluents from the three tests were in compliance with the City Code of Boca Raton. As for conductivity, because no limit is specified, no conclusion can be drawn.

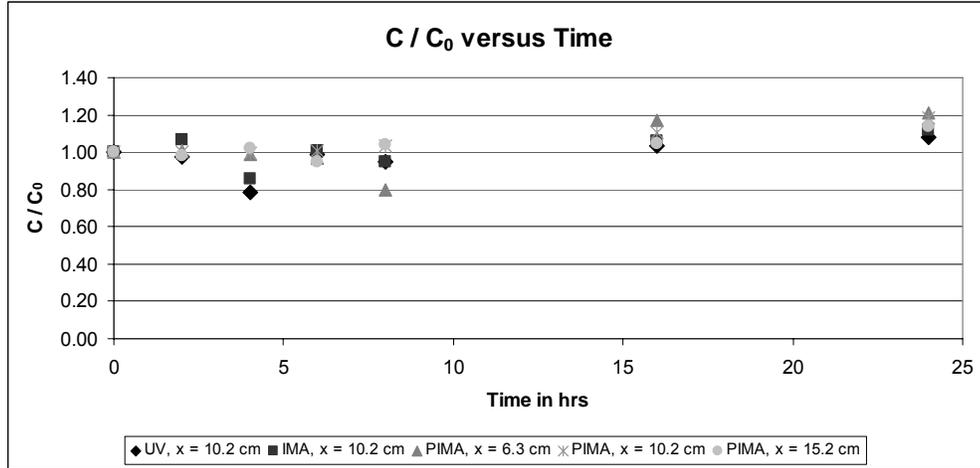


Figure 31. Summary of individual simulated conductivity experimental results using PIMA

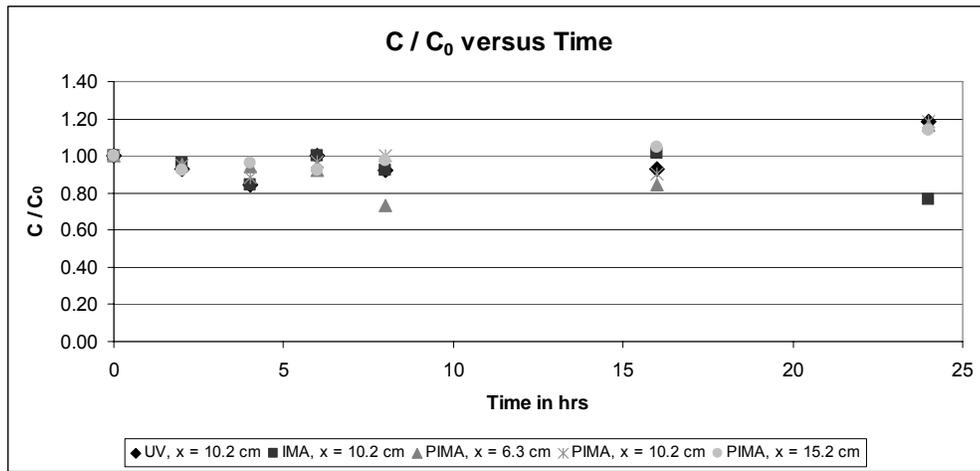


Figure 32. Summary of individual simulated TDS experimental results  
 Note: Due to concentration monitoring sensitivity issues encountered during the low level experiment, these results do not appear in this figure.

Table 28. Summary of simulated conductivity experimental results for the low concentration level (2,750  $\mu$ S/cm) using PIMA.

| Process           | C / C <sub>0</sub> |
|-------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
|                   | 0 hr               | 2 hrs              | 6 hrs              | 16 hrs             | 24 hrs             |
| IMA, x = 10.2 cm  | 1.00               | 1.27               | 1.00               | 1.03               | 1.06               |
| UV, x = 10.2 cm   | 1.00               | 1.03               | 0.97               | 0.97               | 1.03               |
| PIMA, x = 6.3 cm  | 1.00               | 1.00               | 1.06               | 1.30               | 1.42               |
| PIMA, x = 6.3 cm  | 1.00               | 1.03               | 1.00               | 1.06               | 1.12               |
| PIMA, x = 10.2 cm | 1.00               | 1.06               | 1.06               | 1.21               | 1.30               |
| PIMA, x = 15.2 cm | 1.00               | 1.06               | 1.06               | 1.18               | 1.15               |
| PIMA, x = 15.2 cm | 1.00               | 1.06               | 0.97               | 0.94               | 1.03               |

The same conclusions than these concerning conductivity can be formulated concerning TDS. This is correlated to the relationship between conductivity and TDS discussed earlier. Table 29 presents the results of this experiment concerning TDS. Due to the sensitivity of the Pocket Pal TDS tester and to the dilution factor, TDS concentration readings vary only from 10 to 20 mg/L. This is the reason why the results presented range from 0 to 2.

**Table 29. Summary of simulated TDS experimental results for the low concentration level (830 mg/L) using PIMA**

| Process           | $C / C_0$ |
|-------------------|-----------|-----------|-----------|-----------|-----------|
|                   | 0 hr      | 2 hrs     | 6 hrs     | 16 hrs    | 24 hrs    |
| IMA, x = 10.2 cm  | 1.00      | 2.40      | 1.00      | 1.00      | 1.00      |
| UV, x = 10.2 cm   | 1.00      | 1.00      | 1.00      | 1.00      | 1.00      |
| PIMA, x = 6.3 cm  | 1.00      | 0.00      | 1.00      | 2.00      | 2.00      |
| PIMA, x = 6.3 cm  | 1.00      | 1.50      | 1.00      | 2.00      | 2.00      |
| PIMA, x = 10.2 cm | 1.00      | 2.00      | 1.00      | 2.00      | 2.00      |
| PIMA, x = 15.2 cm | 1.00      | 1.50      | 1.00      | 2.00      | 2.00      |
| PIMA, x = 15.2 cm | 1.00      | 2.00      | 1.00      | 1.00      | 2.00      |

The same conclusions concerning conductivity can be formulated concerning TDS. As was mentioned previously, this is correlated to the relationship between conductivity and TDS discussed earlier. Table 30 presents the results of this high level experiment concerning TDS.

**Table 30. Summary of simulated TDS experimental results for the low concentration level (40.00 g/L) using PIMA**

| Process           | $C / C_0$ |
|-------------------|-----------|-----------|-----------|-----------|-----------|
|                   | 0 hrs     | 2 hrs     | 6 hrs     | 16 hrs    | 24 hrs    |
| IMA, x = 10.2 cm  | 1.00      | 1.00      | 1.00      | 1.00      | 0.97      |
| UV, x = 10.2 cm   | 1.00      | 0.94      | 1.00      | 0.94      | 1.03      |
| PIMA, x = 6.3 cm  | 1.00      | 0.97      | 0.88      | 1.13      | 1.13      |
| PIMA, x = 6.3 cm  | 1.00      | 1.00      | 0.97      | 1.03      | 0.97      |
| PIMA, x = 10.2 cm | 1.00      | 0.97      | 0.94      | 0.97      | 1.06      |
| PIMA, x = 10.2 cm | 1.00      | 0.97      | 1.00      | *         | 1.00      |
| PIMA, x = 15.2 cm | 1.00      | 0.94      | 0.88      | 1.03      | 1.06      |
| PIMA, x = 15.2 cm | 1.00      | 0.91      | 0.97      | 1.00      | 1.03      |

\* Sample was lost during the measurement.

### 3.1.3 Biochemical Oxygen Demand (BOD<sub>5</sub>)

Three scoping experiments on Biochemical Oxygen Demand (BOD<sub>5</sub>) were conducted. The initial concentrations were 55, 120, and 425 mg/L as O<sub>2</sub>, respectively for the low (experiment No. 11), medium (experiment No. 07) and high (experiment No. 10) concentration levels. As explained in earlier, BOD<sub>5</sub> experiments were monitored only after sixteen hours of treatment.

#### 3.1.3.1 Low BOD<sub>5</sub> concentration level

Experiment No. 11 was conducted on the low concentration level, which started with a BOD<sub>5</sub> value of 55 mg/L as O<sub>2</sub>. The influent was prepared with 10.0 mL of BOD<sub>5</sub> Standard Solution (3.00 g/L of glucose and 3.00 g/L of glutamic acid) diluted in 250 mL of reagent water. During this experiment, temperature was not recorded due to the unavailability of the computer system. The IMA and PIMA processes demonstrated an identical removal on the order of 40 percent; the BOD<sub>5</sub> was reduced to 34 mg/L as O<sub>2</sub> in both cases. Table 31 presents the results of this experiment. The dose of iron was 2.0 g for the IMA and PIMA processes. Due to technical limitations, the UV process was not tested during this experiment. The air flow was constant during the sixteen hours of the experiment. As the initial BOD<sub>5</sub> content was already in compliance with the sewer discharge criteria, the effluents from this experiment were also in compliance.

**Table 31. Summary of simulated BOD<sub>5</sub> experimental results for the low concentration level (55 mg/L)**

| Process           | C / C <sub>0</sub> | C / C <sub>0</sub> |
|-------------------|--------------------|--------------------|
|                   | 0 hr               | 16 hrs             |
| IMA, x = 10.2 cm  | 1.00               | 0.62               |
| PIMA, x = 10.2 cm | 1.00               | 0.61               |

#### 3.1.3.2 Medium BOD<sub>5</sub> concentration level

The next experiment (No. 07) was performed on the medium concentration level. The initial concentration was 120 mg/L as O<sub>2</sub>, prepared with 25.0 mL of BOD<sub>5</sub> Standard Solution (3.00 g/L of glucose and 3.00 g/L of glutamic acid) diluted in 250 mL of reagent water. During this experiment, a UV process control was analyzed. Table 32 presents the results of this experiment. The control showed 100 percent removal of BOD<sub>5</sub>, and the PIMA process achieved 55 percent removal, lowering the BOD<sub>5</sub> to 56 mg/L as O<sub>2</sub>. This total removal obtained with the UV process is logical. Using data obtained from Dobrović et al. (2007), after 16 hours of treatment and applying their hypothesis on BOD<sub>5</sub> (first order degradation reaction of organic matter with a reaction constant of  $6.8 \times 10^{-3} \text{ min}^{-1}$ ), the effluent BOD<sub>5</sub> value can be estimated

to be 0.17 mg/L as O<sub>2</sub> with UV alone. The dose of iron was 2.0 g for the PIMA process and 0 g for the UV control. The air flow was constant during the sixteen hours of the experiment. The temperature of the atmosphere inside the safety cabinet was recorded between 36 - 37°C. As the initial BOD<sub>5</sub> content was already in compliance with the sewer discharge criteria, the effluents from this experiment were also in compliance.

**Table 32. Summary of simulated BOD<sub>5</sub> experimental results for the medium concentration level (120 mg/L)**

| Process           | C / C <sub>0</sub> | C / C <sub>0</sub> |
|-------------------|--------------------|--------------------|
|                   | 0 hr               | 16 hrs             |
| UV, x = 10.2 cm   | 1.00               | 0.00               |
| PIMA, x = 10.2 cm | 1.00               | 0.45               |

### 3.1.3.3 High BOD<sub>5</sub> concentration level

The last experiment (No. 10) was performed on the high concentration level. The initial BOD<sub>5</sub> concentration was 425 mg/L as O<sub>2</sub>, prepared by diluting 40.0 mL of the BOD<sub>5</sub> Standard Solution (3.00 g/L of glucose and 3.00 g/L of glutamic acid) in 250 mL of deionized water). Table 33 presents the results of this experiment. A noticeable difference is observed between the IMA control process and the PIMA sample. The former achieved a removal of 38 percent (corresponding to a decrease of 119 mg/L), whereas the latter achieved a removal of 44 percent (corresponding to a decrease of 187 mg/L). The final BOD<sub>5</sub> concentration of the sample treated with the PIMA process was then 238 mg/L as O<sub>2</sub>, which is below the allowable sewer discharge concentration (400 mg/L) of the City of Boca Raton. The dose of iron was 2.0 g for both processes. The air flow was constant during the sixteen hours of the experiment. The temperature of the atmosphere inside the safety cabinet was recorded between 32 - 33°C. The level of removal achieved during this experiment was acceptable since the effluent meets the allowable sewer discharge criteria (400 mg/L as O<sub>2</sub>) for the public sewer network of the City of Boca Raton. After sixteen hours, the PIMA and IMA effluents could have already been authorized for discharge.

**Table 33. Summary of simulated BOD<sub>5</sub> experimental results for the high concentration level (425 mg/L).**

| Process           | C / C <sub>0</sub> | C / C <sub>0</sub> |
|-------------------|--------------------|--------------------|
|                   | 0 hr               | 16 hrs             |
| IMA, x = 10.2 cm  | 1.00               | 0.72               |
| PIMA, x = 10.2 cm | 1.00               | 0.56               |

### 3.1.3.4 Summary of BOD<sub>5</sub> experiments with PIMA

The results of these three experiments conducted on BOD<sub>5</sub> are summarized in Figure 33. The graph represents the average removal percentages of BOD<sub>5</sub> after running the reactor for 16 hours without distinction given to initial concentration. Only IMA and PIMA processes are shown. The two plots corroborate the conclusion drawn previously: the addition of UV radiation improved the efficiency of the IMA process. The removal is increased from 33 percent without UV to 46 percent with UV. The results obtained during the first experiment seem also to show that the UV process can achieve complete mineralization of the model organics used in this experiment (glucose and glutamic acid). Regarding the sewer discharge limit, low and medium initial concentrations were already under the limits, and for the high concentration level, the targeted goal was reached by the PIMA process, which reduced the BOD<sub>5</sub> content to a value lower than 400 mg/L as O<sub>2</sub>. All these results tend to indicate that iron acts as an inhibitor for organic content degradation by reducing the removal rate. This might be due to the shadow generated by the steel wool (as illustrated in Figure 34), which prevented the total irradiation of the samples.

The results obtained during these three experiments delivered only the processes efficiency after sixteen hours. But it would be interesting, in order to optimize the PIMA process, to know the efficiency after a shorter time. The removal of organics may occur during the first hours of treatment, but the experiments conducted do not make a conclusion possible. Consequently, an additional experiment (No. 16) was run for four hours only. Results are presented in the next paragraph.

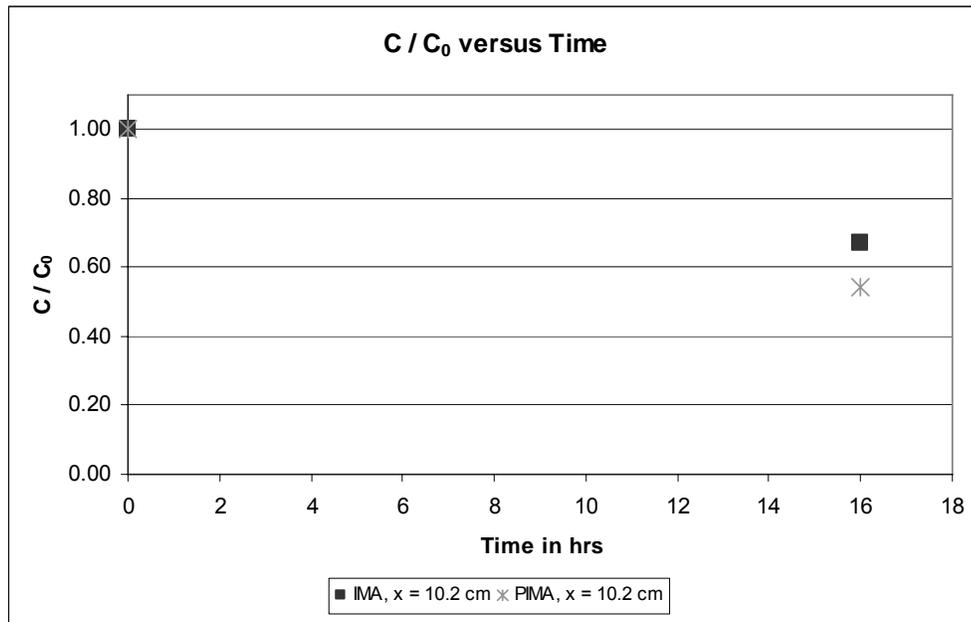
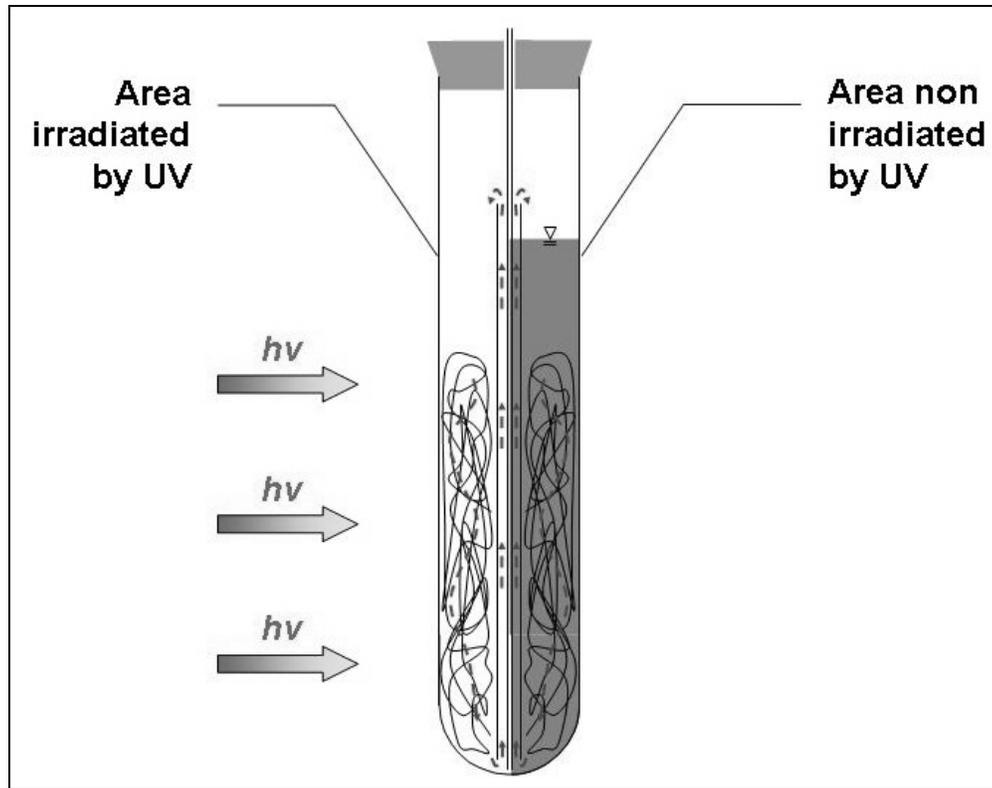


Figure 33. Summary of simulated BOD<sub>5</sub> experimental results (initial experiments)



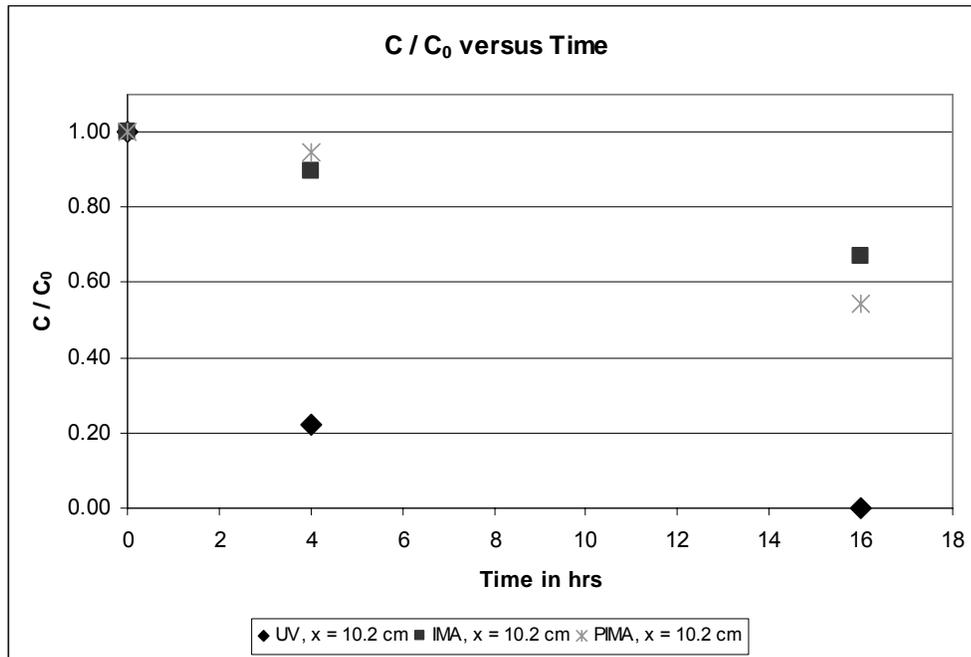
**Figure 34. Shadow induced by the steel wool**

An additional experiment (experiment No. 16) was conducted with an initial BOD<sub>5</sub> value of 20 mg/L as O<sub>2</sub>, prepared by diluting 25 mL of BOD<sub>5</sub> Standard Solution (3.00 g/L of glucose and 3.00 g/L of glutamic acid) in 500 mL of reagent water. This initial value is lower than the value expected from the previous experiment. The reason for this discrepancy is not certain; however, dilution water or seed used could have accounted for this result. Nevertheless, as results are presented as a ratio of C/C<sub>0</sub> and results after treatment are logical, this is not an invalidating issue. Table 34 presents the results of this experiment. On average, the IMA and PIMA processes demonstrated a similar removal in the order of 10 percent. The BOD<sub>5</sub> was reduced to respectively 17.6 mg/L as O<sub>2</sub> and an average of 18.5 mg/L as O<sub>2</sub>. On the other hand, the UV process achieved a removal of 78 percent, reducing the BOD<sub>5</sub> to 4.3 mg/L as O<sub>2</sub>. The dose of iron was 2.0 g for the IMA and PIMA processes. The air flow was constant during the four hours of the experiment. The temperature was recorded around 30 - 31°C at the mid-distance test tube (set-up before experiment No. 13). The detention time was four hours.

**Table 34. Summary of individual simulated BOD<sub>5</sub> experimental results for the complementary experiment (20 mg/L as O<sub>2</sub>)**

| Process           | $C / C_0$ |       |
|-------------------|-----------|-------|
|                   | 0 hr      | 4 hrs |
| IMA, x = 10.2 cm  | 1.00      | 0.90  |
| UV, x = 10.2 cm   | 1.00      | 0.22  |
| PIMA, x = 10.2 cm | 1.00      | 0.83  |
| PIMA, x = 10.2 cm | 1.00      | 1.06  |

As already noticed during the 16-hour experiment, this test demonstrated that the PIMA and IMA processes, contrary to the UV process, required a longer detention time than 4 hours to achieve an acceptable removal. Iron seems to inhibit the removal action of UV radiation. Figure 35 is the best way to illustrate this statement. Soluble iron is not responsible for this conclusion. In fact the Fenton and Photo-Fenton use ferrous ions to achieve similar levels of treatment. The reactor design may be the reason. Steel wool is generated large areas of shadow, which prevented the radiation of UV as mentioned in the previous paragraph, particularly if complete mixing conditions were not achieved in the reactor.



**Figure 35. Summary of individual simulated BOD<sub>5</sub> experimental results**

### 3.1.4 Ammonia

Three scoping tests concerning ammonia were performed: experiments No. 03, 08 and 09. The initial concentrations were respectively 110, 540, and 930 mg/L as NH<sub>3</sub>-N for the low, medium and high concentration levels.

#### 3.1.4.1 Low ammonia concentration level

The first experiment (experiment No. 09) was performed on the low concentration level of 110 mg/L as NH<sub>3</sub>-N. The effluent was prepared by dissolving 0.204 g of NH<sub>4</sub>Cl salt in 1.0 L of reagent water. Concentrations were monitored after zero, two, six, sixteen, and twenty-four hours of treatment. Table 35 presents the results of this experiment. The dose of iron was 2.0 g per sample, and the air flow was constant during the whole experiment. This experiment did not show any removal. The IMA and UV control processes and the PIMA at the three different distances had no effect on the simulated leachate. The concentrations did not decrease over time. The temperature inside the safety cabinet was recorded at the equilibrium value of 36°C.

**Table 35. Summary of simulated ammonia experimental results for the low concentration level (110 mg/L)**

| Process           | C / C <sub>0</sub> |
|-------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
|                   | 0 hr               | 2 hrs              | 6 hrs              | 16 hrs             | 24 hrs             |
| IMA, x = 10.2 cm  | 1.00               | 1.00               | 1.02               | 1.05               | 1.05               |
| UV, x = 10.2 cm   | 1.00               | 0.99               | 1.02               | 1.02               | 0.96               |
| PIMA, x = 6.3 cm  | 1.00               | 0.96               | 1.13               | 1.19               | 1.52               |
| PIMA, x = 6.3 cm  | 1.00               | 0.97               | 1.03               | 1.13               | 1.10               |
| PIMA, x = 10.2 cm | 1.00               | 1.01               | 1.05               | 1.12               | 1.12               |
| PIMA, x = 10.2 cm | 1.00               | 0.98               | 1.05               | 1.15               | 1.18               |
| PIMA, x = 15.2 cm | 1.00               | 0.96               | 0.97               | 1.07               | 1.12               |
| PIMA, x = 15.2 cm | 1.00               | 0.97               | 0.99               | 1.04               | 1.06               |

#### 3.1.4.2 Medium ammonia concentration level

The second experiment (experiment No. 08) was performed on the medium concentration level: 540 mg/L as NH<sub>3</sub>-N. The effluent was prepared by adding to 1.33 g of NH<sub>4</sub>Cl salt in 1.0 L of reagent water. Concentrations were monitored after zero, two, six, sixteen, and twenty-four hours of treatment. Table 36 presents the results of this experiment. The dose of iron was 2.0 g per sample, and the air flow was constant during the whole experiment. The three processes showed an average removal of 24 percent of the ammonia concentration during the first two hours of treatment. But as treatment continued, no additional action was noticeable for any of the processes. The temperature inside the safety cabinet was recorded at the

equilibrium value of 38°C.

**Table 36. Summary of simulated ammonia experimental results for the medium concentration level (540 mg/L)**

| Process           | $C / C_0$ |
|-------------------|-----------|-----------|-----------|-----------|-----------|
|                   | 0 hr      | 2 hrs     | 6 hrs     | 16 hrs    | 24 hrs    |
| IMA, x = 10.2 cm  | 1.00      | 0.69      | 0.71      | 0.76      | 0.82      |
| UV, x = 10.2 cm   | 1.00      | 0.78      | 0.81      | 0.80      | 0.80      |
| PIMA, x = 6.3 cm  | 1.00      | 0.76      | 0.78      | 0.75      | 0.70      |
| PIMA, x = 6.3 cm  | 1.00      | 0.74      | 0.76      | 0.84      | 0.59      |
| PIMA, x = 10.2 cm | 1.00      | 0.79      | 0.77      | 0.84      | 0.90      |
| PIMA, x = 10.2 cm | 1.00      | 0.77      | 0.79      | 0.79      | 0.77      |
| PIMA, x = 15.2 cm | 1.00      | 0.79      | 0.76      | 0.76      | 0.79      |
| PIMA, x = 15.2 cm | 1.00      | 0.77      | 0.62      | 0.80      | 0.82      |

### 3.1.4.3 High ammonia concentration level

The third experiment (experiment No. 03) was performed on the high concentration level: 930 mg/L as  $\text{NH}_3\text{-N}$ . The influent was prepared with of 0.5 L of Nitrogen Standard Solution at 1,000 mg/L as  $\text{NH}_3\text{-N}$ . Concentrations were monitored after zero, two, four, and twenty-four hours of treatment. Table 37 presents the results of this experiment. The dose of iron was 2.0 g per sample, and the air flow was constant during the whole experiment. Similar to the first experiment, the three processes did not show any substantial removal of ammonia. The temperature inside the safety cabinet was recorded at the equilibrium value of 29°C.

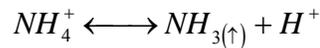
**Table 37. Summary of simulated ammonia experimental results for the high concentration level (930 mg/L)**

| Process           | $C / C_0$ | $C / C_0$ | $C / C_0$ | $C / C_0$ |
|-------------------|-----------|-----------|-----------|-----------|
|                   | 0 hrs     | 2 hrs     | 4 hrs     | 24 hrs    |
| IMA, x = 10.2 cm  | 1.00      | 1.01      | 1.03      | 1.08      |
| UV, x = 10.2 cm   | 1.00      | 0.98      | 0.97      | 1.12      |
| PIMA, x = 6.3 cm  | 1.00      | 0.92      | 0.91      | 0.99      |
| PIMA, x = 6.3 cm  | 1.00      | 1.00      | 0.99      | 1.10      |
| PIMA, x = 10.2 cm | 1.00      | 0.97      | 1.06      | 1.03      |
| PIMA, x = 15.2 cm | 1.00      | 0.96      | 0.99      | 0.87      |

### 3.1.4.4 Summary of ammonia experiments with PIMA

As no sewer discharge limit is specified in the City of Boca Raton, a conclusion concerning the ability to safely discharge the effluents cannot be drawn. However,

concentrations on the order of 500 mg/L as N or higher are known to be bio-toxic. In general, the simulated leachate experiments conducted on ammonia showed unexpected results. Air stripping is known to remove ammonia from wastewater or leachate, but during these three experiments, no observable changes in the ammonia concentrations were noticed for any of the processes. Figure 36 summarizes this tendency. At first, the effect of pH was suspected. The pH was only monitored during the low and medium concentration level experiments. Initial pH was recorded at 6.0. With the exception of the UV process control, where pH dropped to 5.5. During the course of testing, the pH remained essentially stable among the three experiments. This acidic pH is most likely a contributing factor as to why air stripping did not achieve removal of ammonia. The air stripping of ammonia from a liquid requires that the ammonia be present as a gas. Ammonia ions in leachate or in any liquid in general exist in equilibrium with gaseous ammonia as shown in the following equation:



As the pH is increases above 7.0, the equilibrium is shifted to the right, and the ammonium ion is converted to gaseous ammonia, which is readily removed by air stripping (the  $pK_a$  of the couple  $NH_4^+/NH_3$  is 9.2). Lime (CaO) or sodium hydroxide (NaOH) is typically used to increase the pH (USEPA, 2000) in industrial wastewater applications. However, during the three scoping experiments, pH was not adjusted, only recorded. This may be why no removal was observed. Also the fact that ammonia gas is lighter than air does not encourage ammonia to strip and exit the test tube. Complementary experiments were conducted to verify these two hypotheses.

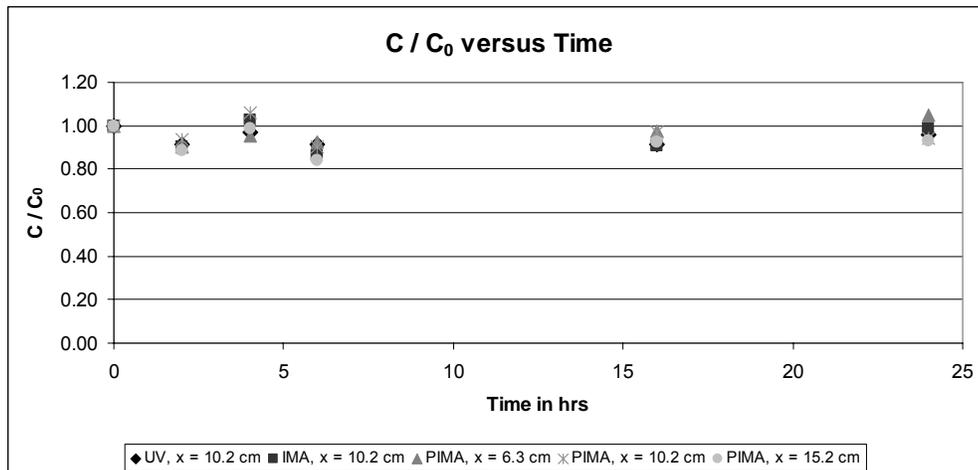


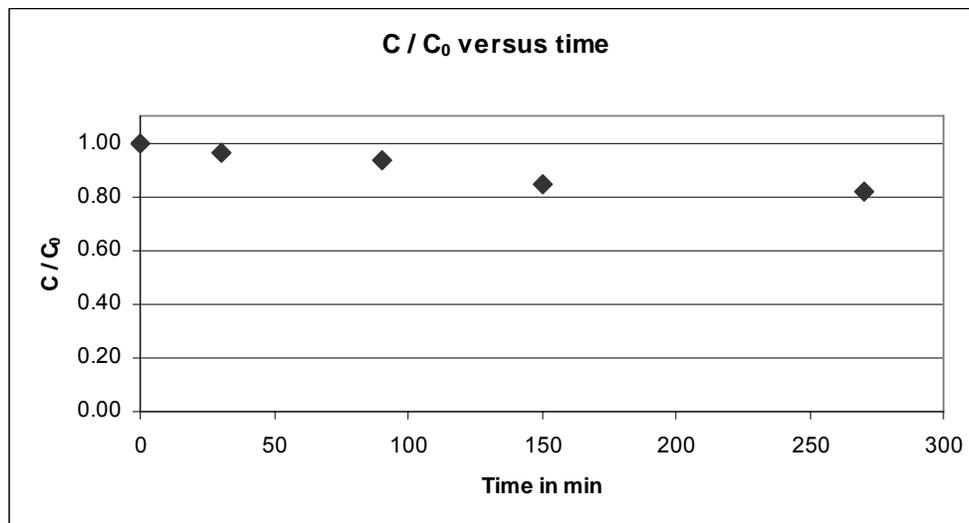
Figure 36. Summary of ammonia experimental results with simulated leachate

In order to verify these experimental results, an additional experiment was performed prior to start of mixed simulated leachate scoping tests. A 200 mL ammonia sample with a concentration of 340 mg/L as  $NH_3-N$  was prepared using

0.34 mg of  $\text{NH}_4\text{Cl}$  salt. The pH was recorded at a value of 6.0. Then, 0.2 mg of  $\text{CaO}$  was added to this solution. The pH was measured again and reached the value of 10, which is above the  $\text{pK}_a$  (9.2) of the couple  $\text{NH}_4^+/\text{NH}_3$  ( $\text{NH}_4^+ \leftrightarrow \text{NH}_3 + \text{H}^+$ ). The sample was then placed in the reactor. The UV lamp was not turned on, only the aeration was initiated. The cap was not placed on top of the test tube reactor to allow the ammonia gas to readily escape. The pH and ammonia levels were recorded after 30, 90, 150, and 270 minutes. Table 38 and Figure 37 summarize the results of this experiment. As a decrease in the ammonia concentration was noticed, the hypothesis expressed in the previous section is validated. The acidic pH and the test tube cap are likely responsible for the absence of ammonia removal noticed during the scoping tests. The pH seems to be the most important factor as a net reduction of the stripping rate is observed when the pH dropped to 9.0 (which is below the  $\text{pK}_a$ ). This confirms the results found by Cho et al. (2002) described earlier in the Introduction section.

**Table 38. First additional individual ammonia experiment results**

| Time in min | pH | Ammonia concentration in mg/L as $\text{NH}_3\text{-N}$ | $C / C_0$ |
|-------------|----|---|-----------|
| 0           | 10 | 341   | 1.00      |
| 30          | 10 | 328   | 0.96      |
| 90          | 10 | 320   | 0.94      |
| 150         | 10 | 288.5   | 0.85      |
| 270         | 9  | 278   | 0.82      |



**Figure 37. Graphical representation of the first additional individual ammonia experience**

A second experiment was conducted between experiments No. 21 and 22 in order

to better examine the inhibiting effect of the test tube cap in the stripping of ammonia. The initial concentration was 322 mg/L as  $\text{NH}_3\text{-N}$ . Without adjustment, pH was 5.5 and remained stable over the 150 min of the experiment. To increase the pH above 9.2, 0.5 g of CaO was added in 420 mL of the solution (80 mL were kept unadjusted for comparison purposes), and the pH rose to 12. Over the duration of the experiment, the pH gradually decreased to 10 through recarbonation during aeration. Ammonia concentration was monitored after 30, 60, 90, and 150 min of simple aeration. Four test tube reactors were used in order to determine the impact of pH adjustment and reactor design:

- Sample 1 contained the pH adjusted solution of ammonia, no cap was used.
- Sample 2 contained the pH adjusted solution of ammonia and an adjusted cap was used. The cap is described in Figure 38 below. A second hole was drilled through the cap and a long glass tube inserted in that hole in order to facilitate the ventilation of the ammonia gas.
- Sample 3 contained the pH adjusted solution of ammonia, and the regular cap was used.
- Sample 4 contained the solution of ammonia, pH was not adjusted and the regular cap used.

Table 39 and Figure 39 summarize the results of this experiment. It compares the influence of pH adjustment above the  $\text{pK}_a$  of the couple  $\text{NH}_4^+/\text{NH}_3$  and the effect of the test tube cap. The first conclusion here is that the pH is one of the most important factors in the stripping of ammonia in this application. The sample without pH adjustment demonstrated the absence of removal while the ammonia concentration diminished in the three others, which were pH adjusted. Of those three samples, the one without the cap and the one with the modified cap showed higher removal than the one with the regular cap. This also demonstrates the influence of the difference in density between air and ammonia, and therefore of the reactor design in the process overall performance. The modified cap was then utilized during the real leachate experiments No. 22 and 23. However the modified cap was difficult to implement. The reason was that the real leachate samples exhibited the tendency to produce foam during aeration. Such foam will generate liquid droplets and bubbles that would effectively close the ventilation pipe. During the two experiments with real leachate, the foaming generated by aeration mixing created problems with treatment performance, even if the exit pipe was set at a higher level.

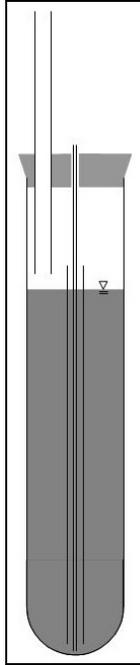


Figure 38. Schematic of test tube with a modified cap

Table 39. Second additional individual ammonia experiment results

| Process                      | $C / C_0$ |
|------------------------------|-----------|-----------|-----------|-----------|-----------|
|                              | 0         | 30        | 60        | 90        | 150       |
| pH adjusted, no cap          | 1.00      | 1.05      | 0.92      | 0.89      | 0.78      |
| pH adjusted, modified cap    | 1.00      | 1.00      | 1.02      | 0.76      | 0.71      |
| pH adjusted, regular cap     | 1.00      | 0.98      | 1.00      | 0.96      | 0.91      |
| pH not adjusted, regular cap | 1.00      | 0.99      | 1.00      | 0.97      | 0.98      |

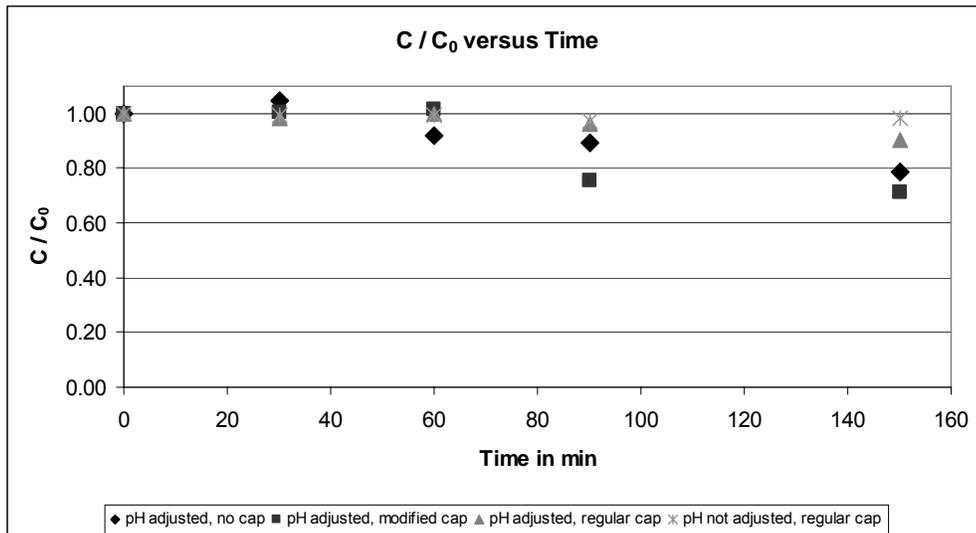


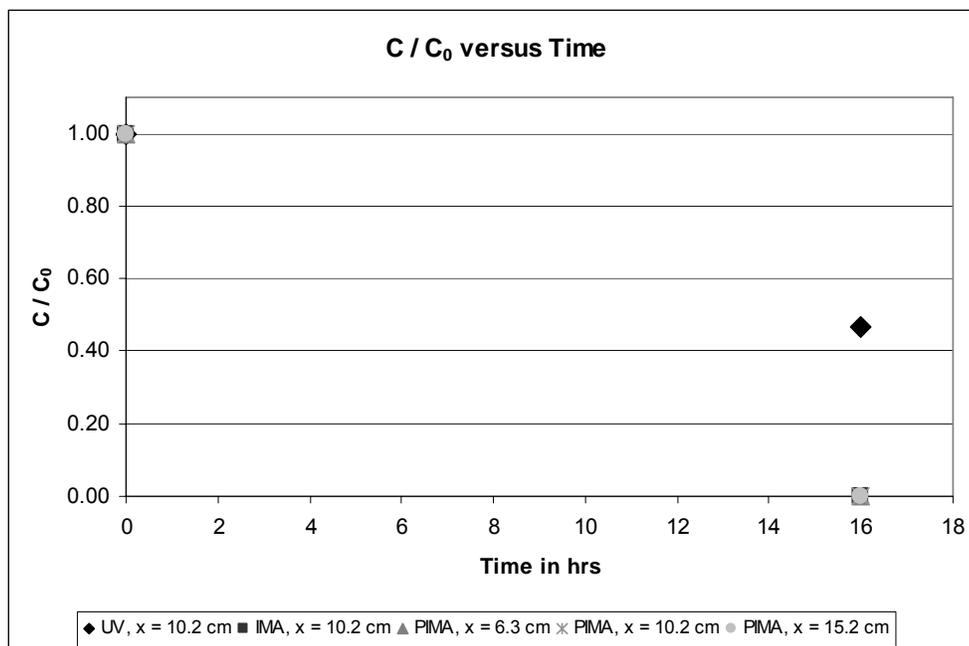
Figure 39. Graphical representation of the second additional individual ammonia experience

### 3.1.5 Lead (Pb)

One scoping experiment (experiment No. 14) on lead was performed. As the scoping tests for the other components showed the non-necessity to pursue the experiment beyond twenty-four hours, the lead experiment was only run for sixteen hours (just as for the BOD<sub>5</sub>). Samples were sent to a contract laboratory in order to determine the initial and remaining lead concentrations in the influent and effluent simulated leachates. The initial lead concentration was 0.30 mg/L (3.0 mL of the Lead Standard Solution, 100 mg/L as Pb<sup>2+</sup>, diluted in 1.0 L of reagent water), which corresponds to the medium level determined from the literature review. Table 40 and Figure 40 summarize the results of this experiment.

**Table 40. Simulated lead experimental results for the individual medium concentration level (0.30 mg/L)**

| Process           | C / C <sub>0</sub> |           |
|-------------------|--------------------|-----------|
|                   | 0 hr               | 16 hrs    |
| IMA, x = 10.2 cm  | 1                  | 0.00033   |
| UV, x = 10.2 cm   | 1                  | 0.46667   |
| PIMA, x = 6.3 cm  | 1                  | < 0.00029 |
| PIMA, x = 6.3 cm  | 1                  | 0.00033   |
| PIMA, x = 10.2 cm | 1                  | < 0.00029 |
| PIMA, x = 10.2 cm | 1                  | 0.00297   |
| PIMA, x = 15.2 cm | 1                  | < 0.00029 |
| PIMA, x = 15.2 cm | 1                  | < 0.00029 |



**Figure 40. Individual simulated lead experimental results**

The UV control process showed a removal of 54 percent and lowered the lead concentration to 0.14 mg/L. Removal of lead by UV was not expected, and such removal was not reported in the literature. On the other hand, and as expected after the literature review, the IMA and PIMA processes demonstrated excellent removal power. Of the 7 samples (1 IMA and 6 PIMA), 4 were below the MDL of 0.000088 mg/L (4 PIMA samples) and the 3 others (1 IMA and 2 PIMA) were very close to that level. This corresponds to a removal percentage greater than 99.96. The removal obtained for lead does not vary with the distance of the reactor from the UV source: the three exposure distances demonstrated similar results. The dose of iron was 2.0 g per sample, and the air flow was held constant during the whole experiment. The temperature was recorded around 32 - 33°C at the mid-distance test tube (set up before experiment No. 13). As samples were sent to an external laboratory, it was also requested to evaluate the concentration of dissolved iron in the effluent after 16 hours of treatment. Results have already been discussed previously.

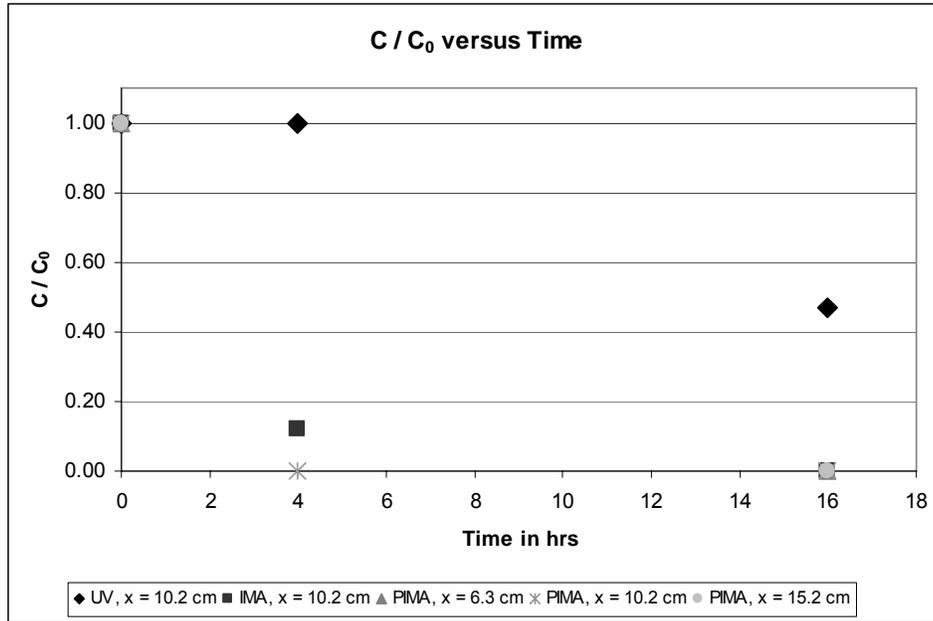
Another experiment (experiment No. 16) was conducted at the same time as the additional experiment that was run for BOD<sub>5</sub> described earlier. The detention time was four hours. Samples were sent to the contract laboratory in order to determine the initial and remaining lead concentrations. Initial lead concentration was 0.29 mg/L (corresponding to 1.5 mL of Lead Standard Solution, 100 mg/L as Pb<sup>2+</sup>, diluted in 0.5 mL of reagent water), which corresponds to the medium level determined from the literature review. Table 41 presents the results of this experiment. The removal achieved during this experience was lower than during the sixteen hours experiment. The PIMA process at mid-distance achieved an average removal greater than 92 percent: the final concentration of one sample was below the MDL of 0.0023 mg/L, and the other replicate had 0.044 mg/L after treatment. This variability is attributed

to mass transfer limitations due to the irreproducible packing density of the iron wool and the mixing conditions. The IMA control test tube showed remaining Pb results lower than one of the PIMA replicates. Concerning the UV process, after four hours, no removal was observed. This seems contradictory to the removal observed during the 16-hour experiment. The literature does not report any interactions between UV and lead in water. These results from the two control processes demonstrate the utility of adding UV to the IMA process because the kinetics of the reaction are accelerated. The dose of iron was 2.0 g for the IMA and PIMA processes. The air flow was constant during the four hours of the experiment. The temperature was recorded around 30 - 31°C at the mid-distance test tube (set up before experiment No. 13). The difference noticed between the two PIMA samples may also be explained by a difference in pH. High pH eases the removal of metals, when a low pH makes it less favored (ions are dissolved). The pH of the first sample was recorded 6.0, the pH of the second sample was 7.0.

**Table 41. Additional simulated lead experimental results for the individual medium concentration level (0.29 mg/L)**

| <b>Process</b>    | <b>C / C<sub>0</sub></b> | <b>C / C<sub>0</sub></b> |
|-------------------|--------------------------|--------------------------|
|                   | 0 hr                     | 4 hrs                    |
| IMA, x = 10.2 cm  | 1.00                     | 0.12069                  |
| UV, x = 10.2 cm   | 1.00                     | 1.00000                  |
| PIMA, x = 10.2 cm | 1.00                     | 0.15172                  |
| PIMA, x = 10.2 cm | 1.00                     | < 0.00793                |

The next graph (Figure 41) is a representation of the results of both experiments performed on lead.



**Figure 41. Summary of individual simulated lead experimental results**

### 3.1.6 Findings of PIMA Simulated Leachate Individual Scoping Tests

Overall, 14 experiments were conducted during the individual scoping phase of the project. The literature review demonstrated that 6 components of leachate (i.e. ammonia, BOD<sub>5</sub>, COD, TDS, conductivity and lead) are the most environmentally relevant. This first phase was dedicated to testing the PIMA process on those 6 components at three different initial concentrations: low, medium and high levels as determined from the review of leachate quality data. Table 42 shows the best removal percentage obtained after 16 hours of treatment (unless stated otherwise in the remarks) and the initial concentration values.

**Table 42. Removal percentages observed after 16 hours of treatment during the individual scoping tests**

|  | COD  |   |   | Conductivity                                      |   |  | TDS                               |   |   |
|--|--|---|---|---|---|--|-----------------------------------|---|---|
|  | Low  | Medium                                      | High  | Low   | Medium  | High   | Low                               | Medium                                      | High  |
| <b>Starting concentration or value</b> | 1.05   | 3.30  | 10.90   | 2,750   | 16,250  | 81,625   | 0.83                              | 8.12  | 40.00   |
| IMA, x = 10.2 cm                       | 21   | 53  | 39  | -3  | -14   | -2   | -                                 | -3  | 0   |
| UV, x = 10.2 cm                        | -  | 11  | 3   | 3   | -19   | 2  | -                                 | 8   | 6   |
| <b>Process</b>                         |  |   |   |   |   |  |                                   |   |   |
| PIMA, x = 6.3 cm                       | 54   | 42  | 35  | -26   | -16   | -9   | -                                 | 38  | -8  |
| PIMA, x = 10.2 cm                      | 51   | 49  | 19  | -12   | -14   | 0  | -                                 | 13  | 3   |
| PIMA, x = 15.2 cm                      | 44   | 52  | 32  | 6   | -12   | -3   | -                                 | -8  | -1  |
|  | concentrations in g/L as O <sub>2</sub>          |   |   | values in µS/cm                                   |   |  | concentrations in g/L             |   |   |
| <b>Remarks</b>                         | Values after 24 hrs, no data available at 16 hrs | COD did not decrease between 16 and 24 hrs. | COD slightly decreased between 16 and 24 hrs. | Conductivity increased between 16 and 24 hrs.     | Conductivity increased between 16 and 24 hrs.     | Conductivity remained relatively stable between 16 and 24 hrs. | Sensitivity issue.                | TDS highly increased between 16 and 24 hrs. | TDS slightly increased between 16 and 24 hrs. |
|  | <b>BOD<sub>5</sub></b>                           |   |   | <b>Ammonia</b>                                    |   |  | <b>Lead</b>                       |   |   |
|  | Low  | Medium                                      | High  | Low   | Medium  | High   | Medium                            |   |   |
| <b>Starting concentration or value</b> | 55   | 120   | 425   | 110   | 540   | 930  | 0.30                              |   |   |
| IMA, x = 10.2 cm                       | 38   | -   | 28  | -5  | 24  | -8   | 99.96                             |   |   |
| UV, x = 10.2 cm                        | -  | 100   | -   | -2  | 20  | -12  | 53.33                             |   |   |
| <b>Process</b>                         |  |   |   |   |   |  |                                   |   |   |
| PIMA, x = 6.3 cm                       | -  | -   | -   | -16   | 21  | -4   | 99.97                             |   |   |
| PIMA, x = 10.2 cm                      | 39   | 55  | 44  | -13   | 19  | -3   | 99.97                             |   |   |
| PIMA, x = 15.2 cm                      | -  | -   | -   | -5  | 22  | 13   | 99.97                             |   |   |
|  | concentrations in mg/L as O <sub>2</sub>         |   |   | concentrations in mg/L as NH <sub>3</sub> -N      |   |  | concentration in mg/L             |   |   |
| <b>Remarks</b>                         | BOD <sub>5</sub> was not monitored at 24 hrs.    |   |   | Ammonia remained unchanged between 16 and 24 hrs. | Ammonia remained unchanged between 16 and 24 hrs. | Values after 24 hrs, no data available at 16 hrs.              | Lead was not monitored at 24 hrs. |   |   |

- No results obtained (experiment not completed)

The purpose of this phase was to grasp the behavior of the reactor, acquire experience with regard to the detection methods, and establish preliminary performance data on individual constituents in simulated leachates. Several key points were found during this phase of testing:

- The reactor design has been updated several times.
  - A thin shield has been placed around the IMA test tube control to insure that no light radiation from the visible domain is penetrating the borosilicate material. The impact of this shielding has been clearly identified.
  - The temperature probe no longer records the temperature of the air in the safety cabinet. It was first designed as a safety measure to control the cooling system of the reactor. While still fulfilling this function, it is now recording the temperature of a water sample in a temperature control tube, and gives a better estimate of the leachate temperatures in each individual test tube reactor during treatment.
  - Preliminary results also showed that there is no real value in varying the distances of irradiation: the differences noticed were negligible. As a result, in the next two phases, the test tubes will all be sited at 10.2 cm from the UV lamp. Figure 42 below is a view from above of this new reactor arrangement.

- The choice of the form of the iron reactant seems not to be optimal because of the obstruction of UV radiation. However, iron powder has already been demonstrated ineffective. Consequently, steel wool will still be used during this project.
- Also according to the results obtained, the experimental protocol has been updated for the next phases. The last 8 hours of treatment have not demonstrated a strong influence on treatment performance for any of the parameters in the scoping tests. The concentration of COD, ammonia, TDS and conductivity measurements will then be performed after zero, two, six, and sixteen hours of treatment. Concerning BOD<sub>5</sub> and lead, they will still only be monitored after sixteen hours and only one measurement will be performed.
- During the experiments, the PIMA demonstrated its removal power for some of the components taken individually. On COD, an average removal of 37 percent was achieved. On BOD<sub>5</sub>, this removal attained an average of 54 percent. Confirming the literature review and in particular the work done by Meeroff et al. (2006), the best results were obtained on lead, which demonstrated an observed removal greater than 99.99 percent. Nevertheless, some issues were encountered with ammonia, TDS and conductivity. Concerning ammonia, pH and reactor configuration have been identified as the cause for the relatively lower than expected observed removal. Concerning TDS and conductivity, the initial removal was offset by the dissolution of iron from the steel wool reactant.

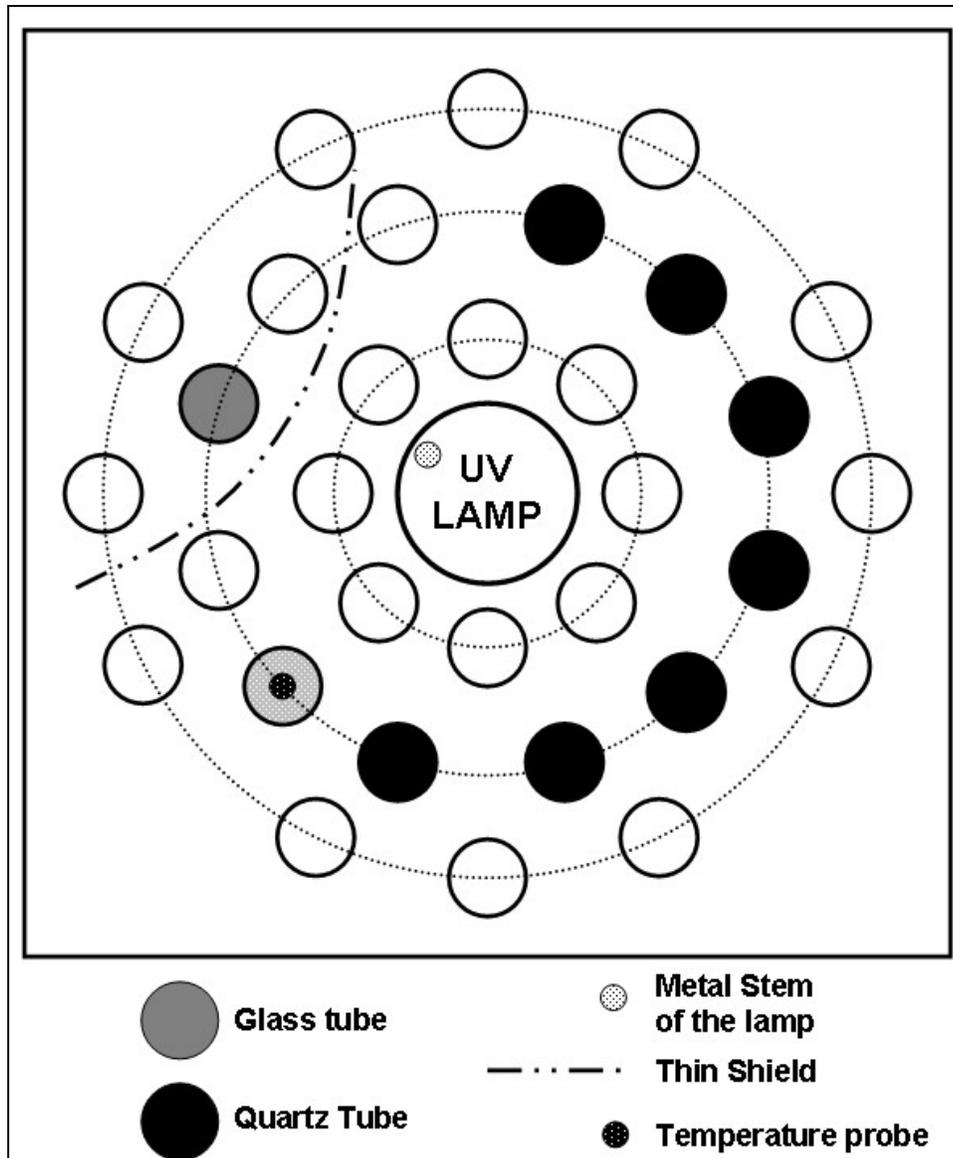


Figure 42. Reactor configuration update after first phase of experiments

### 3.2 PIMA MIXTURE SCOPING TESTS: SIMULATED LEACHATE

After applying the three processes (PIMA, IMA, and UV) on individual components and establishing preliminary performance data, a simulated leachate containing all six components was prepared and subjected to treatment. Table 43 summarizes the order of the scoping tests on the simulated mixture leachate experiments (No. 15, 17, and 18).

**Table 43. Order of execution of the simulated mixture leachate experiments for PIMA**

| Experiment Number | Component tested | Level  | Date      | Shield used? |
|-------------------|------------------|--------|-----------|--------------|
| 15                | Mixture          | Medium | 13-Feb-07 | Yes          |
| 17                | Mixture          | Low    | 13-Mar-07 | Yes          |
| 18                | Mixture          | High   | 20-Mar-07 | Yes          |

Beginning with experiment No. 17 on the low level, this section presents the results obtained during this second phase of experiments. Table 44 summarizes the starting concentration of every component tested during this phase. The same amount of each component was added during these experiments as was done during the individual scoping tests in the previous section.

**Table 44. Initial concentrations of mixture simulated leachate tests with PIMA**

|  |              | Level |        |         |
|--|--------------|-------|--------|---------|
|  |              | Low   | Medium | High    |
| <b>COD, in g/L as O<sub>2</sub></b>              | Theoretical  | 0.05  | 3.00   | 14.00   |
|  | Experimental | 0.74  | 3.83   | 11.60   |
| <b>Conductivity in <math>\mu</math>S/cm</b>      | Theoretical  | 1,000 | 11,600 | 95,000  |
|  | Experimental | 3,915 | 28,250 | 78,750  |
| <b>TDS in g/L</b>                                | Theoretical  | 0.90  | 9.30   | 88.00   |
|  | Experimental | 0.17  | 13.34  | 43.75   |
| <b>BOD<sub>5</sub>, in mg/L as O<sub>2</sub></b> | Theoretical  | 0     | 150    | 445     |
|  | Experimental | > 417 | -      | > 1,650 |
| <b>Ammonia, in mg/L as NH<sub>3</sub>-N</b>      | Theoretical  | 0     | 500    | 1,350   |
|  | Experimental | 52.5  | 470    | -       |
| <b>Lead, in mg/L</b>                             | Theoretical  | 0.00  | 0.03   | 0.10    |
|  | Experimental | 0.07  | 0.30   | 0.30    |

- Measure not completed during this experiment.

### 3.2.1 Low concentration levels

For this experiment (experiment No.17), the five constituents were mixed in their low concentration levels. Initial concentrations were respectively:

- COD = 740 mg/L as O<sub>2</sub>
- Conductivity = 3,915  $\mu$ S/cm
- TDS = 165 mg/L
- BOD<sub>5</sub> = 415 mg/L as O<sub>2</sub>
- Ammonia = 52.5 mg/L as NH<sub>3</sub>-N
- Pb = 0.07 mg/L

The initial pH of the simulated, low strength leachate was 5.0 and rose to a value of 6.0 after 2 hours of treatment. Only the pH of the UV process reactor stayed stable around the 5.0 value. The pH was not adjusted for this experiment. The dose of iron was 2.0 g for all IMA and PIMA reactions. The temperature was recorded with the temperature monitoring tube. The equilibrium value was approximately 30°C. Concentrations were monitored after zero, two, six, and sixteen hours. All of the test tube reactors were situated at the middle distance from the UV lamp as explained earlier. The following paragraphs detail the removal efficiencies obtained for each parameter.

### 3.2.1.1 Chemical Oxygen Demand (COD)

Regarding COD, the initial concentration was 740 mg/L as O<sub>2</sub> (0.5 g of KHP were dissolved in a 1.0 L flask filled with reagent water and the other constituents). Table 45 summarizes the results at each sampling time. The results obtained during this experiment are not in complete agreement with those obtained during the individual scoping tests. Indeed, the UV process achieved a similar removal compared to the PIMA process (40 percent removal, which equals to 296 mg/L as O<sub>2</sub>). Both PIMA and UV alone achieved a better removal than the IMA, which reduced the COD concentration by only 28 percent (i.e. 207 mg/L as O<sub>2</sub>). As the starting concentration is below the authorized limit for safe sewer discharge for the City of Boca Raton, the final concentrations are also below this limit.

**Table 45. Summary of simulated COD experimental results for the low concentration level mixture (740 mg/L as O<sub>2</sub>)**

| Process           | C / C <sub>0</sub> |
|-------------------|--------------------|--------------------|--------------------|--------------------|
|                   | 0 hr               | 2 hrs              | 6 hrs              | 16 hrs             |
| IMA, x = 10.2 cm  | 1.00               | 0.95               | 0.83               | 0.72               |
| UV, x = 10.2 cm   | 1.00               | 0.90               | 0.84               | 0.60               |
| PIMA, x = 10.2 cm | 1.00               | 0.82               | 0.64               | 0.60               |
| PIMA, x = 10.2 cm | 1.00               | 0.81               | 0.64               | 0.60               |
| PIMA, x = 10.2 cm | 1.00               | 0.84               | 0.68               | 0.61               |
| PIMA, x = 10.2 cm | 1.00               | 1.33               | 0.66               | 0.69               |
| PIMA, x = 10.2 cm | 1.00               | 0.85               | 0.65               | 0.59               |
| PIMA, x = 10.2 cm | 1.00               | 0.86               | 0.69               | 0.63               |

### 3.2.1.2 Conductivity and Total Dissolved Solids (TDS)

Regarding conductivity and TDS, both were simulated using sodium chloride salt. For this experiment, 1.0 g NaCl was dissolved in a 1.0 L flask filled with reagent water and the other constituents mentioned earlier. The conductivity registered was 3915 µS/cm, and the TDS concentration was 1650 mg/L. With the

same amount of salt added in the same volume, these two values are higher than those registered during the individual scoping test. This was caused by mixing with other components that also contained salts such as ammonium chloride, for instance.

Table 46 summarizes the results for conductivity, and Table 47 summarizes the results for TDS. The results obtained during this experiment are similar to those obtained previously during the individual scoping tests. Conductivity and TDS are unaffected by any of the processes. And due to the same sensitivity issue that occurred during the individual tests, the TDS values registered here are all equal. Initial and final TDS concentrations are not in compliance with the City of Boca Raton sewer discharge limits for TDS.

**Table 46. Summary of simulated conductivity experimental results for the low concentration level mixture (3,915  $\mu\text{S}/\text{cm}$ )**

| Process           | $C / C_0$ | $C / C_0$ | $C / C_0$ | $C / C_0$ |
|-------------------|-----------|-----------|-----------|-----------|
|                   | 0 hr      | 2 hrs     | 6 hrs     | 16 hrs    |
| IMA, x = 10.2 cm  | 1.00      | 1.02      | 1.00      | 0.98      |
| UV, x = 10.2 cm   | 1.00      | 1.04      | 0.98      | 0.98      |
| PIMA, x = 10.2 cm | 1.00      | 1.00      | 0.96      | 0.94      |
| PIMA, x = 10.2 cm | 1.00      | 0.98      | 0.91      | 0.94      |
| PIMA, x = 10.2 cm | 1.00      | 0.96      | 0.96      | 1.00      |
| PIMA, x = 10.2 cm | 1.00      | 0.96      | 0.87      | 0.94      |
| PIMA, x = 10.2 cm | 1.00      | 0.98      | 0.96      | 0.96      |
| PIMA, x = 10.2 cm | 1.00      | 0.98      | 0.94      | 0.96      |

**Table 47. Summary of simulated TDS experimental results for the low concentration level mixture (165 mg/L)**

| Process           | $C / C_0$ | $C / C_0$ | $C / C_0$ | $C / C_0$ |
|-------------------|-----------|-----------|-----------|-----------|
|                   | 0 hr      | 2 hrs     | 6 hrs     | 16 hrs    |
| IMA, x = 10.2 cm  | 1.00      | 1.00      | 1.00      | 1.00      |
| UV, x = 10.2 cm   | 1.00      | 1.00      | 1.00      | 1.00      |
| PIMA, x = 10.2 cm | 1.00      | 1.00      | 1.00      | 1.00      |
| PIMA, x = 10.2 cm | 1.00      | 1.00      | 1.00      | 1.00      |
| PIMA, x = 10.2 cm | 1.00      | 1.00      | 1.00      | 1.00      |
| PIMA, x = 10.2 cm | 1.00      | 1.00      | 1.00      | 1.00      |
| PIMA, x = 10.2 cm | 1.00      | 1.00      | 1.00      | 1.00      |
| PIMA, x = 10.2 cm | 1.00      | 1.00      | 1.00      | 1.00      |

### 3.2.1.3 Biochemical Oxygen Demand (BOD<sub>5</sub>)

Regarding BOD<sub>5</sub>, the initial concentration was greater than 417 mg/L as O<sub>2</sub>. BOD<sub>5</sub> was simulated with 20.0 mL of BOD Standard Solution, 3.00 g/L of glucose

and 3.00 g/L of glutamic acid, diluted in the 1.0 L flask filled with reagent water and the other components. The initial BOD<sub>5</sub> concentration expected was about 55 mg/L as O<sub>2</sub>, as recorded during the low level individual test. Dilutions were prepared consequently 5.0, 10.0 and 50.0 mL as stated in the Methodology section. However, the initial value was much higher than expected; resulting in over-ranging the dilutions set up for the measurements. Consequently, the initial BOD<sub>5</sub> can only be estimated as higher than 417 mg/L as O<sub>2</sub>. This phenomenon is likely due to the mixing with the other components, most notably KHP for COD simulation.

Table 48 summarizes the results for this experiment. The data obtained during this experiment are in agreement with the conclusions drawn during the first previous experimental phase. The best removal is obtained with UV with a removal higher than 65 percent, followed by the PIMA process (removal higher than 48 percent) and finally the IMA (removal higher than 37 percent). The level of treatment achieved during this experiment lowered the BOD<sub>5</sub> value from a value higher than the permissible threshold to an allowable range.

**Table 48. Summary of simulated BOD<sub>5</sub> experimental results for the low concentration level mixture (> 417 mg/L as O<sub>2</sub>)**

| Process           | C <sub>0</sub> in mg/L<br>as O <sub>2</sub> | C in mg/L as<br>O <sub>2</sub> |        | C / C <sub>0</sub> |
|-------------------|---|--------------------------------|--------|--------------------|
|                   | 0 hr  | 16 hrs                         | 16 hrs |                    |
| IMA, x = 10.2 cm  | > 417                                       | 262                            |        | < 0.63             |
| UV, x = 10.2 cm   | > 417                                       | 147                            |        | < 0.35             |
| PIMA, x = 10.2 cm | > 417                                       | 177                            |        | < 0.42             |
| PIMA, x = 10.2 cm | > 417                                       | 259                            |        | < 0.62             |

### 3.2.1.4 Ammonia

Regarding ammonia, the initial concentration was 52.5 mg/L as NH<sub>3</sub>-N (0.21 g of NH<sub>4</sub>Cl were diluted in a 1.0 L flask filled with reagent water and the other constituents). This value is lower than the value that could have been expected after the individual low level experiment. However, the results obtained during this experiment are in complete agreement with those obtained during the individual scoping tests. Experimental results are presented in Table 49. The three processes tested (UV, IMA, and PIMA) do not achieve the acceptable removal performance with regard to ammonia, without pH adjustment. Since no pH adjustment was made, the acidic pH was the main explanation for this absence of stripping.

**Table 49. Summary of simulated ammonia experimental results for the low concentration level mixture (52.5 mg/L as NH<sub>3</sub>-N)**

| Process           | C / C <sub>0</sub> |
|-------------------|--------------------|--------------------|--------------------|--------------------|
|                   | 0 hr               | 2 hrs              | 6 hrs              | 16 hrs             |
| IMA, x = 10.2 cm  | 1.00               | 1.14               | 1.10               | 1.13               |
| UV, x = 10.2 cm   | 1.00               | 1.14               | 1.29               | 1.25               |
| PIMA, x = 10.2 cm | 1.00               | 1.13               | 1.16               | 1.14               |
| PIMA, x = 10.2 cm | 1.00               | 1.13               | 1.08               | 1.13               |
| PIMA, x = 10.2 cm | 1.00               | 1.10               | 1.14               | 1.19               |
| PIMA, x = 10.2 cm | 1.00               | 1.08               | 1.08               | 1.17               |
| PIMA, x = 10.2 cm | 1.00               | 1.11               | 1.13               | 1.13               |
| PIMA, x = 10.2 cm | 1.00               | 1.08               | 1.10               | 1.13               |

### 3.2.1.5 Lead

Regarding lead, the initial concentration was measured at 0.0686 mg/L. It was simulated with 0.5 mL of the Lead Standard Solution, 100 mg/L as Pb<sup>2+</sup>, diluted in the 1.0 L flask containing the other components and filled with reagent water. This relative difference of 37 percent is not explainable. The usual experimental protocol was used; the pipette was checked for accuracy before use. The other components are not known to contain any traces of lead. The laboratory might be the source of this discrepancy. The MDL setting for this experiment was 0.0023 mg/L. Although it may be entirely possible that one of the components may have complexed with lead, which would have masked its signature.

During this experiment, the control process effluents were used to monitor and compare their relative efficiency on the biochemical oxygen demand. Therefore, lead was tested on four PIMA test tube reactors. Table 50 summarizes the results. Lead readings were very homogeneous with a standard deviation of only 0.009. After 16 hours of treatment, a mean removal efficiency approaching 77.2 percent was achieved. This value is not as high as the removal experienced during the individual scoping tests. However this is not a surprise as the starting concentration was lower and the starting concentration dependence has been demonstrated in individual leachate tests. As the initial concentration was lower than the allowable sewer discharge for the City of Boca Raton, the concentration recorded in the effluent is also below the limit.

**Table 50. Summary of simulated lead experimental results for the low concentration level mixture (0.07 mg/L)**

| Process           | $C / C_0$ | $C / C_0$ |
|-------------------|-----------|-----------|
|                   | 0 hr      | 16 hrs    |
| PIMA, x = 10.2 cm | 1.00      | 0.2391    |
| PIMA, x = 10.2 cm | 1.00      | 0.2172    |
| PIMA, x = 10.2 cm | 1.00      | 0.2259    |
| PIMA, x = 10.2 cm | 1.00      | 0.2289    |

### 3.2.2 Medium concentration levels

For this experiment (experiment No. 15), the five components were mixed in their medium concentration levels. Initial concentrations were respectively:

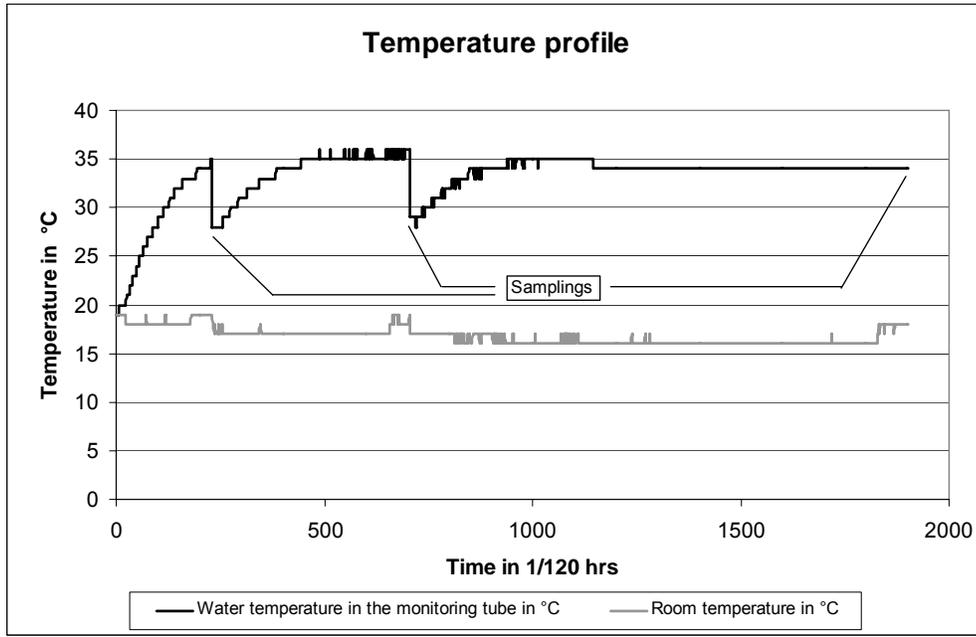
- COD = 3830 mg/L as O<sub>2</sub>
- Conductivity = 28,250 μS/cm
- TDS = 13,335 mg/L
- BOD<sub>5</sub> = not measured
- Ammonia = 470 mg/L as NH<sub>3</sub>-N
- Pb = 0.3 mg/L

No BOD<sub>5</sub> measurements were performed during this experiment.

The initial pH of the simulated low strength leachate was 4.5 and rose to the value of 6.0 after 2 hours of treatment and stayed stable afterwards, except for the pH in the UV process reactor, which has stayed stable over time at 4.5. The pH was not adjusted for this experiment. The dose of iron was 2.0 g for all IMA and PIMA reactions. After treatment, the concentration of soluble iron was measured in the IMA and in the 3 PIMA effluent replicates (data were already reported in Table 14Table 15). The impact of the difference noted seems difficult to establish with certainty. During this experiment on COD, the IMA sample (which contained the highest recorded amount of iron) showed the same level of removal than the PIMA process sample, which had the lowest concentration of dissolved iron. The two other PIMA replicates had a concentration of iron lower than the IMA sample, but higher than the first PIMA sample, and showed a lower COD removal. The iron monitoring conducted during experiment No. 17 leads to the same inconclusive trend.

The temperature was recorded with the temperature monitoring tube. The equilibrium value was approximately 34 - 35°C. Concentrations were monitored after zero, two, six, and sixteen hours. All the test tube reactors were situated at the middle distance from the UV lamp as explained in the conclusions of the individual tests. Figure 43 shows the temperature profile for experiment No. 15 that was run for 16 hours. One time unit corresponds to 30 seconds. The gap required to complete the sample collection is not shown in the graph, but the amount of time required for the

sample collection process was approximately 30 minutes. As explained in the Methodology section, the temperature probe was set up in a temperature monitoring tube. This tube was sited in the middle circle of the reactor and provided a better representation of the temperature profile of a leachate sample.



**Figure 43. Temperature profile of experiment No. 15**

The following paragraphs describe the removals achieved for each parameter.

### 3.2.2.1 Chemical Oxygen Demand (COD)

Regarding COD, the initial concentration was 3,830 mg/L as O<sub>2</sub> (influent prepared by adding 2.7 g of KHP to the 1.0 L flask filled with reagent water containing the other constituents). Table 51 summarizes the results at each sampling time. The data obtained during this experiment confirm those obtained during the individual scoping tests. Indeed, the UV process achieved a very slim removal of only 3 percent (i.e. 105 g of COD have been degraded). As observed during the middle level individual experiment, the IMA achieve a slightly better removal than the PIMA: 36 percent for the IMA (i.e. 1,380 g of COD have been degraded) compared to 28 average percent for the PIMA (i.e. 1,073 g of COD have been degraded).

It also appeared that during this experiment the first 2 hours of treatment did not have any effect on the COD content of the simulated leachate. The reaction required more than 2 hours to start degrading COD. This phenomenon only occurred during this experiment and no explanation can be found. The initial concentration was well

above the authorized limit value for sewer discharge in the City of Boca Raton (800 mg/L), but none of the three processes achieved permissible levels in the effluent after 16 hours of treatment.

**Table 51. Summary of simulated COD experimental results for the middle concentration level mixture (3,830 mg/L as O<sub>2</sub>)**

| Process           | C / C <sub>0</sub> |
|-------------------|--------------------|--------------------|--------------------|--------------------|
|                   | 0 hr               | 2 hrs              | 6 hrs              | 16 hrs             |
| IMA, x = 10.2 cm  | 1.00               | 1.03               | 0.88               | 0.64               |
| UV, x = 10.2 cm   | 1.00               | 1.01               | 1.05               | 0.97               |
| PIMA, x = 10.2 cm | 1.00               | 1.00               | 0.81               | 0.64               |
| PIMA, x = 10.2 cm | 1.00               | 1.00               | 0.78               | 0.74               |
| PIMA, x = 10.2 cm | 1.00               | 1.03               | 0.87               | 0.73               |
| PIMA, x = 10.2 cm | 1.00               | 0.98               | 0.81               | 0.72               |
| PIMA, x = 10.2 cm | 1.00               | 1.00               | 0.83               | 0.69               |
| PIMA, x = 10.2 cm | 1.00               | 1.04               | 0.87               | 0.78               |

### 3.2.2.2 Conductivity and Total Dissolved Solids (TDS)

For this test, 7.9 grams of NaCl were dissolved in the 1.0 L solution containing the other constituents. Table 52 and Table 53 summarize the data for this experiment. As occurred during the low level experiments, using a similar mass of salt, the initial conductivity and TDS values are higher than during the individual test because of the other components added. Initial conductivity was recorded at 28,250 µS/cm and TDS at 13,335 mg/L. Nevertheless, it is not surprising to notice that the three processes did not have any action on these two parameters. All previous conclusions from the individual scoping tests are confirmed here. Also, initial and final TDS concentrations are not in compliance with the City of Boca Raton sewer discharge limits.

**Table 52. Summary of simulated conductivity experimental results for the middle concentration level mixture (28,250 µS/cm)**

| Process           | C / C <sub>0</sub> |
|-------------------|--------------------|--------------------|--------------------|--------------------|
|                   | 0 hr               | 2 hrs              | 6 hrs              | 16 hrs             |
| IMA, x = 10.2 cm  | 1.00               | 1.11               | 0.97               | 0.98               |
| UV, x = 10.2 cm   | 1.00               | 0.99               | 0.97               | 0.98               |
| PIMA, x = 10.2 cm | 1.00               | 1.01               | 0.99               | 1.01               |
| PIMA, x = 10.2 cm | 1.00               | 1.00               | 0.99               | 1.01               |
| PIMA, x = 10.2 cm | 1.00               | 1.00               | 0.97               | 1.03               |
| PIMA, x = 10.2 cm | 1.00               | 1.03               | 0.99               | 1.01               |
| PIMA, x = 10.2 cm | 1.00               | 0.98               | 0.97               | 0.98               |
| PIMA, x = 10.2 cm | 1.00               | 0.99               | 0.99               | 1.00               |

**Table 53. Summary of simulated TDS experimental results for the middle concentration level mixture (13,335 mg/L)**

| Process           | C / C <sub>0</sub> |
|-------------------|--------------------|--------------------|--------------------|--------------------|
|                   | 0 hr               | 2 hrs              | 6 hrs              | 16 hrs             |
| IMA, x = 10.2 cm  | 1.00               | 1.13               | 1.00               | 1.00               |
| UV, x = 10.2 cm   | 1.00               | 1.00               | 1.00               | 1.00               |
| PIMA, x = 10.2 cm | 1.00               | 1.00               | 0.97               | 1.00               |
| PIMA, x = 10.2 cm | 1.00               | 1.00               | 1.00               | 1.06               |
| PIMA, x = 10.2 cm | 1.00               | 1.00               | 1.00               | 1.06               |
| PIMA, x = 10.2 cm | 1.00               | 1.06               | 1.00               | 1.00               |
| PIMA, x = 10.2 cm | 1.00               | 1.00               | 1.00               | 1.00               |
| PIMA, x = 10.2 cm | 1.00               | 1.00               | 1.00               | 1.00               |

### 3.2.2.3 Biochemical Oxygen Demand (BOD<sub>5</sub>)

Unfortunately, the solution prepared for this experiment was discarded by mistake between the beginning of the experiment and the time that the BOD<sub>5</sub> measurement should have started. Thus no results for BOD<sub>5</sub> for the medium mixture concentration level are available.

### 3.2.2.4 Ammonia

Regarding ammonia, the initial concentration was 467.5 mg/L as NH<sub>3</sub>-N (1.48 g of NH<sub>4</sub>Cl were dissolved in the 1.0 L flask filled with reagent water containing the other constituents). The experimental data are listed in Table 54. The initial ammonia was reduced by an average of 10 percent during the first two hours of treatment. This is independent of the process. After this initial low removal, no observable changes can be noticed. This phenomenon is very similar to the individual scoping test with simulated medium level ammonia. The pH was not adjusted and remained in the acidic range during the experiment. This is once again the main reason for the poor performance of the process.

**Table 54. Summary of simulated ammonia experimental results for the low concentration level mixture (470 mg/L as NH<sub>3</sub>-N)**

| Process           | $C / C_0$ |       |       |        |
|-------------------|-----------|-------|-------|--------|
|                   | 0 hr      | 2 hrs | 6 hrs | 16 hrs |
| IMA, x = 10.2 cm  | 1.00      | 0.96  | 0.91  | 0.90   |
| UV, x = 10.2 cm   | 1.00      | 0.89  | 0.88  | 0.88   |
| PIMA, x = 10.2 cm | 1.00      | 0.93  | 0.95  | 0.95   |
| PIMA, x = 10.2 cm | 1.00      | 0.87  | 0.95  | 0.90   |
| PIMA, x = 10.2 cm | 1.00      | 0.88  | 0.96  | 0.92   |
| PIMA, x = 10.2 cm | 1.00      | 0.90  | 0.90  | 0.93   |
| PIMA, x = 10.2 cm | 1.00      | 0.90  | 0.89  | 0.92   |
| PIMA, x = 10.2 cm | 1.00      | 0.86  | 0.91  | 0.94   |

### 3.2.2.5 Lead

Regarding lead, the initial concentration was measured at 0.30 mg/L. It was simulated with 3.0 mL of the Lead Standard Solution, 100 mg/L as Pb<sup>2+</sup>, diluted in a 1.0 L flask containing the other components and filled with reagent water. The three processes were compared during this experiment where the MDL was 0.0023 mg/L. Experimental data are summarized in Table 55. As occurred during the individual scoping tests with lead, this experiment demonstrated the limited removal of the UV process at only 3.3 percent. The IMA process efficiency is enhanced by UV. After 16 hours, IMA reduced 95 percent of the initial lead, and the three PIMA processes achieved an average of 98.13 percent removal of lead. This removal efficiency is lower than the removal registered during the individual scoping test. An interaction with the other components is the most likely explanation. As the initial concentration is lower than the allowable sewer discharge for the City of Boca Raton, the concentration recorded in the effluent is also below the limit.

**Table 55. Summary of simulated lead experimental results for the middle concentration level mixture (0.30 mg/L)**

| Process           | $C / C_0$ |        |
|-------------------|-----------|--------|
|                   | 0 hr      | 16 hrs |
| IMA, x = 10.2 cm  | 1.00      | 0.0500 |
| UV, x = 10.2 cm   | 1.00      | 0.9667 |
| PIMA, x = 10.2 cm | 1.00      | 0.0123 |
| PIMA, x = 10.2 cm | 1.00      | 0.0197 |
| PIMA, x = 10.2 cm | 1.00      | 0.0240 |

### 3.2.3 High concentration levels

For this experiment (experiment No. 18), the five chemicals were mixed in their high concentration levels. Initial concentrations were respectively:

- COD = 11,600 mg/L as O<sub>2</sub>
- Conductivity = 78,750 μS/cm
- TDS = 43,760 mg/L
- BOD<sub>5</sub> > 1650 as O<sub>2</sub>
- Ammonia = not measured
- Pb = 0.35 mg/L

Due to a reagent shortage that occurred during the experiment, ammonia could not be measured.

The initial pH of the simulated low strength leachate was 4.0 and rose to the value of 6.0 after 2 hours of treatment. Only the pH in the UV process reactor stayed stable over time at 4.0. The pH was not adjusted for this experiment. The dose of iron was 2.0 g for all IMA and PIMA reactors. The temperature was recorded with the temperature monitoring tube. The equilibrium value was approximately 29 - 30°C. Concentrations were monitored after zero, two, six, and sixteen hours. All test tube reactors were situated at the middle distance from the UV lamp as explained in the conclusions of the individual tests. The following paragraphs describe the removal efficiencies obtained for each parameter.

#### 3.2.3.1 Chemical Oxygen Demand (COD)

Regarding COD, the initial concentration was 11,600 mg/L as O<sub>2</sub> (6.0 g of KHP were dissolved in a 1.0 L flask filled with reagent water containing the other constituents). Table 56 summarizes the results at each sampling time. The data obtained during this experiment also confirm those obtained during the individual scoping tests. The UV process achieved a low removal of only 14 percent (i.e. 1,580 g of COD have been degraded). As observed during the high level individual experiment, the IMA achieved a lower removal than the PIMA: 20 percent for the IMA (i.e. 2,320 g of COD have been degraded) compared to 33 average percent for the PIMA (i.e. 3,830 g of COD have been degraded). Some values were not available due to particles that were not settling; (this may be the result of interferences or elevated ionic strength). In fact, chloride ions have been identified as a potential interference for measurement of COD with the colorimetric method. During this experiment, samples were diluted 20 times, and the chloride concentration was reduced to less than 2,200 mg/L (as all TDS are not due to NaCl but also to the other salts added in the mixture). For diluted samples, Hach suggest a maximum chloride concentration of 1,000 mg/L. High chlorides tend to result in a positive interference, which would explain the lower perceived removal. Similarly to the medium level

simulated mixture experiment, the initial concentration is above the authorized limit value for the City of Boca Raton (800 mg/L) and none of the three processes achieved to lower the value to the permissible level.

**Table 56. Summary of simulated COD experimental results for the high concentration level mixture (11,600 mg/L as O<sub>2</sub>)**

| Process           | C / C <sub>0</sub> |
|-------------------|--------------------|--------------------|--------------------|--------------------|
|                   | 0 hrs              | 2 hrs              | 6 hrs              | 16 hrs             |
| IMA, x = 10.2 cm  | 1.00               | 0.88               | 0.82               | 0.80               |
| UV, x = 10.2 cm   | 1.00               | 0.92               | 1.00               | 0.86               |
| PIMA, x = 10.2 cm | 1.00               | 0.76               | *                  | 0.66               |
| PIMA, x = 10.2 cm | 1.00               | 0.95               | *                  | 0.71               |
| PIMA, x = 10.2 cm | 1.00               | 0.92               | *                  | 0.59               |
| PIMA, x = 10.2 cm | 1.00               | 0.89               | 0.80               | 0.60               |
| PIMA, x = 10.2 cm | 1.00               | 0.93               | 0.79               | 0.75               |
| PIMA, x = 10.2 cm | 1.00               | 1.02               | 0.79               | 0.69               |

\* The measurement of COD was not possible due to non-settling particles in the cuvette.

### 3.2.3.2 Conductivity and Total Dissolved Solids (TDS)

For this experiment, 30.2 grams of NaCl were used. Initial conductivity was recorded at 78,750 µS/cm and initial TDS at 43,750 mg/L. As shown in Table 57 and Table 58, a removal of 20 percent was observed during the first two hours of treatment, but no additional treatment is performed afterwards. The levels even demonstrated a tendency to increase after this initial but unanticipated removal. Also, as initial TDS concentrations are not in compliance with the City of Boca Raton sewer discharge limits, none of the three processes achieved the required removal.

**Table 57. Summary of simulated conductivity experimental results for the high concentration level mixture (78,750 µS/cm)**

| Process           | C / C <sub>0</sub> |
|-------------------|--------------------|--------------------|--------------------|--------------------|
|                   | 0 hrs              | 2 hrs              | 6 hrs              | 16 hrs             |
| IMA, x = 10.2 cm  | 1.00               | 0.81               | 0.83               | 0.86               |
| UV, x = 10.2 cm   | 1.00               | 0.84               | 0.80               | 0.81               |
| PIMA, x = 10.2 cm | 1.00               | 0.83               | 0.86               | 0.84               |
| PIMA, x = 10.2 cm | 1.00               | 0.83               | 0.87               | 0.89               |
| PIMA, x = 10.2 cm | 1.00               | 0.85               | 0.84               | 0.97               |
| PIMA, x = 10.2 cm | 1.00               | 0.86               | 0.86               | 0.94               |
| PIMA, x = 10.2 cm | 1.00               | 0.79               | 0.88               | 0.89               |
| PIMA, x = 10.2 cm | 1.00               | 0.82               | 0.81               | 0.90               |

**Table 58. Summary of simulated TDS experimental results for the high concentration level mixture (43,750 mg/L)**

| Process           | C / C <sub>0</sub> |
|-------------------|--------------------|--------------------|--------------------|--------------------|
|                   | 0 hr               | 2 hrs              | 6 hrs              | 16 hrs             |
| IMA, x = 10.2 cm  | 1.00               | 0.74               | 0.74               | 0.77               |
| UV, x = 10.2 cm   | 1.00               | 0.80               | 0.77               | 0.80               |
| PIMA, x = 10.2 cm | 1.00               | 0.77               | 0.80               | 0.74               |
| PIMA, x = 10.2 cm | 1.00               | 0.80               | 0.80               | 0.80               |
| PIMA, x = 10.2 cm | 1.00               | 0.80               | 0.77               | 0.89               |
| PIMA, x = 10.2 cm | 1.00               | 0.80               | 0.80               | 0.83               |
| PIMA, x = 10.2 cm | 1.00               | 0.80               | 0.80               | 0.80               |
| PIMA, x = 10.2 cm | 1.00               | 0.77               | 0.77               | 0.83               |

### 3.2.3.3 Biochemical Oxygen Demand (BOD<sub>5</sub>)

Regarding BOD<sub>5</sub>, the initial concentration was higher than 1,650 mg/L as O<sub>2</sub>. BOD<sub>5</sub> was simulated with 117 mL of BOD Standard Solution, 3.00 g/L of glucose and 3.00 g/L of glutamic acid, diluted in the 1.0 L flask filled with reagent water and the other components. Lessons have been learned from the low level experiment, and dilutions were prepared consequently (1, 2 and 5 for the BOD<sub>5</sub> before treatment and 2, 5 and 10 mL after 16 hours). However, the results were still beyond the dilution range anticipated, and the samples were not diluted enough to allow for accurate determination of the BOD measurements. This is probably due to the presence of the KHP, as explained during the low level experiment, or weaker seed. As a result, the initial concentration was measured as higher than 1,650 mg/L as O<sub>2</sub>, but cannot be estimated with certainty. Table 59 summarizes the performance data for the simulated mixture. During this experiment, only the PIMA process was tested for BOD<sub>5</sub> (the UV and IMA control reactor were used to generate lead removal performance data). After 16 hours of PIMA treatment, the remaining concentration was recorded to be higher than 860 mg/L as O<sub>2</sub> on average, but can also not be estimated with certainty. Due to this double inequality, no removal percentage is estimated. Final concentrations are likely not in the permissible range for discharge to the City of Boca Raton sewer network.

**Table 59. Summary of simulated BOD<sub>5</sub> experimental results for the low concentration level mixture (> 1,650 mg/L as O<sub>2</sub>)**

| Process           | C <sub>0</sub> in mg/L<br>as O <sub>2</sub> | C in mg/L as<br>O <sub>2</sub> |
|-------------------|---|--------------------------------|
|                   | 0 hr  | 16 hrs                         |
| PIMA, x = 10.2 cm | > 1,650                                     | > 844                          |
| PIMA, x = 10.2 cm | > 1,650                                     | > 851                          |
| PIMA, x = 10.2 cm | > 1,650                                     | > 861                          |
| PIMA, x = 10.2 cm | > 1,650                                     | > 880                          |

### 3.2.3.4 Ammonia

Another issue was encountered during the ammonia measurement. A shortage of one of the reagents required to conduct the colorimetric test caused the data to be lost. As a result, no ammonia removal data are available for the high level mixture.

### 3.2.3.5 Lead

Regarding lead, the initial concentration was measured at 0.35 mg/L. It was simulated with 3.0 mL of the Lead Standard Solution, 100 mg/L as Pb<sup>2+</sup>, diluted in the 1.0 L flask containing the other components and filled with reagent water. The three processes (PIMA, IMA, and UV) were compared during this experiment where the MDL was 0.000088 mg/L. Experimental data are shown in Table 60. As seen during the individual scoping tests, this experiment demonstrated a limited removal (79.2 percent) of lead by the UV process alone. However, there is an important difference between this experiment and the previous one (experiment No. 15). Initial concentrations were similar, but removal is different: better treatment was achieved during this experiment. The IMA and PIMA processes demonstrated once again their high efficiency on reducing the lead concentration by more than 99.9 percent, in 16 hours. As the initial concentration is lower than the allowable discharge for the City of Boca Raton, the concentration recorded in the effluent is also below the limit.

**Table 60. Summary of simulated lead experimental results for the high concentration level mixture (0.30 mg/L)**

| Process           | C / C <sub>0</sub> | C / C <sub>0</sub> |
|-------------------|--------------------|--------------------|
|                   | 0 hr               | 16 hrs             |
| IMA, x = 10.2 cm  | 1.00               | 0.0003             |
| UV, x = 10.2 cm   | 1.00               | 0.2086             |
| PIMA, x = 10.2 cm | 1.00               | 0.0003             |
| PIMA, x = 10.2 cm | 1.00               | 0.0007             |

### 3.2.4 Findings of PIMA Simulated Leachate Mixture Scoping Tests

Table 61 shows the best removal percentages obtained after 16 hours of treatment and their initial concentration values. The performance of the three processes on mixture scoping tests will be illustrated with the same type of graphs as those used for the individual tests: removal at each time is the average of all the removals obtained for the process during the three experiments, including replicates.

**Table 61. Summary of removal percentages observed after 16 hours of treatment during the mixture scoping tests with PIMA**

|   | COD                                      |        |         | Conductivity                                 |        |        | TDS                   |                   |         |
|---|--|--------|---------|--|--------|--------|-----------------------|-------------------|---------|
|   | Low                                      | Medium | High    | Low  | Medium | High   | Low                   | Medium            | High    |
| <b>Starting concentration or value</b>  | 0.74                                     | 3.83   | 11.60   | 3,915  | 28,250 | 78,750 | 0.17                  | 13.34             | 43.75   |
| IMA, x = 10.2 cm  | 28                                       | 36     | 20      | 2  | 2      | 14     | 0                     | 0                 | 23      |
| <b>Process</b> UV, x = 10.2 cm  | 40                                       | 3      | 14      | 2  | 2      | 19     | 0                     | 0                 | 20      |
| PIMA, x = 10.2 cm   | 38                                       | 28     | 33      | 5  | 0      | 10     | 0                     | -2                | 19      |
| <b>Remarks</b>  | concentrations in g/L as O <sub>2</sub>  |        |         | values in µS/cm                              |        |        | concentrations in g/L |                   |         |
|   |  |        |         |  |        |        | Sensitivity issue     | Sensitivity issue |         |
|   | BOD <sub>5</sub>                         |        |         | Ammonia                                      |        |        | Lead                  |                   |         |
|   | Low                                      | Medium | High    | Low  | Medium | High   | Low                   | Medium            | High    |
| <b>Starting concentration or value</b>  | > 417                                    | -      | > 1,650 | 52.5   | 470    | -      | 0.07                  | 0.3               | 0.3     |
| IMA, x = 10.2 cm  | > 37                                     | -      | -       | -13  | 10     | -      | -                     | 95                | > 99.97 |
| <b>Process</b> UV, x = 10.2 cm  | > 65                                     | -      | -       | -25  | 12     | -      | -                     | 3                 | 79      |
| PIMA, x = 10.2 cm   | > 48                                     | -      | > 860 * | -15  | 7      | -      | 77                    | 98                | > 99.95 |
| <b>Remarks</b>  | concentrations in mg/L as O <sub>2</sub> |        |         | concentrations in mg/L as NH <sub>3</sub> -N |        |        | concentration in mg/L |                   |         |
| * This is not a percentage but the measured concentration: the actual percentage can not be estimated due to the double inequality. |  |        |         |  |        |        |                       |                   |         |
| - No results obtained (experiment not completed)  |  |        |         |  |        |        |                       |                   |         |

The results obtained for COD removal during the mixture scoping tests follow the same trends as those obtained during the individual tests. Of the three processes, the one using only UV gave the lowest COD degradation performance. The IMA process is shown to be enhanced by UV radiation. Although the impact is negligible at short reaction times (i.e. less than 2 hours of treatment), it increases with time and demonstrates the benefits of using both iron and UV light together in the PIMA process. Figure 44 shows this phenomenon. However, the percentage of removal achieved during these three experiments did not reach the values obtained during the individual COD scoping tests. This is especially true for the low and medium levels. Figure 45 illustrates this comparison. The presence of the other components is the most viable explanation for this lower than expected removal. Also, even the PIMA process cannot decrease the COD concentration to a level permissible for discharge to the sewer network in the City of Boca Raton, under the conditions of the bench scale laboratory reactor.

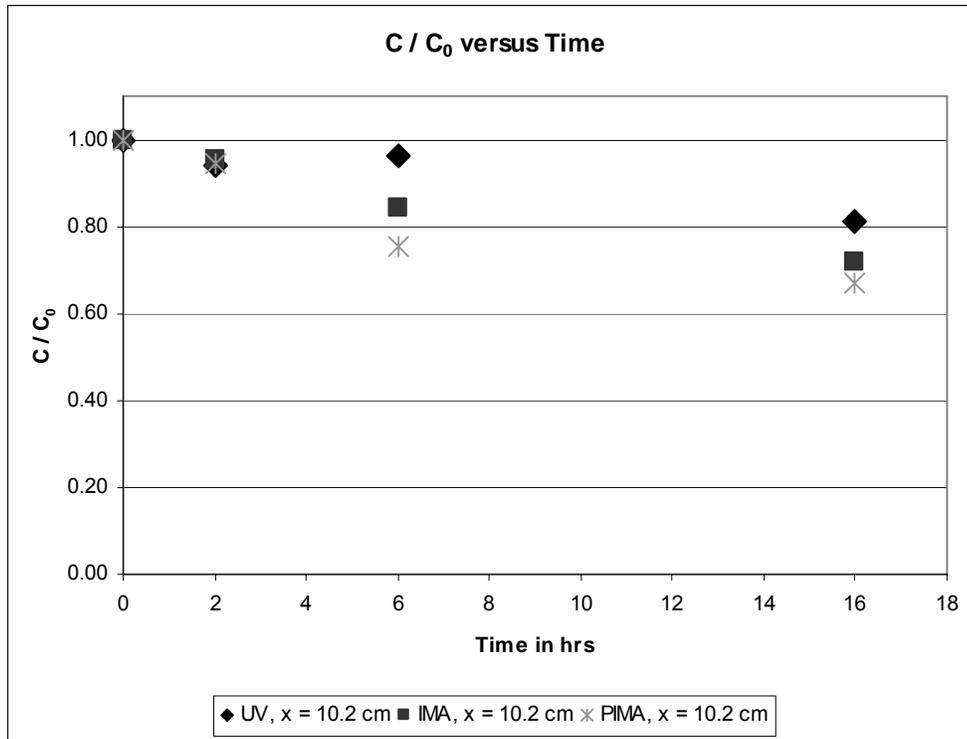


Figure 44. Summary of mixture simulated COD experimental results

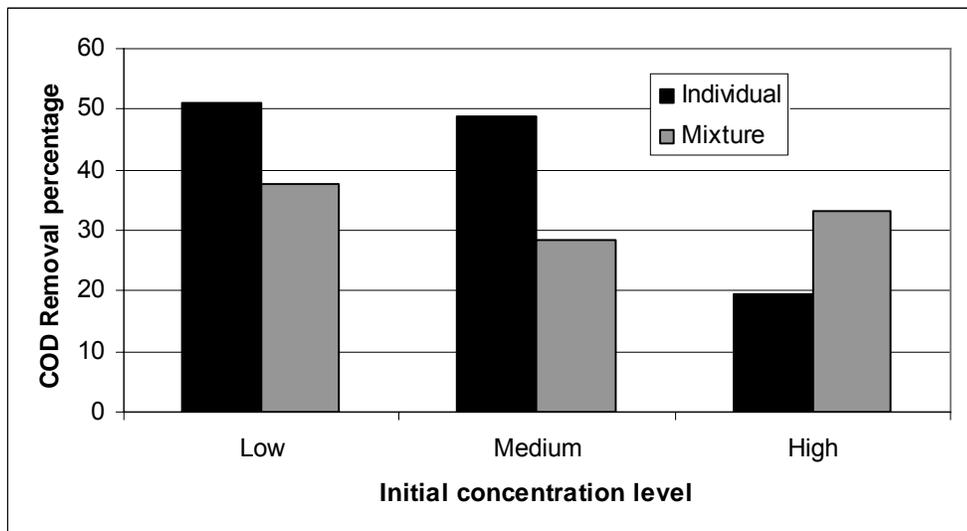


Figure 45. COD removal comparison of the PIMA process

The results obtained on conductivity and TDS during the mixture scoping tests confirm those obtained during the individual tests. None of the processes has a measurable impact on the NaCl salt concentration. Figure 46 and Figure 47 illustrate this statement. As observed previously, values have the tendency to decrease in the first hours of treatment and then increase as the treatment continues. Consequently, a

safe sewer discharge TDS concentration is never reached by either the IMA, UV or PIMA processes.

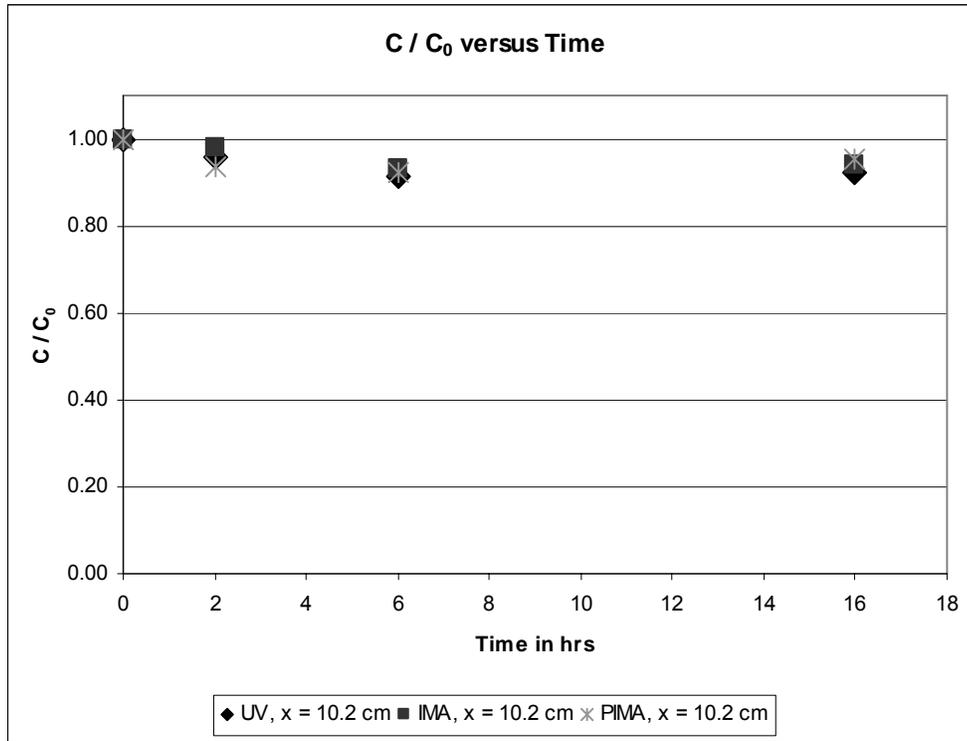


Figure 46. Summary of mixture simulated conductivity experimental results

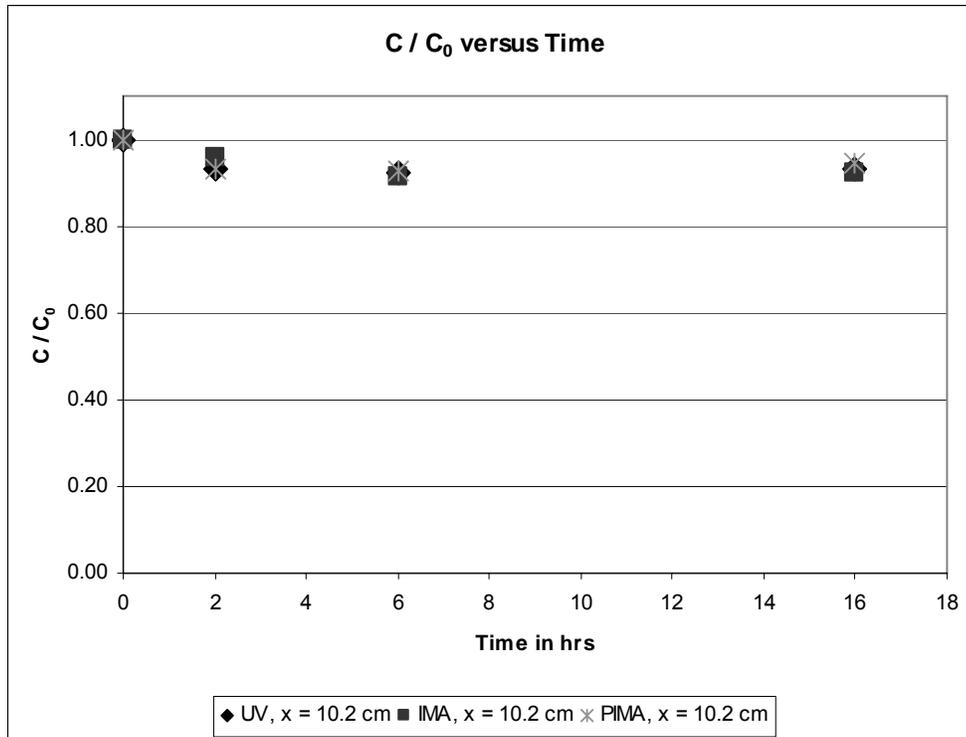
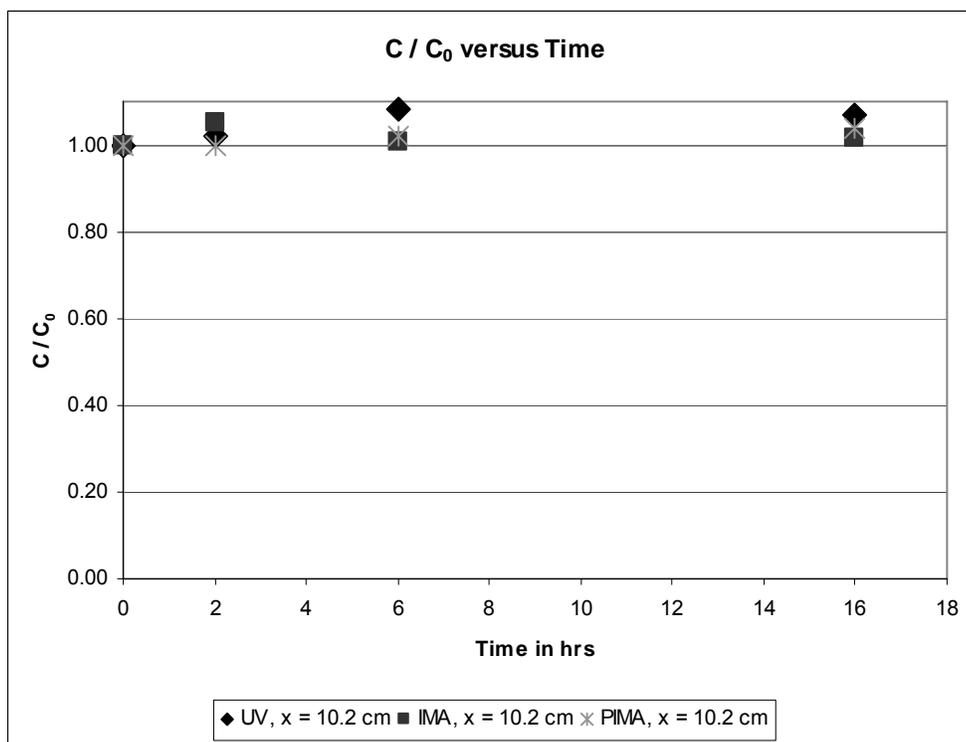


Figure 47. Summary of mixture simulated TDS experimental results

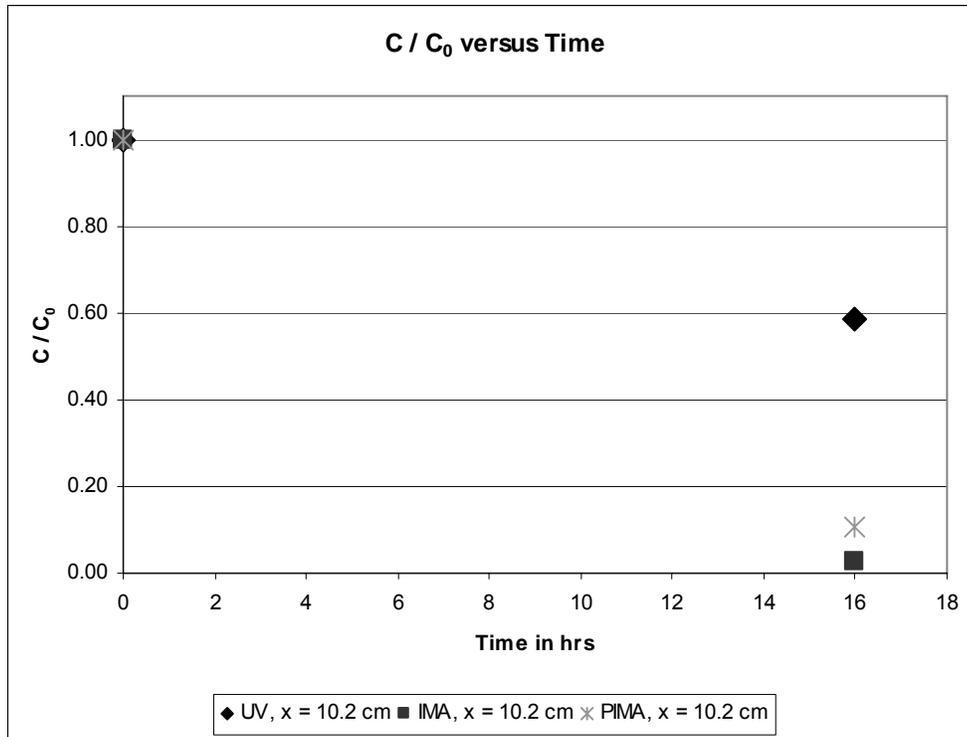
The results obtained on BOD<sub>5</sub> during the mixture scoping tests also confirm those obtained during the individual tests. The UV control process presents the best biochemical degradation capacities of the three processes. This justifies why the PIMA process achieves a better purification than the IMA process. The discrepancy between the concentrations noticed during the individual tests and mixture tests seems to demonstrate that some of the recalcitrant COD is converted into BOD<sub>5</sub> confirming the expectations of an energized process.

The results obtained on ammonia during the mixture scoping tests also followed the same pattern as the results encountered during the individual ammonia tests. None of the three processes tested had an impact on the ammonia concentration. Figure 48 illustrates this statement. As there is no ammonia limit listed for safe sewer discharge in the City of Boca Raton Code, no conclusion can be drawn concerning the ability to discharge the effluent. However, the ammonia stripping is limited at laboratory scale due to pH issues and reactor configuration. The pH in the laboratory scale reactor was too low to induce the transfer of NH<sub>4</sub><sup>+</sup> to NH<sub>3(g)</sub>. Appropriate pH adjustment (pH > 10) would allow ammonia stripping but at the same time, it would also increase the cost of treatment and complicate the discharge of the effluent, since pH should be between 6.0 and 8.5 for permissible discharge. Thus a re-carbonation step may be required to bring the pH back down prior to discharge. In addition, pH adjustment may have consequences on process removal efficiencies for other constituents, since Fenton-like processes are known to be more efficient at lower pH.



**Figure 48. Summary of mixture simulated ammonia experimental results**

Without surprise, results obtained on lead during the mixture scoping tests confirm those obtained during the individual tests. Figure 49 summarizes the process performance results on lead. The UV control process presents the lowest removal capacities. The IMA process can achieve a removal almost as powerful as the PIMA process. As every initial concentration tested is below the safe discharge limit, the effluent could eventually be discharged to the sewer network.



**Figure 49. Summary of mixture simulated lead experimental results**

To conclude on the mixture scoping test, it can be said that observed removal capacities conform to the expectations from the individual scoping tests. However, overall treatment performance is not high enough to achieve the goal of safe discharge of the effluent to a public sewer system network. And the results show that PIMA performs just as well as other known AOPs and EPs. But those techniques have been well studied and developed. This is why the PIMA process has to be tested on real leachate samples. The results of this last phase of testing are presented in the next section.

### **3.3 PIMA MIXTURE SCOPING TESTS: REAL LEACHATE**

Five experiments were conducted using real leachate samples from the Class I landfill of the Solid Waste Authority of Palm Beach County. Table 62 gives the details of these experiments, and the raw data tables are located in Appendix B.

**Table 62. List of real leachate experimental conditions using PIMA**

| Experiment Number | Collection date | Rainfall in inches in the previous |        |       | Experiment date | Shield used? |
|-------------------|-----------------|------------------------------------|--------|-------|-----------------|--------------|
|                   |                 | 24 hours                           | 3 days | 7days |                 |              |
| 19                | 30-Apr-07       | 0.00                               | 0.00   | 0.00  | 2-May-07        | Yes          |
| 20                | 8-May-07        | 0.00                               | 0.68   | 0.68  | 9-May-07        | Yes          |
| 21                | 18-May-07       | 1.03                               | 1.03   | 1.14  | 21-May-07       | Yes          |
| 22                | 24-May-07       | 0.00                               | 0.03   | 0.03  | 28-May-07       | Yes          |
| 23                | 6-Jun-07        | 0.09                               | 1.05   | 4.78  | 7-Jun-07        | Yes          |

The monitoring profile of the first two experiments (experiments No. 19 and 20) conducted on real leachate samples differs from the previous experimental setup. Only four test tubes were used for the PIMA process and two were used respectively for the IMA and UV control processes. Thus, during these two experiments:

- Ammonia was monitored after two, four, six, ten, and sixteen hours. Samples were sent to the same laboratory as the one used for the lead measurements.
- TDS and conductivity were monitored after two, four, six, ten, and sixteen hours and monitored as before in the simulated leachate tests.
- COD was monitored after two, four, six, ten, and sixteen hours and monitored as before in the simulated leachate tests.
- BOD<sub>5</sub> was measured after sixteen hours of treatment for the PIMA and IMA processes.
- Lead was also monitored after sixteen hours for the PIMA and UV processes.

Experiments performed afterwards (experiments No. 21, 22, and 23) were monitored with the same monitoring program as the simulated leachate. During these three experiments, the impact of iron dosage on PIMA performance was studied by using different amounts of steel wool (2.0, 1.0, and 0.5 grams).

The pH was recorded for each of the experiments. The initial pH was 7.0 for the five experiments. Over the course of the sixteen hours of treatment, pH increased to a range of 7.5 to 8.5. Those values are in the acceptable range for direct discharge to the City of Boca Raton sewer network.

Temperature was monitored with the temperature monitoring test tube. Equilibrium temperature was between 35°C and 40°C for the five experiments. The temperature profile is similar to the profile registered during experiment No. 15 presented in Figure 43 earlier. Figure 50 shows the actual temperature profile of the last experiment, experiment No. 23.

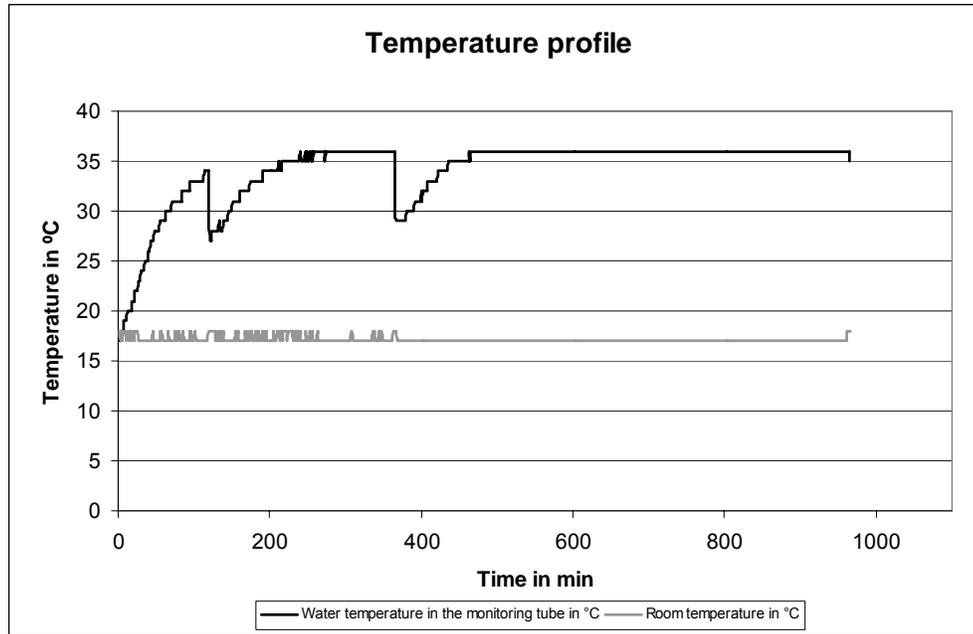


Figure 50. Temperature profile of experiment No. 23

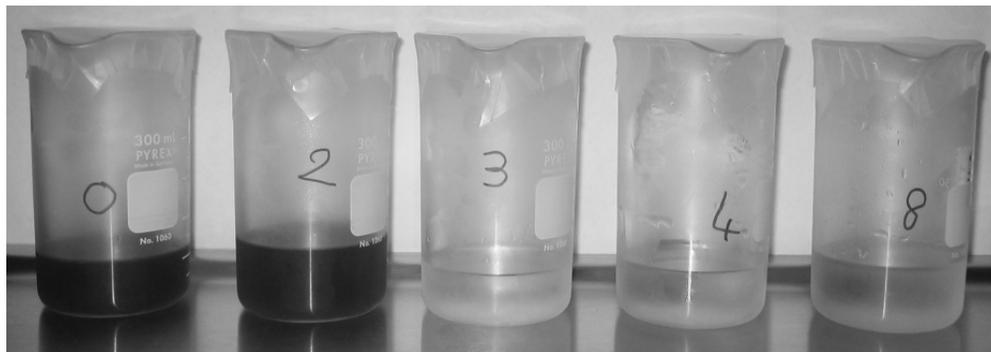
A bacterial analysis was conducted by MICRIM LABS Inc. (Fort Lauderdale, FL) during the fourth experiment (experiment No. 22). Bacteria (*Bacillus* sp., *Pseudomonas stutzeri*, *Pseudomonas fluorescens*, *Pseudomonas alcaligenes*, *Micrococcus luteus*, and coagulase-negative *Staphylococcus*) and fungus (*Aspergillus niger*) were present in the raw leachate. After 16 hours of PIMA treatment, no sign of viable bacterial or fungal activity was found in the effluent. This demonstrates the disinfection power of the PIMA process. This finding was expected as UV alone is a well-known disinfectant (Metcalf and Eddy 2003). It would also have been interesting to evaluate the disinfection action of the IMA process. However, this was not performed during this project.

Color and odor were also a concern during the real leachate testing phase. Regarding odor, no beneficial effect of treatment was noticed during the experiment, although there was no attempt to quantify the odors present. A pungent odor was detected at all sampling times for all experiments with real leachate. Regarding color, however, PIMA and IMA were very efficient in improving the sample clarity. Raw leachate was characterized by a very dark brown color, even after filtration. No actual color measurements were recorded, but Figure 51 is evidence of the color removal capacity of the PIMA process. The UV control process by itself is inefficient for color removal, but the PIMA process can achieve, after filtration, an effluent of very high quality in terms of color. The Color Test Kit from Hach (Loveland, CO), was used to approximate the color of the samples, based on the pictures taken (the kit was not available at the time of the experiment). Raw leachate and UV treated leachate are out of the range of the equipment and would have required dilution. Color of the PIMA treated leachate samples is estimated, in APHA Platinum Cobalt units, as follows:

- Sample No.3: Color = 0-10 PCU
- Sample No.4: Color = 50-60 PCU
- Sample No.8: Color = 20-30 PCU

The modified cap (designed to facilitate ammonia removal) was used during the five experiments with real leachate. No improvement in any of the constituents was noticeable; especially concerning ammonia, for which pH is definitely the main responsible factor. No pH adjustments were made.

Aeration was very difficult to control during these experiments. Samples were generating foam that was bubbling out of the test tube through the hole in the cap or modified cap. This amplified the difficulties, already mentioned, due to the laboratory scale reactor design.



**Figure 51. Comparative of the color removal between raw leachate and treated leachate**  
 Note: Sample 0 is raw leachate, sample 2 is UV treated leachate, and samples 3, 4, and 8 are PIMA treated leachate. The picture has been converted to grayscale.

Table 63 shows the water quality data of the leachate samples collected. Compared with the data collected across the State of Florida, it appears that the operating Class I landfill of the Solid Waste Authority of Palm Beach County (Palm Beach, FL) is generating leachate of relatively high strength. The COD, conductivity, TDS, BOD<sub>5</sub>, ammonia are all above the average concentrations listed in Table 4. The only exception is lead which is present at very low levels. Table 64 contains the complete leachate composition of the real leachate samples collected in the investigation of PIMA.

**Table 63. Quality data of leachate from the operating Class I landfill of the Solid Waste Authority of Palm Beach County collected from the 30<sup>th</sup> of April 2007 to the 6<sup>th</sup> of June 2007**

| Parameters                                   | Concentrations  |         |
|--|-----------------|---------|
|  | Range           | Average |
| COD, in mg/L as O <sub>2</sub>               | 2,950 - 5,850   | 4,200   |
| Conductivity in µS/cm                        | 41,250 - 51,250 | 43,950  |
| TDS in mg/L                                  | 20,000 - 31,250 | 23,650  |
| BOD <sub>5</sub> , in mg/L as O <sub>2</sub> | 95 - 670        | 425     |
| Ammonia, in mg/L as NH <sub>3</sub> -N       | 800 - 1,200     | 1,000   |
| Lead, in mg/L                                | 0.0021 - 0.0054 | 0.0032  |
| pH   | 7.0 - 7.0       | 7.0     |

**Table 64. Water quality data of leachate samples collected**

| Parameters                                   | Experiment No. |         |          |         |         |
|--|----------------|---------|----------|---------|---------|
|  | 19             | 20      | 21       | 22      | 23      |
| COD, in mg/L as O <sub>2</sub>               | 5,865          | 3,765   | 3,360    | 5,170   | 2,950   |
| Conductivity in µS/cm                        | 51,250         | 41,583  | 31,250 * | 41,250  | 41,333  |
| TDS in mg/L                                  | 26,250         | 20,833  | 20,000   | 31,250  | 20,000  |
| BOD <sub>5</sub> , in mg/L as O <sub>2</sub> | 511            | 666     | -        | -       | 96      |
| Ammonia, in mg/L as NH <sub>3</sub> -N       | 1,000          | 1,040   | 805      | 1,213   | 932     |
| Lead, in mg/L                                | 0.00540        | 0.00250 | -        | 0.00290 | 0.00210 |
| pH   | 7.0            | 7.0     | 7.0      | 7.0     | 7.0     |

- Measure not completed during this experiment.  
 \* Conductivity estimated by their empirical relationship (Snoeyink and Jenkins, 1980)

Variations in rainfall registered during the study seem to have an impact on the leachate quality. For example, initial COD was higher for experiments No. 19 and 22 than for experiments No. 20, 21, and 23 where sampling occurred a few days after a heavy rain event (see Figure 20).

The following paragraphs discuss the performance of the PIMA process and compare them with the IMA and UV control processes. Complete performance data are summarized by constituent in the sections below.

### 3.3.1 Chemical Oxygen Demand (COD)

The average initial COD concentration was 4,220 mg/L as O<sub>2</sub> with a standard deviation of 1,250 mg/L as O<sub>2</sub>. Figure 52 presents a summary of the experiments performed on COD with real leachates and shows the average removal at each monitoring step. The first three experiments were conducted using the Reactor Digestion Method (DR4000 Procedure), High Range Plus. The last two were monitored with the Reactor Digestion Method (DR4000 Procedure), High Range. Both methods are described in the methodology section.

The PIMA process did not demonstrate its promising results observed during the simulated leachate experiments. In fact, no removal was achieved: the COD concentration remained stable around its initial value. This phenomenon does not concern only the PIMA process, but all three processes and might be due to the loss of liquid content during treatment caused by foaming, which may have artificially concentrated the pollutants. Also as shown in Figure 52, varying the dose of iron did not affect the performance of the PIMA process.

The accuracy of the values is not in doubt. Due to the dilution necessary to perform the measurements and the presence of multiple ions in solution, the dose of chloride cannot be held responsible for this absence of removal. In order to find another explanation, alkalinity was monitored during experiment No. 23, and was recorded at a level higher than 240 mg/L as CaCO<sub>3</sub>. At a pH close to 8, bicarbonates (HCO<sub>3</sub><sup>-</sup>) and carbonates (CO<sub>3</sub><sup>2-</sup>) are favored. The issue is that both HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup> are known hydroxyl radical scavengers. Acidic pH would have favored the generation of the hydroxyl radical but inhibited ammonia removal. In the simulated leachates, the alkalinity was very low, but such high levels of alkalinity in the real leachates may be one reason for these unexpectedly low removal results. Steensen (1997) states that alkalinity should be completely removed in order to achieve effective oxidation.

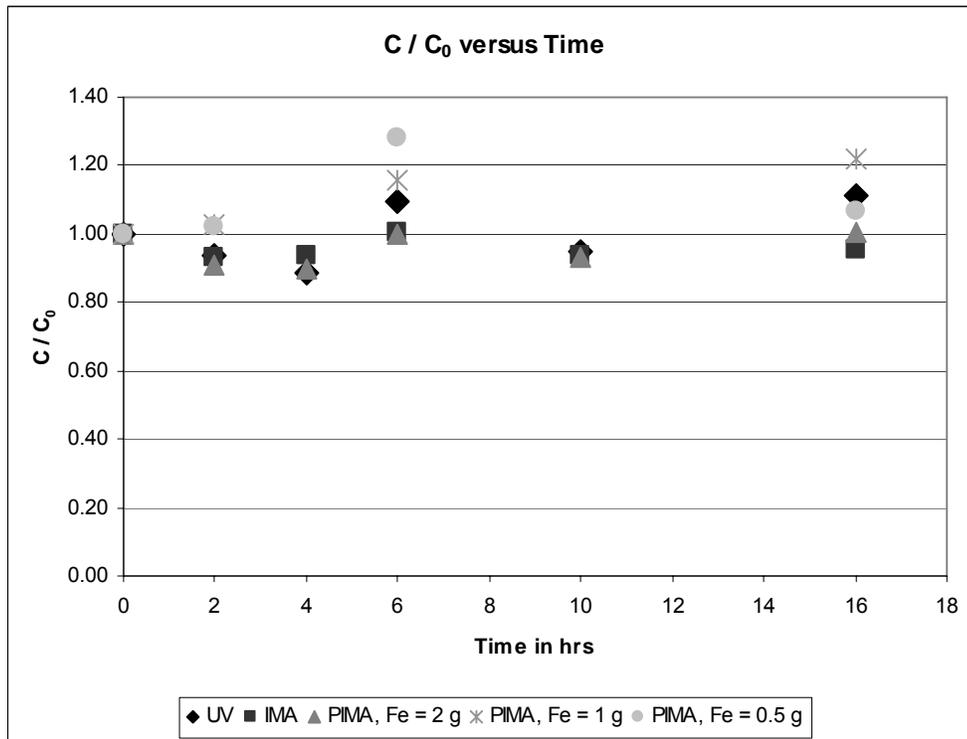
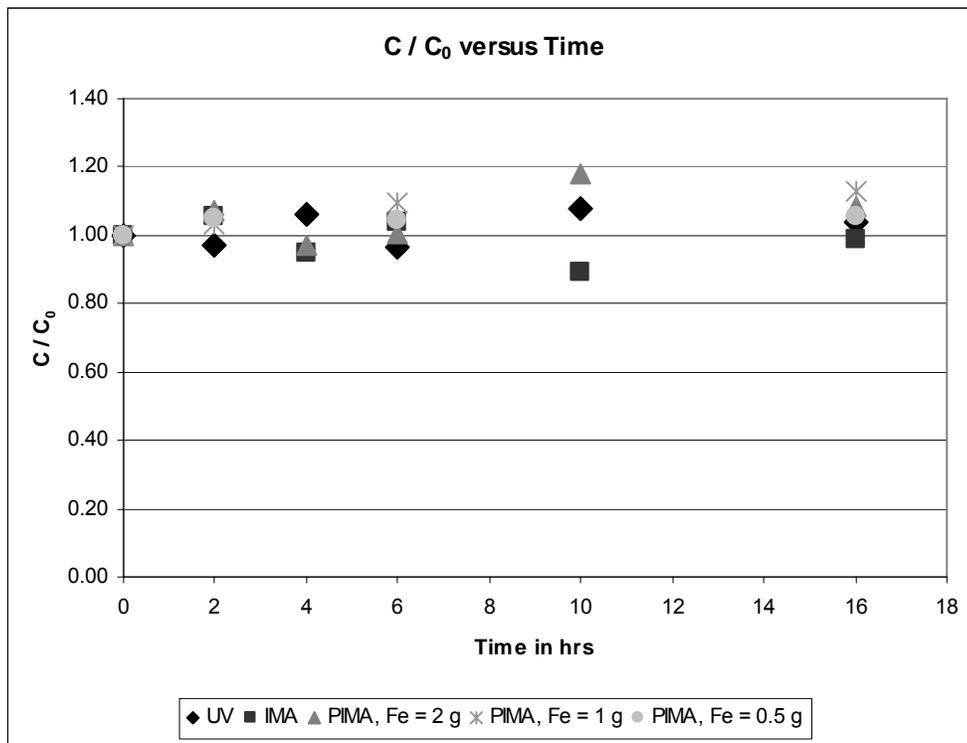


Figure 52. Summary of real leachate experiments concerning COD

### 3.3.2 Conductivity and Total Dissolved Solids (TDS)

The average initial conductivity value was 43,850  $\mu\text{S}/\text{cm}$  with a standard deviation of 4,900  $\mu\text{S}/\text{cm}$ . Figure 53 presents the summary of the experiments performed on conductivity. Regarding TDS, the average initial value was 23,665 mg/L with a standard deviation of 5,000 mg/L. Figure 54 presents the summary of the experiments performed on TDS. Both figures show the average removal at each monitoring step. The performance of the three processes (UV control, IMA control, and PIMA) confirms the conclusion drawn during the simulated leachate phase. No actual removal is achieved. Conductivity and TDS remain unchanged over the course of the sixteen hours of reaction.



**Figure 53. Summary of real leachate experiments of conductivity**

Note: Conductivity was not monitored during experiment No. 21 because the Pocket Pal Tester was not available.

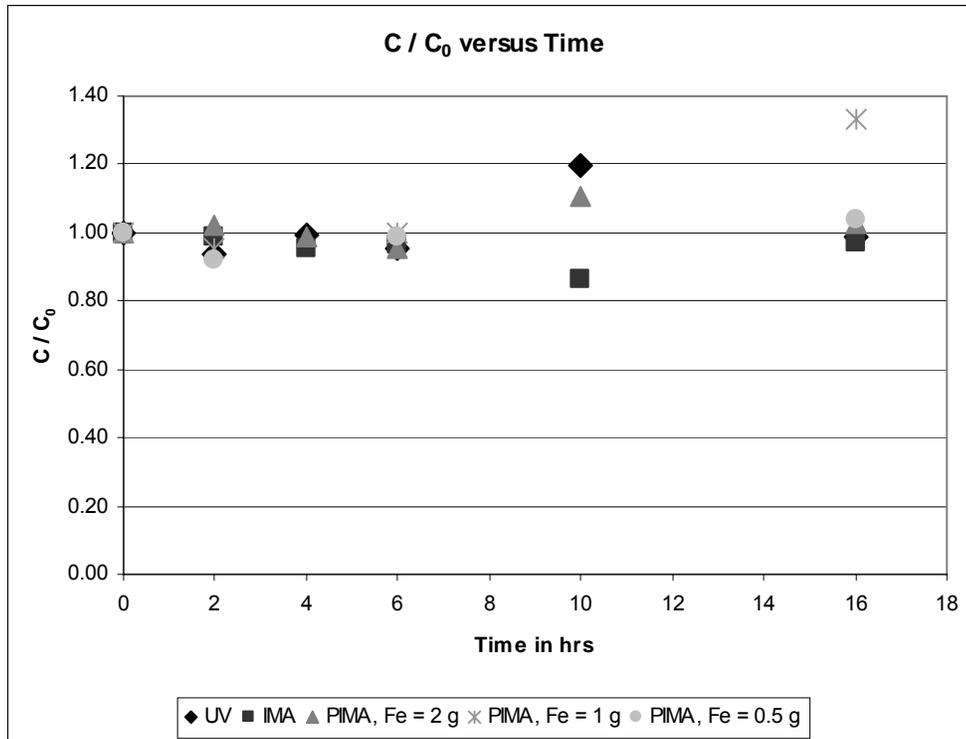
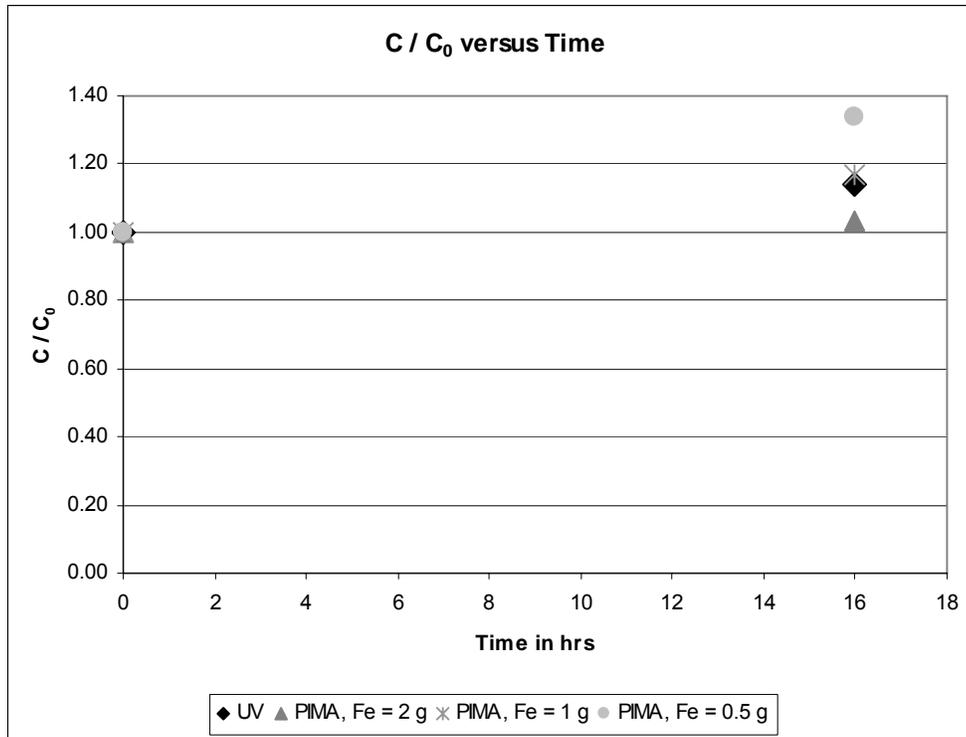


Figure 54. Summary of real leachate experiments of TDS

### 3.3.3 Biochemical Oxygen Demand (BOD<sub>5</sub>)

The average initial BOD<sub>5</sub> concentration was 425 mg/L as O<sub>2</sub> with a standard deviation of 295 mg/L as O<sub>2</sub>. Figure 55 presents the summary of the experiments performed on BOD<sub>5</sub>. The simulated leachate BOD<sub>5</sub> experiments demonstrated that the UV control and the PIMA processes were the most capable for biological content removal. This is why the IMA process was not controlled for BOD<sub>5</sub> in real leachate tests. Just as seen with the COD results, the UV control and the PIMA processes appear to be incapable of appreciably lowering the BOD<sub>5</sub> content of the real leachate. If UV could achieve great removal during the first phase of testing with simulated leachates, performance considerably decreased during this phase with real leachates. This conclusion is also true for the PIMA process. The BOD<sub>5</sub> behavior mimicked the COD with the same tendency to concentrate rather than mineralize due to foaming and radical scavenging due to high alkalinity. Furthermore, due to the absence of observed removal for both COD and BOD<sub>5</sub>, it is not possible to interpret the effect of the COD/BOD ratio, with respect to gaining a better understanding of the reaction mechanism involved in the PIMA process for real leachate.



**Figure 55. Summary of real leachate experiments of BOD<sub>5</sub>**

Note: BOD<sub>5</sub> was not monitored during experiment No. 21 because the thevacuum filtration unit was not available. BOD<sub>5</sub> was not monitored during experiment No. 22 because results were unusable due to the use of very high strength seed.

### 3.3.4 Ammonia

The average initial ammonia value was 1,000 mg/L as NH<sub>3</sub>-N with a standard deviation of 150 mg/L as NH<sub>3</sub>-N. Figure 56 presents the summary of the experiments performed on ammonia and shows the average removal at each monitoring step. The performance of the three processes (UV control, IMA control, and PIMA) confirms the conclusion drawn during the simulated leachate phase. No actual removal is achieved without pH adjustment. In simulated leachate tests of individual constituents and mixtures, pH has been demonstrated to be the main reason for the lack of observed ammonia stripping. But if high pH would have promoted the stripping of ammonia, it may also have inhibited the generation rate of hydroxyl radical by enhancing bicarbonate scavenging (Steensen 1997).

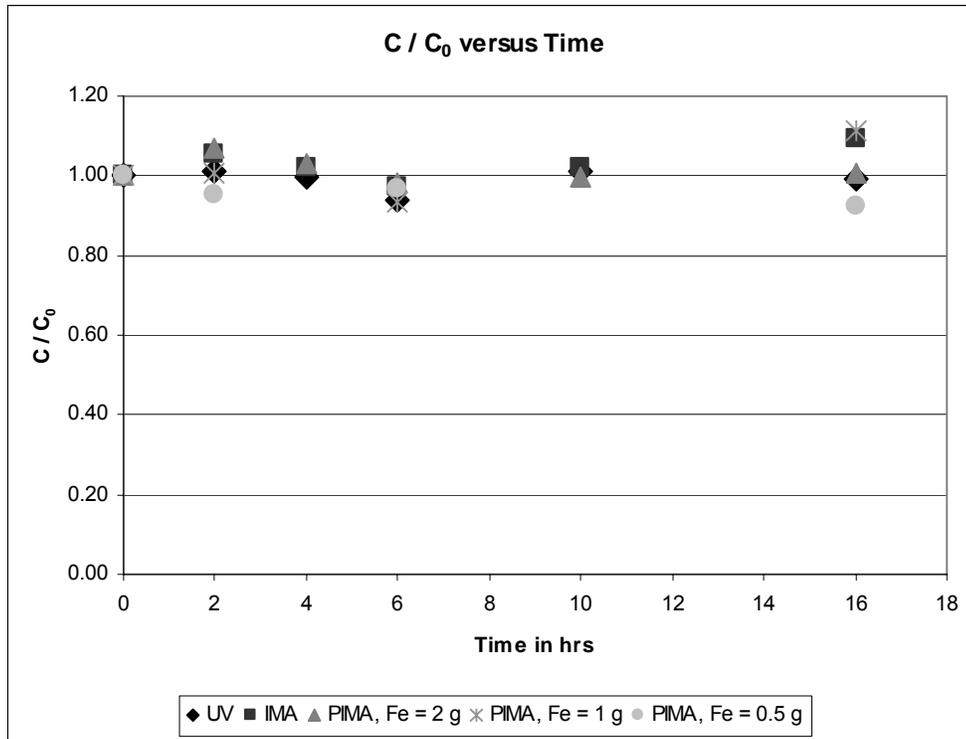


Figure 56. Summary of real leachate experiments of ammonia

### 3.3.5 Lead

The average initial lead concentration was 0.003225 mg/L with a standard deviation of 0.001486 mg/L. Figure 57 presents the summary of the experiments performed on lead. The average initial concentration of lead in the influent is very low. No simulated leachate experiment was performed at such a low initial level. However, lead is the component on which the PIMA demonstrated its most significant removal efficiency. Its performance is well improved compared to the UV control process as occurred during every test of the first phase with simulated leachates. The removal achieved by the PIMA process with a dose of iron equal to 1.0 g is also greater than the PIMA process with a dose of iron equal to 2.0 or 0.5 g. The overall removal achieved during these real leachate tests is lower than expected during the simulated tests. This is attributable to the very low initial concentration. The effect of starting concentration was already noticed during the mixture scoping tests. Alternatively, interactions between lead and organic compounds could also be occurring (organic chelation and photo-inhibition or inorganic competition for oxidant).

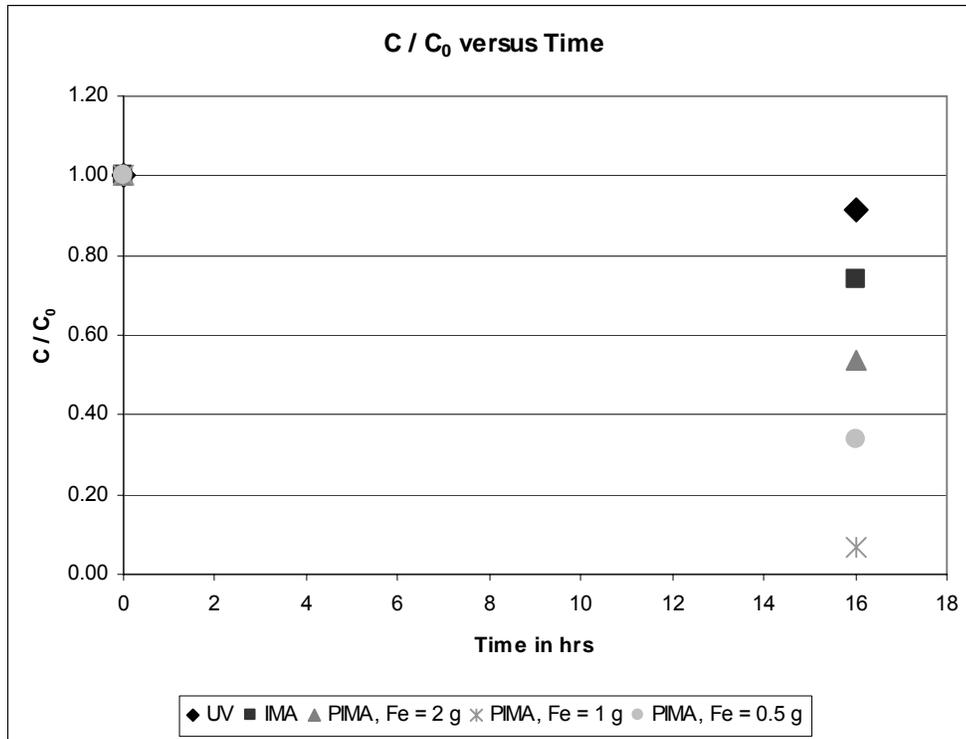


Figure 57. Summary of real leachate experiments of lead

### 3.3.6 Findings of PIMA Real Leachate Tests

The PIMA process showed promising performance results on simulated leachates. Removal capacities were along the same order compared to the already well-developed advanced oxidation processes and energized processes investigated in the literature review. However, the same level of treatment was not achieved during the real leachate experiment phase. COD and BOD<sub>5</sub> were the most promising parameters after simulated leachate tests, but the PIMA process did not reduce organic constituent concentrations in the real leachate samples. The impact of the initial dose of iron is difficult to evaluate as removals were limited. However, lead results seem to indicate that a ratio of 1.0 gram of iron per 80 mL of sample gives the best removal results. Up to this point, all simulated leachate tests used 2.0 g of iron. This effect deserves further investigation to determine the optimum dosage of iron wool. Of the 6 components monitored during this second phase, removal was measured only on lead. Color was also greatly improved by the PIMA process. However, neither the UV nor the IMA control processes showed any signs of lowering pollutant concentrations. Several reasons can explain this phenomenon:

- The design of the reactor needs to be improved to allow fine control of aeration. In its current design, mixing and aeration cannot be considered homogeneous or reproducible. Liquid content evaporates or bubbles out of the test tube reactors, and excessive foaming were both experimental issues. At full scale, leachate foaming and other losses would not be expected to

occur at inhibitory levels due to the scale of the reactors needed.

- If UV enhances the dissolution of iron to ferric precipitates, the steel wool prevents the radiation from uniformly striking the leachate sample by generating large areas of shadow. Figure 34 is the illustration of this statement.
- The pH is not adjusted and remains at a neutral condition. This does not encourage the generation of hydroxyl radicals (which is favored at acidic pH). At more circumneutral pH values, alkalinity then favors the bicarbonate form and reduces the oxidation power of the PIMA process by acting as a radical scavenger. Furthermore, this neutral pH does not promote the stripping of ammonia which, conversely, requires an alkaline pH.
- The nature of the compounds used to simulate the leachate may also be an issue. For example, glucose may have been more easily degradable than the components found in real leachate.

Overall, the pollutant concentrations in the real leachate influent were such that, the leachate would not have been allowed to be directly discharged to the sewer network in the City of Boca Raton. After treatment, since no major reductions in pollutant concentrations were observed, the treated effluent would not have been accepted either. With the limitations of the laboratory scale reactor, the Photochemical Iron Mediated Aeration process is not yet capable of achieving the required level of treatment to allow a safe discharge to the sewer network and not impair the wastewater treatment plant's daily operations. Additional development is necessary to limit the impact of the constraints encountered during this project.

### **3.4 PHOTOCATALYTIC OXIDATION: SIMULATED LEACHATE**

The second technology that was evaluated in this study was photocatalytic oxidation with  $\text{TiO}_2$  particles activated by UV light. The following sections detail the laboratory scale results for testing of synthetic and real leachates with photocatalytic oxidation processes in different configurations.

#### **3.4.1 Scoping Tests with $\text{TiO}_2$ -Magnetite Particles**

##### **3.4.1.1 Ammonia**

On June 21, 2007, the first scoping test was conducted using the  $\text{TiO}_2$ -magnetite particles provided by the Northeastern University of China to treat a simulated leachate contaminated with ammonia prepared by adding 0.503 g of  $\text{NH}_4\text{Cl}$  in reagent water. The dose of photocatalytic particles was 0.512 g in 250 mL of sample. Figure 58 shows a photograph of the experimental set-up. Note that the reactor is different than the PIMA test tube reactors. The photocatalytic particles were used "as-is" without prior conditioning or washing.

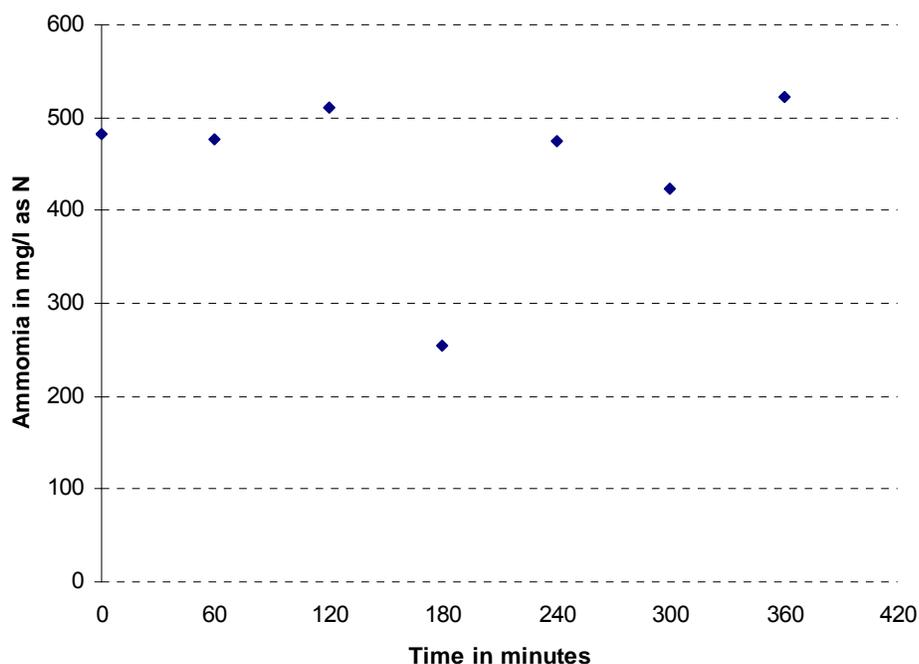


**Figure 58. Simulated leachate contaminated with ammonia being treated with  $\text{TiO}_2$ -magnetite particles**

The initial ammonia concentration was expected to be 526 mg/L as N, and the measured value was 482.5 mg/L as N (relative error = 8.26 percent). Table 65 summarizes the results for the first experiment. As shown in Figure 59, removal only occurred at 180 minutes; however, it is believed that this value is an outlier and may have been the result of an inaccurate dilution rather than real removal. Temporarily ignoring this outlier, the other times during this reaction, essentially no treatment was observed. The temperature in the reaction tube was below  $37^\circ\text{C}$  throughout the duration of the test, although some measurable amount of water was lost due to evaporation. The solution was mixed properly by the addition of air and the magnetic stirrer to ensure complete mix conditions.

**Table 65. Summary of results for photocatalytic oxidation scoping tests on simulated leachates containing ammonia (Experiment A)**

| Time (min) | pH  | Instrument Reading | Dilution Factor | Ammonia (mg/L as N) |
|------------|-----|--------------------|-----------------|---------------------|
| 0          | 6.0 | 3.86               | 125             | 482.5               |
| 60         | 5.5 | 3.81               | 125             | 476.2               |
| 120        | 5.0 | 4.08               | 125             | 510.0               |
| 180        | 4.5 | 2.03               | 125             | 253.8               |
| 240        | 4.5 | 3.79               | 125             | 473.8               |
| 300        | 4.5 | 3.38               | 125             | 422.5               |
| 360        | 4.5 | 4.18               | 125             | 522.5               |



**Figure 59. Ammonia results for the first photocatalytic oxidation experiment.**

### 3.4.1.2 Chemical Oxygen Demand (COD)

On June 26, 2007, the second scoping experiment was conducted using the TiO<sub>2</sub>-magnetite particles provided by the Northeastern University of China to treat a simulated leachate contaminated with KHP prepared by adding 1.0 g of KHP in reagent water. The dose of photocatalytic particles was 0.416 g in 250 mL of sample. Again, these particles were used “as-is” without prior conditioning or washing. Figure 60 shows a photograph of the experimental set-up.

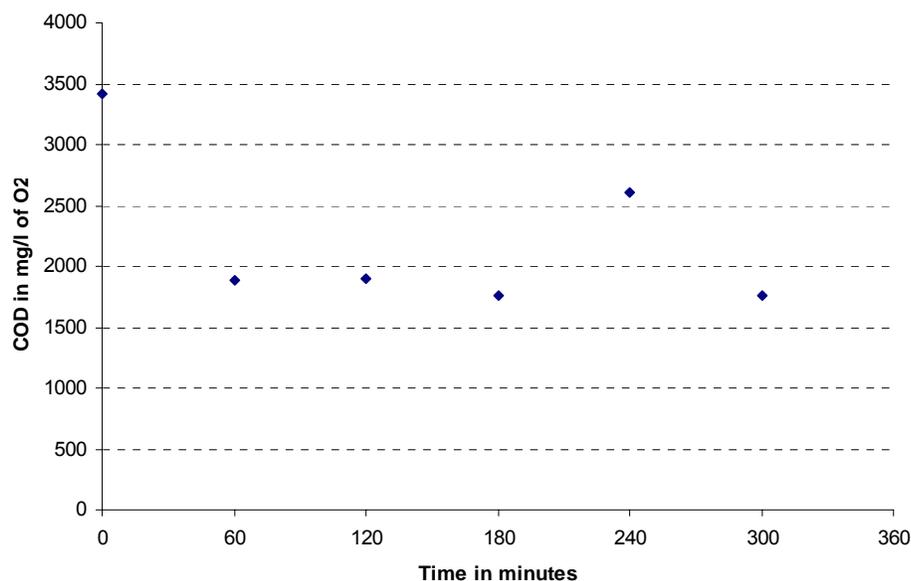


**Figure 60. Simulated leachate contaminated with KHP being treated with  $\text{TiO}_2$ -magnetite particles**

The final results are presented in Table 66 and Figure 61. The initial COD concentration expected was 4700 mg/L, and the measured value was 3416 mg/L (relative error = 27.3 percent). Nearly 45 percent of the original COD was removed in the first 60 minutes of the reaction time, and for the most part, the removal efficiency did not seem to change much as the reaction time was extended beyond one hour. At 240 minutes, an outlier was encountered that was most likely a dilution error. It was noticed that as the reaction proceeded, the color of the solution darkened with time. Furthermore, an attempt was made to recover the particles by evaporating the remaining sample in a porcelain drying dish in the drying oven at 70-105°C. The particles remaining after drying were very dark in color, even after washing them with reagent water several times and repeating the drying procedure. For these tests, a quality control check was performed using standard KHP calibration check reagent certified at 150 mg/L and 300mg/L. The readings of those checks are listed in Table 66. The maximum removal was on the order of 49 percent and occurred after 3 hours.

**Table 66. Summary of results for photocatalytic oxidation scoping tests on simulated leachates containing COD (Experiment B)**

| Time (min) | pH  | Instrument Reading | Dilution Factor | COD (mg/L as O <sub>2</sub> )  |
|------------|-----|--------------------|-----------------|--------------------------------|
| 0          | 4.5 | 854                | 4               | 3416                           |
| 60         | 4.5 | 472                | 4               | 1888                           |
| 120        | 4.5 | 476                | 4               | 1904                           |
| 180        | 4.5 | 439                | 4               | 1756                           |
| 240        | 4.5 | 653                | 4               | 2612                           |
| 300        | 4.5 | 440                | 4               | 1760                           |
| QA/QC      | n/a | 155                | 1               | 155 (rel. error = 3.3 percent) |
| QA/QC      | n/a | 305                | 1               | 305 (rel. error = 1.7 percent) |



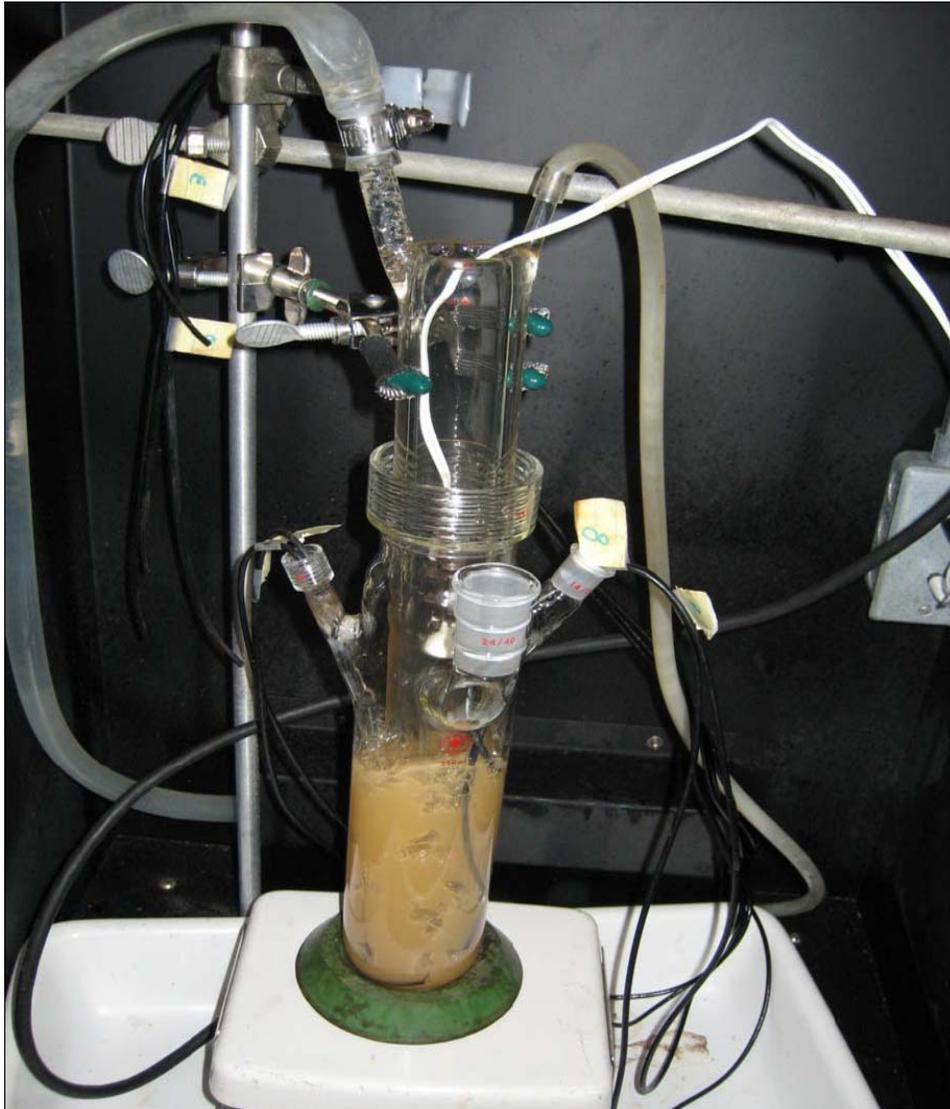
**Figure 61. COD results for the second photocatalytic oxidation experiment**

### 3.4.2 Scoping Tests with Recovered TiO<sub>2</sub>-Magnetite Particles

In the previous set of experiments, new TiO<sub>2</sub>-magnetite particles that had never been used before were added to the sample. The results of those experiments revealed that the new particles did not perform as well as expected. The next step was to see if the TiO<sub>2</sub>-magnetite particles could be recovered and reused.

#### 3.4.1.1 Ammonia

On July 6, 2007, an experiment was conducted to investigate the effect of reusing the TiO<sub>2</sub>-magnetite particles from the first two experiments to treat a simulated leachate contaminated with ammonium chloride prepared by adding 0.594 g of NH<sub>4</sub>Cl in reagent water. The dose of photocatalytic particles was 0.543 g in 250 mL of sample.

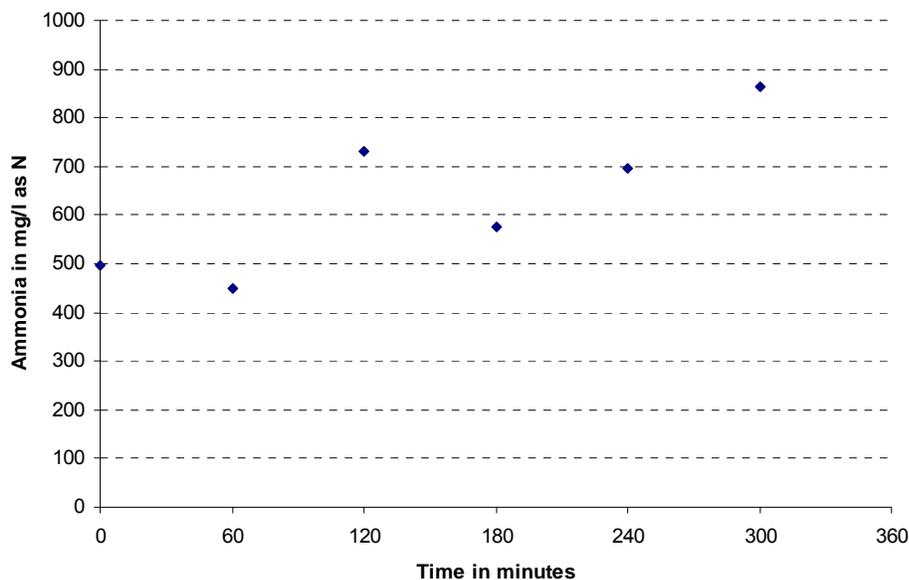


**Figure 62. Simulated leachate contaminated with ammonia being treated with recovered  $\text{TiO}_2$ -magnetite particles**

The results are presented in Table 67 and Figure 63. The initial COD concentration expected was 4700 mg/L, and the measured value was 3416 mg/L (relative error = 27.3 percent). The initial ammonia concentration expected was 622 mg/L as N, and the measured value was 497 mg/L as N (relative error = 20 percent). The data shows that after a small decrease of 10%, the ammonia levels climbed above the initial concentration. This is likely due to evaporation or loss of liquid during the reaction induced by turbulent mixing conditions, aeration, and high temperatures.

**Table 67. Summary of results for photocatalytic oxidation scoping tests on simulated leachates containing ammonia (Experiment C)**

| Time (min) | pH  | Instrument Reading | Dilution Factor | COD (mg/L as O <sub>2</sub> ) |
|------------|-----|--------------------|-----------------|-------------------------------|
| 0          | 5.5 | 3.98               | 125             | 497                           |
| 60         | 5.5 | 3.60               | 125             | 450                           |
| 120        | 5.5 | 5.85               | 125             | 731                           |
| 180        | 5.5 | 4.60               | 125             | 575                           |
| 240        | 5.5 | 5.57               | 125             | 696                           |
| 300        | 5.5 | 6.92               | 125             | 865                           |



**Figure 63. Results for photocatalytic oxidation scoping tests on simulated leachates containing ammonia (Experiment C)**

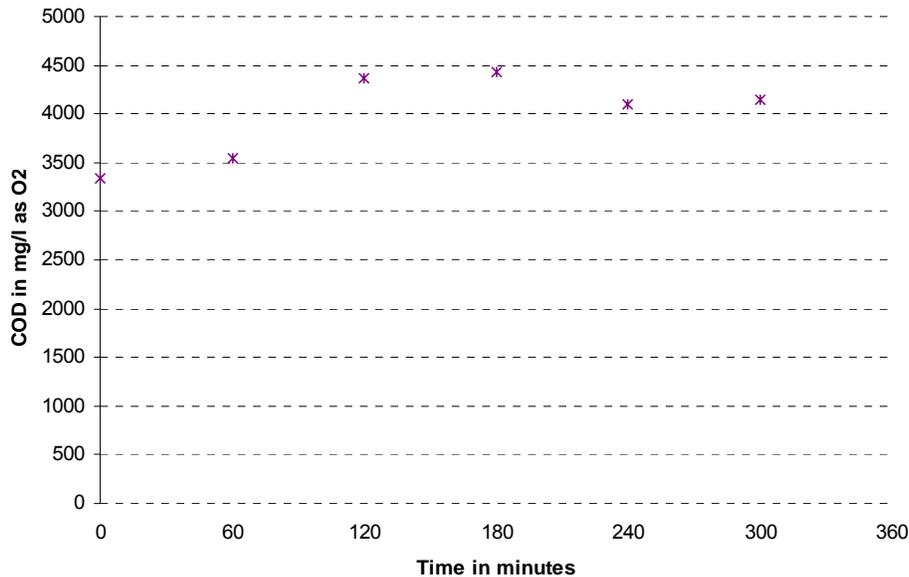
### 3.4.2.2 Chemical Oxygen Demand (COD)

On June 28, 2007, the next scoping experiment was conducted using the TiO<sub>2</sub>-magnetite particles provided by the Northeastern University of China to treat a simulated leachate contaminated with KHP prepared by adding 1.0 g of KHP in reagent water. The dose of photocatalytic particles was 0.427 g in 250 mL of sample. The particles were recovered using the process outlined in the Methodology. The used photocatalysts from the first two experiments were treated, conditioned, and washed, and then combined together to be available for use again in the experiment.

The results of this experiment are presented in Table 68 and Figure 64. The expected initial COD concentration was 4700 mg/L, and the measured value was 3332 mg/L (relative error = 29.2 percent). As the data clearly shows, no effect of treatment was observed using the recovered photocatalysts.

**Table 68. Summary of results for photocatalytic oxidation scoping tests on simulated leachates containing COD treated with recovered photocatalytic particles (Experiment D)**

| Time (min) | pH  | Instrument Reading | Dilution Factor | COD (mg/L as O <sub>2</sub> ) |
|------------|-----|--------------------|-----------------|-------------------------------|
| 0          | 4.5 | 833                | 4               | 3332                          |
| 60         | 4.5 | 888                | 4               | 3552                          |
| 120        | 4.5 | 1091               | 4               | 4364                          |
| 180        | 4.5 | 1106               | 4               | 4424                          |
| 240        | 4.5 | 1023               | 4               | 4092                          |
| 300        | 4.5 | 1036               | 4               | 4144                          |



**Figure 64. COD results for the photocatalytic oxidation experiment using recovered TiO<sub>2</sub>-magnetite particles**

### 3.4.3 Scoping Tests with Degussa P25 TiO<sub>2</sub> Particles

Since the TiO<sub>2</sub>-magnetite particles did not show any removal capacity for ammonia or COD after recovery, the used photocatalysts were sent out for surface chemistry analysis to determine if the coating had been eroded or electroplating had occurred. Results were inconclusive. Thus for subsequent experiments, it was desired to test pure TiO<sub>2</sub> microparticles obtained from a commercial source (Degussa P25).

#### 3.4.3.1 Ammonia

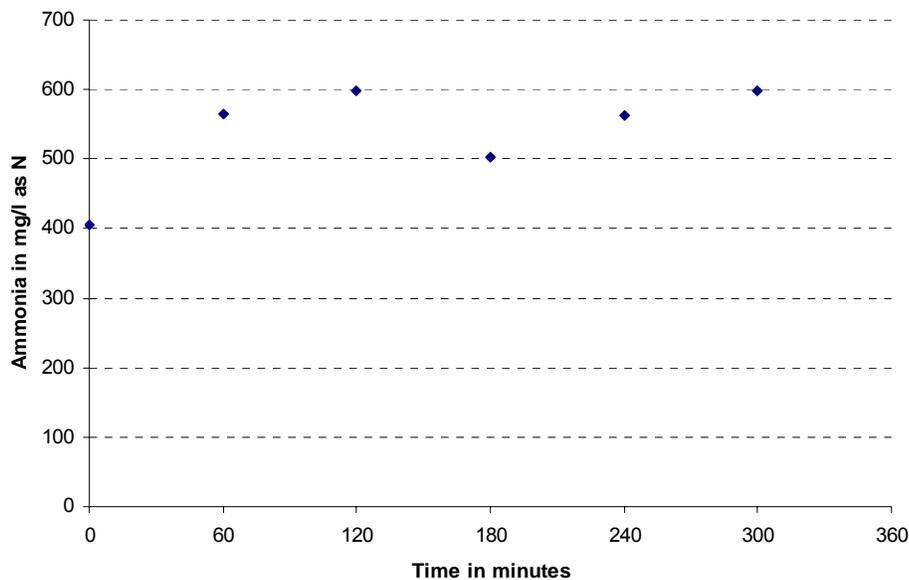
On July 10, 2007, the next scoping experiment was conducted using the TiO<sub>2</sub> microparticles of Degussa P25 provided by the University of Florida to treat a simulated leachate contaminated with ammonia prepared by adding 0.518 g of NH<sub>4</sub>Cl in reagent water. The dose of photocatalytic particles (Degussa P25) was 0.153 g in

250 mL of sample.

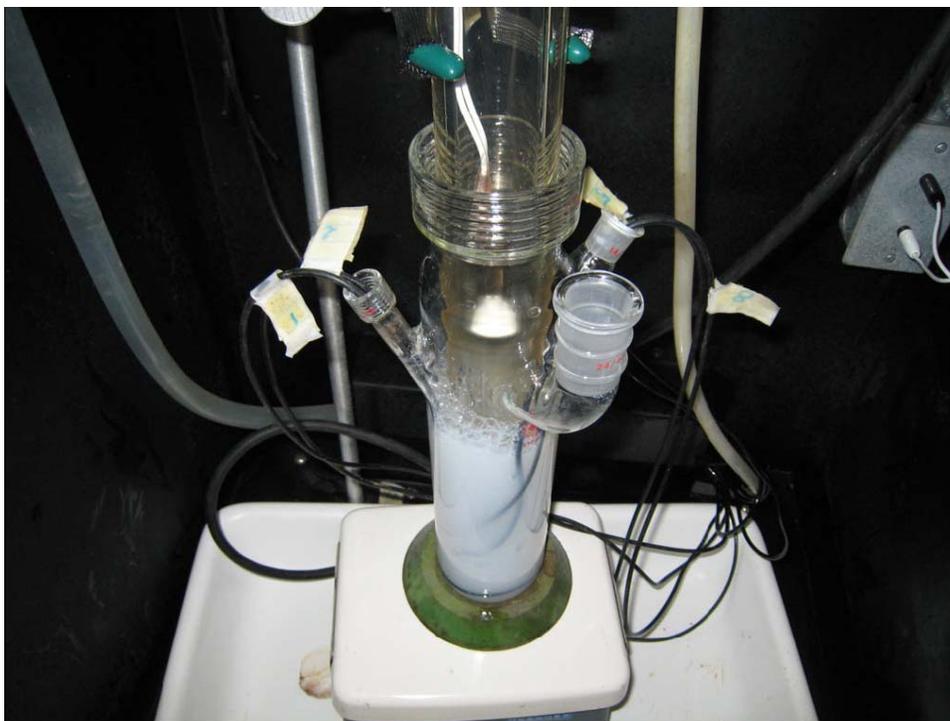
The expected initial ammonia concentration was 542 mg/L as N, but the actual measurement of the influent was 405 mg/L as N (relative error = 25.3 percent). Table 69 and Figure 65 summarize the results for this experiment. No effect of treatment was observed. Figure 66 and Figure 67 show how the solution containing the simulated leachate and the photocatalytic particles change color with respect to time. The photographs show how the mixture becomes darker white from the initial influent to 300 minutes of treatment. Figure 68 shows the color of the particles after recovery. The particles seem to have maintained the initial color, however, in later tests, this is not always the case.

**Table 69. Summary of results for photocatalytic oxidation scoping tests on simulated leachates containing ammonia treated with Degussa P25 photocatalytic particles (Experiment E)**

| Time (minutes) | pH of solution | Reading of instrument | Dilution Factor | Ammonia (mg/L as N) |
|----------------|----------------|-----------------------|-----------------|---------------------|
| 0              | 5.5            | 3.24                  | 125             | 405                 |
| 60             | 5.5            | 4.52                  | 125             | 565                 |
| 120            | 5.5            | 4.79                  | 125             | 599                 |
| 180            | 5.5            | 4.02                  | 125             | 502                 |
| 240            | 5.5            | 4.51                  | 125             | 564                 |
| 300            | 5.5            | 4.78                  | 125             | 598                 |



**Figure 65. Results for photocatalytic oxidation scoping tests on simulated leachates containing ammonia treated with Degussa P25 (Experiment E)**



**Figure 66.** Photocatalytic oxidation scoping test on simulated leachate containing ammonia at  $t = 0$  using Degussa P25



**Figure 67.** Photocatalytic oxidation scoping test on simulated leachate containing ammonia at  $t = 300$  minutes using Degussa P25



**Figure 68. TiO<sub>2</sub> particle recovery process after an ammonia removal experiment**

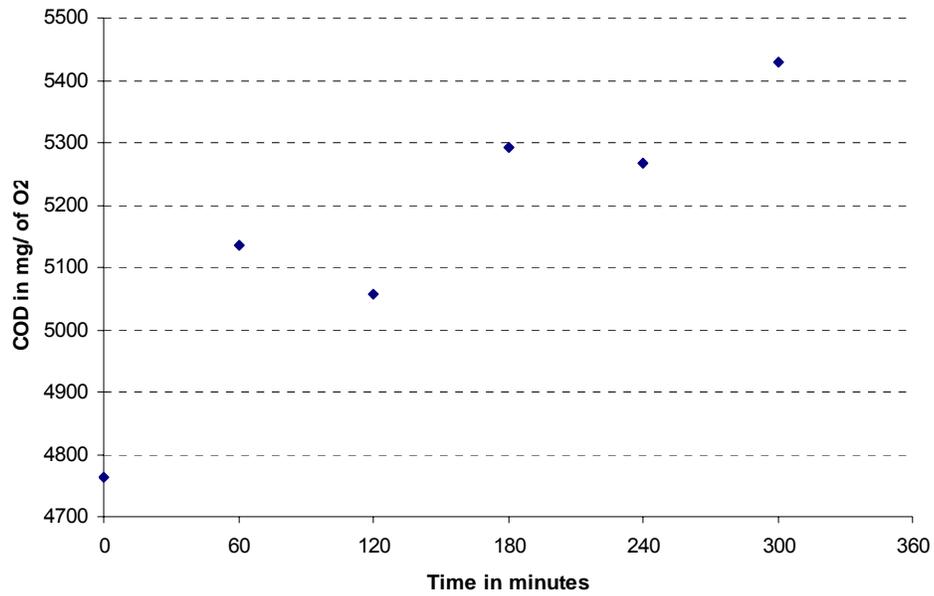
### **3.4.3.2 Chemical Oxygen Demand (COD)**

On July 9, 2007, the next scoping experiment was conducted using the TiO<sub>2</sub> microparticles of Degussa P25 provided by the University of Florida to treat a simulated leachate contaminated with COD prepared by adding 1.0 g of KHP in reagent water. The dose of photocatalytic particles (Degussa P25) was 0.219 g in 250 mL of sample.

The expected initial COD concentration was 4700 mg/L as O<sub>2</sub>, but the actual measurement of the influent was 4764 mg/L as O<sub>2</sub> (relative error = 1.36 percent). Table 70 and Figure 69 summarize the results of this experiment. Although the TiO<sub>2</sub> particles dissolved fully in the solution, which was a bright white color (Figure 70), just as seen in the previous ammonia experiment, the solution became brown in color (Figure 71) after just 1 hour of treatment. No effect of treatment was observed, and the remaining particles after recovery and drying were very dark and sticky (Figure 72). No explanation for this phenomenon is speculated.

**Table 70. Summary of results for photocatalytic oxidation scoping tests on simulated leachate containing COD treated with Degussa P25 photocatalytic particles (Experiment F)**

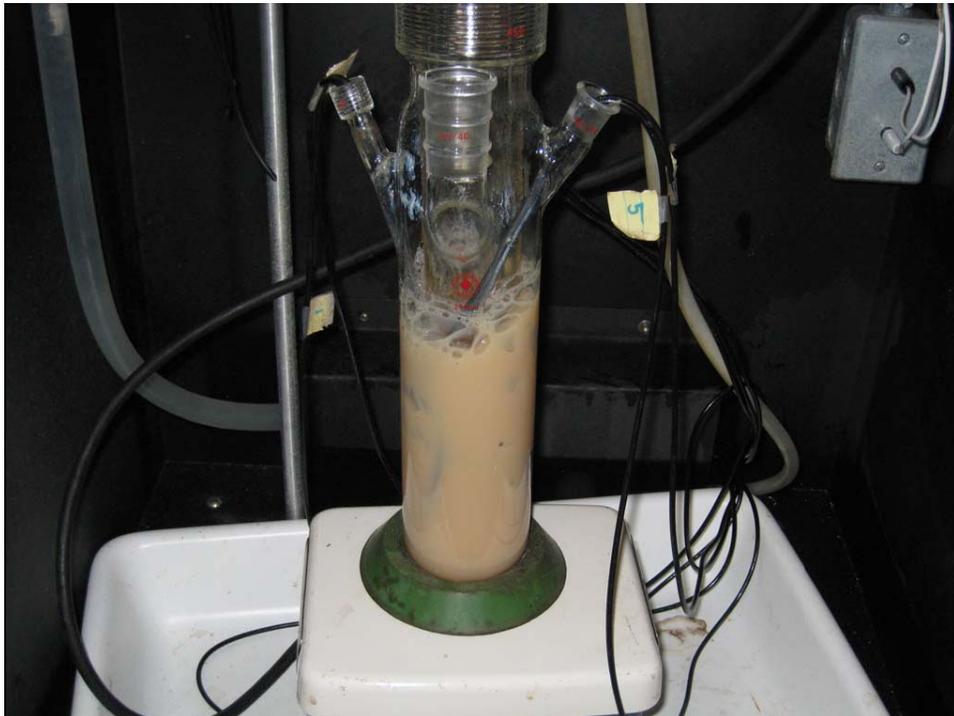
| Time (minutes) | pH  | Instrument Reading | Dilution Factor | COD (mg/L as O <sub>2</sub> ) |
|----------------|-----|--------------------|-----------------|-------------------------------|
| 0              | 4.5 | 1191               | 4               | 4764                          |
| 60             | 4.5 | 1284               | 4               | 5136                          |
| 120            | 4.5 | 1264               | 4               | 5056                          |
| 180            | 4.5 | 1323               | 4               | 5292                          |
| 240            | 4.5 | 1317               | 4               | 5268                          |
| 300            | 4.5 | 1357               | 4               | 5428                          |



**Figure 69. Summary of results for photocatalytic oxidation scoping tests on simulated leachate containing COD treated with Degussa P25 photocatalytic particles (Experiment F)**



**Figure 70.** Photocatalytic oxidation scoping test on simulated leachate containing COD at  $t = 0$  using Degussa P25



**Figure 71.** Photocatalytic oxidation scoping test on simulated leachate containing COD at  $t = 60$  minutes using Degussa P25



Figure 72. Degussa P25 particle recovery process after a COD removal experiment

### 3.4.4 Scoping Tests with Heat-Treated TiO<sub>2</sub>-Magnetite Particles

On July 12, 2007, the next scoping experiment was conducted using the recovered TiO<sub>2</sub>-magnetite particles that had been heat-treated to regenerate the surface coating. The experiment involved treatment of a simulated leachate contaminated with COD prepared by adding 1.0 g of KHP in reagent water. The dose of photocatalytic particles was 0.511 g in 250 mL of sample.

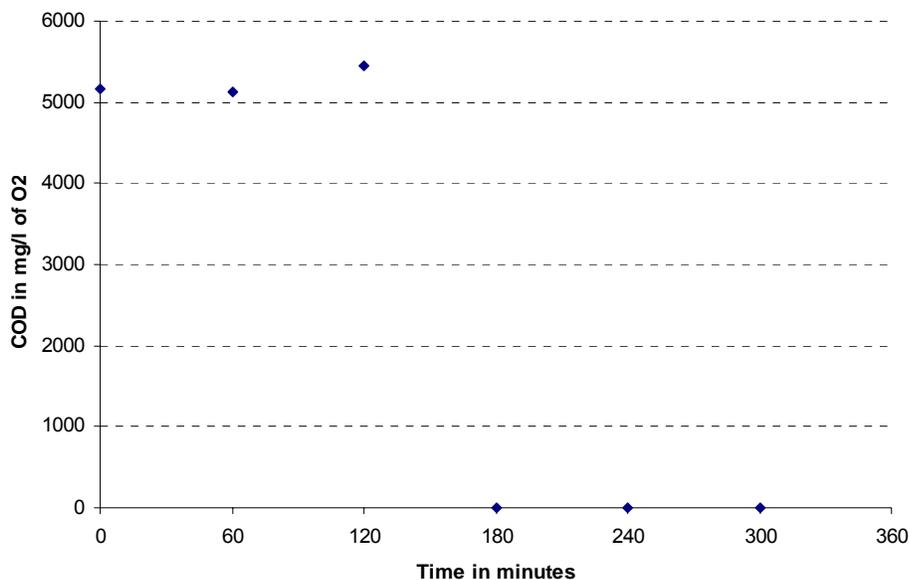
The expected initial COD concentration was 4700 mg/L as O<sub>2</sub>, but the actual measurement of the influent was 5164 mg/L as O<sub>2</sub> (relative error = 9.87 percent). Table 71 and Figure 73 summarize the results of this experiment.

**Table 71. Summary of results for photocatalytic oxidation scoping tests on simulated leachate containing COD treated with recovered photocatalytic TiO<sub>2</sub>-magnetite particles (Experiment G)**

| Time (minutes) | pH  | Instrument Reading | Dilution Factor | COD (mg/L as O <sub>2</sub> ) |
|----------------|-----|--------------------|-----------------|-------------------------------|
| 0              | 4.5 | 1291               | 4               | 5164                          |
| 60             | 4.5 | 1283               | 4               | 5132                          |
| 120            | 4.5 | 1364               | 4               | 5456                          |
| 180            | 4.5 | OR                 | 4               | OR                            |
| 240            | 4.5 | OR                 | 4               | OR                            |
| 300            | 4.5 | OR                 | 4               | OR                            |

OR = out of range high

In this experiment, no effect of treatment was observed. However, the UV lamp was unusually hot to the touch, and considerable amount of water evaporated during the duration of testing. After 3 hours of treatment, the COD levels were over the range of the instrument because the sample was concentrated in the reactor by the abnormally high temperatures. It is speculated that the cooling system may have malfunctioned. As seen with the previous experiment, the solution darkened with time, and the recovered particles were very dark in color.



**Figure 73. Results for photocatalytic oxidation scoping tests on simulated leachate containing COD treated with recovered photocatalytic TiO<sub>2</sub>-magnetite particles (Experiment G)**

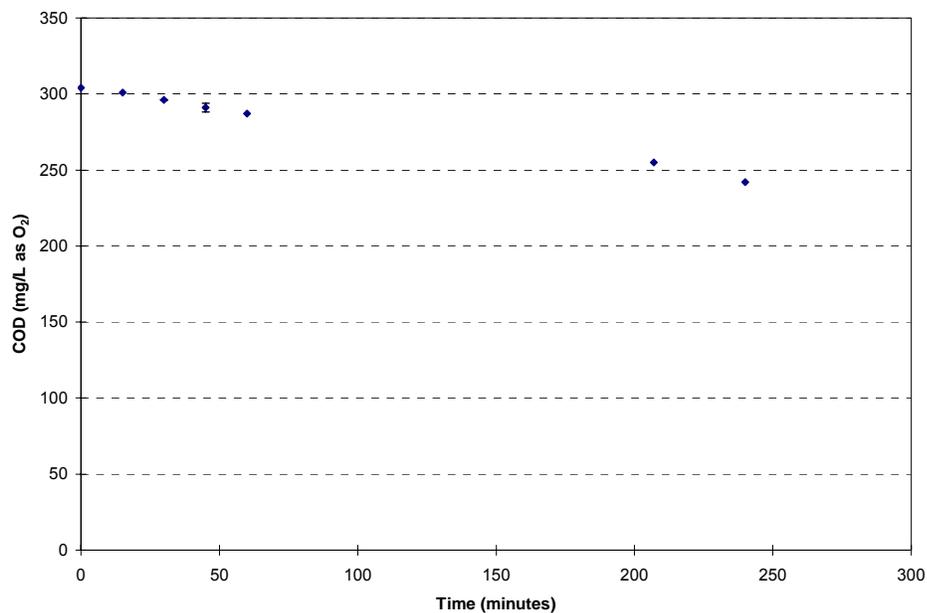
### 3.4.5 Additional Scoping Tests with Photocatalytic Particles

Because the previous tests conducted with photocatalytic particles were unsuccessful due to the overheating caused by the powerful UV lamp, it was desired to test the process using a lower UV intensity, which would allow the temperature to be controlled more precisely. A custom conical shaped reactor with a 15W UV lamp was obtained from the FAU Honors Chemistry Department (see Figure 74) for additional trials of the TiO<sub>2</sub>-magnetite particles with simulated leachate containing COD. The simulated leachate was prepared using 3.348 g/L KHP solution tested with 0.278 g/L of recovered TiO<sub>2</sub>-magnetite powder that was heat-treated in an attempt to rid the surface of any adsorbed organics that might be blocking the formation of holes and radicals by photocatalysis.



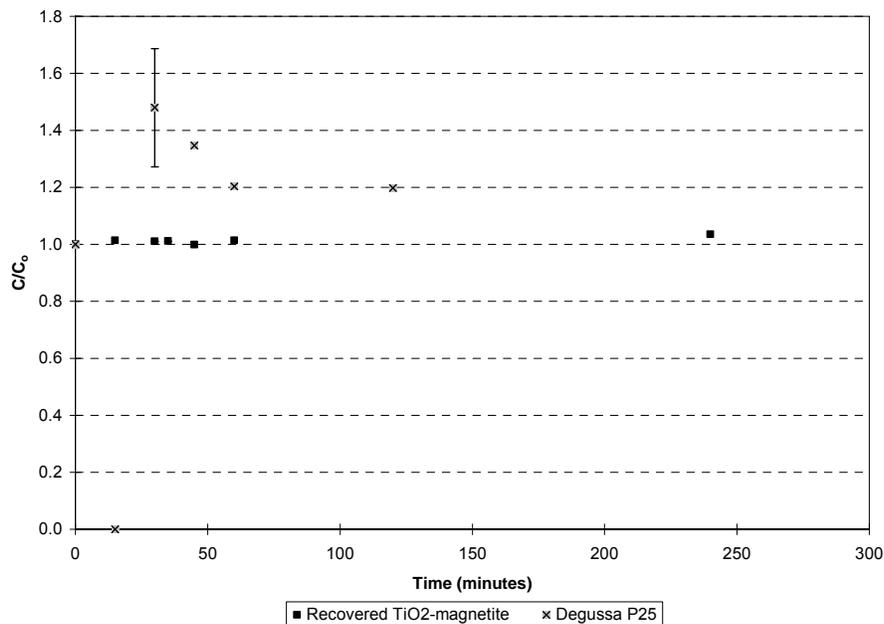
**Figure 74. Photograph of the custom conical shaped reactor with 15 W UV pen-ray lamp**

The results of this experiment (October 15, 2007) are plotted in Figure 75. For the entire duration of the experiment until 240 minutes, no effect of treatment is observed. The primary reasons for this are that: 1) the initial concentration of KHP (4096 mg/L as O<sub>2</sub>) is too strong for the experimental conditions, 2) the dose of photocatalytic particles (0.278 g per 250 mL) simply cannot provide sufficient reagent surface area for the reaction, 3) the UV light intensity (15W) is too weak compared to the time scale of the experiment, and/or 4) the photocatalytic particles that have been heat-treated and reused multiple times may be spent. The QA/QC calibration check for this experiment was 1.3% relative error.



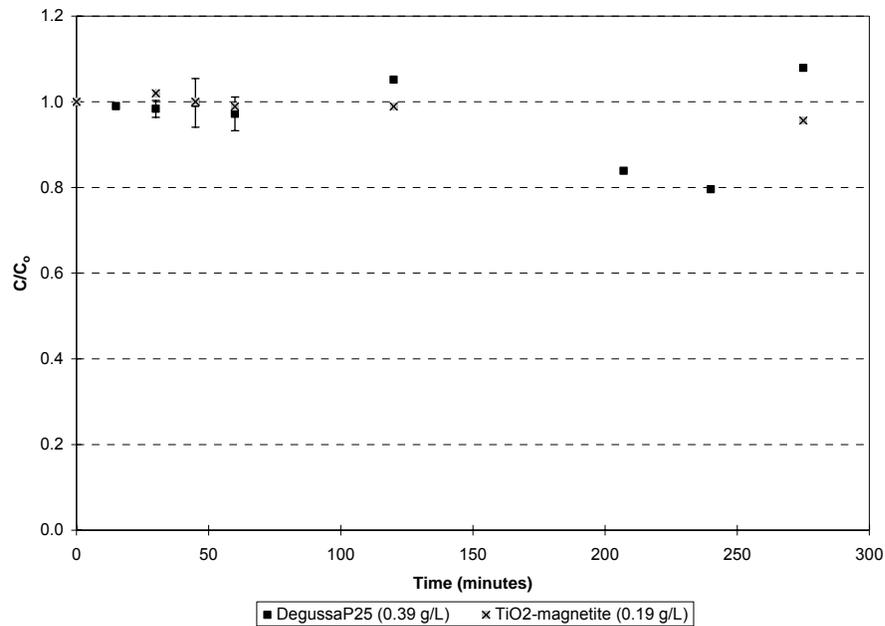
**Figure 75. Summary of results for photocatalytic oxidation scoping tests on simulated leachate containing COD treated with heat-treated recovered TiO<sub>2</sub>-magnetite photocatalytic particles**

Using the same influent solution, the action of the recovered TiO<sub>2</sub>-magnetite particles was compared against commercially available Degussa P25 in Figure 76. Essentially no effects were observed for either catalyst under these conditions.



**Figure 76. Comparison of preliminary tests with recovered TiO<sub>2</sub>-magnetite photocatalysts against Degussa P25 using the 15 W UV pen-ray lamp to treat 0.84 g/L as O<sub>2</sub>**

A second set of tests were conducted on October 22, 2007, under similar conditions as the previous experiment, except that: 1) instead of the heat-treated recovered photocatalytic particles, virgin Degussa P25 powder was substituted and 2) the initial concentration of KHP was reduced by about one-quarter to 0.213 g/L KHP. The results of this experiment are summarized in Figure 77. Clearly, the Degussa P25 photocatalysts were unable to achieve substantial removal of the KHP model contaminant using the 15 W pen-ray lamp. As a further comparison, unused TiO<sub>2</sub>-magnetite particles were tested without UV radiation to determine if adsorption processes play an important role. At a dose of 0.19 g/L, essentially no adsorption was observed during the time scale of the reaction (over 4 hours), as shown in Figure 77.

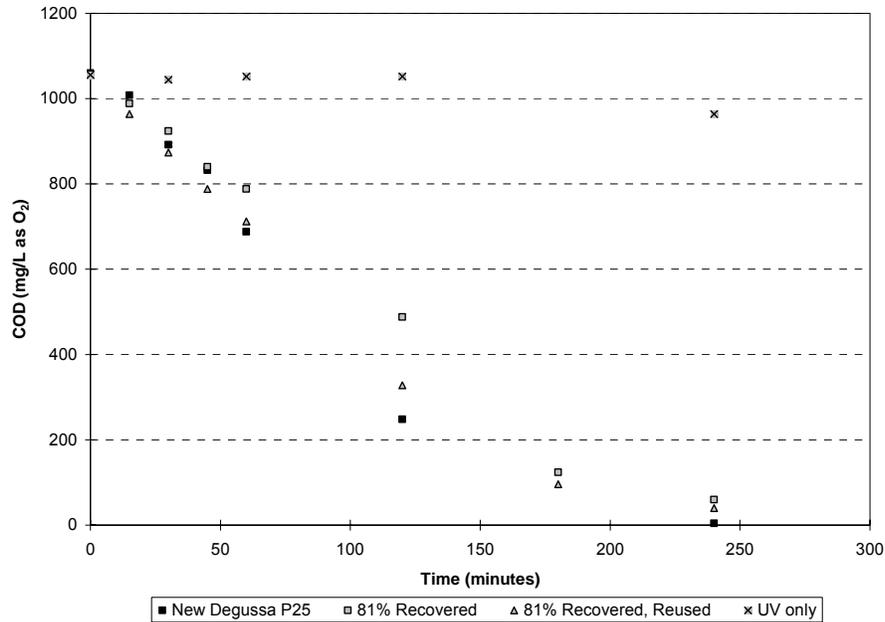


**Figure 77. Results of simulated leachate test (0.231 g/L KHP solution) tested using TiO<sub>2</sub>-magnetite particles (at 0.19 g/L) and DegussaP25 powder (0.39 g/L) with a 15W UV lamp**

### 3.4.6 Scoping Tests of Photocatalytic Particle Recovery Using KHP

Four experiments were conducted between November 27, 2007 and December 4, 2007 to test the ability of the photocatalyst to perform after recovery. For all of these experiments, the 450 W lamp was used to replace the ineffective 15 W pen-ray lamp. In these tests, 375 mL of a 0.84 g/L KHP solution with 1.01 g of TiO<sub>2</sub> (Degussa P25) were added to the reactor. Samples were collected at: 0, 15, 30, 45, 60, 120, 180, and 240 minutes. After the experiment, TiO<sub>2</sub> particles were recovered in a centrifuge following the procedure outlined in the Methodology section. Particle recovery was on the order of 80-85 percent. Therefore, new Degussa P25 particles were added to the subsequent test samples to make-up the difference in the 1.01 g of TiO<sub>2</sub> dose. The

initial COD value for the KHP test solution varied from 1056 – 1060 mg/L as O<sub>2</sub>. The results of this experiment are summarized in Figure 78.

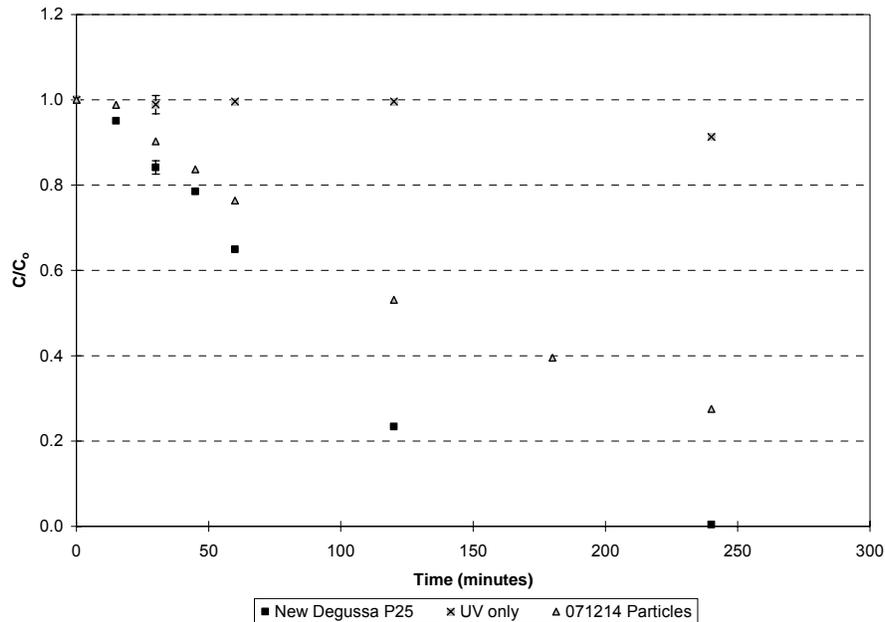


**Figure 78. COD treatment test of recovered TiO<sub>2</sub> Degussa P25**

The experimental results indicate that the Degussa P25 photocatalytic particles are capable of reducing the COD concentration in simulated leachates from a starting concentration of 1060 mg/L as O<sub>2</sub> to below the permissible sewer discharge limit for the City of Boca Raton (800 mg/L as O<sub>2</sub>) in approximately 45 - 60 minutes under the experimental conditions tested. Furthermore, after 4 hours of treatment, 94 to 99 percent of the original COD content was removed by the photocatalytic oxidation process. The results also indicate that very little difference is observed when reusing the photocatalytic particles multiple times. The UV control process showed essentially no removal during the same period.

### 3.4.6 Scoping Tests of Synthesized Photocatalytic Particles Using KHP

Experiments were conducted on December 20, 2007 to test the ability of the laboratory synthesized photocatalysts to perform COD removal compared to the commercially available Degussa P25 photocatalyst. In these tests, 375 mL of a 0.84 g/L KHP solution with 1.0 g of TiO<sub>2</sub> (Degussa P25 or laboratory synthesized photocatalyst particles) were added to the reactor. Samples were collected at: 0, 15, 30, 45, 60, 120, 180, and 240 minutes. The initial COD value for the KHP test solution varied from 1032 – 1060 mg/L as O<sub>2</sub>. The results of this experiment are summarized in Figure 79.



**Figure 79. Comparison of Degussa P25 and photocatalytic particles synthesized in the laboratory on December 14, 2007**

The experimental results indicate that the laboratory synthesized particles are capable of reducing the COD concentration in simulated leachates from a starting concentration of 1060 mg/L as O<sub>2</sub> to below the permissible sewer discharge limit for the City of Boca Raton (800 mg/L as O<sub>2</sub>) in approximately 45 - 60 minutes under the experimental conditions tested. Furthermore, the degradation rate of KHP for the laboratory synthesized particles is similar to the degradation rate of the commercially available Degussa P25 photocatalytic particles. Using the time required to achieve the permissible sewer discharge level as a comparison, the Degussa P25 outperforms the laboratory synthesized particles by about 19 percent. The Degussa P25 required 48 minutes to reach 800 mg/L as O<sub>2</sub>, and the laboratory particles required 57 minutes to reach the same level. Furthermore, the Degussa P25 reaches complete mineralization after 4 hours, but the laboratory particles achieve only 78 percent removal after 4 hours. The UV control process showed essentially no removal during the same period.

If first order degradation is assumed (see Figure 80), the decay coefficient for the Degussa P25 is  $k = -0.024/\text{min}$  ( $r^2 = 0.938$ ), and the decay coefficient for the laboratory synthesized particles (071214) is  $k = -0.006/\text{min}$  ( $r^2 = 0.997$ ). This is a difference of a factor of 4, although the Degussa P25 data does not fit as well to the first order approximation.

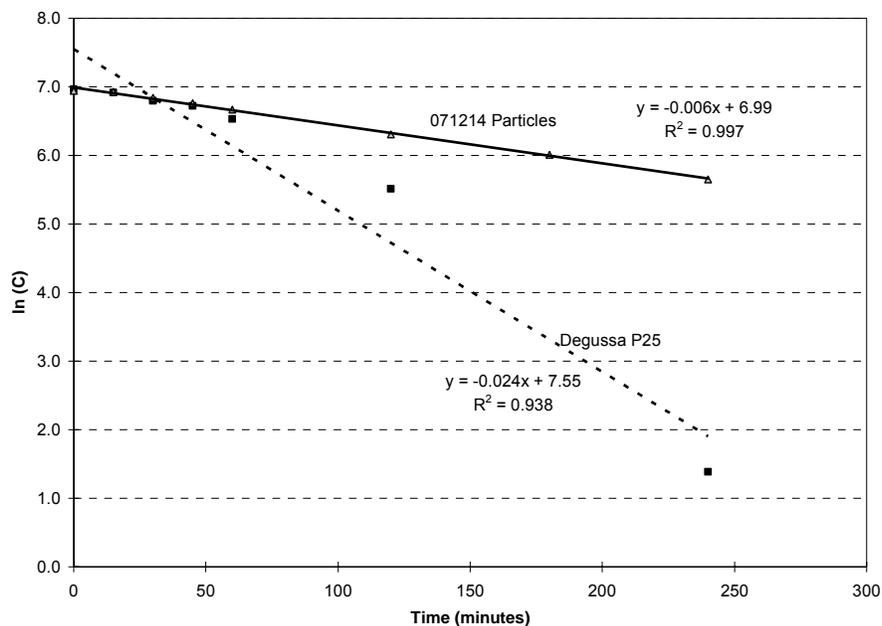
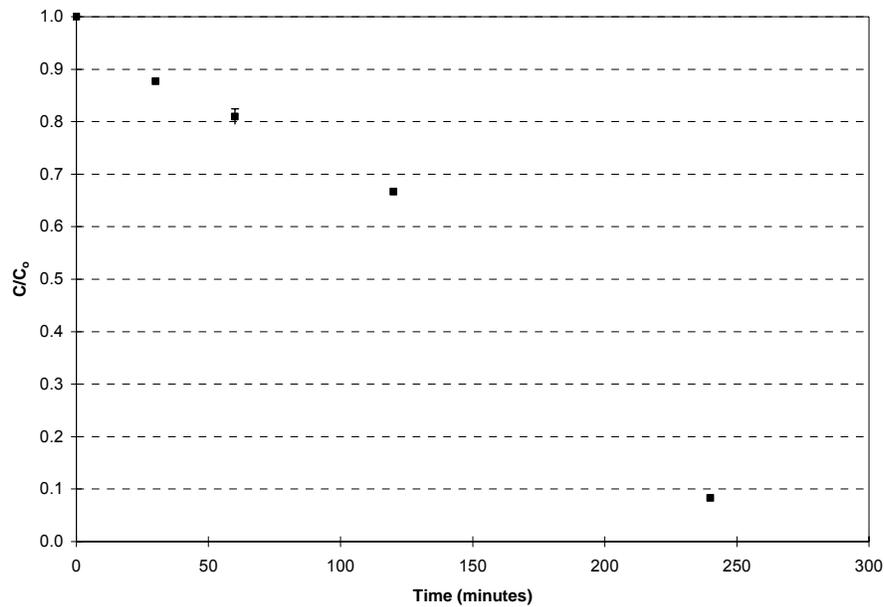


Figure 80. Plot of first order degradation constants comparing Degussa P25 and 071214

### 3.4.7 Photocatalytic Scoping Tests of Other Model Organic Compounds

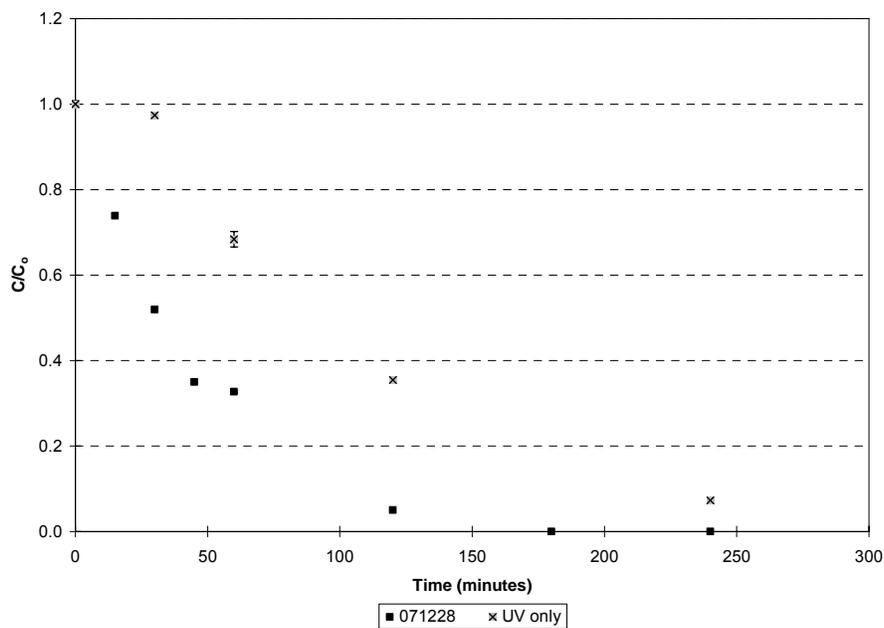
Two experiments were conducted between January 3, 2008 and January 5, 2008 to determine the efficiency of the process with a different model organic compound. Up until this point, KHP has been the only model organic compound tested. Experiments conducted in the literature have focused on many different model compounds. The work of Grzechulska and Morawski (2003), Ilisz et al. (2002), and Kanki et al. (2005) reported on the removal of phenol. Therefore, experiments were designed to investigate the removal of efficiency of phenol and also isobutanol.

First, the experiment with phenol tested the photosensitivity of the model compound in our laboratory scale reactor. The results of the UV only test are shown in Figure 81. Within 4 hours of treatment with just the UV lamp, less than 10% of the material is remaining.



**Figure 81. Results of phenol photosensitivity test using the 450W lamp without photocatalyst**

The results are shown in Figure 82, and although the isobutanol is photosensitive, the photocatalytic process outperforms ultraviolet light radiation during the first four hours of treatment. The photocatalytic process achieves full mineralization within 120 – 180 minutes, while the UV lamp by itself still cannot achieve mineralization after 240 minutes of treatment.



**Figure 82. Comparison of laboratory synthesized TiO<sub>2</sub> (071228) against UV for treatment of isobutanol**

### 3.4.8 Findings of Photocatalytic Oxidation Simulated Leachate Tests

A summary of the photocatalytic oxidation tests conducted on simulated leachates is found in Table 72.

**Table 72. Summary of photocatalytic oxidation tests conducted on simulated leachates**

| No. | Date       | Constituent | Conc (g/L) | Photocatalyst          | Dose (g/L) | Recovered | Virgin | Lamp |
|-----|------------|-------------|------------|------------------------|------------|-----------|--------|------|
| 1   | 11/27/2007 | KHP         | 0.837      | Degussa P25            | 4.06       | 0.00      | 4.06   | 450  |
| 2   | 11/30/2007 | KHP         | 0.838      | Degussa P25            | 4.06       | 3.28      | 0.78   | 450  |
| 3   | 12/04/2007 | KHP         | 0.838      | Degussa P25            | 4.06       | 3.28      | 0.78   | 450  |
| 4   | 12/06/2007 | KHP         | 0.839      | None                   | 0.00       | 0.00      | 0.00   | 450  |
| 5   | 12/20/2007 | KHP         | 0.839      | 071214<br>(6 days old) | 4.05       | 0.00      | 4.05   | 450  |
| 6   | 01/03/2008 | Isobutanol  | 0.408      | 071228<br>(4 days old) | 4.06       | 0.00      | 4.06   | 450  |
| 7   | 01/05/2008 | Isobutanol  | 0.408      | None                   | 0.00       | 0.00      | 0.00   | 450  |
| 8   | 01/11/2008 | Phenol      | 0.251      | None                   | 0.00       | 0.00      | 0.00   | 450  |

On the basis of the results of the experiments detailed in this section, the following are a summary of the major findings:

- New TiO<sub>2</sub>-magnetite particles were successful in reducing the COD concentration of simulated leachates to 48.6 percent of the original concentration value. These photocatalytic particles were recovered by drying overnight at 70-105°C.
- However, experiments conducted with used, recovered TiO<sub>2</sub>-magnetite particles show no success in reducing ammonia or COD in simulated leachates. This was attributed to over-saturation of the surface or degradation of the photocatalytic coating during recovery.
- Heat-treatment to regenerate the coating had no effect.
- Commercially available TiO<sub>2</sub> powder (Degussa P25) was also found to be incapable of reducing the ammonia content in simulated leachate without pH adjustment. However, Degussa P25 was successful in removing COD in simulated leachate. In under 45-60 minutes, the levels were reduced to below the safe sewer discharge limits, and complete mineralization was recorded in under 4 hours of treatment.

### 3.5 PHOTOCATALYTIC OXIDATION: REAL LEACHATE

A summary of the photocatalytic oxidation tests conducted on real leachates is found in Table 73.

**Table 73. Summary of photocatalytic oxidation tests conducted on real leachates**

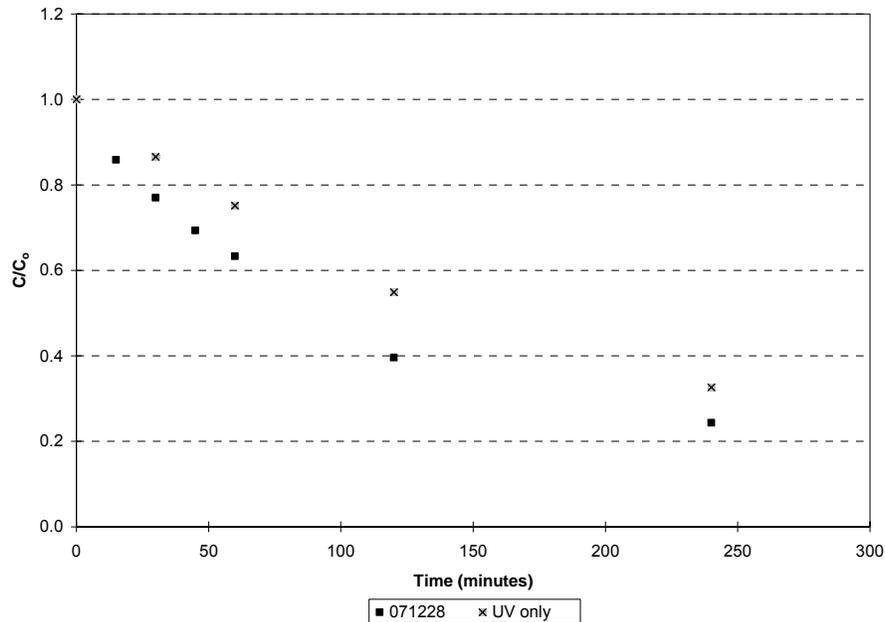
| No. | Date       | Constituent                       | Conc (g/L) | Photocatalyst | Dose (g/L) | Recovered | Virgin | Filtered |
|-----|------------|-----------------------------------|------------|---------------|------------|-----------|--------|----------|
| 9   | 01/24/2008 | Broward County Leachate (12/2006) | 0.691      | Mixed         | 4.06       | 3.89      | 0.17   | No       |
| 10  | 01/19/2008 | Broward County Leachate (12/2006) | 0.691      | None          | 0.00       | 0.00      | 0.00   | No       |
| 11  | 01/27/2008 | Polk County Leachate (08/2004)    | 0.932      | Mixed         | 4.05       | 4.05      | 0.00   | No       |
| 12  | 01/25/2008 | Polk County Leachate (08/2004)    | 0.941      | None          | 0.00       | 0.00      | 0.00   | No       |
| 13  | 01/22/2008 | Polk County Leachate (08/2004)    | 0.876      | Mixed         | 4.07       | 4.07      | 0.00   | Yes      |
| 14  | 01/21/2008 | Polk County Leachate (08/2004)    | 0.944      | None          | 0.00       | 0.00      | 0.00   | Yes      |

### 3.5.1 Broward County Leachate Tests

In December 2006, Broward County leachate was collected for experiments of photocatalytic oxidation with real leachate. On January 24, 2008, two tests were conducted. The first test used mixed photocatalysts in the following amounts:

- 0.8544 g of 071228 laboratory synthesized photocatalyst, which had been recovered and reused twice already
- 0.1199 g of 071214 laboratory synthesized photocatalyst, which had been recovered and reused twice already
- 0.0417 g of virgin Degussa P25

The mixed photocatalyst was required because insufficient material was available to run the experiment with a single photocatalyst at a dose of 4.0 g/L of effective TiO<sub>2</sub>. The initial starting concentration of COD was 691 mg/L as O<sub>2</sub>, but the starting solution had to be diluted 7.2 times by reagent water to produce enough sample for the photoreaction (250 mL), so the actual starting concentration in the reactor was measured at 96 mg/L as O<sub>2</sub>, which is already below the sewer discharge limits of the City of Boca Raton. Nevertheless, the process was tested against UV only, and results are presented in Figure 83.

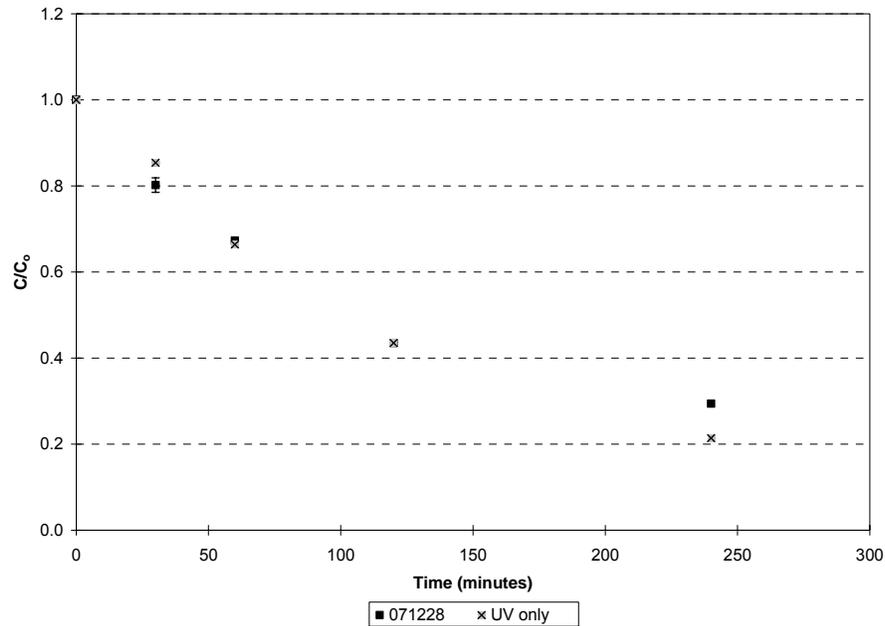


**Figure 83. Comparison of laboratory synthesized TiO<sub>2</sub> (071228) against UV for treatment of real leachate (Broward County December 2006)**

### 3.5.2 Polk County Leachate Tests

In August 2004, leachate from the Polk County landfill was collected for experiments of photocatalytic oxidation with real leachate. On January 22, 2008, a series of four tests were conducted. Two of the tests used the laboratory synthesized 071228 photocatalysts at a dose of 4.0 g/L of effective TiO<sub>2</sub>. The initial starting concentration of COD was  $920 \pm 32$  mg/L as O<sub>2</sub>, but the starting solution had to be diluted 2.8 times by reagent water to produce enough sample for the photoreaction (250 mL), so the actual starting concentration in the reactor was measured at 330 mg/L as O<sub>2</sub>, which is already below the sewer discharge limits of the City of Boca Raton.

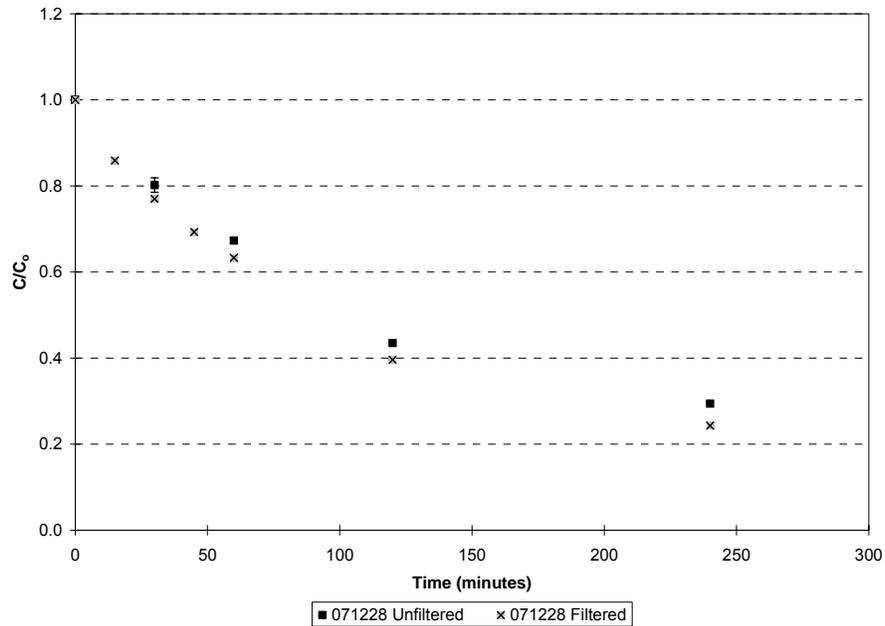
First, the photocatalytic process using the reused laboratory synthesized photocatalyst particles was tested against UV only, and the results are summarized in Figure 84. Very little difference was noted between the two processes in this experiment, but the leachate is aged and the starting concentration is already below the treatment objective. It would be desired to test the same experiment with fresh leachate that is of much higher COD concentration, if possible.



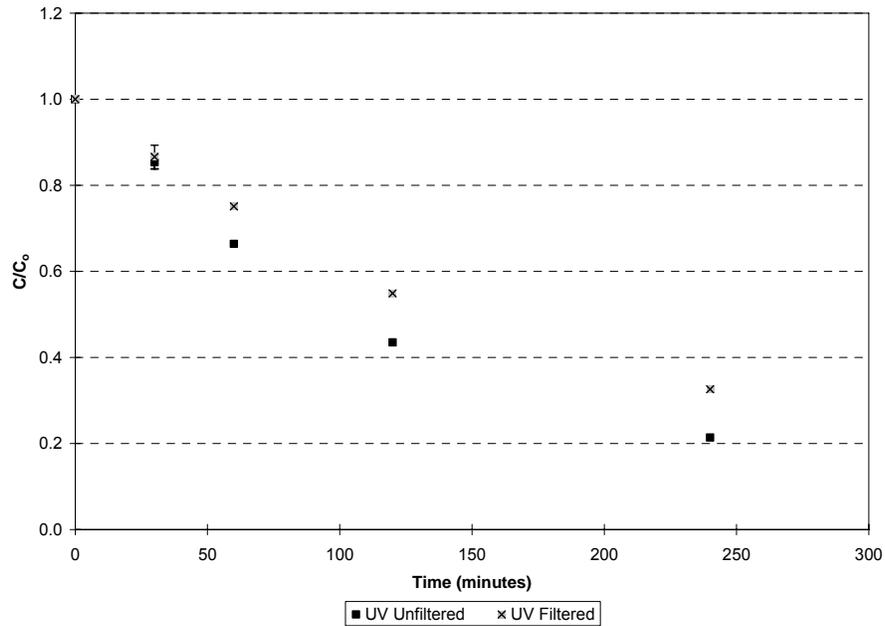
**Figure 84. Comparison of recovered photocatalytic particle oxidation and UV only for the Polk County leachate (August 15, 2004)**

### 3.5.3 Effect of Filtration

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. Therefore, it was desired to test the effect of pre-filtration on both processes with real leachate. Figure 85 shows the results for the photocatalytic process. Figure 86 shows the results for the UV process. In both cases, no differences were observed; however, it is important to note that the real leachate matrix was of very low strength.



**Figure 85. Comparison of recovered photocatalytic particle oxidation with and without filtration for the Polk County leachate (August 15, 2004)**



**Figure 86. Comparison of UV treatment with and without filtration for the Polk County leachate (August 15, 2004)**

## 4. CONCLUSION AND RECOMMENDATIONS

Leachate is highly loaded with dissolved and suspended materials (organic or inorganic compounds, such as heavy metals, ammonia, dissolved and suspended solids, COD and BOD<sub>5</sub>, etc). The quality and quantity of leachate are highly variable and unpredictable on a daily scale. Thus leachate cannot be considered as a typical wastewater. The concentrations of the constituents are too elevated compared to a typical (or even high strength) municipal wastewater. As a result, leachate should not be handled as such. Nevertheless, some facilities are still not pre-treating their leachate. This is why leachate must be managed properly before it is safely discharged back to the environment.

To remedy this issue, several engineering alternatives are available. Conventional options based on physical and chemical characteristics of the leachate and subsequent treatment demonstrated interesting results for specific parameters. For instance, filtration shows excellent results on TDS but does not achieve a sufficient removal of COD; air stripping can only be used to remove ammonia; biological systems are not well-suited for the removal of bio-toxics from water and are inefficient in dealing with wastes of variable quality, such as leachate. Thus post-treatment, using constructed wetlands, combined physical/chemical/biological treatment, or evaporative systems, is necessary. Unfortunately, most current processes cannot adequately address inorganics and organics simultaneously.

Based on the oxidation power of the hydroxyl radical (OH<sup>•</sup>), Advanced Oxidation Processes (AOPs) and Energized Processes (EPs) seem to achieve better removal efficiencies for several constituents simultaneously. Cost and the number of processes required to treat leachate are then reduced. In evaluating the engineering alternatives for longterm leachate management in this study, several trends have been identified:

- Conventional treatment techniques that are commonly used in water treatment, such as biological, physical and chemical methods, have demonstrated their limited efficiency on leachate. Based on the alternative analysis scoring and ranking elaborated during this project, these conventional treatment techniques, applied on leachate, were not recommended as suitable alternatives for longterm leachate management.
- Alternative treatment techniques, utilizing powerful and indiscriminate oxidants such as ozone, hydrogen peroxide, UV, or advanced oxidation processes, are becoming more popular as research demonstrates encouraging capacities at laboratory and pilot scale. The Photochemical Iron Mediated Aeration process is among these emerging techniques. It is an energized process, combining the oxidation power of the IMA process with UV. Based on the same alternative analysis ranking matrix, these alternative treatment techniques, applied on leachate, obtained better scores compared to conventional treatment techniques.

As mentioned before, Table 7 lists the advantages and inconveniences of all the treatment methods inventoried during this study. Each engineering alternative was ranked according to process efficiency, footprint, residuals generated, and environmental considerations. This matrix was produced exclusively with laboratory scale data: no actual survey of operational leachate treatment facilities was conducted, although with the assistance of the Technical Advisory Group and the Florida Department of Environmental Protection Southeast District Office, different landfill managers were surveyed to provide more accurate data with personal input on treatment efficiency and daily operations of certain systems. The consensus long-term leachate management option is to safely discharge to a sewer network. This option provides the most flexibility given the certainty of more stringent regulations in the future. Provided that the leachate is unable to meet the local sewer discharge regulations, some type of on-site treatment would be required. According to Table 74, there are a variety of options that could be employed to deal with site-specific issues.

Using the laboratory scale reactor, and according to the ranking established during this project, the PIMA process obtained a score of 29 for the treatment of Class I landfill leachate. This is among the lowest scores obtained by an energized process. Based on the simulated tests, PIMA would obtain a score of 36, which is in the average of all the available leachate treatment techniques. Compared to the five best techniques presented in Table 74 and based on the present research, the PIMA process on real leachate at laboratory scale suffers from less than promising removal performances. However, the rankings at this point are not definitive. First because the preliminary cost analysis was not completed during the time of this project. And secondly, this project is the first to report experiments conducted on the PIMA process with leachate. This technology is still at a very young stage of development; and additional improvements are necessary for PIMA to mature to a point in which full scale testing can be contemplated. This development should be made according to the recommendations formulated in the next two sections.

**Table 74. Comparison between the best treatment techniques and the new PIMA process**

| <b>Technology</b>                               | <b>Type</b> | <b>Efficiency</b> | <b>Residuals</b> | <b>Footprint</b> | <b>Other</b> | <b>Total Weighted Score</b> |
|---|-------------|-------------------|------------------|------------------|--------------|-----------------------------|
| Photocatalytic Oxidation (simulated leachate)   | EP          | 4                 | 4                | 3                | 4            | 47                          |
| Municipal Sewer Discharge without Pre-Treatment | None        | 2                 | 4                | 5                | 4            | 39                          |
| Leachate Recirculation Bioreactor               | On-site     | 4                 | 2                | 3                | 3            | 39                          |
| Membrane Filtration                             | On-site     | 5                 | 1                | 3                | 2            | 38                          |
| Iron-Mediated Aeration                          | AOP         | 4                 | 1                | 3                | 3            | 37                          |
| Carbon Adsorption                               | On-site     | 3                 | 2                | 3                | 2            | 30                          |
| Ultraviolet Processes                           | EP          | 2                 | 4                | 3                | 2            | 29                          |

| Technology  | Type    | Efficiency | Residuals | Footprint | Other | Total Weighted Score |
|---|---------|------------|-----------|-----------|-------|----------------------|
| UV and Ozone and Hydrogen Peroxide                        | EP      | 3          | 2         | 2         | 2     | 29                   |
| Aerobic and Anaerobic Biological Processes                | On-site | 2          | 2         | 2         | 2     | 24                   |
| Air Stripping   | On-site | 1          | 3         | 3         | 2     | 22                   |
| Photochemical Iron Mediated Aeration (simulated leachate) | EP      | 4          | 1         | 2         | 3     | 36                   |
| Photochemical Iron Mediated Aeration (real leachate)      | EP      | 2          | 2         | 3         | 3     | 29                   |

#### 4.1 PHOTOCATALYTIC IRON MEDIATED AERATION

One of the objectives of this study was to develop laboratory scale performance data for the PIMA process and the photocatalytic oxidation process with TiO<sub>2</sub>-magnetite. The first year of the study focused primarily on PIMA. Two experimental phases were necessary in order to evaluate its performance. The first was dedicated to tests of simulated leachate, and during the second phase, the process was applied to leachate samples from an operating Class I landfill (Solid Waste Authority of Palm Beach County). The designated goal of the process was to lower the concentration of the pollutants contained in leachate in order to safely discharge the effluent to a public sewer network.

Performance data was established by monitoring the COD, conductivity, TDS, BOD<sub>5</sub>, ammonia, and lead content of leachate. The first phase was divided into two separate steps. The first consisted of testing each component to measure the removal power of this treatment method. The PIMA process achieved promising removal efficiencies for COD (removal up to 50-60 percent for the medium level), BOD<sub>5</sub> (removal up to 50 percent for the medium level), and lead (removal greater than 99.9 percent). The PIMA process managed to be competitive with the other AOP processes with regards to the removal of COD (50-60%). Its performance was slightly better than the IMA control process, but well improved compared to the UV control process. However, no removal of conductivity, TDS, or ammonia was observed during any of the simulated leachate tests. Unexpectedly, air stripping (which occurs as a byproduct of circulation of air in the test chamber) by itself should have reduced the ammonia contained in simulated leachates. However, no removal action was detected for ammonia. The test chamber geometry and pH effects are likely implicated. The lack of pH adjustment to a value in excess of 10 is identified as the main obstacle for ammonia removal. Regarding TDS and conductivity, the removal action is counterbalanced due to the dissolution of iron into the liquid phase as a byproduct of iron-mediated aeration. Tests on the amount of dissolved iron indicated that this is partially responsible.

The results of individual simulated leachate tests were confirmed by mixture scoping tests. This second step of the first phase demonstrated the benefits of combining both UV light and iron wool in leachate treatment. PIMA process performance for COD (removal up to 30 percent for the medium level), BOD<sub>5</sub> (removal greater than 50 percent for the medium level), and lead (removal greater than 98 percent) were improved compared to the IMA and UV control processes. But once again, conductivity, TDS, and ammonia were not affected by any of the three processes. The concentrations of all constituents that were initially in violation in the influent were still not in compliance with the City of Boca Raton Code after sixteen hours of PIMA treatment. Thus the level of removal achieved by the PIMA process would not have permitted the discharge of the effluent in the sewer network, unless reactors are operated for extended detention times or operated in series or with recycle.

The second phase of PIMA testing involved actual leachate samples collected from the Solid Waste Authority of Palm Beach County. This leachate was of medium-high strength. The five experiments conducted with real leachate demonstrated the limited effectiveness of the laboratory scale reactor. From simulated leachate tests, no effects were expected with regards to ammonia, conductivity, or TDS and none were observed. Odor also did not seem to be affected by PIMA treatment. However, with regard to COD or BOD<sub>5</sub>, the laboratory scale reactor, which performed well with synthetic leachate, did not perform as well with real leachate. Neither COD nor BOD<sub>5</sub> were lowered appreciably after sixteen hours of treatment, presumably because of the high alkalinity, which acted as a radical scavenger and also because of the foaming caused by aeration, which may have led to mass transfer limitations and inefficient mixing. Lead was the only component affected by the treatment in real leachate. As a result, the PIMA effluent was not in compliance with the City of Boca Raton sewer discharge limits. Regarding other metallic contaminants, IMA and PIMA results reported for lead treatment by Englehardt et al. (2005) and Meeroff et al. (2006) were confirmed during this project. Englehardt et al. (2002) also investigated the removal of other metals, i.e. Pb (average removal of 97.9 percent), As(V) (average removal of 99.97 percent), As(III) (average removal of 99.97 percent), Hg (average removal of 98.8 percent), Cd (average removal of 99.3 percent), Cr (average removal of 99.3 percent), V (average removal of 98.9 percent), and Ni (average removal of 62.6 percent). Thus IMA treatment is feasible for a large number of metallic constituents alone or in mixtures, and since PIMA is basically a similar treatment process, it is expected that PIMA will also work well for other metals. This hypothesis should be confirmed by further research, however.

On a more subjective scale, color was another component of real leachate that was greatly improved by PIMA and also IMA, but not by the UV process alone. Color can be caused by numerous pollutants. One of them is humic acids, which are naturally-occurring complexed forms of COD. Observing color removal without a corresponding change in the COD concentration would signal that the oxidation of the color-forming humic acids yields less complex intermediate forms of COD but

does not proceed all the way to carbon dioxide mineralization. The PIMA process also showed disinfection capabilities due to the combined action of direct UV radiation and hydroxyl radical oxidation.

All of the data generated during the experiments were analyzed in order to find a reaction order for the PIMA mechanism. Zero, first and second order curve fits were tested but none of the experiments (individual and mixture simulated tests or real leachate tests) corresponded to these simplified reaction orders. This might indicate a complex mechanism of multiple rate-limiting steps occurring simultaneously.

## 4.2 PIMA RECOMMENDATIONS

During this project, no statistical analysis was performed. After refining the PIMA process and conducting more conclusive experiments, such analyses would, for instance, establish the reliability of the data and also help to develop a better understanding of the impact of each process parameter: UV intensity, detention time, initial dose of steel wool, etc.

Throughout the laboratory scale PIMA process development, several factors have been identified as responsible for the lack of removal observed during the real leachate experiments:

- The pH has two effects that are counter-productive in this application. Elevated pH aids the stripping of ammonia and the precipitation and co-precipitation of metals, but tends to reduce the generation rate of the hydroxyl radical. On the other hand, a low pH tends to hinder the stripping of ammonia and limit the removal of inorganics but enhances the formation of  $\text{OH}^\bullet$ .
- Linked to the pH, alkalinity has been identified as a second detrimental factor. Bicarbonates and carbonates ( $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$ ) are known radical scavengers and slow down reactions involving hydroxyl radical oxidation. Carbonic acid (favored at low pH and low alkalinity) does not have such an effect. The influence of radical scavenging must be investigated further to determine if an optimum alkalinity/pH range can be attained that would allow for simultaneous treatment of leachate constituents; otherwise, the process would have to be split into separate air stripping with pH adjustment for ammonia removal and then PIMA treatment with pH adjustment or elimination of alkalinity prior to removal of biodegradable and recalcitrant organics and inorganics.

Alkalinity and pH could be evaluated by, for instance, splitting the process into two successive steps. The first one, conducted at high pH ( $\text{pH} > 10$ ) would lower ammonia and metals but not affect COD or BOD. The second step, at low pH ( $\text{pH} < 5$ ), would promote the generation of hydroxyl radicals to enhance removal of

COD, BOD<sub>5</sub>, and inorganics. Color and color-associated COD removal should also be the subject of further investigation. Instead of using KHP to simulate COD, humic acids might be used instead, and extending the detention time to more than sixteen hours could help determine the mechanism involved in COD and color removal. A stagnant COD concentration observed at the same time as a decrease in color would be the sign of the conversion of complex, high molecular weight COD to simpler, low molecular weight intermediates. Furthermore, simultaneously analyzing the BOD<sub>5</sub> or adding TOC analysis would also help clarify the removal mechanism and help to answer the question: is refractory COD ultimately converted into readily biodegradable BOD as mentioned by Suty et al. (2004).

If the IMA results obtained during this project are compared with the work done by Englehardt et al. (2005), the process performance for ammonia or conductivity was not reproduced. This is why, despite the reactor updates already done, some constraints remain an issue and should be sorted out to improve the PIMA process, specifically:

- The most noticeable issue in the reactor design is the aeration and mixing system. The design does not allow for precise control of the aeration rate in multiple test tubes and therefore, the mixing and aeration in each of the replicates is not reproducible. The compromise between effective and excessive mixing was difficult to adjust during laboratory scale testing, especially as the reactor is enclosed in a photochemical safety cabinet to prevent exposure of the researchers to UV radiation. Although the impact of variable aeration rates and incomplete mixing is significant at laboratory scale, the issue is expected to diminish at field scale due to the larger reactor volume compared to the volume of air bubbles.
- The nature of the iron wool reactant also reduces the reproducibility of the process treatment efficiency. First of all, the distribution of fibers and the packing density is not reproducible, even on a mass per volume basis. Also, the packing density was observed to interfere with UV light transmission by generating large areas of shadows. Thus, a large amount of the sample is not irradiated directly and because the steel wool does not move during treatment; if mixing is not operating properly, the process effectiveness may be greatly impaired. Eventually, a more adequate solution (iron filings for example) may be found in order to limit this issue and to reuse the remaining iron sludge after treatment. Trials conducted with pure iron fibers may be another alternative if the mixing system can be improved. This specific issue should be sorted out before attempting to test the process at field scale, although shadows would not be expected to be a concern at field scale because mixing and aeration will be more controllable and also the UV lamps would be placed in an overlapping pattern, which was not done in laboratory scale. Regarding iron, the level of soluble iron and precipitate should be monitored more closely so as to evaluate its impact on the process performance and on sludge generation.

- Regarding the iron residuals generation, no tests were conducted during this project regarding the toxicity of the iron sludge. A Toxicity Characteristic Leaching Procedure (TCLP) analysis (EPA method# 1311) would be the most appropriate means to evaluate the composition of the residuals. This would clarify the fate of lead and other heavy metals during treatment. Specific questions that need to be answered in this analysis will address the removal mechanism. In other words, do the inorganic pollutants adsorb to the steel wool or do they precipitate/co-precipitate and settle out in the bottom sludge? The results of the TCLP test would also tell if the sludge could be landfilled or if the material must be handled as a hazardous waste.
- The efficiency of the UV source can also impact the laboratory scale results. According to the manufacturer, the average lifetime of the lamp is 1,000 hours, but the energy measured during this study declined in less time. To determine the precise effect, a lamp emitting only a narrow band UV radiation could also improve the productivity of the process. As stated earlier overlapping UV lamps might also be effective. In addition, the UV intensity issue must also be optimized because the higher the energy output required, the higher the cost of the system.
- The dose of iron used is also a potential issue. Many of the laboratory scale tests were conducted using a dose of 2.0 grams per 80 mL of sample. If scaled up, this dose requires 25 grams of iron per liter of leachate treated. If the iron is not recovered after treatment, a tremendous amount of iron would be necessary (approximately 20 metric tons for the treatment of 50,000 gallons of leachate per day), and unfortunately, the world market price of metals is on a rising trend due to very high demand. This would also generate large quantities of bottom sludge and residuals that would have to be managed. Even by reducing the dose in half, which seemed to work better in real leachate testing, the amount of iron used in the field scale unit would be on the order of several metric tons per day.

The literature reported on the IMA process shows that the reaction mechanism is not completely understood. In addition, the interaction of UV energy with the other reactants has to be accounted for the treatment performance. After this project, we can speculate that the following steps are involved in the PIMA process:

- The oxidation of  $\text{Fe}_{(s)}$  to  $\text{Fe}^{2+}$ , under an aerated environment enhanced by UV irradiation
- The generation of hydroxyl radicals, according to a Photo-Fenton reaction
- The oxidation action of hydroxyl radical, which seems to have the most valuable impact
- The co-precipitation action of ferric precipitates
- The stripping action of aeration, which seems to have a very limited effect in laboratory scale, due to pH issues

- The direct photolysis action of UV energy

From the results of this study, the laboratory scale PIMA process would not produce an effluent with a water quality high enough to allow discharge into a sewer network. Based on the treatment efficiency on simulated leachate, the PIMA process would obtain a total score of 36 in our alternative analysis selection matrix. This is slightly below the average score of the other EPs. But based on the real leachate process efficiency, this score would fall to an even lower value under the limitations of the laboratory scale reactor. These conclusions need further development to be validated. The re-engineering of the reactor would be the first step to improve mixing and aeration and to generate more homogeneous UV radiation. Implementing the process with additional treatment stages, such as pH and alkalinity adjustments should be investigated in order to complete the validation of these conclusions. Tests with samples from different landfills should also be considered. Finally, development of a refined cost analysis would complete the evaluation of the different landfill leachate treatment techniques. Based on the information collected during the literature review, a preliminary cost analysis was initiated during this project, but because processes were evaluated only at a laboratory scale, the outcomes of this analysis are not yet publishable.

#### **4.3 PHOTOCATALYTIC OXIDATION**

A number of scoping tests were conducted on COD and ammonia using various types of photocatalytic particles. The TiO<sub>2</sub> -magnetite nanoparticles showed the capability to degrade KHP in shorter reaction times than the PIMA, IMA, and UV processes. However, after the first use, the results were not reproducible. It is speculated that some type of surface interaction degraded the photocatalytic coating or the highly concentrated simulated leachate supersaturated the surface or something occurred with the silica layer that binds the magnetite core to the photocatalytic surface. Attempts to determine the reason for the inability to recover and reuse the particles were inconclusive. Using microparticles provided by the University of Florida and also commercially available Degussa P25 photocatalysts also performed well against COD. However, initial attempts to recover and reuse the particles by drying without filtration met with failure to reproduce the removal efficiencies seen in the first use. Later experiments employed the use of centrifugal separation. Under these conditions, the TiO<sub>2</sub> particles were recoverable at around 80-85 percent and reusable with essentially no loss in removal efficiency with up to four repeated uses. Although ammonia removal was not successful at laboratory scale without pH adjustment, the TiO<sub>2</sub> particles tested were able to completely mineralize KHP, phenol, and isobutanol in synthetic leachates.

Our laboratory also developed a method to manufacture custom TiO<sub>2</sub> particles and compared the results to the commercially available TiO<sub>2</sub> (Degussa P25). Although the Degussa P25 performed slightly better in synthetic leachates, the results

were nearly identical in terms of the process kinetics and reaction times to achieve the sewer discharge limits and complete mineralization.

Finally, the custom TiO<sub>2</sub> particles made in our laboratory were capable of decomposing COD in real leachates from local area sanitary landfills. In these experiments, the photocatalytic oxidation process outperformed UV treatment, and the effects of filtration were insignificant at low starting COD concentrations.

#### **4.4 PHOTOCATALYTIC OXIDATION RECOMMENDATIONS**

During this project, no statistical analysis was performed. After refining the photocatalytic process and conducting more conclusive experiments, such analyses would, for instance, establish the reliability of the data and also help to develop a better understanding of the impact of each process parameter: UV intensity, detention time, initial dose of photocatalyst, etc. In addition, the TiO<sub>2</sub>-magnetite particles were not fully tested because after recovery, the particles were not reusable for some unknown reason. This critical issue must be determined to allow for further testing of TiO<sub>2</sub>-magnetite, which offers a simple method for recovery in which centrifugation and heat-treatment are not necessary to regenerate the catalyst for the next batch.

It is promising that the newer particles manufactured in our laboratory, performed well against COD. This should allow for experiments with higher catalyst doses, which may decrease reaction times or allow the process to handle even higher initial concentrations of pollutants.

Throughout the laboratory scale photocatalytic oxidation process development, several factors have been identified as requiring further investigation apart from the general recommendations above:

- Instead of KHP, phenol, and isobutanol for the simulated COD test, something that is not as photosensitive should be tested to see if the photocatalyst can perform against truly recalcitrant model compounds. If photosensitive target compounds such as isobutanol and phenol are used in simulated leachates, then lower UV intensities may be useful to determine the actual effects of photocatalytic oxidation versus ultraviolet radiation by itself.
- In addition to COD, the same parameters that were tested for the PIMA process should be tested for the photocatalytic oxidation process. These include: ammonia, BOD<sub>5</sub>, dissolved solids, conductivity, and heavy metals (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 pH should be controlled in some experiments so as to determine the optimum pH value for maximum decomposition.
- The flow rate of the cooling water can be increased or other measures taken to reduce the operating temperatures of the UV lamp, if it reaches very high temperatures during treatment at laboratory scale.
- The effect of air should also be monitored by conducting some experiments without the air supply to see if it is actually needed because the TiO<sub>2</sub>-magnetite particles can be theoretically mixed using a magnetic field, so air would only be necessary if it participates in the reaction.
- 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.
- In terms of the photocatalytic particles synthesized in the laboratory, the purity can be increased by using higher calcination temperatures. This will allow the yield of more crystallized TiO<sub>2</sub> to increase. However, the nominal size of the particles will also be expected to increase, reducing the surface area to volume ratio and the efficiency per gram. If a compromise can be reached that achieves both higher purity without increasing the particle diameters too much, this would increase process efficiency and is certainly worth investigating further.
- In the last set of photocatalytic oxidation tests, the real leachates were tested in dilutions because insufficient volumes were available. In subsequent tests, it is desired to test only undiluted leachates sampled the same day as testing.

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## APPENDIX A: LEACHATE COMPOSITION IN FLORIDIAN LANDFILLS

| SOURCE                                    |         | Ward et al. (2002)               |                          |                                 |                               |                   |  | Solid Waste Authority of Palm Beach County                         |  |
|---|---------|----------------------------------|--------------------------|---------------------------------|-------------------------------|-------------------|--|--|--|
| Lead in mg/L                              | Range   |                                  |                          | 0.04 - 0.10                     |                               |                   |  |  |  |
|   | Average | < 0.04                           | < 0.04                   | 0.06                            | < 0.04                        |                   |  |  |  |
| Conductivity in $\mu\text{S}/\text{cm}$   | Range   | 13,200 - 15,200                  | 3,100 - 8,400            | 2,600 - 9,500                   | 6,500 - 8,600                 | 3,200 - 12,100    | 1,000 - 14,200   | 1,245 - 95,000   | 2,320 - 7,370  |
|   | Average | 14,100                           | 6,200                    | 5,200                           | 7,600                         | 8,300             | 9,600  | 40,470   | 5,090  |
| TSS in mg/L                               | Range   |                                  |                          |                                 |                               |                   |  |  |  |
|   | Average |                                  |                          |                                 |                               |                   |  |  |  |
| TDS in mg/L                               | Range   |                                  |                          |                                 |                               |                   |  | 900 - 88,000   | 220 - 4,100  |
|   | Average |                                  |                          |                                 |                               |                   |  | 27,690   | 2,770  |
| Ammonia in mg/L as $\text{NH}_3\text{-N}$ | Range   |                                  |                          |                                 |                               |                   |  |  |  |
|   | Average |                                  |                          |                                 |                               |                   |  |  |  |
| COD in mg/L                               | Range   | 1,070 - 2,584                    | 522 - 827                | 242 - 440                       | 902 - 1,616                   | 416 - 1,208       | 10,530 - 13,960  |  |  |
|   | Average | 1,850                            | 636                      | 351                             | 1,165                         | 857               | 12,245   |  |  |
| BOD <sub>5</sub> in mg/L                  | Range   | 89 - 204                         | 14 - 30                  | 13 - 21                         | 55 - 77                       | 13 - 66           |  |  |  |
|   | Average | 140                              | 22                       | 15                              | 66                            | 42                |  |  |  |
| pH  | Range   | 7.3 - 7.6                        | 6.5 - 7.4                | 6.8 - 7.5                       | 7.3 - 7.8                     | 7.5 - 7.9         | 7.3 - 7.8  | 2.0 - 11.3   | 6.5 - 8.1  |
|   | Average | 7.5                              | 7.0                      | 7.2                             | 7.5                           | 7.7               | 7.6  | 6.8  | 7.1  |
| <b>LANDFILL CHARACTERISTICS</b>           |         | Landfill with leachate recycling | Landfill in a rural area | Capped landfill in a rural area | Landfill in a semi urban area | Regional landfill | Landfill with enhanced biological treatment in an urban area | Class I landfill at the Solid Waste Authority in Palm Beach County | Class III landfill at the Solid Waste Authority in Palm Beach County |

| SOURCE                               |         | St. Lucie County Glades Road Landfill Water Quality Report January 2005, prepared by CDM |               |               | St. Lucie County Baling & Recycling Facility Water Quality Report July 2005, prepared by CDM, Eric Grotke |       |       | Okeechobee County 2nd 2005 Semi-annual Water Quality Monitoring Report Berman Road Landfill, Leachate analysis report by STL (Severn Trent) Denver |        |
|--------------------------------------|---------|--|---------------|---------------|---|-------|-------|--|--------|
| Lead in mg/L                         | Range   |  |               | 0.03          | 0.01  | BDL   | 0.006 | BDL  | BDL    |
|                                      | Average |  | BDL           | 0.03          | 0.01  | BDL   | 0.006 | BDL  | BDL    |
| Conductivity in $\mu$ S/cm           | Range   |  |               |               |   |       |       |  |        |
|                                      | Average |  |               |               |   |       |       |  |        |
| TSS in mg/L                          | Range   |  |               |               |   |       |       |  |        |
|                                      | Average |  |               |               |   |       |       |  |        |
| TDS in mg/L                          | Range   | 800 - 1,400  | 4,000 - 8,000 | 3,500 - 8,000 |   |       |       |  |        |
|                                      | Average |  |               |               | 830   | 7,400 | 7,800 | 13,000   | 19,000 |
| Ammonia in mg/L as NH <sub>3</sub> N | Range   | 3 - 15   | 500 - 800     | 400 - 700     |   |       |       |  |        |
|                                      | Average |  |               |               | 28  | 940   | 710   | 1,300  | 1,300  |
| COD in mg/L                          | Range   | 55 - 150   | 1,500 - 5,000 | 1,000 - 2,500 |   |       |       |  |        |
|                                      | Average |  |               |               | 110   | 5,400 | 4,300 |  |        |
| BOD <sub>5</sub> in mg/L             | Range   |  |               |               |   |       |       |  |        |
|                                      | Average |  |               |               |   |       |       |  |        |
| pH                                   | Range   |  |               |               |   |       |       |  |        |
|                                      | Average |  |               |               | 7.1   | 8.0   | 7.7   | 7.3  | 7.5    |
| LANDFILL CHARACTERISTICS             |         | St. Lucie County landfills   |               |               |   |       |       | Okeechobee County Landfill   |        |

| SOURCE                                  |         | 2nd Semi-annual GWMR 2004<br>Broward County Interim<br>Contingency Landfill |       | Miami-Dade County South Dade<br>Landfill First Semi-annual<br>Monitoring Report 2005 |       | 2004 2nd Semi-annual Monitoring<br>Sampling Report for the Resources<br>Recovery and 58th Street Landfill |            |
|---|---------|---|-------|--|-------|---|------------|
| Lead in mg/L                            | Range   |   |       |  |       |   |            |
|   | Average | 0.03  | 0.07  | 0.016  | 0.018 | BDL   | BDL        |
| Conductivity in $\mu$ S/cm              | Range   |   |       |  |       |   |            |
|   | Average |   |       |  |       |   |            |
| TSS in mg/L                             | Range   |   |       |  |       |   |            |
|   | Average |   |       |  |       |   |            |
| TDS in mg/L                             | Range   |   |       |  |       |   |            |
|   | Average | 540   | 3,300 | 10,000   | 9,200 | 7,090   |            |
| Ammonia in mg/L as NH <sub>3</sub><br>N | Range   |   |       |  |       |   |            |
|   | Average | 9.6   | 40    | 790  | 570   |   | 98         |
| COD in mg/L                             | Range   |   |       |  |       |   |            |
|   | Average |   |       |  |       |   |            |
| BOD <sub>5</sub> in mg/L                | Range   |   |       |  |       |   | 14.1 - 445 |
|   | Average |   |       | 250  | 550   | 98  |            |
| pH                                      | Range   |   |       |  |       |   |            |
|   | Average | 7.3   | 7.5   | 7.8  | 7.5   | 8.3   | 8.3        |
| <b>LANDFILL CHARACTERISTICS</b>         |         | Broward County Landfills  |       | Miami-Dade County Landfills  |       |   |            |

| SOURCE                   |         | 2005 1st Semi-annual Monitoring Sampling Report for the Resources Recovery and 58th Street Landfill |     | 2005 1st Semi-annual GWMR Medley Landfill & Recycling Center |        | Statom et al. (2004)                                    | SUMMARY        |
|--------------------------|---------|---|-----|--|--------|---|----------------|
| Lead in mg/L             | Range   |   |     |  |        | <0.004 - 0.11   | BDL - 0.1      |
|                          | Average |   |     | < 0.04   | < 0.04 |   | 0.03           |
| Conductivity in µS/cm    | Range   |   |     |  |        | 3,600 - 15,000  | 1,000 - 95,000 |
|                          | Average |   |     |  |        | 7,642   | 11,578         |
| TSS in mg/L              | Range   |   |     |  |        |   |                |
|                          | Average |   |     |  |        |   |                |
| TDS in mg/L              | Range   |   |     |  |        | 1,630 - 6,400   | 900 - 88,000   |
|                          | Average | 20,000  |     | 7,400  |        | 3,441   | 9,297          |
| Ammonia in mg/L as NH3-N | Range   |   |     |  |        | 6 - 1,350   | BDL - 1,350    |
|                          | Average | 52  | BDL | 500.00   | 0.60   | 473   | 487            |
| COD in mg/L              | Range   |   |     |  |        | 222 - 2,000   | 55 - 13,960    |
|                          | Average |   |     |  |        | 835   | 2,775          |
| BOD <sub>5</sub> in mg/L | Range   |   |     |  |        | 1 - 184   | BDL - 445      |
|                          | Average | 130   | BDL |  |        | 47  | 137            |
| pH                       | Range   |   |     |  |        | 6.56 - 8.01   | 2.0 - 11.3     |
|                          | Average | 7.5   | 7.2 | 7.6  | 7.7    | 7.1   | 7.5            |
| LANDFILL CHARACTERISTICS |         | Miami-Dade County Landfills   |     |  |        | Closed Dyer Boulevard Landfill, Palm Beach County (MSW) |                |

## APPENDIX B: PIMA REAL LEACHATE EXPERIMENTAL RESULTS

### Experiment No. 19, COD results

| Process           | $C / C_0$<br>0 hr | $C / C_0$<br>2 hrs | $C / C_0$<br>4 hrs | $C / C_0$<br>6 hrs | $C / C_0$<br>10 hrs | $C / C_0$<br>16 hrs |
|-------------------|-------------------|--------------------|--------------------|--------------------|---------------------|---------------------|
| IMA, x = 10.2 cm  | 1.00              | 0.73               | 0.63               |                    | 0.62                |                     |
| IMA, x = 10.2 cm  | 1.00              | 0.61               |                    | 0.65               |                     | 0.68                |
| UV, x = 10.2 cm   | 1.00              | 0.71               | 0.71               |                    | 0.81                |                     |
| UV, x = 10.2 cm   | 1.00              | 0.68               |                    | 0.71               |                     | 0.72                |
| PIMA, x = 10.2 cm | 1.00              | 0.56               | 0.69               |                    | 0.66                |                     |
| PIMA, x = 10.2 cm | 1.00              | 0.77               |                    | 0.71               |                     | *                   |
| PIMA, x = 10.2 cm | 1.00              | 0.63               |                    | 0.66               |                     | 0.62                |
| PIMA, x = 10.2 cm | 1.00              | 0.69               |                    | 0.67               |                     | 0.60                |

\* Sample was lost during the measurement.  
Initial COD = 5,865 mg/L as O<sub>2</sub>

### Experiment No. 20, COD results

| Process           | $C / C_0$<br>0 hr | $C / C_0$<br>2 hrs | $C / C_0$<br>4 hrs | $C / C_0$<br>6 hrs | $C / C_0$<br>10 hrs | $C / C_0$<br>16 hrs |
|-------------------|-------------------|--------------------|--------------------|--------------------|---------------------|---------------------|
| IMA, x = 10.2 cm  | 1.00              | 1.07               | 1.24               |                    | 1.25                |                     |
| IMA, x = 10.2 cm  | 1.00              | 1.04               |                    | 1.09               |                     | 1.01                |
| UV, x = 10.2 cm   | 1.00              | 1.11               | 1.06               |                    | 1.09                |                     |
| UV, x = 10.2 cm   | 1.00              | 1.12               |                    | 1.12               |                     | 1.14                |
| PIMA, x = 10.2 cm | 1.00              | 1.11               |                    | 1.08               |                     | 1.17                |
| PIMA, x = 10.2 cm | 1.00              | 1.07               |                    | 1.00               |                     | 0.97                |
| PIMA, x = 10.2 cm | 1.00              | 1.07               | 1.11               |                    | 1.21                |                     |
| PIMA, x = 10.2 cm | 1.00              | 0.98               |                    | 1.05               |                     | 1.05                |

Initial COD = 3,765 mg/L as O<sub>2</sub>

### Experiment No. 21, COD results

| Process           | Dose of Iron<br>in g | $C / C_0$<br>0 hrs | $C / C_0$<br>2 hrs | $C / C_0$<br>6 hrs | $C / C_0$<br>16 hrs |
|-------------------|----------------------|--------------------|--------------------|--------------------|---------------------|
| IMA, x = 10.2 cm  | 2.1                  | 1.00               | 1.10               | 1.14               | 1.08                |
| UV, x = 10.2 cm   | 0.0                  | 1.00               | 0.95               | 1.03               | 1.36                |
| PIMA, x = 10.2 cm | 2.1                  | 1.00               | 1.07               | 1.32               | 1.24                |
| PIMA, x = 10.2 cm | 2.0                  | 1.00               | 0.97               | 1.14               | 1.24                |
| PIMA, x = 10.2 cm | 1.0                  | 1.00               | 1.28               | 1.27               | 1.54                |
| PIMA, x = 10.2 cm | 1.0                  | 1.00               | 1.03               | 1.34               | 1.65                |
| PIMA, x = 10.2 cm | 0.5                  | 1.00               | 1.08               | 1.49               | 1.12                |
| PIMA, x = 10.2 cm | 0.5                  | 1.00               | 1.00               | 1.50               | 1.28                |

Initial COD = 3,360 mg/L as O<sub>2</sub>

**Experiment No. 22, COD results**

| Process           | Dose of Iron<br>in g | C / C <sub>0</sub> |
|-------------------|----------------------|--------------------|--------------------|--------------------|--------------------|
|                   |                      | 0 hrs              | 2 hrs              | 6 hrs              | 16 hrs             |
| IMA, x = 10.2 cm  | 1.9                  | 1.00               | 0.96               | 1.12               | 1.05               |
| UV, x = 10.2 cm   | 0.0                  | 1.00               | 1.00               | 1.12               | 1.29               |
| PIMA, x = 10.2 cm | 2.1                  | 1.00               | 1.01               | 1.03               | 1.13               |
| PIMA, x = 10.2 cm | 2.0                  | 1.00               | 1.01               | 1.15               | 1.23               |
| PIMA, x = 10.2 cm | 1.0                  | 1.00               | 1.05               | 1.31               | 1.19               |
| PIMA, x = 10.2 cm | 1.0                  | 1.00               | 1.00               | 1.12               | 1.10               |
| PIMA, x = 10.2 cm | 0.5                  | 1.00               | 1.09               | 1.52               | 1.07               |
| PIMA, x = 10.2 cm | 0.5                  | 1.00               | 1.08               | 1.23               | 1.17               |

Initial COD = 5,170 mg/L as O<sub>2</sub>

**Experiment No. 23, COD results**

| Process           | Dose of Iron<br>in g | C / C <sub>0</sub> |
|-------------------|----------------------|--------------------|--------------------|--------------------|--------------------|
|                   |                      | 0 hrs              | 2 hrs              | 6 hrs              | 16 hrs             |
| IMA, x = 10.2 cm  | 2.1                  | 1.00               | 0.95               | *                  | 0.95               |
| UV, x = 10.2 cm   | 0.0                  | 1.00               | 0.97               | 1.50               | 1.05               |
| PIMA, x = 10.2 cm | 2.0                  | 1.00               | 0.94               | 1.25               | 0.99               |
| PIMA, x = 10.2 cm | 2.0                  | 1.00               | 0.87               | 0.94               | 0.84               |
| PIMA, x = 10.2 cm | 1.1                  | 1.00               | 0.92               | 1.01               | 0.99               |
| PIMA, x = 10.2 cm | 1.0                  | 1.00               | 0.87               | 0.89               | 0.85               |
| PIMA, x = 10.2 cm | 0.5                  | 1.00               | 0.93               | 0.96               | 0.88               |
| PIMA, x = 10.2 cm | 0.5                  | 1.00               | 0.95               | 1.00               | 0.86               |

\* Sample was lost during the measurement.  
Initial COD = 2,950 mg/L as O<sub>2</sub>

### Experiment No. 19, Conductivity results

| Process           | C / C <sub>0</sub> |
|-------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
|                   | 0 hr               | 2 hrs              | 4 hrs              | 6 hrs              | 10 hrs             | 16 hrs             |
| IMA, x = 10.2 cm  | 1.00               | 1.09               | 0.94               |                    | 0.81               |                    |
| IMA, x = 10.2 cm  | 1.00               | 1.20               |                    | 1.14               |                    | 1.05               |
| UV, x = 10.2 cm   | 1.00               | 0.90               | 1.16               |                    | 1.16               |                    |
| UV, x = 10.2 cm   | 1.00               | 1.07               |                    | 1.03               |                    | 1.04               |
| PIMA, x = 10.2 cm | 1.00               | 1.59               | 0.97               |                    | 1.35               |                    |
| PIMA, x = 10.2 cm | 1.00               | 1.04               |                    | 1.04               |                    | *                  |
| PIMA, x = 10.2 cm | 1.00               | 1.13               |                    | 0.98               |                    | 1.08               |
| PIMA, x = 10.2 cm | 1.00               | 1.23               |                    | 1.01               |                    | 1.04               |

\* Sample was lost during the measurement.  
Initial Conductivity = 51,250  $\mu\text{S}/\text{cm}^2$

### Experiment No. 20, Conductivity results

| Process           | C / C <sub>0</sub> |
|-------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
|                   | 0 hr               | 2 hrs              | 4 hrs              | 6 hrs              | 10 hrs             | 16 hrs             |
| IMA, x = 10.2 cm  | 1.00               | 0.91               | 0.95               |                    | 0.97               |                    |
| IMA, x = 10.2 cm  | 1.00               | 1.03               |                    | 0.91               |                    | 0.71               |
| UV, x = 10.2 cm   | 1.00               | 0.88               | 0.96               |                    | 1.00               |                    |
| UV, x = 10.2 cm   | 1.00               | 0.95               |                    | 0.75               |                    | 0.99               |
| PIMA, x = 10.2 cm | 1.00               | 0.92               |                    | 0.94               |                    | 1.13               |
| PIMA, x = 10.2 cm | 1.00               | 0.96               |                    | 0.99               |                    | 0.91               |
| PIMA, x = 10.2 cm | 1.00               | 0.93               | 0.97               |                    | 1.01               |                    |
| PIMA, x = 10.2 cm | 1.00               | 0.93               |                    | 0.91               |                    | 1.22               |

Initial Conductivity = 41,585  $\mu\text{S}/\text{cm}^2$

### Experiment No. 22, Conductivity results

| Process           | Dose of Iron<br>in g | C / C <sub>0</sub> |
|-------------------|----------------------|--------------------|--------------------|--------------------|--------------------|
|                   |                      | 0 hrs              | 2 hrs              | 6 hrs              | 16 hrs             |
| IMA, x = 10.2 cm  | 1.9                  | 1.00               | 1.29               | 1.32               | 1.38               |
| IMA, x = 10.2 cm  | 0.0                  | 1.00               | 1.21               | 1.33               | 1.31               |
| UV, x = 10.2 cm   | 2.1                  | 1.00               | 1.24               | 1.34               | 1.38               |
| UV, x = 10.2 cm   | 2.0                  | 1.00               | 1.21               | 1.28               | 1.32               |
| PIMA, x = 10.2 cm | 1.0                  | 1.00               | 1.26               | 1.37               | 1.41               |
| PIMA, x = 10.2 cm | 1.0                  | 1.00               | 1.26               | 1.34               | 1.42               |
| PIMA, x = 10.2 cm | 0.5                  | 1.00               | 1.29               | 1.32               | 1.28               |
| PIMA, x = 10.2 cm | 0.5                  | 1.00               | 1.30               | 1.19               | 1.34               |

Initial Conductivity = 41,250  $\mu\text{S}/\text{cm}^2$

**Experiment No. 23, Conductivity results**

| Process           | Dose of Iron<br>in g | C / C <sub>0</sub> |
|-------------------|----------------------|--------------------|--------------------|--------------------|--------------------|
|                   |                      | 0 hrs              | 2 hrs              | 6 hrs              | 16 hrs             |
| IMA, x = 10.2 cm  | 2.1                  | 1.00               | 0.82               | 0.79               | 0.81               |
| IMA, x = 10.2 cm  | 0.0                  | 1.00               | 0.82               | 0.77               | 0.81               |
| UV, x = 10.2 cm   | 2.0                  | 1.00               | 0.83               | 0.76               | 0.81               |
| UV, x = 10.2 cm   | 2.0                  | 1.00               | 0.85               | 0.80               | 0.83               |
| PIMA, x = 10.2 cm | 1.1                  | 1.00               | 0.81               | 0.81               | 0.84               |
| PIMA, x = 10.2 cm | 1.0                  | 1.00               | 0.81               | 0.85               | 0.83               |
| PIMA, x = 10.2 cm | 0.5                  | 1.00               | 0.73               | 0.83               | 0.82               |
| PIMA, x = 10.2 cm | 0.5                  | 1.00               | 0.88               | 0.83               | 0.78               |

Initial Conductivity = 41,335 µS/cm<sup>2</sup>

**Experiment No. 19, TDS results**

| Process           | C / C <sub>0</sub> |
|-------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
|                   | 0 hr               | 2 hrs              | 4 hrs              | 6 hrs              | 10 hrs             | 16 hrs             |
| IMA, x = 10.2 cm  | 1.00               | 1.02               | 0.95               |                    | 0.76               |                    |
| IMA, x = 10.2 cm  | 1.00               | 1.14               |                    | 1.14               |                    | 1.02               |
| UV, x = 10.2 cm   | 1.00               | 0.89               | 1.14               |                    | 1.43               |                    |
| UV, x = 10.2 cm   | 1.00               | 1.02               |                    | 1.02               |                    | 1.02               |
| PIMA, x = 10.2 cm | 1.00               | 1.52               | 1.02               |                    | 1.33               |                    |
| PIMA, x = 10.2 cm | 1.00               | 1.02               |                    | 1.08               |                    | *                  |
| PIMA, x = 10.2 cm | 1.00               | 1.05               |                    | 1.02               |                    | 1.08               |
| PIMA, x = 10.2 cm | 1.00               | 1.14               |                    | 1.02               |                    | 1.02               |

\* Sample was lost during the measurement.  
Initial TDS = 26,250 mg/L

**Experiment No. 20, TDS results**

| Process           | C / C <sub>0</sub> |
|-------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
|                   | 0 hr               | 2 hrs              | 4 hrs              | 6 hrs              | 10 hrs             | 16 hrs             |
| IMA, x = 10.2 cm  | 1.00               | 0.96               | 0.96               |                    | 0.96               |                    |
| IMA, x = 10.2 cm  | 1.00               | 0.96               |                    | 0.72               |                    | 0.88               |
| UV, x = 10.2 cm   | 1.00               | 0.80               | 0.84               |                    | 0.96               |                    |
| UV, x = 10.2 cm   | 1.00               | 0.96               |                    | 0.88               |                    | 0.96               |
| PIMA, x = 10.2 cm | 1.00               | 0.96               |                    | 0.84               |                    | 1.08               |
| PIMA, x = 10.2 cm | 1.00               | 0.96               |                    | 0.88               |                    | 1.04               |
| PIMA, x = 10.2 cm | 1.00               | 0.88               | 0.96               |                    | 0.88               |                    |
| PIMA, x = 10.2 cm | 1.00               | 0.88               |                    | 0.96               |                    | 1.12               |

Initial TDS = 20,885 mg/L

**Experiment No. 21, TDS results**

| Process           | Dose of Iron<br>in g | C / C <sub>0</sub> |
|-------------------|----------------------|--------------------|--------------------|--------------------|--------------------|
|                   |                      | 0 hrs              | 2 hrs              | 6 hrs              | 16 hrs             |
| IMA, x = 10.2 cm  | 2.1                  | 1.00               | 0.83               | 1.00               | 1.00               |
| UV, x = 10.2 cm   | 0.0                  | 1.00               | 0.94               | 0.94               | 1.00               |
| PIMA, x = 10.2 cm | 2.1                  | 1.00               | 1.00               | 1.00               | 1.06               |
| PIMA, x = 10.2 cm | 2.0                  | 1.00               | 1.00               | 1.00               | 1.00               |
| PIMA, x = 10.2 cm | 1.0                  | 1.00               | 1.00               | 1.00               | 2.13               |
| PIMA, x = 10.2 cm | 1.0                  | 1.00               | 0.94               | 1.06               | 1.92               |
| PIMA, x = 10.2 cm | 0.5                  | 1.00               | 0.92               | 1.08               | 1.33               |
| PIMA, x = 10.2 cm | 0.5                  | 1.00               | 0.92               | 1.00               | 1.00               |

Initial TDS = 20,000 mg/L

**Experiment No. 22, TDS results**

| Process           | Dose of Iron<br>in g | C / C <sub>0</sub> |
|-------------------|----------------------|--------------------|--------------------|--------------------|--------------------|
|                   |                      | 0 hrs              | 2 hrs              | 6 hrs              | 16 hrs             |
| IMA, x = 10.2 cm  | 1.9                  | 1.00               | 1.07               | 1.01               | 1.01               |
| UV, x = 10.2 cm   | 0.0                  | 1.00               | 1.01               | 1.01               | 1.01               |
| PIMA, x = 10.2 cm | 2.1                  | 1.00               | 1.01               | 0.91               | 1.08               |
| PIMA, x = 10.2 cm | 2.0                  | 1.00               | 1.01               | 0.96               | 1.01               |
| PIMA, x = 10.2 cm | 1.0                  | 1.00               | 1.01               | 1.07               | 1.07               |
| PIMA, x = 10.2 cm | 1.0                  | 1.00               | 1.01               | 1.07               | 1.01               |
| PIMA, x = 10.2 cm | 0.5                  | 1.00               | 1.01               | 1.01               | 1.01               |
| PIMA, x = 10.2 cm | 0.5                  | 1.00               | 1.01               | 1.01               | 1.01               |

Initial TDS = 31,250 mg/L

**Experiment No. 23, TDS results**

| Process           | Dose of Iron<br>in g | C / C <sub>0</sub> |
|-------------------|----------------------|--------------------|--------------------|--------------------|--------------------|
|                   |                      | 0 hrs              | 2 hrs              | 6 hrs              | 16 hrs             |
| IMA, x = 10.2 cm  | 2.1                  | 1.00               | 0.94               | 0.94               | 0.94               |
| UV, x = 10.2 cm   | 0.0                  | 1.00               | 0.94               | 0.92               | 0.94               |
| PIMA, x = 10.2 cm | 2.0                  | 1.00               | 0.92               | 0.88               | 0.94               |
| PIMA, x = 10.2 cm | 2.0                  | 1.00               | 0.92               | 0.94               | 0.88               |
| PIMA, x = 10.2 cm | 1.1                  | 1.00               | 0.88               | 0.88               | 0.94               |
| PIMA, x = 10.2 cm | 1.0                  | 1.00               | 0.88               | 0.92               | 0.94               |
| PIMA, x = 10.2 cm | 0.5                  | 1.00               | 0.75               | 0.94               | 0.94               |
| PIMA, x = 10.2 cm | 0.5                  | 1.00               | 0.92               | 0.88               | 0.94               |

Initial TDS = 20,000 mg/L

### Experiment No. 19, BOD<sub>5</sub> results

| Process           | $C / C_0$ | $C / C_0$ |
|-------------------|-----------|-----------|
|                   | 0 hr      | 16 hrs    |
| UV, x = 10.2 cm   | 1.00      | 1.29      |
| PIMA, x = 10.2 cm | 1.00      | 1.01      |

Initial BOD<sub>5</sub> = 510 mg/L as O<sub>2</sub>

### Experiment No. 20, BOD<sub>5</sub> results

| Process           | $C / C_0$ | $C / C_0$ |
|-------------------|-----------|-----------|
|                   | 0 hr      | 16 hrs    |
| UV, x = 10.2 cm   | 1.00      | 0.99      |
| PIMA, x = 10.2 cm | 1.00      | 0.80      |

Initial BOD<sub>5</sub> = 666 mg/L as O<sub>2</sub>

### Experiment No. 23, BOD<sub>5</sub> results

| Process           | $C / C_0$ | $C / C_0$ |
|-------------------|-----------|-----------|
|                   | 0 hr      | 16 hrs    |
| PIMA, x = 10.2 cm | 2.0       | 1.30      |
| PIMA, x = 10.2 cm | 1.0       | 1.17      |
| PIMA, x = 10.2 cm | 0.5       | 1.34      |

Initial BOD<sub>5</sub> = 96 mg/L as O<sub>2</sub>

**Experiment No. 19, Ammonia results**

| Process           | $C / C_0$ |
|-------------------|-----------|-----------|-----------|-----------|-----------|
|                   | 0 hr      | 2 hrs     | 4 hrs     | 10 hrs    | 16 hrs    |
| IMA, x = 10.2 cm  | 1.00      | 1.04      | 1.02      | 1.01      |           |
| UV, x = 10.2 cm   | 1.00      | 1.06      | 0.99      | 1.04      |           |
| UV, x = 10.2 cm   | 1.00      |           |           |           | 0.96      |
| PIMA, x = 10.2 cm | 1.00      | 0.96      | 1.04      | 0.98      |           |
| PIMA, x = 10.2 cm | 1.00      |           |           |           | 0.96      |
| PIMA, x = 10.2 cm | 1.00      |           |           |           | 0.96      |

Initial Ammonia = 1,000 mg/L as NH<sub>3</sub>-N

**Experiment No. 20, Ammonia results**

| Process           | $C / C_0$ |
|-------------------|-----------|-----------|-----------|-----------|-----------|
|                   | 0 hr      | 2 hrs     | 4 hrs     | 10 hrs    | 16 hrs    |
| IMA, x = 10.2 cm  | 1.00      | 1.03      | 1.02      | 1.03      |           |
| UV, x = 10.2 cm   | 1.00      | 1.00      | 1.01      | 0.98      |           |
| PIMA, x = 10.2 cm | 1.00      | 0.94      | 1.02      | 1.02      |           |
| PIMA, x = 10.2 cm | 1.00      |           |           |           | 0.92      |
| PIMA, x = 10.2 cm | 1.00      |           |           |           | 0.97      |

Initial Ammonia = 1,040 mg/L as NH<sub>3</sub>-N

**Experiment No. 21, Ammonia results**

| Process           | Dose of Iron<br>in g | $C / C_0$ | $C / C_0$ | $C / C_0$ | $C / C_0$ |
|-------------------|----------------------|-----------|-----------|-----------|-----------|
|                   |                      | 0 hrs     | 2 hrs     | 6 hrs     | 16 hrs    |
| IMA, x = 10.2 cm  | 2.1                  | 1.00      | 1.06      | 1.03      | 1.21      |
| UV, x = 10.2 cm   | 0.0                  | 1.00      | 1.09      | 1.18      | 1.08      |
| PIMA, x = 10.2 cm | 2.1                  | 1.00      | 1.18      | 1.18      | 1.08      |
| PIMA, x = 10.2 cm | 2.0                  | 1.00      | 1.15      | 1.15      | 1.00      |
| PIMA, x = 10.2 cm | 1.0                  | 1.00      | 1.11      | 0.92      | 1.17      |
| PIMA, x = 10.2 cm | 1.0                  | 1.00      | 1.02      | 1.15      | 1.76      |
| PIMA, x = 10.2 cm | 0.5                  | 1.00      | 1.12      | 1.14      | 1.12      |
| PIMA, x = 10.2 cm | 0.5                  | 1.00      | 0.90      | 1.14      | 0.72      |

Initial Ammonia = 805 mg/L as NH<sub>3</sub>-N

**Experiment No. 22, Ammonia results**

| Process           | Dose of Iron<br>in g | C / C <sub>0</sub> |
|-------------------|----------------------|--------------------|--------------------|--------------------|--------------------|
|                   |                      | 0 hrs              | 2 hrs              | 6 hrs              | 16 hrs             |
| IMA, x = 10.2 cm  | 1.9                  | 1.00               | 1.11               | 0.94               | 1.06               |
| UV, x = 10.2 cm   | 0.0                  | 1.00               | 0.96               | 0.65               | 1.06               |
| PIMA, x = 10.2 cm | 2.1                  | 1.00               | 1.19               | 0.95               | 0.96               |
| PIMA, x = 10.2 cm | 2.0                  | 1.00               | 1.07               | 0.93               | 1.07               |
| PIMA, x = 10.2 cm | 1.0                  | 1.00               | 1.07               | 0.97               | 1.00               |
| PIMA, x = 10.2 cm | 1.0                  | 1.00               | 0.95               | 0.65               | 0.97               |
| PIMA, x = 10.2 cm | 0.5                  | 1.00               | 0.96               | 1.05               | 1.08               |
| PIMA, x = 10.2 cm | 0.5                  | 1.00               | 0.99               | 0.80               | 1.00               |

Initial Ammonia = 1,215 mg/L as NH<sub>3</sub>-N

**Experiment No. 23, Ammonia results**

| Process           | Dose of Iron<br>in g | C / C <sub>0</sub> |
|-------------------|----------------------|--------------------|--------------------|--------------------|--------------------|
|                   |                      | 0 hrs              | 2 hrs              | 6 hrs              | 16 hrs             |
| IMA, x = 10.2 cm  | 2.1                  | 1.00               | 1.04               | 0.95               | 1.02               |
| UV, x = 10.2 cm   | 0.0                  | 1.00               | 0.95               | 0.98               | 0.88               |
| PIMA, x = 10.2 cm | 2.0                  | 1.00               | 1.03               | 0.95               | 0.95               |
| PIMA, x = 10.2 cm | 2.0                  | 1.00               | 1.02               | 0.73               | 0.95               |
| PIMA, x = 10.2 cm | 1.1                  | 1.00               | 1.00               | 0.90               | 0.90               |
| PIMA, x = 10.2 cm | 1.0                  | 1.00               | 0.88               | 1.02               | 0.92               |
| PIMA, x = 10.2 cm | 0.5                  | 1.00               | 0.92               | 0.94               | 0.84               |
| PIMA, x = 10.2 cm | 0.5                  | 1.00               | 0.84               | 0.75               | 0.79               |

Initial Ammonia = 930 mg/L as NH<sub>3</sub>-N

**Experiment No. 19, Lead results**

| <b>Process</b>    | <b>C / C<sub>0</sub></b> | <b>C / C<sub>0</sub></b> |
|-------------------|--------------------------|--------------------------|
|                   | 0 hr                     | 16 hrs                   |
| IMA, x = 10.2 cm  | 1.00                     | 1.3333                   |
| PIMA, x = 10.2 cm | 1.00                     | 1.0926                   |

Initial Lead = 0.00540 mg/L

**Experiment No. 20, Lead results**

| <b>Process</b>    | <b>C / C<sub>0</sub></b> | <b>C / C<sub>0</sub></b> |
|-------------------|--------------------------|--------------------------|
|                   | 0 hr                     | 16 hrs                   |
| IMA, x = 10.2 cm  | 1.00                     | < 0.92                   |
| UV, x = 10.2 cm   | 1.00                     | < 0.92                   |
| PIMA, x = 10.2 cm | 1.00                     | < 0.92                   |

Initial Lead = 0.00250 mg/L

**Experiment No. 22, Lead results**

| <b>Process</b>    | <b>Dose of Iron<br/>in g</b> | <b>C / C<sub>0</sub></b> | <b>C / C<sub>0</sub></b> |
|-------------------|------------------------------|--------------------------|--------------------------|
|                   |                              | 0 hrs                    | 16 hrs                   |
| IMA, x = 10.2 cm  | 1.9                          | 1.00                     | 0.138                    |
| UV, x = 10.2 cm   | 0.0                          | 1.00                     | 1.690                    |
| PIMA, x = 10.2 cm | 2.1                          | 1.00                     | 0.141                    |
| PIMA, x = 10.2 cm | 2.0                          | 1.00                     | 0.324                    |
| PIMA, x = 10.2 cm | 1.0                          | 1.00                     | 0.069                    |
| PIMA, x = 10.2 cm | 1.0                          | 1.00                     | 0.128                    |
| PIMA, x = 10.2 cm | 0.5                          | 1.00                     | 0.152                    |
| PIMA, x = 10.2 cm | 0.5                          | 1.00                     | 0.248                    |

Initial Lead = 0.00290 mg/L

**Experiment No. 23, Lead results**

| <b>Process</b>    | <b>Dose of Iron<br/>in g</b> | <b>C / C<sub>0</sub></b> | <b>C / C<sub>0</sub></b> |
|-------------------|------------------------------|--------------------------|--------------------------|
|                   |                              | 0 hrs                    | 16 hrs                   |
| IMA, x = 10.2 cm  | 2.1                          | 1.00                     | 0.571                    |
| UV, x = 10.2 cm   | 0.0                          | 1.00                     | 0.138                    |
| PIMA, x = 10.2 cm | 2.0                          | 1.00                     | 0.524                    |
| PIMA, x = 10.2 cm | 2.0                          | 1.00                     | 0.219                    |
| PIMA, x = 10.2 cm | 1.1                          | 1.00                     | < 0.042                  |
| PIMA, x = 10.2 cm | 1.0                          | 1.00                     | < 0.042                  |
| PIMA, x = 10.2 cm | 0.5                          | 1.00                     | < 0.042                  |
| PIMA, x = 10.2 cm | 0.5                          | 1.00                     | 0.905                    |

Initial Lead = 0.00210 mg/L