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**Aerated Recirculation and Pressurized Suspended Fiber Biofiltration  
for the Treatment of Landfill Leachate**

October 31, 2014

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# FINAL REPORT

November 1, 2013 to October 31, 2014

**PROJECT TITLE:** Aerated Recirculation and Pressurized Suspended Fiber Biofiltration for the Treatment of Landfill Leachate

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**KEY WORDS:** Aeration, Recirculation, Landfill Leachate, Organic, Ammonia, Chloride, Biofiltration, and Suspended Fiber.

## **ABSTRACT** (1 page only)

Recirculating leachate appears to be one of the least expensive methods for partial treatment and disposal of landfill leachate at properly designed and operated landfill sites. The leachate recirculation not only improves the leachate quality, but also shortens the time required for landfill stabilization. In addition, aerated leachate recirculation may bring air into the landfill, leading to aerobic degradation of organic compounds and precipitation of heavy metals. Aerated recirculation also promotes nitrification, which makes it possible to remove nitrogen through denitrification after oxygen is consumed at the bottom part of the landfill. Although aerated leachate recirculation has these advantages, leachate is only partially treated. The leachate must be further treated in order to meet the discharge requirements. In this research, aerated recirculation and pressurized suspended fiber biofiltration were tested for the treatment of leachate from landfills in Northwest Florida. The pressurized suspended fiber biofilter was configured to allow biological contact oxidation, a novel and efficient treatment process for enhanced organic and iron removal. In between aerated leachate recirculation and pressurized suspended fiber biofiltration, ammonium and chloride in the leachate were removed through denitrification and the ultra-high lime with aluminum process. From this research, the best operation parameters were identified for leachate recirculation, denitrification, the ultra-high lime with aluminum process, and pressurized suspended fiber biofiltration operations. Cost and space saving were analyzed and compared with that of the conventional aerobic activated sludge systems.

**Metrics:**

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

<b>Last name, first name</b>	<b>Rank</b>	<b>Department</b>	<b>Professor</b>	<b>Institution</b>
WeijieXie	M.S.	Civil and Environmental Engineering	Gang Chen	Florida State University
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Boya Wang	M.S.	Civil and Environmental Engineering	Gang Chen	Florida State University

2. List undergraduate researchers working on this Hinkley Center project

<b>Last name, first name</b>	<b>Department</b>	<b>Professor</b>	<b>Institution</b>
Emily Nabong	Civil and Environmental Engineering	Gang Chen	Florida State University

3. List research publications resulting from this Hinkley Center project

Wang, B., Grasel, P., Millington, G., Hallas, J., Ahmad, H. and Chen, G. “Aerated Recirculation and Pressurized Suspended Fiber Biofiltration for the Treatment of Landfill Leachate”, Environ. Technol. To be submitted (2014).

4. List research presentations resulting from this Hinkley Center project

Lee, Y. and Chen, G. “Aerated Recirculation and Pressurized Suspended Fiber Biofiltration for the Treatment of Landfill Leachate”. 99th Annual American Society of Microbiology Southeastern Branch Conference, Auburn, AL. Nov 7, 2013.

5. How have the research results from this Hinkley Center project been leveraged to secure additional research funding?

“Advanced Oxidation, Recirculation and Pressurized Suspended Fiber Biofiltration for the Treatment of Landfill Leachate” by Gang Chen and Kamal Tawfiq has been submitted to Environmental Research and Education Foundation in response to Environmental Research and Education Foundation Issues Targeted Request for Proposals: High Need Topics in Solid Waste Research.

6. What new collaborations were initiated based on this Hinkley Center project?

We have initiated collaboration with John Hallas from Talquin Electric Cooperative, Inc. and Hafiz Ahmad from Florida State University at Panama City Campus from this research.

7. How have the results from this Hinkley Center funded project been used (not will be used) by the FDEP or other stakeholders? (1 paragraph maximum).

We share the results with FDEP through TAG members of Gary Millington, FDEP Subsection Manager, and Peter Grasel, who is in charge of ground water modeling and monitoring and old landfills. In addition, we discuss the results with Talquin Electric

Cooperative, Inc., which operates seven wastewater treatment plants, as well as managers of Leon County Solid Waste Facility and Springhill Landfill.

## **EXECUTIVE SUMMARY**

November 1, 2013 to October 31, 2014

**PROJECT TITLE:** Aerated Recirculation and Pressurized Suspended Fiber Biofiltration for the Treatment of Landfill Leachate

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**AFFILIATION:** Department of Civil and Environmental Engineering, FAMU-FSU College of Engineering

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**PROJECT TAG MEMBERS:** Peter Grasel, Gary Millington, John Hallas, Brian Lee Moody, Hafiz Ahmad and Tarek Abichou

**COMPLETION DATE:** October 31, 2014

### **Objective:**

In this research, leachate from landfills in Northwest Florida was treated by aerated recirculation, denitrification, the ultra-high lime with aluminum process, and suspended fiber biofiltration. The suspended fiber biofilter was designed and operated under pressurized aeration conditions to achieve biological contact oxidation, which can remove organic compounds and iron more efficiently. The specific objectives of this research project include:

1. Aerated Leachate Recirculation. A laboratory scale experiment apparatus was set up to simulate aerated landfill leachate recirculation. Organic compound decomposition and heavy metal removal were investigated and recirculation ratio and aeration levels were tested.

2. Denitrification and the Ultra-High Lime with Aluminum Process. A denitrification reaction tank and an ultra-high lime with aluminum process reactor were arranged in between aerated leachate recirculation and pressurized suspended fiber biofiltration. Ammonium and chloride removal was examined by means of denitrification and the ultra-high lime with aluminum process.

3. Pressurized Suspended Fiber Biofiltration. A custom-made pressurized suspended fiber biofilter was set up and tested for organic and iron removal by biological contact oxidation. Factors that may impact this process such as dissolved oxygen and alkalinity were explored for this part of research.

4. System Optimization and Cost Analysis. The best operation parameters were identified for aerated leachate recirculation, denitrification, the ultra-high lime with aluminum process, and pressurized suspended fiber biofiltration. Cost and space saving

were analyzed and compared with that of conventional treatment processes and reported in this research.

### **Methodology:**

Landfill leachate recirculation can improve the leachate quality and shorten the time required for landfill stabilization from several decades to 2 - 3 years. However, after recirculation, more efficient treatment methods are required to further treat the leachate in order to meet the discharge requirements. Pressurized suspended fiber biofiltration can remove organic compounds and heavy metals more efficiently than conventional biological methods through biological contact oxidation. Especially, the biological contact oxidation has extreme advantages in iron removal by fixing iron onto the filter media. Consequently, there is minimal ferric iron suspending in the solution that can escape the filter. Besides organic contaminants and heavy metals, landfill leachate also contains high concentrations of ammonium and chloride, which are released from hydrolysis of proteins of the solid waste and ashes of waste-to-energy processes. To efficiently remove ammonium and chloride, denitrification and the ultra-high lime with aluminum process can be arranged in between aerated leachate recirculation and pressurized suspended fiber biofiltration. The combined aerated leachate recirculation and pressurized suspended fiber biofiltration, together with denitrification and the ultra-high lime with aluminum process provide a new alternative means for the treatment of landfill leachate with high organic, nitrogen, chloride and iron contents.

### **Results:**

At a recirculation cycle of 4, 50% of the treated leachate was aerated and re-circulated back and the other 50% of the treated leachate was further treated in a pressurized fiber biofilter after denitrification and the ultra-high lime with aluminum process. In this research, variable dissolved oxygen concentrations from 3.0 mg/L to 6.0 mg/L were tested in the recirculation reactor for enhanced organic decomposition and ammonium oxidation. To ensure the ammonium in the landfill leachate was completely oxidized to nitrate during aerated leachate recirculation and before the landfill leachate was introduced to denitrification reactor, a dissolved oxygen level of 5.0 mg/L was maintained. At this dissolved oxygen level, nearly all of the ammonium in the landfill leachate was oxidized to nitrate. Denitrification was a function of input nitrogen and hydraulic loading of the denitrification reactor. A higher input nitrogen level displayed a greater removal in the denitrification reactor. Chloride removal was a function of pH. With the increase of pH, chloride removal was enhanced accordingly. At pH of 7, around 30% chloride was removed. However, at pH of 8, the removal rate increased to 55%; at pH of 10, the removal reached 95%. Finally, COD of the landfill leachate can achieve as low as 8 mg/L and iron can be as low as 0.02 mg/L after the final treatment by the pressurized fiber biofiltration.

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# 1. Introduction

## 1.1 Leachate Recirculation

Landfilling is widely adopted as one of the most economical processes of solid waste disposal. At the same time, landfill leachate is a great environmental concern because of its complex composition and high contaminant concentrations (Ragle et al., 1995). Landfill leachate is the liquid generated from the moisture associated with the solid waste deposited in the landfill cell, which mainly is created when infiltrating rainwater dissolves contaminants within the landfill waste and seeps out the bottom of the landfill cell into the leachate collection system. To prevent/reduce pollution of the natural environment, biological treatment, adsorption using various adsorbents, precipitation, ion exchange, coagulation-flocculation, chemical and electrochemical oxidation, and reverse osmosis are the common treatment processes for the landfill leachate (Coban et al., 2012; Renou et al., 2008; Wintheiser, 1998). Recirculating leachate appears to be one of the least expensive methods for partial treatment and disposal of leachate at properly designed and operated landfill sites (Figure 1) (Reinhart and AlYousfi, 1996; Yang et al., 2012). Through leachate recirculation, organic contents and heavy metals can be significantly reduced. It has been reported that up to 84% BOD, 86% COD, 90% iron and manganese can be removed after 4 months' recirculation (Figure 2) (Bilgili et al., 2007; Martins et al., 2010). It should be noted that COD values in Figure 2 would increase at the beginning of the operations owing to release and hydrolysis of organic waste in the landfill. The leachate recirculation not only improves the leachate quality, but also shortens the time required for landfill stabilization from several decades to 2 – 3 years. There are different methods and designs to recirculate leachate, which include spraying the leachate onto the working face, digging ponds or trenches into the landfill and filling them with leachate, and installing subsurface leach fields or injection wells. Mixing of leachate with an absorbent material and disposing of the mixture in the landfill has also been practiced.

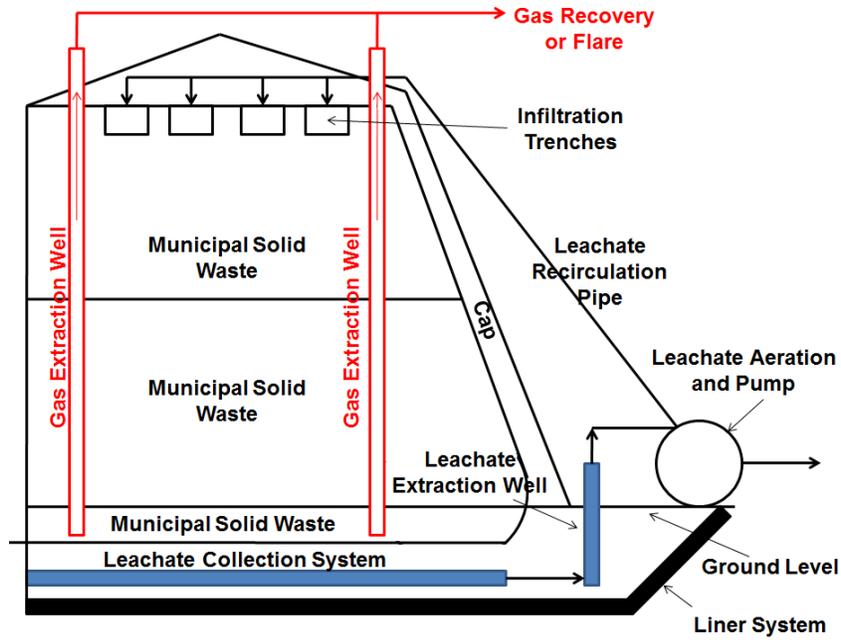


Figure 1. Landfill Leachate Recirculation Operations

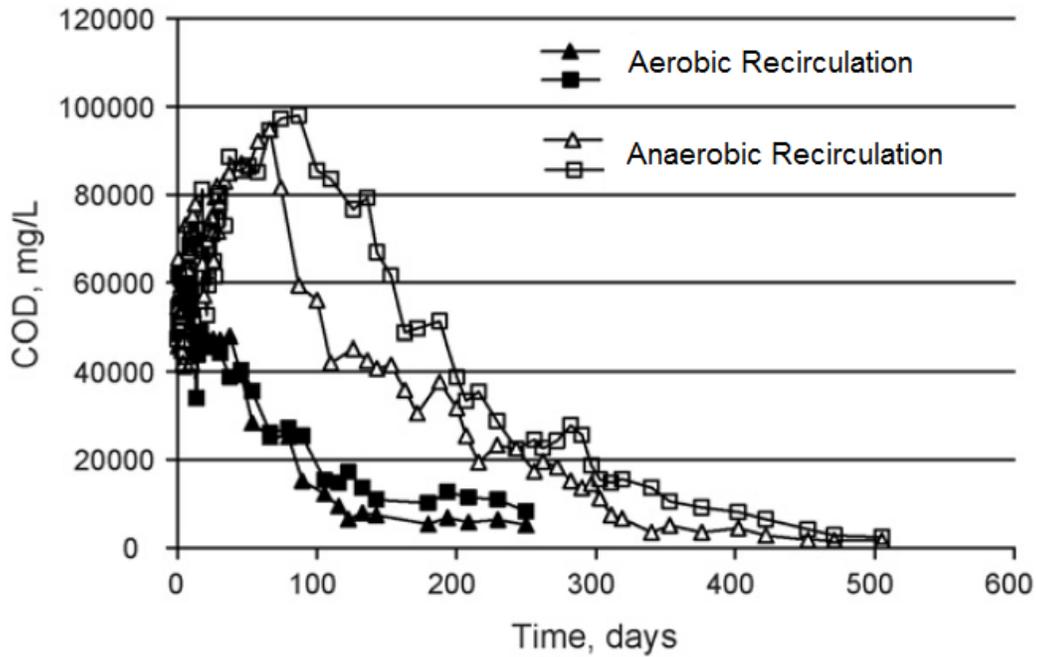
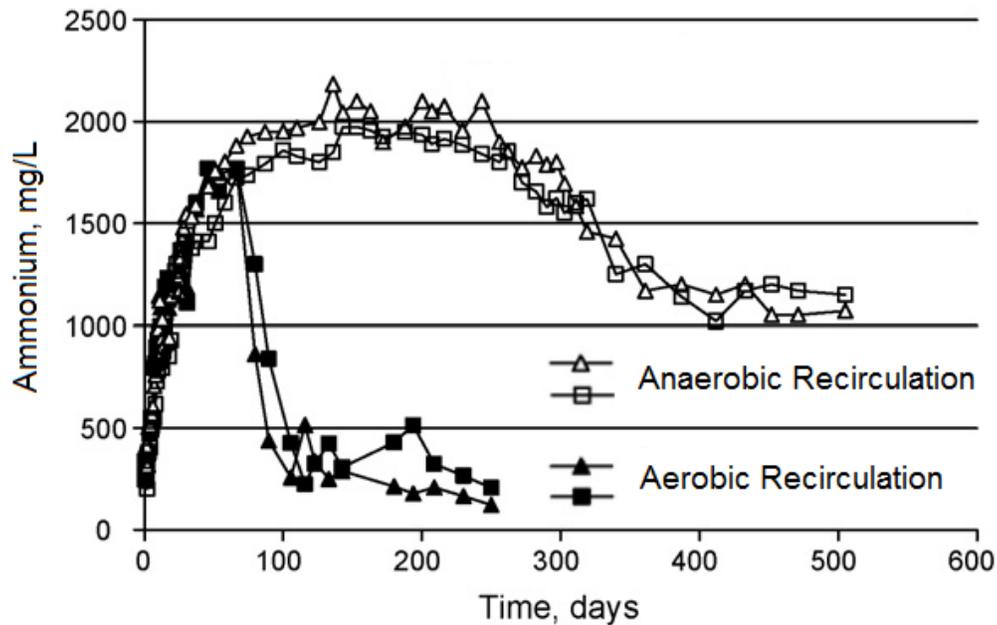


Figure 2. COD Removal after Leachate Recirculation

The biological reactions during leachate recirculation are basically anaerobic. However, aerobic conditions may prevail if the recirculated leachate is aerated. Recently, increased interest has been focused on introducing air into the waste mass for aerobic degradation of solid wastes since aerobic processes have been promoted as a method for accelerating solid waste stabilization. Studies of aerobic biodegradation processes have demonstrated that the organic parts of the refuse can be degraded in a relatively shorter time when compared with those of anaerobic degradation processes (Figure 2) (Bilgili et al., 2007; Nikolaou et al., 2010). The concept of aerobic degradation by introducing air into a landfill presents significant alternatives in waste management both for existing and new systems. In addition to promotion of aerobic organic decomposition, aerated recirculation can also help iron precipitation as well as nitrogen nitrification. In Northwest Florida, high concentrations of iron have been observed in the landfill leachate, which is believed to be released to the landfill leachate from iron-rich soil owing to changes in pH and redox conditions induced by organic waste decomposition. Therefore, aerated leachate recirculation has obvious benefits in this region. With depleting carbonaceous organic compounds in the leachate, nitrifying microorganisms are able to thrive where nitrification will readily occur. The main source of nitrogen in the landfill leachate is ammonium, which is released from the hydrolysis of proteins. The release of ammonium in the landfill continues over a long period of time when compared with that of carbon compounds since the hydrolysis of the polypeptide chains is energetically disadvantaged. Through nitrification, ammonium is oxidized to nitrate, which can be removed from the landfill through denitrification under anoxic conditions at the bottom part of the landfill. Just like COD, ammonium would increase at the beginning of the operations owing to the hydrolysis of polypeptide chains (Figure 3) (Bilgili et al., 2007).

It is obvious ammonium is oxidized during aerobic recirculation. However, for anaerobic recirculation, ammonium oxidation was not significant. Although aerated leachate recirculation has above advantages, leachate is only partially treated through aerobic recirculation. The leachate must be further treated in order to meet the discharge requirements. Especially, since leachate is partially treated after aerated recirculation, more efficient treatment methods are required to further treat the leachate.



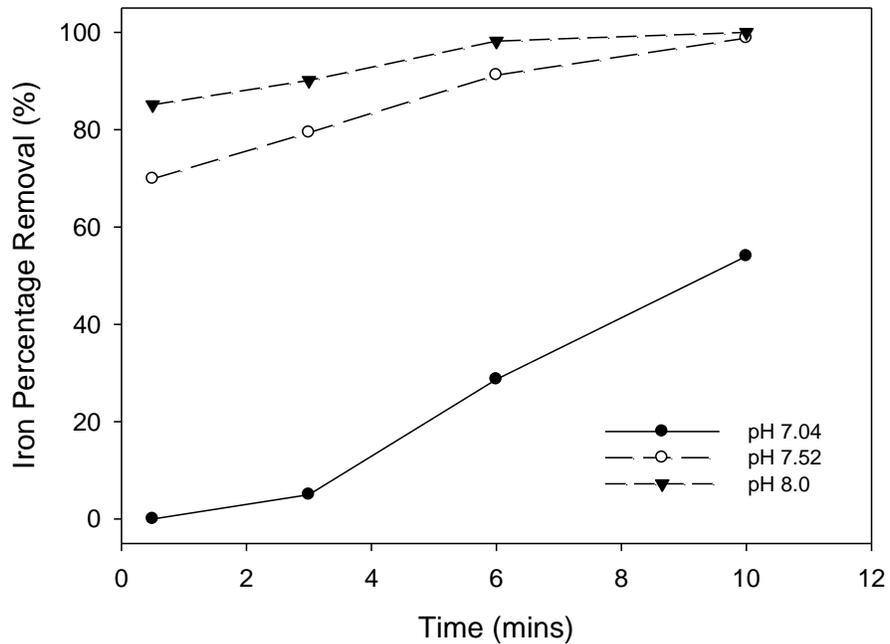
**Figure 3. Ammonia Removal after Leachate Recirculation**

## 1.2 Aerated Biofiltration of Landfill Leachate

The biological treatment of wastewater with a biofilter is among the oldest and most well characterized technologies. The biological aerated filter — a wastewater treatment technology developed in the 1980s, is similar to a traditional filter in many ways, but also possesses several advantages over conventional wastewater treatment technologies, such as activated sludge and feed water filtration (Ramadori et al., 2006). These systems have also been described as intermittent (medium) filters, packed bed filters (PBFs), trickling filters (TFs), attached growth processes, and fixed film processes. The fundamental components of a biofilter system include: (1) a medium upon which a microbial community (biofilm) develops, (2) a container or excavated pit to house the medium, (3) a system for applying the water to be treated to the medium, and (4) a system for collection and distribution of the treated water. The characteristics of the filtering medium dictate, to a large degree, the biological aerated filter performance. Popular filtering media include sand, macadam, slag, coke, anthracite coal, zeolite and

bioceramsite, etc. Zeolite and bioceramsite have certain advantages, including a rough surface, large adsorptive capacity and long-term resistance to degradation, which make them two of the most widely utilized filtering media (Ilies and Mavinic, 2001).

During biofiltration operations, the growth of microorganisms develops biofilms on the medium surfaces and the microorganisms in the biofilms absorb soluble and colloidal waste materials in the wastewater as it percolates over the medium surfaces. The adsorbed materials are incorporated into a new cell mass or degraded under aerobic conditions to carbon dioxide and water. The BOD can nearly be completely removed if the wastewater retention time in the media is sufficiently long for the microorganisms to absorb wastewater constituents. Besides organic removal, biofilter can also achieve other functions. In our prior research, we used mulch as the biofilter medium for the removal of iron from landfill leachate. After biofiltration, above 80% of iron was removed when the aerated groundwater passed through the biofilter at pH 8.0 (Figure 4).



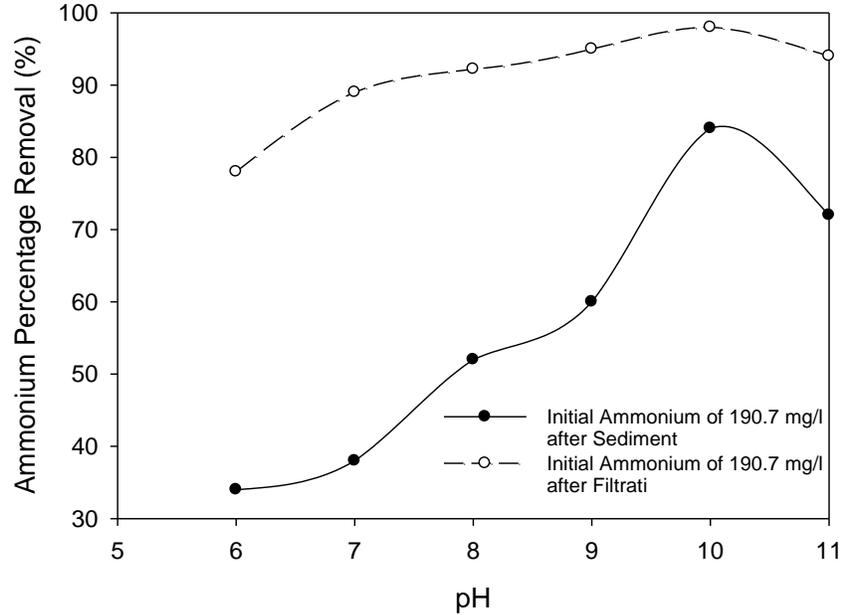
**Figure 4. Iron Removal in a Mulch Biofilter**

At pH 7.52, above 70% was removed. However, at pH 7.04, less than 50% was removed. The iron removal seemed not to be a function of the input iron concentration, but a function of pH. The higher the pH, more iron was removed. The dependence of iron removal with pH was related to the iron transformation. At high pH, iron tended to be existing in the form of ferric iron, consequently, ferric hydroxide was formed, which can be easily precipitated and filtered out during the bilfiltration process.

During the operation of aerated biofiltration, besides physical processes such as straining and sedimentation that remove suspended solids within the pores of the media, chemical adsorption of pollutants onto the medium surfaces also plays a finite role in the removal of some chemical constituents (e.g., phosphorus). Using goethite-coated silica sand, we have also demonstrated that biofiltration can be used to remove phosphorous from landfill leachate. We performed phosphorus adsorption experiments after ammonium removal by magnesium ammonium phosphate (MAP,  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$  or struvite) precipitation (Tunay et al., 2004). For landfill leachate treatment, phosphorus removal usually follows nitrogen removal. Therefore, we first evaluated ammonium removal by MAP precipitation. For MAP precipitation, pH had a great influence on landfill leachate ammonium removal, i.e., ammonium removal increased with the increase of pH until pH increased to 10; after pH 10, ammonium removal decreased with the increase of pH. After MAP precipitation, the treated leachate passed through a goethite-coated silica sand filter for phosphorous removal. For landfill leachate with an initial ammonium content of 190.7 mg/l, the maximum ammonium removal achieved 84% after sedimentation and 98% after filtration at pH 10 (Figure 5). pH impacted ammonium removal since it determined MAP solubility. Although  $\text{H}^+$  concentration did not directly enter the ion-activity product equation,  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$  precipitation was highly pH dependent because the activities of both  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  were pH dependent (Nelson et al., 2003).

In addition to ammonium removal, MAP precipitation also helped the removal of some other pollutants such as suspended solids and heavy metals. The filtration process after MAP precipitation ensured the formed MAP that did not settle in the sedimentation tank was removed. In addition, the filter with goethite-coated silica sand serving as the

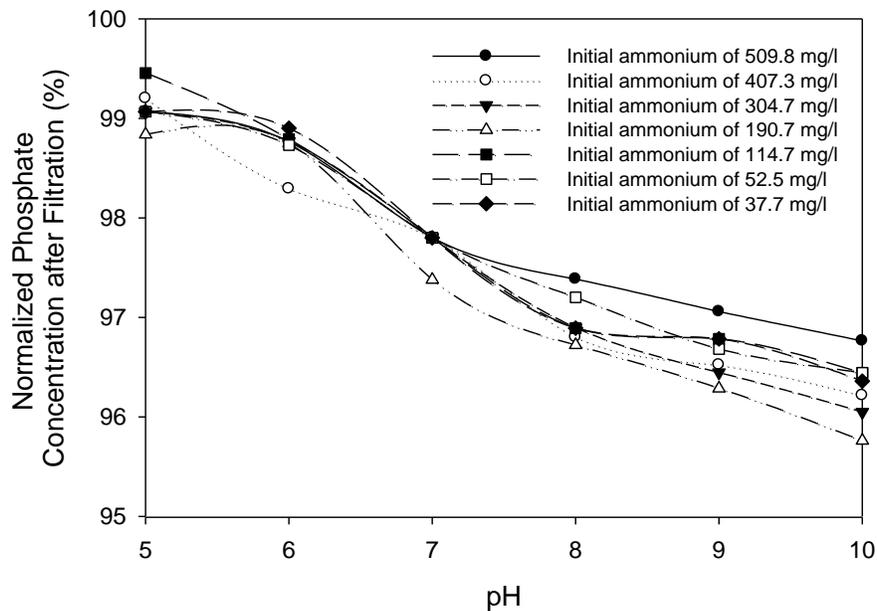
filtering medium removed the phosphorous in the effluent, which was especially important when excess  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  was added. When low dose of  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$



**Figure 5. Ammonium Removal by MAP Precipitation**

was added, no phosphorous was observed after filtration. However, when high dose of  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  was added, phosphorous was able to escape the filter. At  $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-} = 1:1:1.2$ , the effluent was measured for phosphorous concentration under different pH conditions. Phosphorous was found to escape the filter, which was a function of solution pH. Phosphorous concentration in the effluent increased with the increase of pH, i.e., the higher the pH, more phosphorous escaped the filter (Figure 6). Therefore, a low pH was preferred for phosphorous adsorption in goethite-coated silica sand. Chemical adsorption could occur throughout the medium bed; however, adsorption sites in the media were usually limited. The capacity of the media to retain ions depended on the target constituent, pH, and the mineralogy of the media. Phosphorous was one element of concern in wastewater that could be removed in this manner. The mechanism of phosphate adsorption onto goethite-coated silica sand was generally dominated by ligand exchange in which two singly coordinated hydroxyl groups or water molecules were

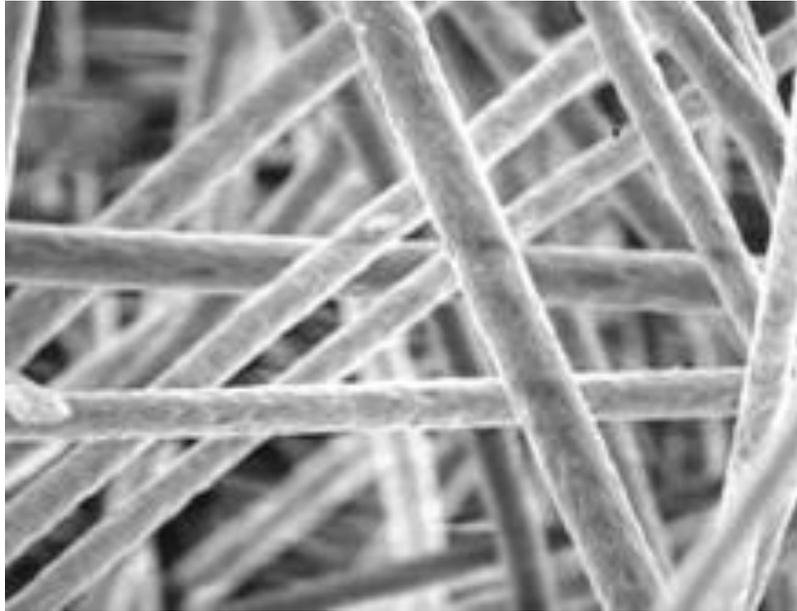
replaced by a single phosphate anion, resulting in the formation of a bidentate, binuclear complex (Bond and Lovley, 2003; Holmes et al., 2004; Tunay et al., 2004). Since  $H_2O$  was a more mobile ligand than  $OH^-$ , sorption was therefore favored at lower pH. Four key characteristics that impacted phosphorus adsorption on the goethite surface included the easiness of hydroxyl release, the specificity toward binding sites, hysteresis, and the surface charges (Bond and Lovley, 2003; Holmes et al., 2004). After adsorption, the phosphate surface complexes were very stable and resulted in slow exchange rates and an apparent irreversibility (hysteresis) of phosphorus adsorption.



**Figure 6. Phosphorous Removal after Biofiltration**

Recently, polypropylene fibers have been utilized as biofilter media (Figure 7) (Cheung et al., 1997; Marti et al., 2008; Nelson et al., 2003). The orientation of fibers in the filters can be categorized as axially aligned, layered and random. Axially aligned biofilters have fibers lying parallel to the direction of flow. Layered biofilters have fibers randomly oriented in the plane normal to the flow direction and the random biofilter have fibers randomly distributed in all three directions. Among the three, axially aligned biofilters are most commonly utilized. These biofilters can be operated in single-pass or multi-pass configurations. In single-pass systems, the hydraulic loading rate (HLR) is equal to the

volume of wastewater per unit time applied to the biofilter medium. The most common expression for the HLR is gallons of wastewater applied per ft<sup>2</sup> of biofilter surface area per day (gal/ft<sup>2</sup>·d).

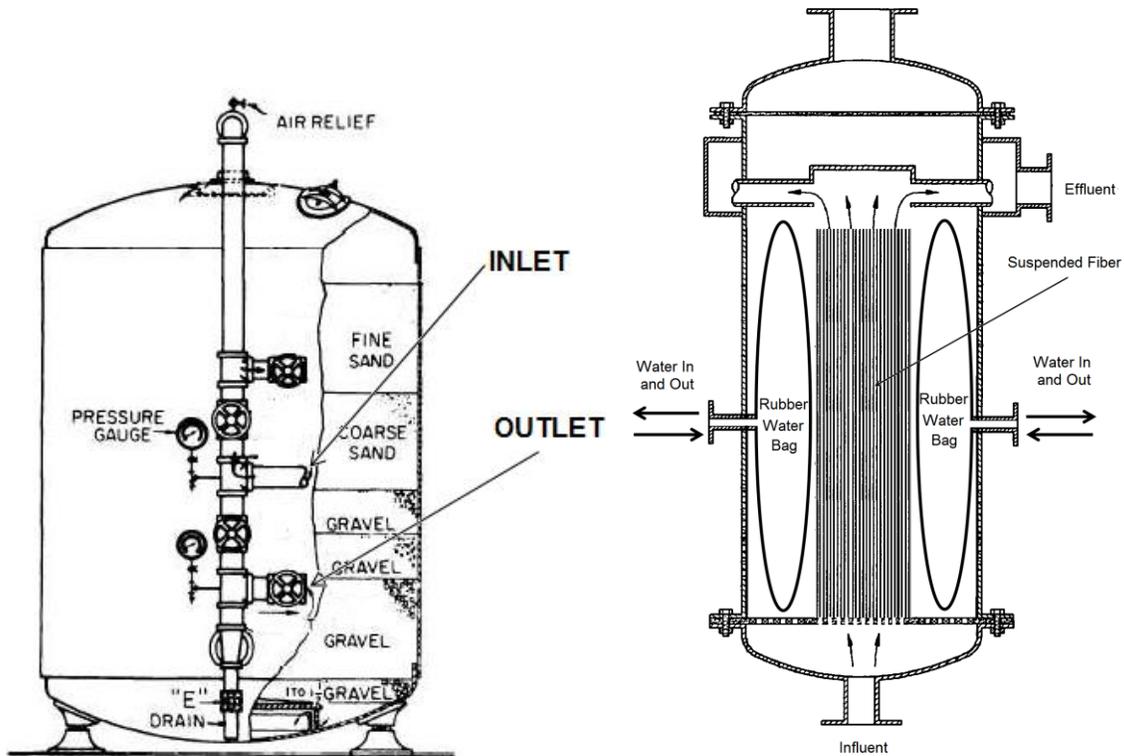


**Figure 7. Microscopic Image of Polypropylene Fiber**

### **1.3 Pressurized Fiber Biofiltration**

Pressurized filters can efficiently achieve the filtration function with limited space and high efficiency (Figure 7) (Ozturk et al., 2003). Vessels of pressurized filters are made to American Society of Mechanical Engineers (ASME) code standards and pressurized filters can operate as stand-alone systems, or combined with other treatment processes. A variety of conventional filtration media can be used in pressurized filters, i.e., activated carbon media in any one of several grades and mesh sizes, etc. Pressurized filters have been utilized in iron and manganese removal from iron-rich groundwater using oxidative media. These iron and manganese removal systems offer a proven, efficient approach of iron and manganese removal. The usage of these systems reduces the chemical feed demand for iron and manganese oxidation. Additionally, these systems can be designed to eliminate the need for backwash storage tanks and backwash pumps through a self-

generated backwash process. When combined with aeration, the pressurized filters achieve three processes, i.e., aeration, oxidation and filtration in a single unit. As a cost-



**Figure 8. Conventional Pressurized Sand Filter (Left) and Pressurized Suspended Fiber Biofilter (Right)**

and space-saving technology, pressurized suspended fiber biofilters have been used for drinking water and wastewater treatment (Figure 8) (Lee et al., 2008). The pressurized suspended filter pore space (and subsequently the retention time) can be adjusted by injecting or retrieving water to or from the water bags, which offers the flexibility to achieve different filtration functions. In addition, the usage of pressurized suspended fiber filters as biofilters have other obvious advantages. For instance, suspended fibers provide a tremendous amount of surface areas in a small volume. Therefore, microorganisms can grow around the fibers at a density of greater than  $1 \times 10^8$  cells per ml, the only means to culture cells at in vivo-like cell density (Chaiprasert et al., 2003). Another advantage of the pressurized suspended fiber filtration is that the oxygen transfer

barrier can be overcome and consequently significantly increased dissolved oxygen level can be achieved. Prior studies have demonstrated that BOD and COD removal increases with the increase of pressure when the pressure is raised up to 6 bar in a laboratory scale rotating biological contactor (Ellis et al., 1992). As an innovative technology for wastewater treatment, the pressurized suspended fiber biofilters also makes biological contact oxidation possible, which can significantly improve BOD and COD removal and decrease the sludge yield. For iron removal, contact oxidation is achieved by microbial mediated iron oxidation and fixation during which ferrous iron is oxidized to ferric iron and fixed onto the filter media. Consequently, there is minimal ferric iron suspending in the solution that can escape the filter.

#### **1.4 Chloride Removal Consideration**

Besides organic contaminants, nutrients and heavy metals, high concentrations of chloride have also been observed in several landfills. For instance, some small counties that have waste-to-energy plants are often unable to use local wastewater treatment plants to dispose the leachate due to high concentrations of chloride in the leachate. These high concentrations of chloride get to the landfills by ashes. The average chloride concentration in landfill leachate is approximately 600 mg/l and the secondary drinking water standard for chloride is 250 mg/l. The elevated concentrations of chloride pose significant challenges to the beneficial waste-to-energy process. If this issue cannot be resolved, the environmental impact of waste-to-energy technology may outweigh the benefits. Chloride tends to percolate and cause surface salt formation and soil alkalinity increase, thereby resulting in loss of soil (Chan et al., 1980). A variety of techniques have been investigated for the removal of chloride, which include ion exchange, reverse osmosis, and norecure, etc. (Ferreira et al., 2004). However, these techniques, though effective, are not feasible from the cost perspective. Therefore, it is the need of time to come up with novel and low cost treatment methods to remove chloride from landfill leachate. As an innovative technology, the ultra-high lime with aluminum process can remove chloride efficiently (Abdel-Wahab and Batchelor, 2006). For this technology, chloride is removed as calcium chloroaluminate [ $\text{Ca}_4\text{Al}_2\text{Cl}_2(\text{OH})_{12}$ ] through precipitation in the presence of calcium and aluminum at high pH. The solubility product ( $K_{sp}$ ) values

of the precipitates of different formula are listed in Table 1 (Birnin-Yauri and Glasser, 1998). In this research, the ultra-high lime with aluminum process will be incorporated into the treatment process for chloride removal. Similarly as MAP precipitation, the micro-flocs of  $\text{Ca}_4\text{Al}_2\text{Cl}_2(\text{OH})_{12}$  precipitate that cannot settle in the sedimentation will be removed in the pressurized suspended fiber biofilter.

**Table 1. Solubility and Free Energy of Precipitate Formula of Calcium Chloroaluminate**

$K_{sp}$	$\text{Log}K_{sp}$ (Observed)	$\text{Log}K_{sp}$ Calculated	$\Delta G$ (293K) (kJ/mol)
$[\text{Ca}^{2+}]^4[\text{Al}(\text{OH})_4]_2[\text{Cl}^-]^2[\text{OH}^-]^4$	-23.476	-24.768	-147.1
$[\text{Ca}^{2+}]^4[\text{Al}(\text{OH})_4]^{1.96}[\text{Cl}^-]^2[\text{OH}^-]^{4.04}$	-25.308	-24.662	-147.1
$[\text{Ca}^{2+}]^4[\text{Al}(\text{OH})_4]^{1.42}[\text{Cl}^-]^2[\text{OH}^-]^{4.58}$	-24.487	-24.785	-146.0
$[\text{Ca}^{2+}]^4[\text{Al}(\text{OH})_4]^{1.34}[\text{Cl}^-]^2[\text{OH}^-]^{4.66}$	-24.467	-24.581	-147.2
$[\text{Ca}^{2+}]^4[\text{Al}(\text{OH})_4]^{1.04}[\text{Cl}^-]^2[\text{OH}^-]^{4.96}$	-24.449	-24.701	-147.7
$[\text{Ca}^{2+}]^4[\text{Al}(\text{OH})_4]^{0.88}[\text{Cl}^-]^2[\text{OH}^-]^{5.12}$	-24.611	-24.799	-147.3
$[\text{Ca}^{2+}]^4[\text{Al}(\text{OH})_4]^{0.86}[\text{Cl}^-]^2[\text{OH}^-]^{5.14}$	-24.768	-24.065	-148.8

## 1.5 Objectives

Landfill operators seek alternatives that can be applied and managed at a low cost, and can be efficient enough to fulfill landfill operation requirements. Currently, the science of bio-energy, featuring wide-ranging fermentation of materials, clear mechanism, simple process and suitable extension of the resources has established its active role in landfill leachate treatment. Landfills are often located in regions where high levels of pollutant removal are required due to the sensitivity of receiving waters. Space constraints may limit the construction of large retention ponds or wetlands, and hence more effective contaminant removal techniques are required. Therefore we argue for the introduction of filter systems using reactive media prepared from natural minerals or from by-products of steel production, such as blast-furnace slag. Such filters could be a possible solution for

the removal of metals and could be used as a pre-treatment step before leachate handling for nitrogen removal in a constructed wetland (Kietlińska, 2003). Filter materials saturated with heavy metals have to be replaced and safely stored. An alternative method could be to leach out the metals with acids under controlled conditions and subsequently concentrate the leachate for further work.

In this research, leachate from landfills in Northwest Florida was treated by aerated recirculation, denitrification, the ultra-high lime with aluminum process, and suspended fiber biofiltration. The suspended fiber biofilter was designed and operated under pressurized aeration conditions to achieve biological contact oxidation, which removed organic compounds and iron more efficiently. The pressurized suspended fiber biofiltration, a cost- and space-saving technology, combined with aerated leachate recirculation, denitrification, and the ultra-high lime with aluminum process, provided a new alternative means for the treatment of landfill leachate with high organic, ammonium, chloride and iron contents. The treatability studies of this research also indicated that the leachate was biologically and physicochemically treatable. The specific objectives of this research project include:

1. Aerated Leachate Recirculation. A laboratory scale experiment apparatus was set up to simulate aerated landfill leachate recirculation. Organic compound decomposition and heavy metal removal was investigated and recirculation ratio and aeration level were tested.

2. Denitrification and the Ultra-High Lime with Aluminum Process. A denitrification reaction tank and the ultra-high with aluminum process reaction tank were arranged in between aerated leachate recirculation and pressurized suspended fiber biofiltration. Ammonium and chloride removal were examined by means of nitrification/denitrification and the ultra-high lime with aluminum process.

3. Pressurized Suspended Fiber Biofiltration. A custom-made pressurized suspended fiber biofilter was set up and tested for organic and iron removal by biological contact oxidation. Factors that may impact this process such as dissolved oxygen and alkalinity were explored for this part of research.

4. System Optimization and Cost Analysis. The best operation parameters were identified for aerated leachate recirculation, denitrification, the ultra-high lime with aluminum process, and pressurized suspended fiber biofiltration. Cost and space saving was analyzed and compared with that of conventional treatment processes and reported in this research.

## 2. Background

### 2.1 Iron Problems in Northwest Florida

Nearby the landfills of Northwest Florida, elevated levels of iron and arsenic, especially iron observations had been made in the groundwater from monitoring wells downgradient of the landfills, which was attributed to the geomicrobial iron and arsenic reduction (Wang et al., 2012). In Florida, soils are mainly composed of Myakka, an acid soil characterized by a subsurface accumulation of humus and Al(III) and Fe(III) oxides. In Northwest Florida, iron content is much higher than the rest of the state with a range of 20 to 200 mg/g soil (Williams et al., 2012). In the subsurface soil, iron exists in the form of Fe(III) oxides. When reducing conditions occur, iron reducing bacteria can reduce various forms of Fe(III)-oxides and generate and release large concentrations of soluble Fe(II). Researchers have discovered that *Shewanella* and *Geobacter* species are capable of conserving energy for growth with the structure Fe (III) bound in smectite clay as the sole electron acceptor (Kostka et al., 2002). Iron reducing bacteria require strict anaerobic conditions and simple organic electron donors, such as acetate, lactate, formate, etc. In addition, the reduction process generates alkalinity. It is also known that iron reducing bacteria can compete with other reducing bacteria such as sulfate reducing bacteria for the same electron donors under specific physicochemical conditions and the predominance of one group over the other can drastically impact the geochemistry of the system. Usually, the activity of both iron reducing bacteria and sulfate reducing bacteria has a greater buffering effect than the iron reducing bacteria alone. The production of sulfide is also greater in the iron reducing bacteria and sulfate reducing bacteria systems, whereas the release of Fe(II) is not necessarily linked to the activity of the iron reducing bacteria. Sulfate reducing bacteria growth does not appear to be a function of the type of electron donors in the systems, but the presence of both iron reducing bacteria and sulfate reducing bacteria limit the growth of iron reducing bacteria in the acetate systems, suggesting that iron reducing bacteria cannot compete with sulfate reducing bacteria when acetate is the only electron donor present.

It has been demonstrated that a pure culture of *Shewanella oneidensis* strain MR-1 as well as enrichment cultures of iron reducing bacteria are capable of conserving energy for growth with the sole electron acceptor being the structure Fe (III) bound in smectite clay:



The above reaction is an important discovery since most of the iron on earth exists in the form of silicate minerals or iron oxides. In addition, initial evidence indicates that a heterogeneous population of *Bacillus* species and *Pseudomonas* species can both contribute to iron reducing (Emde et al., 1992; Ganesh et al., 1997). Inside the landfills, geochemical evidence suggests that the primary terminal electron acceptors for organic matter decomposition are nitrate, Fe (III), sulfate, and carbon dioxide (Caccavo et al., 1992; Reeburgh, 1983). It is frequently reported that there are distinct zones in the landfills in which the metabolism of organic matter is coupled to the reduction of only one of these electron acceptors at any one time (Froelich et al., 1979). Environments in which microorganisms oxidize organic matter with Fe (III) as the sole electron acceptor can only be established if the microorganisms gain energy for maintenance and growth from these reactions (Balashova and Zavarzin, 1979; Senior, 1995). Reducing of Fe (III) by *Bacillus* species and *Pseudomonas* species during growth on organic substrates have also been reported (Lee et al., 2007; Lovley, 1987, 1995; Zavarzina, 2004). The sulfate reduction process is frequently linked to anaerobic iron oxidation processes, which should be directly responsible for groundwater iron contamination (Dinh et al., 2004, Hamilton, 2003; Lee et al., 1995). Two iron oxidation mechanisms, indirect mechanism and direct mechanism, which may occur simultaneously at different extents, are involved in the sulfate reduction process (Dinh et al., 2004).

## 2.2 Landfill as a Bioreactor

In areas where sufficient land is available, sanitary landfill technique is widely used for the disposal of municipal solid wastes. Nevertheless of economic benefits, there are a number of environmental shortcomings related to the sanitary landfill method, one of which is the generation of landfill leachate. Landfill leachate characteristics in terms of quality and quantity are site-specific and vary from one site to the other. The

characterization of leachate provides important information necessary of the design and operation of leachate treatment facilities. Leachate is a very complex liquid that may contain high concentrations of biodegradable and non-biodegradable organic matter, ammonia nitrogen ( $\text{NH}_3\text{-N}$ ), phosphate, heavy metals, sulfide, hardness, acidity, alkalinity etc. Landfill leachate treatment thus represents a portion of the broader nexus between treatment efficiency and treatment costs. Collecting, treating, and discharging landfill leachate to acceptable permit standards requires well-designed and operated treatment facilities. Many methods that are currently used to treat leachate may have several drawbacks. Conventional landfill leachate treatments can be classified into three major groups: (a) leachate recycling/recirculation, (b) leachate aerobic and anaerobic degradation and (c) leachate chemical and physical treatment including chemical oxidation, adsorption, chemical precipitation, coagulation/flocculation, sedimentation/flotation and air stripping, etc. Leachate biological processes are effective for removing organic compounds but do remain inefficient due to large amounts of excessive sludge production, odor generation and high energy consumption. Chemical and physical methods as described above are commonly regarded as higher cost or lower effectiveness. Due to the increased enforcement of discharge regulation and escalating surcharges by public owned treatment works, many landfill leachate facilities are seeking alternative treatment means. Currently, leachate recirculation and use the existing landfill as a bioreactor is drawing more and more attention.

Making landfill a bioreactor for the treatment of leachate treatment is a proven technology for organics and ammonia removal in young and intermediate landfill leachate. This technology is based on biological leachate treatment, which has been carried out successfully for more than thirty years. As a new and promising trend in solid waste management, landfill as a bioreactor (bioreactor landfill) has been recognized as one of the lowest cost methods of leachate treatment. Bioreactor landfills are controlled systems in which moisture control and/or air injection are used as enhancements to create a solid waste environment capable of actively degrading the readily biodegradable organic fraction of the waste. There are many advantages associated with treating the landfill as a bioreactor, including the rapid reduction of biodegradable organic

compounds and heavy metals in leachate. Typical bioreactor landfill operation is to recycle leachate back through the tip, which has been largely used in the past decade because it was one of the least expensive options available [10]. Recently, related research has demonstrated benefits of this technique. It has been reported that leachate recirculation increases the moisture content in a controlled reactor system and provides the distribution of nutrients and enzymes between methanogens and solid/liquids. Significant lowering in methane production and COD was also observed when the recirculated leachate volume was 30% of the initial waste bed volume. The leachate recycle not only improves the leachate quality, but also shortens the time required for landfill stabilization from several decades to 2 - 3 years [53]. Although positive effects have been reported on leachate treatment, the recirculation rate may impact treatment efficiency of solid waste degradation. High recirculation rates may adversely affect anaerobic degradation of solid wastes in the landfills. For instance, leachate recirculation can lead to the inhibition of methanogenesis as it may cause high concentrations of organic acids ( $\text{pH} < 5$ ) which are toxic for the methanogens. Furthermore, if the volume of leachate recirculated is very high, problems such as saturation, ponding and acidic conditions may occur. Landfill as a bioreactor can be operated either under anaerobic conditions or aerobic conditions, both can be achieved by using different operation means. The main advantage of the anaerobic treatment processes is the low energy requirement, because no oxygen has to be supplied.

At the same time, challenges remain for landfill bioreactors, which include the persistence of ammonia-nitrogen in the leachate. Recirculating leachate increases the rate of ammonification and results in accumulation of higher levels of ammonia-nitrogen concentrations, even after the biodegradable organic fractions of the waste are removed. Concomitantly, although the biodegradability of leachate organic compounds declines with time, complex organic compounds such as humic substances and xenobiotic compounds, remain in solution. Thus, leachate, with time, will require a complex sequence of biological, physical, and chemical treatment processes to reach discharge limits. Ammonia removal from leachate is an important aspect in leachate treatment and nitrification is one of the most economical ways to remove ammonia from landfill

leachate. In the top regions of landfills, the leachate treatment of stable nitrification as a result of organic loading occurs under anoxic conditions. Inside the landfill, it is important to maintain a balance between the organic and nitrogen loads that result in a high nitrifier fraction in the biomass. Since nitrifiers have a relatively low cell yield, if there is a change in the available ammonia to biodegradable organic ratio, a shift in the biomass population can easily occur, making the nitrifier mass less adequate. The organic to ammonia ratio in the landfill leachate varies significantly as the leachate ages and this may cause poor performance in the nitrifying systems. Once ammonia is oxidized, nitrogen can be removed from landfill leachate through denitrification, which reduces nitrate to nitrogen gas. This usually happens at the bottom section of landfills, i.e., the denitrification zone. As the leachate ages, the ratio of biodegradable organic to nitrogen drops and external carbon sources such as methanol may be required to achieve higher degree of denitrification. Biological nutrient removal processes in landfills allow for lower operational cost for the leachate treatment.

### **2.3 Landfill Leachate Treatment by Biofiltration**

The high concentrations of organic matters, low biodegradability ratio, heavy metals,  $\text{NH}_3\text{-N}$ , and other pollutants in leachate clearly are the major factors that should be considered when choosing a suitable leachate treatment method. The actual composition of landfill leachate varies dramatically from landfills to landfills. Even within the same landfill, the composition varies over time. Leachate characteristics present high variation due to several factors such as the composition of the solid waste, site hydrology, compaction, cover design, and waste age, etc. New technologies are emerging or introduced for the treatment of landfill leachate. The most noticeable one is the introduction of attached-growth biomass systems, which were introduced due to the problems of sludge bulking or inadequate separability in conventional aerobic systems. These treatment technologies take advantage of biofilm and present the advantage of increased contact areas of active biomass with the contaminants. In addition, nitrification is less affected at low temperatures in attached-growth systems than in suspended-growth systems, and by inhibition due to high nitrogen content. As one of these attached growth systems, trickling filters have been investigated for the biological nitrogen removal for

municipal landfill leachate. Trickling filters remain an interesting and attractive option for nitrification due to low-cost filter media. Moving-bed biofilm reactor (MBBR) (or suspended-carrier biofilm reactor (SCBR) or fluidized bed reactor) is another type of attached-growth biomass systems, which is based on the use of suspended porous polymeric carriers, kept in continuous movement in the aeration tank, while the active biomass grows as a biofilm on the surfaces of them. Main advantages of this method compared to conventional suspended-growth processes include: higher biomass concentrations, no long sludge-settling periods, lower sensitivity to toxic compounds, and both organic and high ammonia removals in a single process. Considering the advantage of anaerobic leachate treatment, anaerobic filters have also been practiced in landfill leachate treatment. The anaerobic filter is a high rate system that gathers the advantages of other anaerobic systems and minimizes the disadvantages. In an up-flow anaerobic filter, biomass is retained as biofilms on support material, such as plastic rings. A hybrid bed filter consists on an up-flow sludge blanket at the bottom and an anaerobic filter on top. This device acts as a gas–solid separator and enhances solid’s retention without causing channeling or short-circuiting. Enhanced performances of such a process result from maximization of the biomass concentration in the reactor. For xenobiotic compound removal, fluidized bed reactors, which combine biodegradation and adsorption processes, have also been practiced. Biological activated carbon fluidized bed process is proven to be much more effective for treating old landfill leachate than the conventional ones such as activated sludge and fixed film processes. Finally, to reduce the treatment costs, constructed wetland, have been explored, especially for nitrogen removal or hybrid systems for both nitrogen and heavy metal treatment.

Among these attached-growth biomass systems, biofiltration has the most promising potential for landfill leachate treatment. For heavy metal removal, several low-cost filter materials have been investigated (Bailey et al., 1999), which could be included in the systems based on filter-bed techniques (Kängsepp et al., 2003). For ammonium removal, experiments have been performed with zeolites to assess their sorption of ammonium nitrogen (Papadopoulos et al., 1996; Demir et al., 2002). For both heavy metal and nitrogen removal from landfill leachate, three filter media, sand, blast-furnace slag (BFS)

and polonite have been investigated, which is based on the determination of contaminant saturation potential of heavy metals and nitrogen in a long-term column study. This method can provide a good indicator of capacity of the filter material to retain elements, which could serve as a parameter for estimating the lifetime of full-scale systems (cf. Ajmal et al., 2001; Drizo et al., 2002). The results demonstrated that these filter media can achieve the treatment goals to different extents. Pressurized biofilters can further enhance contaminant removal from landfill leachate, which have been practiced for organic and inorganic chemicals removal, radiological removal, iron and manganese control, water softening, pH adjustment, etc. Typically, pressurized biofilters are used for the removal of iron and manganese. Greensand filters can also be configured as pressurized filters for the removal of arsenic. Pressurized filters can be used with a variety of conventional filtration media in cylindrical pressurized vessels.

In addition, oxidative media (for iron and manganese removal) and activated carbon media can be used in variable grades and mesh sizes in the pressurized biofilters. Pressurized biofilters are made to ASME code standards in certified fabrication facilities and are in many respects similar to conventional rapid filters (Figure 9). The main differences are that the media is contained in a pressurized vessel (such as a steel tank) and that they are operated under pressure provided by means of a pump or high-pressure water source on the influent side rather than gravity. The high energy requirement of conventional landfill leachate treatment are demanding for the alternative treatment technology which will be cost effective and require less energy for its efficient operation. Pretreatment, such as oxidation, has been introduced before the biofiltration to enhance removal of the contaminants. Therefore, the main parameters controlling the efficiency of biofiltration are linked to leachate quality, filter medium characteristics (medium type, grain size, distribution coefficient, age and general conditions) and operation (hydraulic loading). The addition of pretreatment chemicals may be done under pressure depending on the system configuration. Pressurized biofilters are constructed in vertical or horizontal configurations. Vertical pressurized biofilters are generally used for smaller plants because the design offers the flexibility of incremental plant expansion and the

ability to easily isolate a single filter cell. Horizontal pressurized biofilters typically are used for larger plants since their layout maximizes filter area and minimizes footprint.



**Figure 9. Pressurized Filters for Large-Quantity Treatment**

#### **2.4 Iron Removal by Biofiltration**

There are numerous techniques used for iron removal. These include aeration, softening, chlorination, ozonation and filtration. Aeration is the most commonly practiced method. For the filtration technique, the common media used are activated carbon and clay. The use of limestone for removing metals was also found to be effective (Aziz, 1992, Aziz, 1997, Aziz & Smith, 1992, Aziz & Smith, 1996, Aziz & Modh, 1998, Othman & Aziz, 1999, Othman et al., 1999a, Othman et al., 1999b, Aziz et al., 2000 and Aziz et al., 2001). More than 80% of heavy metals such as iron and others can be removed using a batch or continuous flow filtration process. Some of the removal mechanisms have been established. For example, adsorption has been proposed as iron removal mechanisms. Besides adsorption, iron oxidizing bacteria are also responsible for iron removal. In the landfills, the rate of bacterial mediation of ferrous iron oxidation increases as pH

decreases. Microbial mediated iron oxidation rates begin to exceed chemical oxidation rates at around pH 3.5 to 4. The microbial mediated rate of iron oxidation is roughly two to three orders of magnitude faster than the abiotic oxidation by oxygen at pH 2. Both abiotic and biotic rates tend to increase with increasing temperature. The chemolithotrophic prokaryotes of our interest are *Acidithiobacillus ferrooxidans* (or *Thiobacillus ferrooxidans*) and *Leptospirillum ferrooxidans*, which are known to enhance acid production in metal-leaching environments by oxidizing  $\text{Fe}^{2+}$  and replenishing the oxidant  $\text{Fe}^{3+}$ . Acid-leaching environments support a diverse range of iron- and sulfur-oxidizing chemolithotrophs as well as heterotrophic microorganisms. It has been demonstrated by fluorescent in situ hybridization (FISH) that *A. ferrooxidans* and *L. ferrooxidans* are not the predominant microorganisms responsible for iron oxidation. It was found that *A. ferrooxidans* was prominent in higher pH solutions. Some of the main physiological characteristics are known for these or related organisms. For example, some *Leptospirillum* are chemolithoautotrophs that gain energy by iron oxidation, while some *Leptospirillum* groups are autotrophic, oxidizing iron for energy. *Acidimicrobium* species are iron-oxidizing, heterotrophic bacteria.

### **3. Materials and Methods**

#### **3.1 Landfill Leachate, Soil Sample Collection and Characterization**

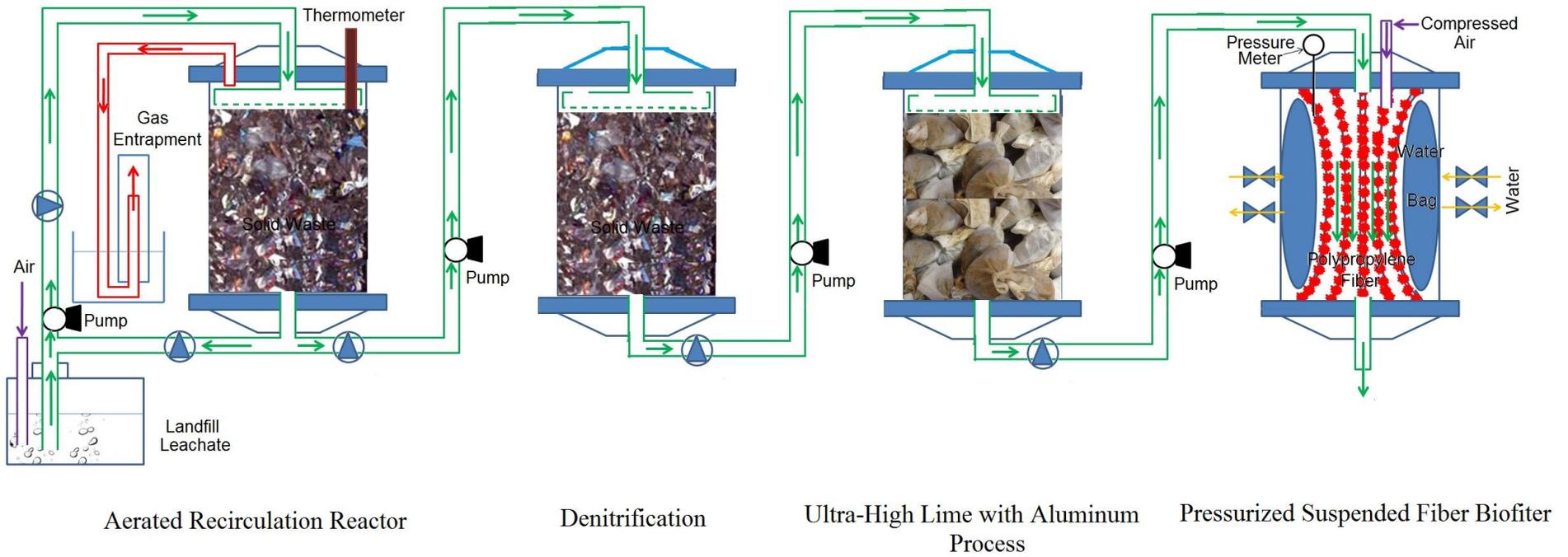
Landfill leachate and solid waste were collected from the Leon County Landfill, located in Tallahassee, FL. and Springhill Landfill, located in Campbellton, FL, Leon County Landfill accepts class III commercial and residential waste through Marpan Recycling, which includes yard trash, C&D debris, processed tires, asbestos, carpet, cardboard, paper, glass, plastic, furniture other than appliances, and other materials approved by Florida Department of Environmental Protection. Yard debris (leaves and limbs) and waste tires are accepted through the Solid Waste Management Facility. Besides, Leon County Landfill also receives electronics, computers and peripherals, televisions, video game systems, handheld electronics, cell phones, household hazardous waste, and styrofoam TM (packaging foam only), etc. Owing to the contract with Marpan Recycling to process and recycle construction debris and packaging material, over 50% of this material is now being recycled rather than buried in a landfill. Currently, the Class III site of Leon County Landfill is closed to the public. But the facility still accepts tires, clean yard waste (no plastic bagged yard waste), wood debris, electronics, recycling and household hazardous waste. Domestic solid wastes from Leon County are processed at the Gum Road Transfer Station and delivered to the Springhill Landfill for disposal. Besides domestic wastes, Springhill Landfill offers the following non-hazardous waste disposal services: Asbestos-Friable, Asbestos-Non-Friable, Auto Shredder Fluff, Biosolids, Construction & Demolition Debris, Drum Management-Liquids, Drum Management-Solids, Industrial & Special Waste, Liquifix (Solidification Services), Municipal Solid Waste, Tires, Yard Waste and CERCLA Waste.

In this research, the leachate was collected in temperature-controlled containers at 4° C and transported to the laboratory immediately. The leachate was stored under refrigeration at 4° C until the reaction. Based on the results of our previous research, we expect the landfill leachate to have a composition of BOD<sub>5</sub> up to 20,000 mg/L, NH<sub>4</sub><sup>+</sup>-N up to 500 mg/L, and phosphorus up to 200 mg/L. The solid waste was ground and sieved before introduced into the laboratory reactors. Soil samples were collected from the landfill site

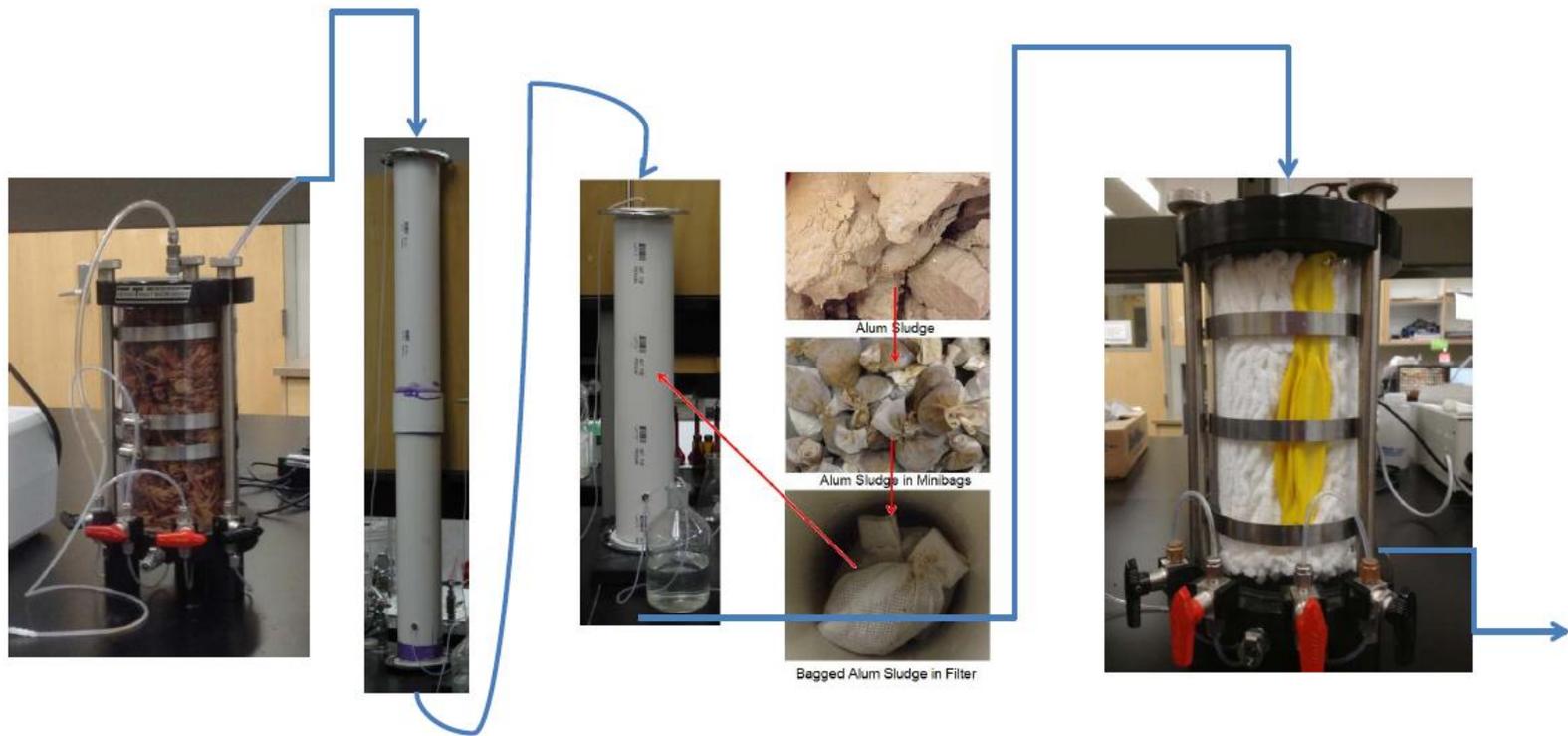
and used as inocula for microbial cultivation. Soil samples were collected 1 to 3 feet below the surface, 100 to 300 feet away from the landfills. The collected soil samples were immediately placed in either a Ziploc bag or a Styrofoam cooler and sealed. All the soil samples were delivered to the laboratory immediately and placed under refrigeration at 4° C until usage in the experiments. To assess the soil iron content, soil samples were first partially thawed and placed in an anaerobic chamber with a maintained H<sub>2</sub>-N<sub>2</sub> atmosphere. The samples were then ground and the weighed samples were placed in a glass reaction vessel and purged with CO<sub>2</sub>-scrubbed air, after which the samples were acidified with hot, 5% perchloric acid to dissolve carbonate precipitates such as siderite, calcite, aragonite, and carbonate forms of green-rust. Evolved CO<sub>2</sub> gas was carried to the coulometer cell containing a CO<sub>2</sub>-sensitive ethanolamine solution and quantitatively titrated. The samples were then reacted with 0.25 M hydroxylamine (NH<sub>2</sub>OH) hydrochloride in 0.25 N HCl and incubated at 60 °C for 2 hrs for iron extraction (Lovley and Phillips, 1988; Roden and Zachara, 1996). Following the extraction, soil iron content was determined using spectrophotometric analysis techniques using a spectrophotometer at the wavelength of 447 nm (Shimadzu UV-1650 PC).

### **3.2 Aerated Leachate Recirculation Investigation**

A laboratory scale recirculation bioreactor was set up to simulate landfill leachate recirculation, which was followed by a denitrification bioreactor, the ultra-high lime with aluminum process, and a pressurized suspended fiber biofilter for this research (Figure 10 and Figure 11). The custom-made recirculation bioreactor had a working volume of 35 L with a height to diameter ratio of 1:1.66 (height = 50 cm and diameter = 30 cm). The reactor was packed with solid waste that was collected from the Leon County Landfill or Springhill Landfill. The solid waste was packed in the bioreactor after grinding and sieving (< 2 mm). Within the bioreactor, a gas entrapment device was arranged. Although methane may be produced, more CO<sub>2</sub> is expected to be produced especially after aerated recirculation.



**Figure 10. Leachate Recirculation Followed by Denitrification, the Ultra-High Lime with Aluminum Process and a Pressurized Suspended Fiber Biofilter ---- Process Illustration**



Aerated Recirculation Reactor

Denitrification

Ultra-High Lime with Aluminum Process

Pressurized Suspended Fiber Biofilter

**Figure 11. Leachate Recirculation Followed by MAP Precipitation and the Ultra-High Lime with Aluminum Process, and a Pressurized Suspended Fiber Biofilter ---- Experimental Setup**

Through leachate aeration and recirculation, organic compounds in the leachate were decomposed and ammonium was oxidized through nitrification. Before the organic degradation and nitrification can happen, the consortia that was responsible for organic degradation and nitrification needed to be cultured first and introduced to the bioreactor. The consortia were cultured using the sampled soil as the inocula under conditions of the bioreactor with collected leachate as the carbon and energy sources for organic decomposition. Nitrifiers are chemolithoautotrophic. Cultivation and enumeration of all nitrifiers (ammonium and nitrite oxidizers) used a medium with the following chemical composition: 0.5 g/L  $(\text{NH}_4)_2\text{SO}_4$ , 1.0 g/L  $\text{K}_2\text{HPO}_4$ , 0.03 g/L  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , 0.3 g/L NaCl, 0.3 g/L  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , 7.5 g/L  $\text{CaCO}_3$ . The second medium (0.006 g/L  $\text{NaNO}_2$ ; 1.0 g/L  $\text{K}_2\text{HPO}_4$ ; 0.3 g/L NaCl; 0.1 g/L  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ; 0.03 g/L  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ; 0.3 g/L  $\text{CaCl}_2$  and 1.0 g/L  $\text{CaCO}_3$ ) was used for the cultivation and enumeration of nitrite oxidizers only. A Most Probable Number (MPN) table was used to determine numbers of nitrifying bacteria. Combined counts of ammonium and nitrite oxidizers were obtained. The consortia were analyzed for the presence of aerobic (facultative) heterotrophs (mainly *Pseudonaomas*), which were further enriched for organic decomposition.

After aeration, landfill leachate collected from the Leon County Landfill or Springhill Landfill was pumped to the bioreactor from the storage reservoir using a peristaltic pump at a flow rate of 100 mL/min. Leachate aeration was achieved in the storage reservoir with air supply at flow rates of 0.2 L/min, 0.5 L/min, 1 L/min and 5 L/min for 15 min by a mass-flow controller (with targeted dissolved oxygen levels of 3 mg/L to 6 mg/L). The air supply and the subsequent targeted dissolved oxygen concentration of 3, 4, 5 and 6 mg/L achieved a stable nitrification condition. Considering the possible organic leaching from the solid waste in the bioreactor, the leachate was recirculated for a couple of months until obvious decrease of organic contents was observed. Then, an aliquot was introduced to the next treatment step and the other aliquot was aerated and recirculated. The same amount of fresh leachate equivalent to that introduced to the next treatment step was added to maintain the same liquid volume of the recirculation bioreactor. Recirculation ratio of 80%, 75%, 50%, 25% and 0% was tested in this research. For this part of the research, dissolved oxygen, chemical oxygen demand (COD), ammonium,

nitrate and iron concentrations were monitored for the leachate before recirculated into the bioreactor and after getting out of the bioreactor. Ammonium and nitrate concentrations were monitored colorimetrically by means of the nesslerization, N-(1-naphthyl)-ethylendiamine dihydrochloride spectrophotometer and thymol spectrophotometry (Mccrady, 1966). Dissolved oxygen concentration was measured directly by a dissolved oxygen meter (WTW Oxi 315i, Cellox 325, Germany). Both ammonium and nitrate concentrations were monitored for up to 12 recirculation cycles. Based on the experimental results, 4 recirculation cycles were selected for further study of the impact of recirculation ratio. With 4 recirculation cycles, recirculation ratio was further studied. Specifically, recirculation ratio of 100%, 75%, 50%, 25% and 0% (with corresponding 0%, 25%, 50%, 75% and 100% added fresh leachate) was tested for nitrification in the recirculation bioreactor.

### **3.3 Iron Oxidation and Removal by Filtration**

Before ferrous iron can be filtered, it needs to be oxidized to a state in which it can form insoluble complexes, which involved the transfer of electrons from ferrous iron to the oxidizing agent. Once ferrous iron was oxidized to ferric iron, the insoluble iron hydroxide complex of  $\text{Fe}(\text{OH})_3$  was formed. Typically, common chemical oxidants including oxygen, chlorine, chlorine dioxide, potassium permanganate and ozone can all be used in landfill leachate treatment to oxidize ferrous iron. Among these oxidants, chlorine and potassium permanganate are frequently applied in landfills and the dosing is relatively easy, requiring simple equipment and is fairly inexpensive. As an oxidant, potassium permanganate is normally more expensive than chlorine and ozone. But for iron removal, it has been reported that ozone is efficient and requires considerably less equipment and capital investment. However, ozone may not be effective for oxidation in the presence of humic or fulvic materials. As the most cost-efficient method of oxidation, the oxygen in air is the most commonly utilized oxidizing agent. Ferrous iron oxidation using oxygen usually combined with pH adjustment and the presence of other oxidizable species hinders ferrous iron. Therefore, the organic contents and alkalinity of the leachate would play important roles in iron oxidation and removal during leachate recirculation. For this part of research, the leachate was aerated with a targeted dissolved oxygen

concentration of 3, 4, 5 and 6 mg/L. Subsequently, iron oxidation and removal were evaluated under these conditions.

### 3.4 Denitrification and Iron Release

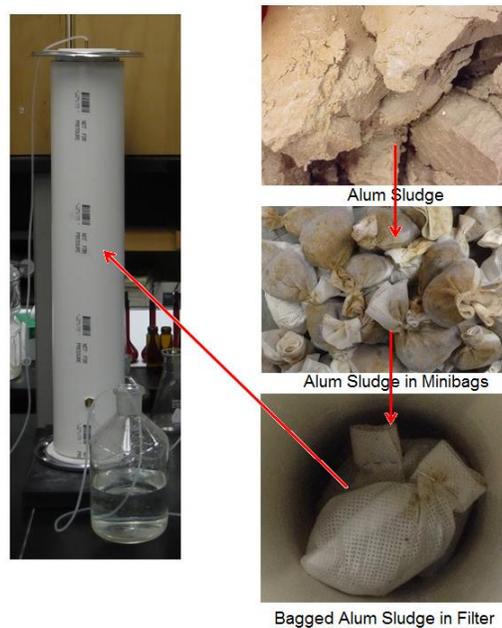
Once leachate was recirculated into the bioreactor, denitrification may occur at the lower section of the reactor once oxygen content became low. At the same time, iron may be released with the decomposition of organic compounds owing to the high iron content in the reactor. This process was simulated by a column with a dimension of 15 cm ID × 75 cm Length. The column was packed with the solid waste collected from Leon County Landfill and Springhill Landfill and was inoculated with consortia cultured with leachate and enrich nitrate using the collected soil as the inocula under conditions of the denitrification and iron reduction. Resazurin (1 mg/L) was added as a redox indicator to indicate contamination by molecular oxygen and cysteine (3.0 g/L) was added to reduce the trace amount of oxygen remaining in the media after autoclaving. The media pH was adjusted to 7.0 with 0.1 M HCl or NaOH. The inoculation was conducted in a serum bottle on a rotary-shaker (150 rpm at 35°C) in the dark for at least 1 week until the formation of black precipitate at the bottom and on the wall of the serum bottles was observed. Then 10 mL enriched culture was transferred into 100 mL fresh culture media for the second phase culture enrichment. After the fourth phase enrichment was completed, consortia were harvested and introduced to the reactor. Control tests were conducted in the absence of consortia to quantify the abiotic losses in the system. Throughout the course of the experiments, COD, ferrous iron, and nitrate concentrations were monitored. For ferrous iron quantification, 1,10-Phenanthroline Method was utilized (Williams et al., 2012). In the presence of 1,10-phenanthroline (C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>·H<sub>2</sub>O), ferrous iron formed a stable, orange-colored complex with the reagent:



For this experiment, 0.0125 M 1,10-phenanthroline was used and ferrous iron concentrations were quantified using the spectrophotometer (Shimadzu UV-1650 PC) at a wavelength of 520 nm.

### 3.5 Chloride Removal by Precipitation

The ultra-high lime with aluminum process was tested in a separate reaction first for chlorine removal. The high pH and calcium content as a result of lime addition allowed chloride removal in the form of calcium chloroaluminate [ $\text{Ca}_4\text{Al}_2\text{Cl}_2(\text{OH})_{12}$ ] with the addition of aluminum. One way in which the ultra-high lime with aluminum process can be made more economically attractive is to reduce the reagent costs. This could be accomplished by using waste alum sludge from water treatment plants as the source of some or all of the aluminum needed. This sludge usually contains approximately 39% aluminum by weight (Huang et al., 2010). For this research, alum sludge was collected from Atlanta-Fulton Water Treatment Plant. After addition of lime and dewatering, the cake-shaped alum sludge had a pH in the range of 12 to 13. The high pH and calcium content of the alum sludge made it possible for chloride to be removed in the form of  $\text{Ca}_4\text{Al}_2\text{Cl}_2(\text{OH})_{12}$ . During chloride removal operation, the most efficient way of using alum sludge was through filtration by using alum sludge as the filtering material. Considering the possible clogging, the alum sludge was bagged before being packed in the filter. For this part of research, a filter with a dimension of 15 cm ID  $\times$  75 cm Length was used (Figure 12).



**Figure 12. Ultra-High Lime with Aluminum Process in a Filter**

To avoid the flow short-cut inside the filter, the filter was operated as a sequencing batch reactor. 5 L of the treated leachate was introduced into the filter with a hydraulic loading of 1, 1.5 and 3 m<sup>3</sup>/m<sup>2</sup>/hr, after which the leachate was introduced to the pressurized fiber biofilter for further treatment and another 5 L of the treated leachate was introduced.

### **3.6 Pressurized Suspended Fiber Biofiltration Performance Evaluation**

The custom-made pressurized suspended fiber biofilter had a volume of 35 L with a height to diameter ratio of 1:1.66 (height = 50 cm and diameter = 30 cm). In the pressurized suspended fiber biofilter, polypropylene fibers were arranged to be suspended in the column (Figure 13). Two water rubber bags were arranged on two side of the column, each with a capacity of 8 L. When the water bags were filled with water, the suspended fibers were squeezed together, producing minimal pore space for enhanced filtration. With the ongoing filtration, microbial growth and metal precipitation, the pore space was occupied and pressure was built up. Consequently, water was withdrawn from the water bags to release filter pore space for further filtration. When the water bags were fully filled, the working volume was a half of the volume of the column.



**Figure 13. Polypropylene Fibers used in Pressurized Biofilter**

In the pressurized suspended fiber biofilter, it was expected organic compounds and iron can be removed through contact oxidation, which depended on the microorganisms to degrade organic compounds and fix iron. These consortia strategically positioned themselves on the suspended fiber to form a biofilm. Bacteria in the biofilm produced a matrix of materials so that they stuck to the fiber. Degradation of complex molecules was known to be carried out better by bacterial cultures in consortia than in monocultures. The performance of consortia for degradation of complex molecules required a stability of association, which can be best achieved by growing compatible cultures in a mixture. Using cultures in consortia for efficient degradation of proteins, carbohydrates and lipids had been demonstrated. This was an importance discovery since proteins, carbohydrates and lipids were major organic components in landfill leachate (Turker and Celen, 2007). Both gram negative bacteria (57%) and gram positive bacteria (43%) were present in almost equal frequencies in the consortia. *Bacillus* dominated the generic composition by 25%, which is followed by *Vibrio* (17%). Dominance of *Bacillus* was in agreement with the findings by Krishnan and Saramma (Chianese et al., 1999). The other genera resembled the *Enterobacteriaceae* group, *Arthrobacter*, *Brevibacterium*, *Aeromonas*, and *Pseudomonas*, etc. Recently, some iron fixation bacteria that can derive energy they need to live and multiply by oxidizing dissolved ferrous iron (or the less frequently available manganese) have also been identified. They are known to grow and proliferate in waters containing as low as 0.1 mg/L of iron. However, at least 0.3 ppm of dissolved oxygen was needed to carry out oxidation (Di Palma et al., 2002). For this research, we cultured organic degrading and iron fixation consortia using collected soil samples as the inocula (Barnes et al., 2007). Continuous cultivation and enrichment were carried out immediately after the samples were transported back to our laboratory. For organic degrading consortia, 10 mg soil was transferred into a 250 mL Erlenmeyer flask containing 100 mL sterilized culture media, containing a composition of 160 mg/L  $\text{KH}_2\text{PO}_4$ , 420 mg/L  $\text{K}_2\text{HPO}_4$ , 50 mg/L  $\text{Na}_2\text{HPO}_4$ , 40 mg/L  $\text{NH}_4\text{Cl}$ , 50 mg/L  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , 50 mg/L  $\text{CaCl}_2$ , 0.5 mg/L  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , 0.05 mg/L  $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ , 0.1 mg/L  $\text{H}_3\text{BO}_3$ , 0.05 mg/L  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ , 0.03 mg/L  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ , 200 mg/L glucose, and 60 mg/L ammonia chloride. The pH of the media was adjusted to 7.4 with 1 M HCl or 1 M NaOH and sterilized by autoclaving (121°C and 1 atm) for 20 min. Glucose was filter-

sterilized and aseptically added to the autoclaved media. The Erlenmeyer flask was capped with a foam stopper and put into a rotary-shaker (150 rpm at 35°C) for at least 1 week until the consortia are observed to be formed. After centrifugation (6000 g, 15 min), the consortia were enriched in 100 mL fresh culture media with 200 mg/L glucose and inoculate the biofilter. For iron fixing bacteria culturing, 10 mg soil was transferred into a 250 mL Erlenmeyer flask containing 100 mL sterilized culture media containing 160 mg/L  $\text{KH}_2\text{PO}_4$ , 420 mg/L  $\text{K}_2\text{HPO}_4$ , 50 mg/L  $\text{Na}_2\text{HPO}_4$ , 40 mg/L  $\text{NH}_4\text{Cl}$ , 50 mg/L  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , 50 mg/L  $\text{CaCl}_2$ , 0.5 mg/L  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , 0.05 mg/L  $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ , 0.1 mg/L  $\text{H}_3\text{BO}_3$ , 0.05 mg/L  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ , 0.03 mg/L  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ , 250 mg/L  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and 60 mg/L ammonia chloride. The pH of the media was adjusted to 7.4 with 1 M HCl or 1 M NaOH and sterilized by autoclaving (121°C and 1 atm) for 20 min. The inoculated Erlenmeyer flask was capped with foam stopper and put into a rotary-shaker (150 rpm at 35°C) for at least 1 week until the iron fixation bacteria are observed. The iron fixation bacteria were then centrifuged and inoculated the biofilter.

During the operation, the water bags were first filled with water and compressed air was supplied to the biofilter at a flow rate of 0.2 L/min, which was controlled by a mass-flow controller. A dissolved oxygen probe was installed to monitor oxygen concentration in the biofilter. Leachate effluent after denitrification and the ultra-high lime with aluminum process was introduced to the biofilter using a peristaltic pump at a flow rate of 50 mL/min. With the ongoing of the biofiltration and building up of the pressure, water was withdrawn decrementally from the water bags to release the pore space and reduce the pressure. Organic decomposition and iron oxidizing were a function of alkalinity and pH. Therefore, alkalinity of the leachate was adjusted to 100, 200, 300, 400, 500 and 600 mg/l as  $\text{CaCO}_3$  with lime before the leachate was introduced to the biofilter. Another advantage of pressurized contact oxidation was the low biomass production. Therefore, the suspended filter can last a long operation period. Once the filter capacity was reached, the filter was backwashed with the water in the water bags totally withdrawn.

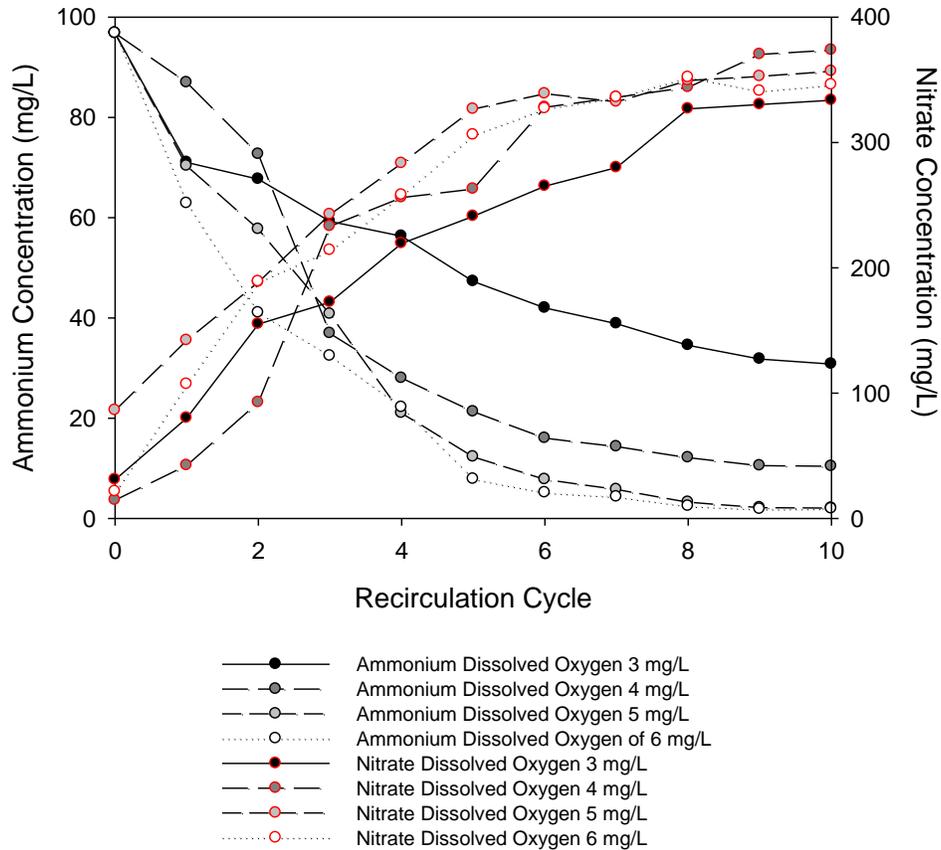
## 4. Results

### 4.1 Soil Characterization

The soil samples were characterized based on sieve analysis and were identified as loamy or fine sand for Leon County and Jackson County landfills. Based on sieve analysis, all the soil samples exhibited a poor grading, i.e., the soil particles were in general similar in size range. The finest particles were screened out by sieve 200 (~ 75 $\mu$ m). Leon County soil had a percentage fine of 5.22% and Jackson County soil had a percentage fine of 4.55%. The soil iron content was 43.8 mg/g for Leon County soil and 34.0 mg/g for Jackson County soil. The average iron content was 38.9 mg/g. It should be noted that only reducible iron contributed to the quantified iron content. There was a general trend that the soil iron content increased with the increase of percentage of finer particles. This is due to the increase in surface area available for iron accumulation. The principal forms of mineralized Fe(III) in the soil of Northwest Florida included amorphous hydrous Fe(III) oxide ( $\text{Fe}_2\text{O}_3 \cdot \text{XH}_2\text{O}$ ), maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ), lepidocrocite ( $\gamma\text{-FeOOH}$ ), hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ), and goethite ( $\alpha\text{-FeOOH}$ ) (Williams et al., 2012).

### 4.2 Nitrification during Aerated Recirculation

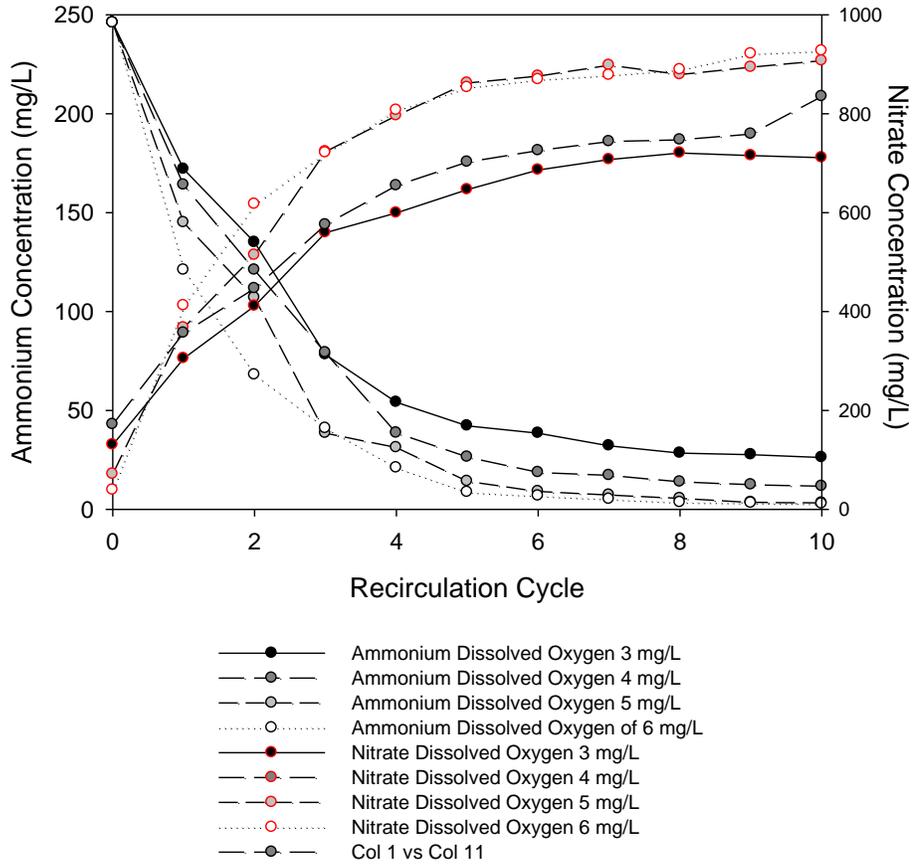
Ammonium oxidation was a function of dissolved oxygen. In this research, dissolved oxygen concentrations from 3.0 mg/L to 6.0 mg/L were tested in the recirculation reactor. At different dissolved oxygen concentration levels, ammonium was converted to nitrate (Figure 14 and Figure 15). The ammonium depletion rate and nitrate production rate (slope of lines in Figure 14 and Figure 15) increased with the increase of the dissolved oxygen concentration. The increase of ammonium depletion rate and nitrate production rate with the increase of the dissolved oxygen concentration was more pronounced at low dissolved oxygen concentrations, i.e., from 3 mg/L to 4 mg/L than at high dissolved oxygen concentrations, i.e., from 5 mg/L to 6 mg/L. In fact, the increase ammonium depletion rate and nitrate production rate with the increase of the dissolved oxygen concentration was minimal after the dissolved oxygen concentration reached 5 mg/L. It was thus assumed that oxygen was no longer the limiting substrate when dissolved oxygen concentration was above 5 mg/L.



**Figure 14. Ammonium Depletion and Nitrate Production for Leon County Landfill Leachate**

As shown in Figure 14 and Figure 15, at dissolved oxygen above 5.0 mg/L, most of the ammonium can be oxidized after 5 recirculation cycles. To ensure the ammonium in the landfill leachate was completely oxidized to nitrate before the landfill leachate was introduced to the next treatment process, dissolved oxygen of 5.0 mg/L was selected for this research. At this dissolved oxygen level, nearly all of the ammonium in the landfill leachate was oxidized to nitrate. By monitoring the nitrate concentration during ammonium oxidation, it was observed that nitrate production increased accordingly with the depletion of ammonium. Minimal nitrite was observed in the reactor, which was confirmed by the mass balance calculation of ammonium depletion and nitrate

production. Sufficient ammonium oxidation also ensured that nitrogen could be effectively removed in the denitrification process.



**Figure 15. Ammonium Depletion and Nitrate Production for Springhill Landfill Leachate**

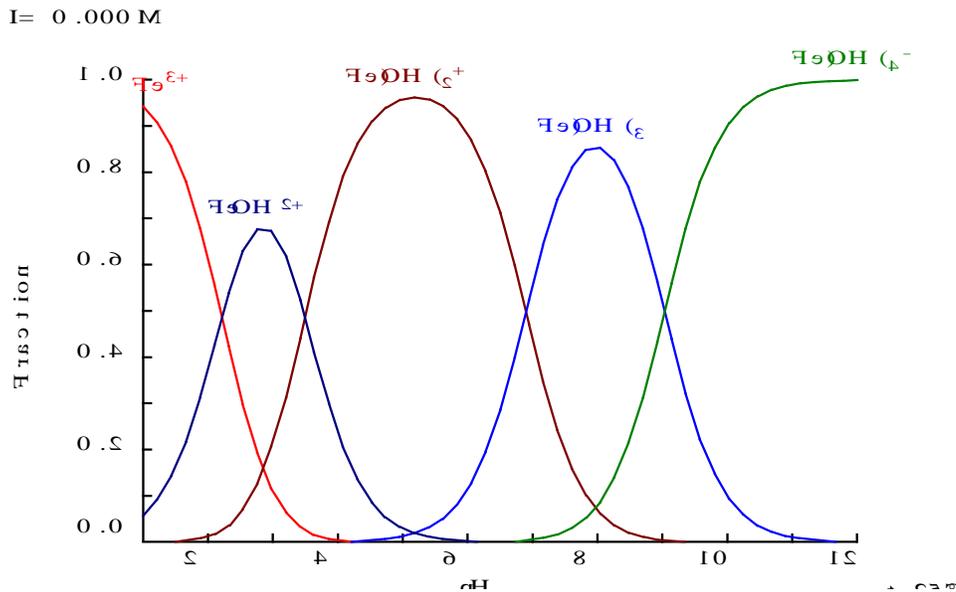
Although Springhill Landfill leachate had obvious higher ammonium concentration than that of Leon County Landfill leachate, the ammonium oxidation and nitrate production had similar observations and trends. At the end of the experiments, the amounts of nitrifiers were assayed via the MPN method for the Leon County Landfill leachate, which were  $0.90 \times 10^6$  cells/mL (Table 2).

**Table 2. Nitrifiers from MPN Method**

Items		Results								
Nitrifiers	Dilution	$10^{-1}$	$10^{-2}$	$10^{-3}$	$10^{-4}$	$10^{-5}$	$10^{-6}$	$10^{-7}$	$10^{-8}$	$10^{-9}$
	Tube Amount	3	3	3	3	3	3	3	3	3
	Positive Tubes	3	3	3	3	3	2	0	0	0
	Biomass	$0.90 \times 10^6$ cells/mL								

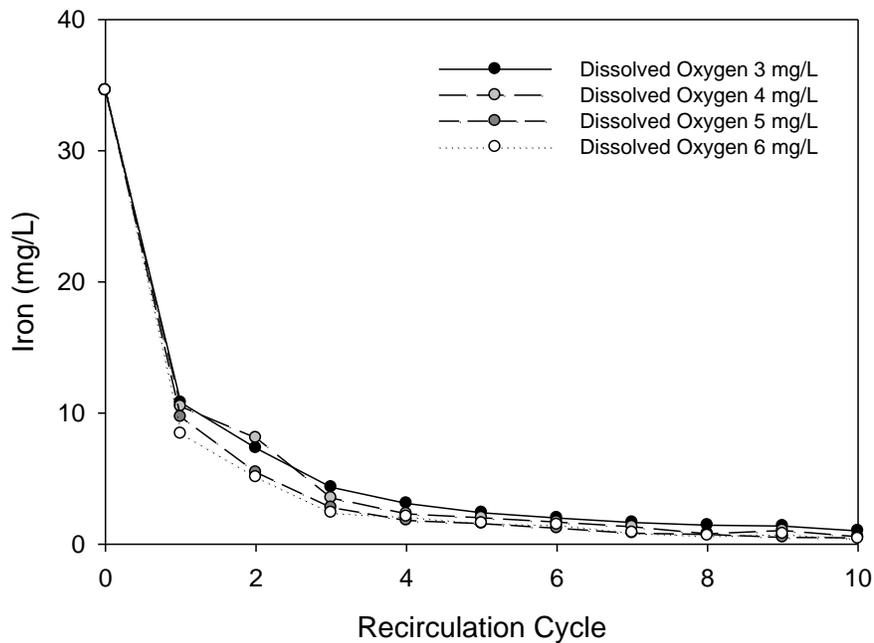
### 4.3 Iron Oxidation and Removal by Filtration

During landfill operations, it is a common practice to compact waste and cover the waste with a layer of soil each day to reduce odors. Therefore, ferrous iron may be released together with organic decomposition. The ferrous iron can be removed by aerated recirculation within the top region of the landfill. The iron removal here is owing to ferrous oxidation and subsequent iron hydroxide precipitation. As shown in Figure 16, iron hydroxide speciation is a function of pH. At pH of 8.0, most of the ferric iron can precipitate in the form of iron hydroxide. At pH of 7.5, around 50% of iron would form iron hydroxide.

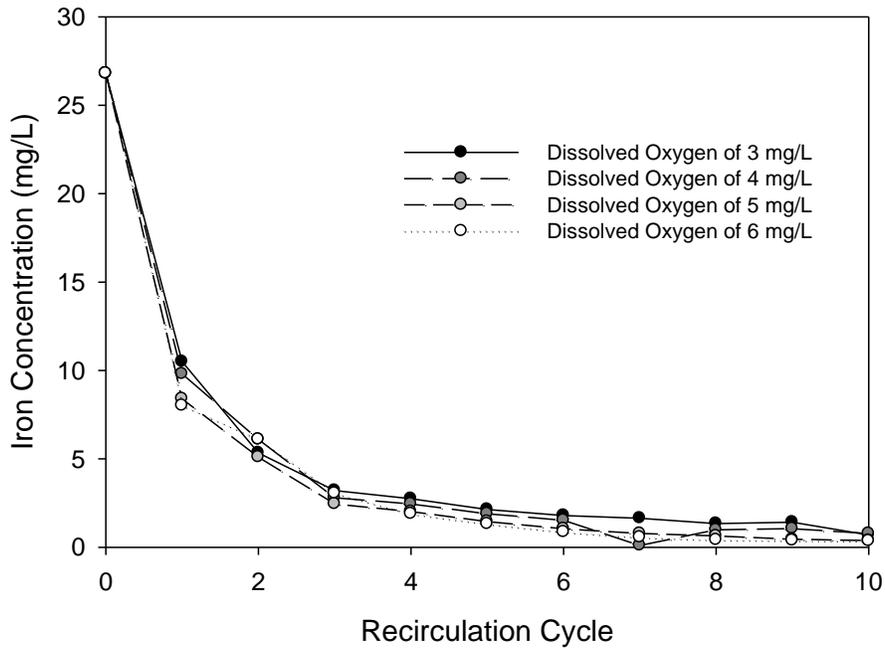


**Figure 16. Iron Speciation as a Function of pH**

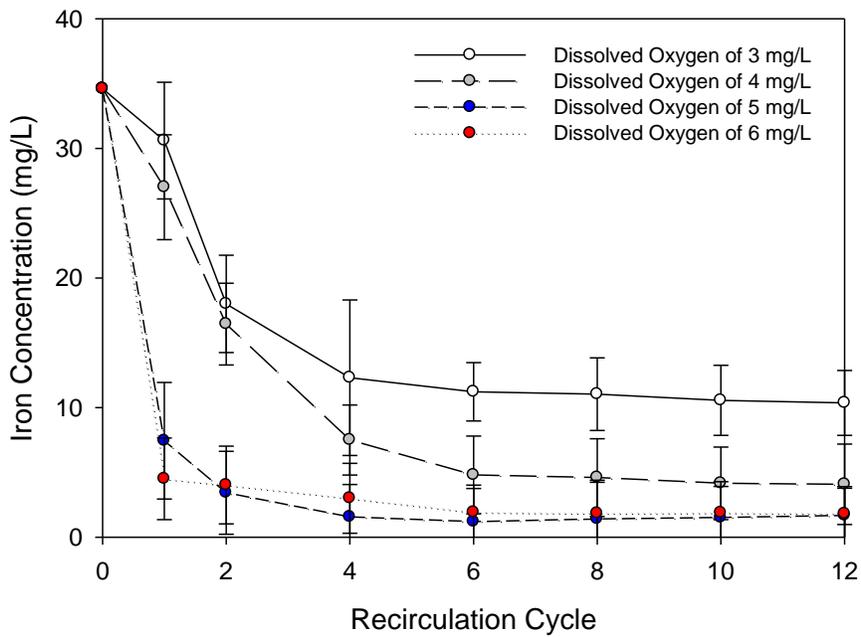
Besides pH, iron removal by aerated recirculation was also a function of aeration rate and the recirculation cycle. At pH of 8.5, further increase of dissolved oxygen above 3.0 mg/L did not make significant difference in iron removal. Above 98% of iron was removed for both Leon County Landfill leachate and Springhill Landfill leachate after 10 recirculation cycles (Figure 17 and Figure 18). At pH 7.5, dissolved oxygen played a more important role in iron oxidation and removal. At this pH level, it seemed that dissolved oxygen of 5 mg/L and above would ensure iron oxidation and removal (Figure 19 and Figure 20). However, for both pH levels, iron removal became stable after 4 recirculation cycles. In our prior research, we discovered that iron removal was not a function of input concentration, but a function of aeration rate and pH. High dissolved oxygen and pH ensured high levels of iron existing in the form of iron hydroxide, which could be consequently removed in the landfill during recirculation by precipitation.



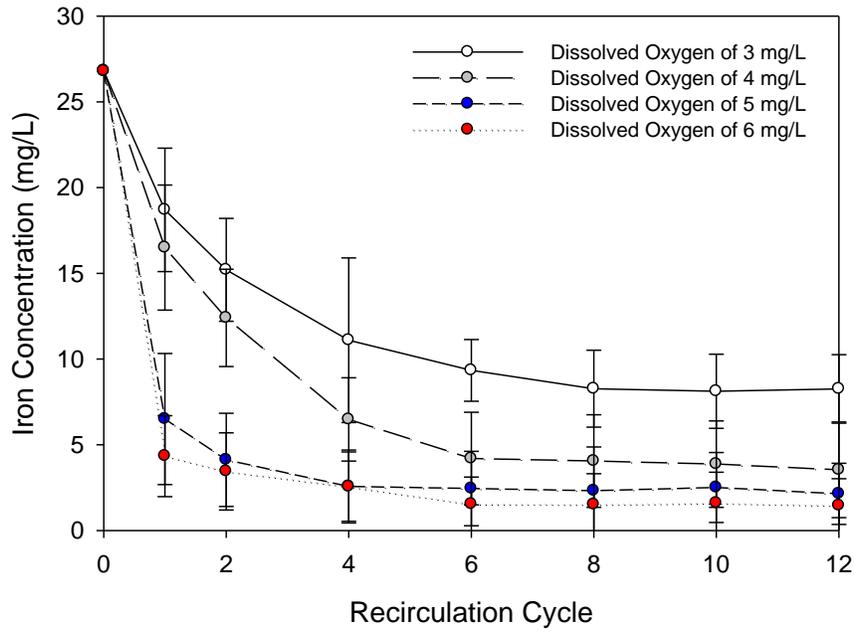
**Figure 17. Iron Removal for Leon County Landfill Leachate at pH 8.5 as a Function of Recirculation Cycle**



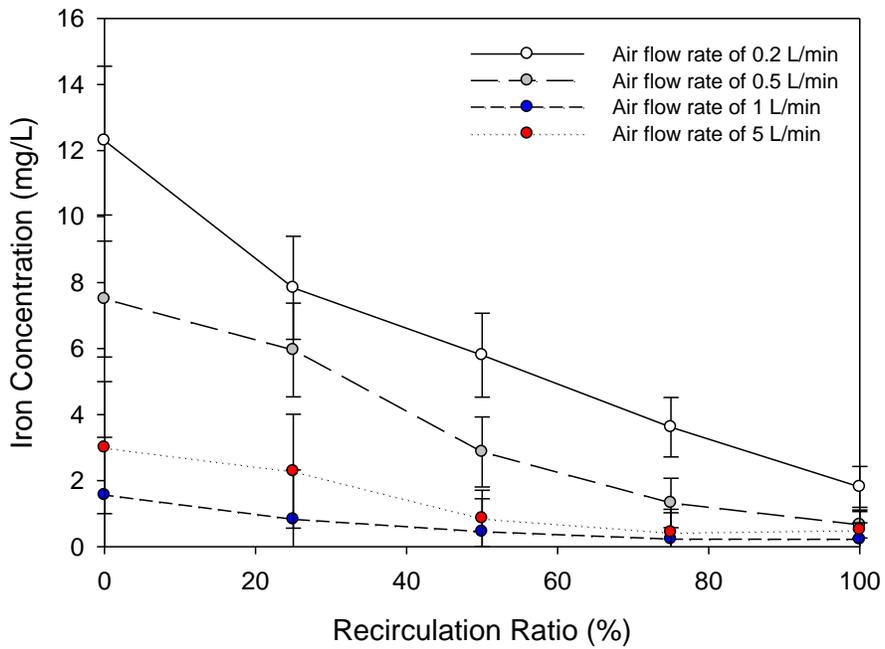
**Figure 18. Iron Removal for Springhill Landfill Leachate at pH 8.5 as a Function of Recirculation Cycle**



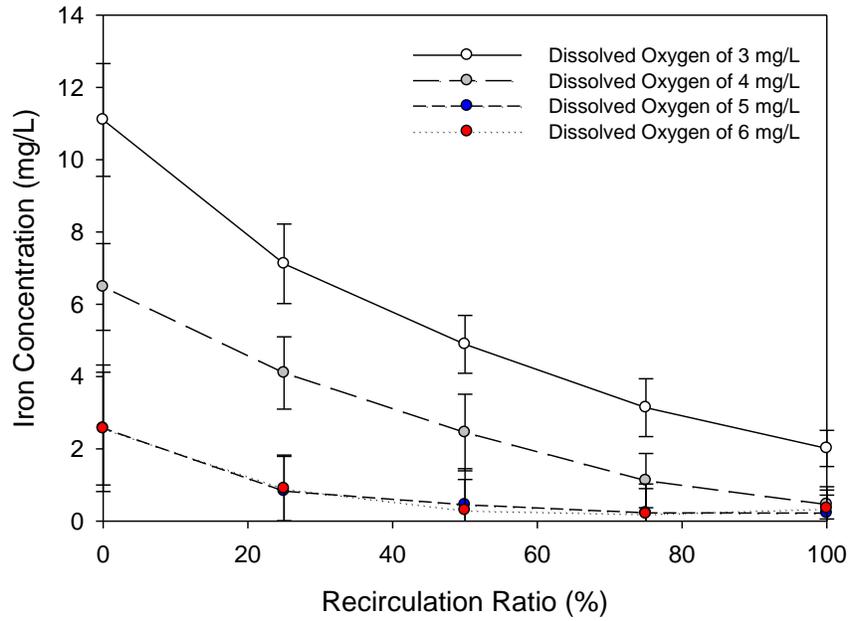
**Figure 19. Iron Removal for Leon County Landfill Leachate at pH 7.5 as a Function of Recirculation Cycle**



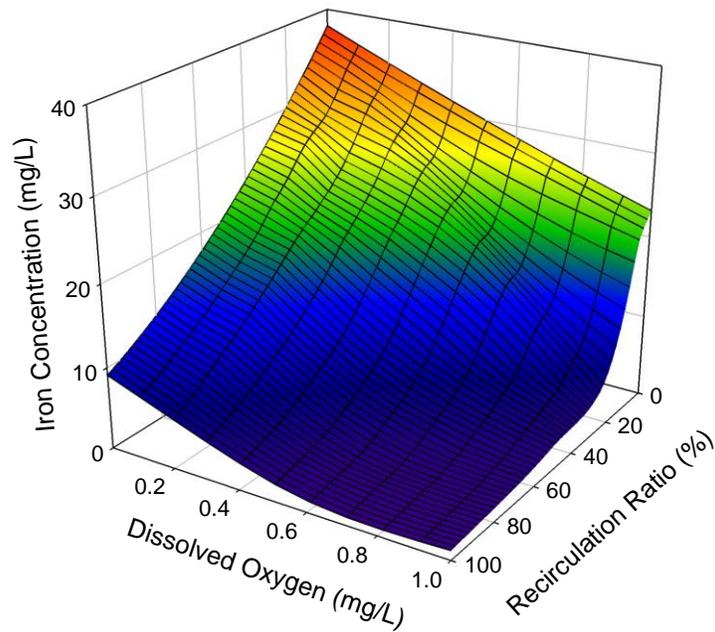
**Figure 20. Iron Removal for Springhill Landfill Leachate at pH 7.5 as a Function of Recirculation Cycle**



**Figure 21. Iron Removal for Leon County Landfill Leachate at pH 7.5 as a Function of Recirculation Ratio**



**Figure 22. Iron Removal for Springhill Landfill Leachate at pH 7.5 as a Function of Recirculation Ratio**

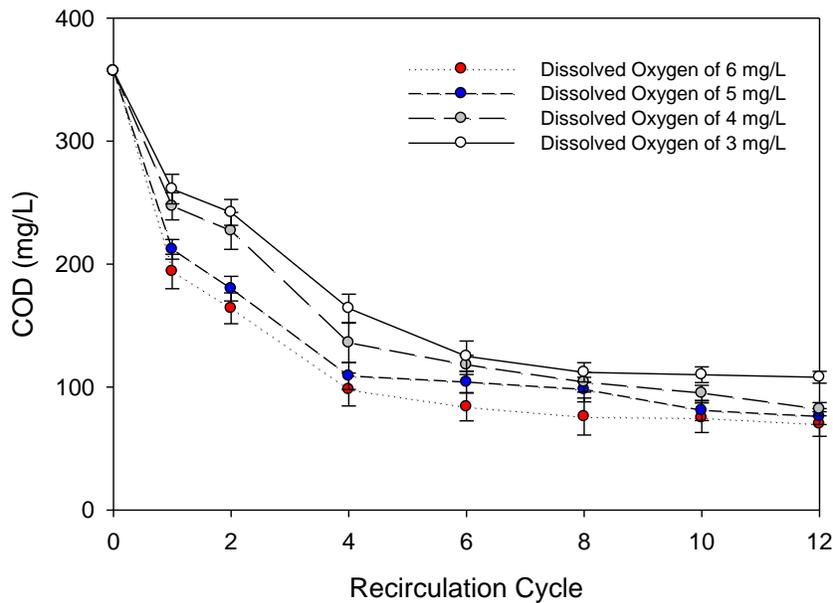


**Figure 23. 3-D Plot of Iron Removal as a Function of Recirculation Ratio and Dissolved Oxygen**

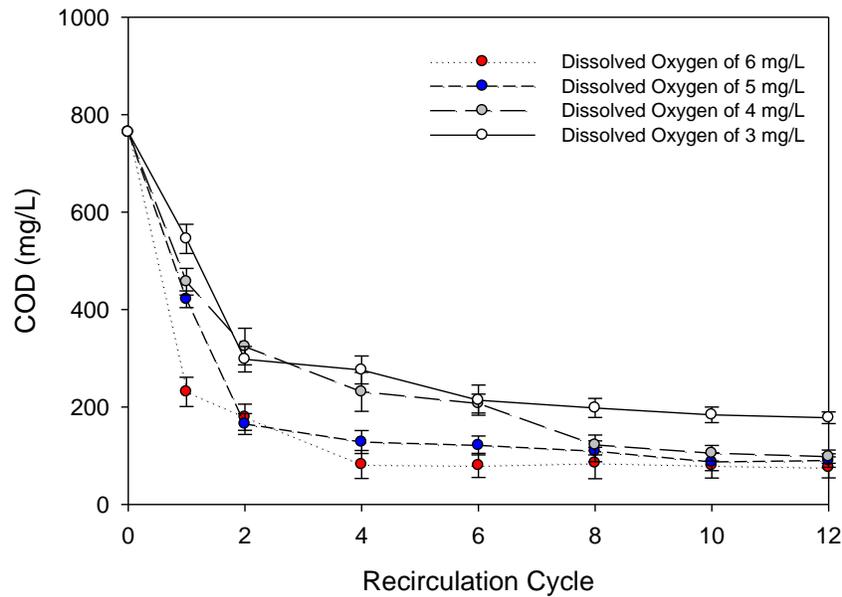
At a recirculation cycle of 4 and pH 7.5, impact of recirculation ratio on iron removal was further investigated. In this process, iron removal also increased with the increase of dissolved oxygen. Again, further increase of dissolved oxygen above 3.0 mg/L did not make significant difference in iron removal (Figure 21 and Figure 22). At this stage, 50% recirculation ratio would produce reasonable iron removal results. For Leon County Landfill leachate treatment, the impact of dissolved oxygen and recirculation ratio was plotted in a 3-D figure to illustrate the importance of both dissolved oxygen and recirculation ratio on iron removal (Figure 23).

#### 4.4 Organic Removal by Recirculation

Organic removal from the landfill leachate collected from the Leon County Landfill and Springhill Landfill was also studied. The organic removal was first tested with the treated leachate totally recirculated back to the recirculation reactor. The impact of recirculation cycle on organic removal was monitored for 12 recirculation cycles. It was discovered that organic removal increased with the increase of dissolved oxygen. However, opposite to iron removal, the enhancement incrementally increased (Figure 24 and Figure 25).

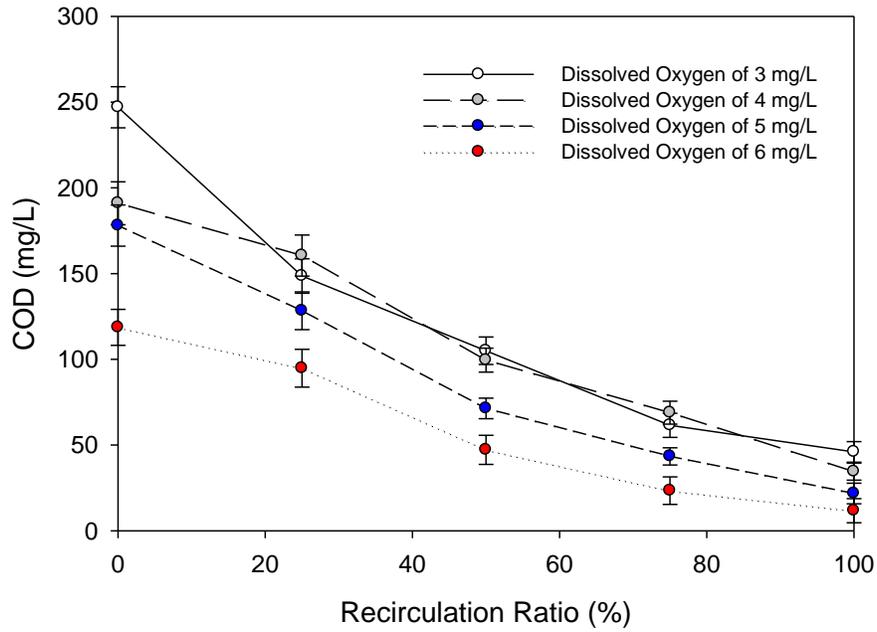


**Figure 24. COD Removal as a Function of Recirculation Cycle for Leon County Landfill Leachate**

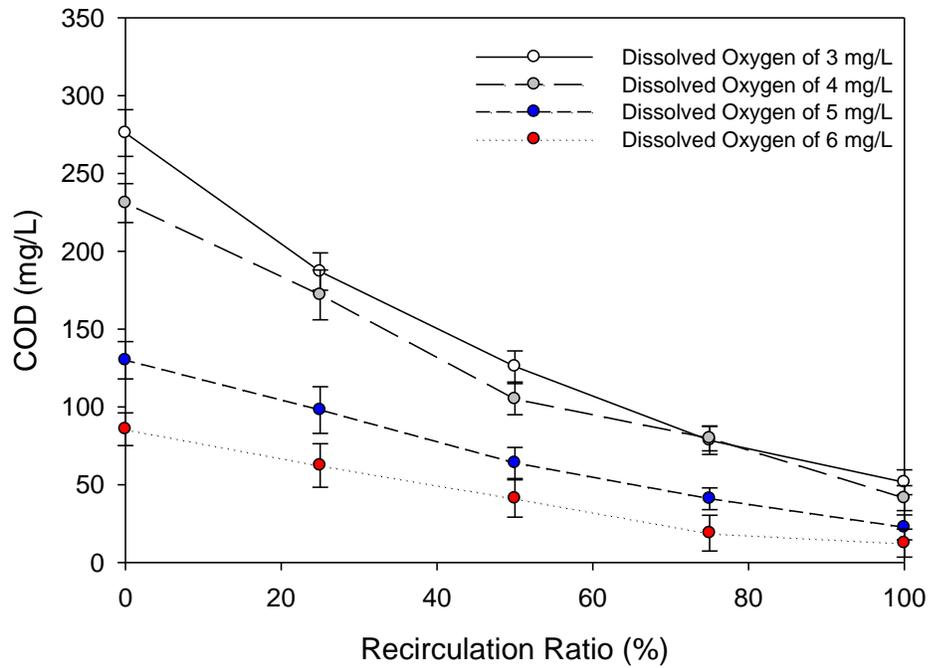


**Figure 25. COD Removal as a Function of Recirculation Cycle for Springhill Landfill Leachate**

After 4 to 5 recirculation cycles, the organic removal became stable. Compared to Leon County Landfill leachate, leachate collected from Springhill Landfill had higher organic contents. The organic removal reached an average of 70% for Leon County Landfill leachate and 80% for Springhill Landfill leachate when organic removal became stable. At a recirculation cycle of 4, the effect of recirculation ratio was investigated. High dissolved oxygen favored organic removal (Figure 26 and Figure 27). Specifically, recirculation ratio of 100%, 75%, 50%, 25% and 0% (with corresponding 0%, 25%, 50%, 75% and 100% added fresh leachate) was tested. Similarly, higher dissolved oxygen resulted in better organic removal for the same recirculation ratio. Although 100% recirculation ratio produced the best results, 100% recirculation was not practical. We chose to adopt 50% recirculation ratio for the following up experiments, i.e., 50% of the treated leachate was introduced to the next treatment step and 50% fresh leachate was added. The unremoved organic and iron would be further removed in the pressurized biofilter.

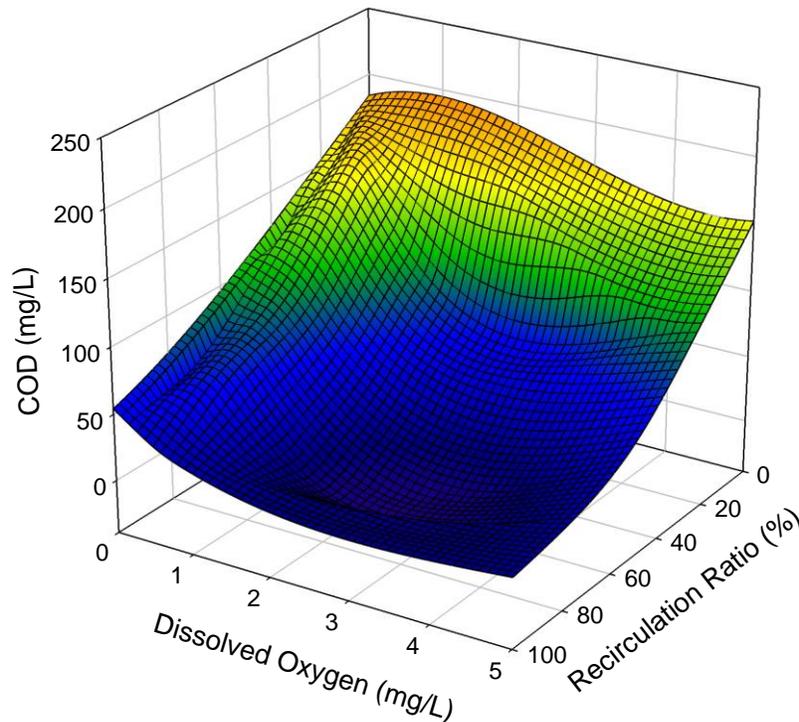


**Figure 26. COD Removal as a Function of Recirculation Ratio for Leon County Landfill Leachate**



**Figure 27. COD Removal as a Function of Recirculation Ratio for Springhill Landfill Leachate**

For Leon County Landfill leachate treatment, the impact of dissolved oxygen and recirculation ratio was plotted in a 3-D figure to illustrate the comparison of these two impact factors. From the 3-D plot, it can be observed that the effect of recirculation ratio on COD removal was more pronounced at lower dissolved oxygen and smaller recirculation ratios than those of higher dissolved oxygen and greater recirculation ratios (Figure 28).



**Figure 28. 3-D Plot of Organic Removal as a Function of Recirculation Ratio and Dissolved Oxygen**

Organic decomposition in the landfill leachate can be described by the Monod equation. Specifically, if microbial activities are coupled with organic depletion and Monod-type kinetics are assumed to describe microbial growth, organic and microbial concentrations over time can be described by following equations (Bhalla and Warheit, 2004):

$$\frac{dS}{dt} = -\frac{1}{Y} \frac{\mu_m SX}{K_s + S} \quad \text{Equation (3)}$$

$$\frac{dX}{dt} = \frac{\mu_m SX}{K_s + S} - \frac{bX}{K_s + S} \quad \text{Equation (4)}$$

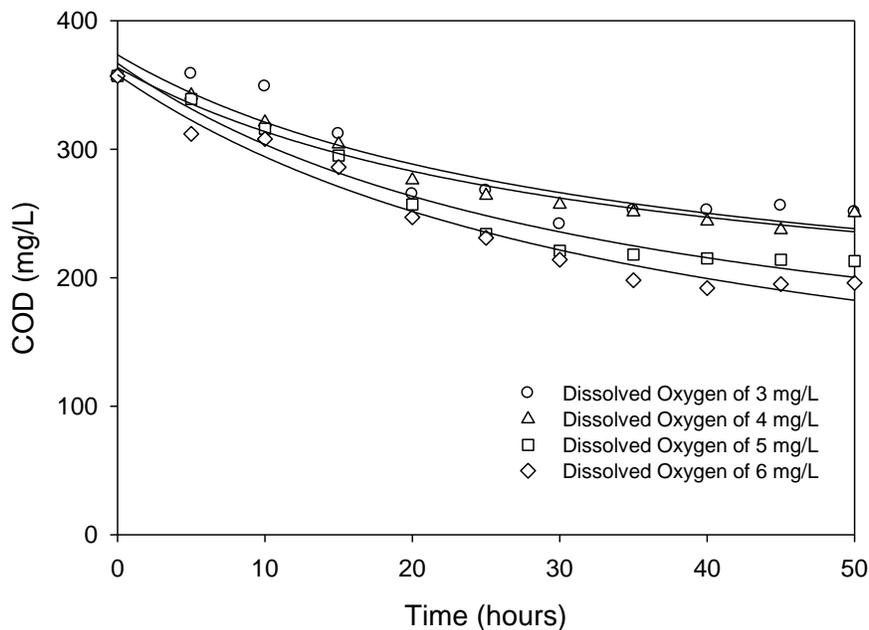
where S is the organic concentration, which is expressed in terms of BOD<sub>5</sub>;  $\mu_m$  is the microbial maximum specific growth rate; X is the microbial concentration; t is the elapsed time; Y is the growth yield coefficient;  $K_s$  is the half-saturation coefficient; and b is the microbial decay coefficient. By ignoring the decay rate coefficient, Y can be used to estimate the microbial production based on organic substrate depletion, such that:

$$Y = -\frac{\Delta X}{\Delta S} \quad \text{Equation (5)}$$

$$X = X_0 + Y(S_0 - S) \quad \text{Equation (6)}$$

By substituting equations (3) and (4) into equation (2), organic depletion can be expressed as:

$$\frac{dS}{dt} = -\frac{1}{Y} \frac{\mu_m S [X_0 + Y(S_0 - S)]}{K_s + S} \quad \text{Equation (7)}$$



**Figure 29. Organic Degradation Simulation based on Monod-Type Microbial Growth Kinetics for Leon County Landfill Leachate**

Organic depletion was simulated by means of non-linear regression of simplex optimization of least squares against Equation (7) to estimate their relevant Monod kinetic parameters (Figure 29). 95% confidence intervals and prognosis intervals were determined for each fitted curve. The statistical analysis was carried out within OriginPro 7.5 (OriginLab, USA). The simulated results are presented in Table 3.

**Table 3. Leon County Landfill Leachate Decomposition Parameters**

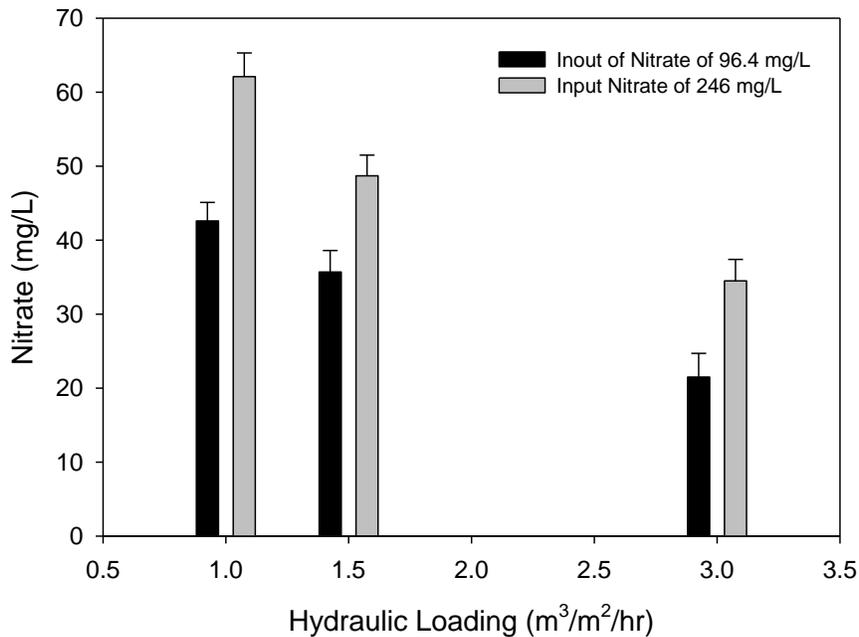
	$K_S$ (mg/L)	Y (g/g)	$\mu_{max}$ (day <sup>-1</sup> )
Leon County	189.5	0.464	0.0073

The consortia had maximum half saturation coefficient value of 189.5 mg/L, which indicated that the consortia had a small affinity to the organic components in the landfill leachate. Growth yield coefficient value was 0.464 g/g and the maximum specific growth rate was 0.0073 hr<sup>-1</sup>.

#### 4.5 Denitrification and Iron Release

Denitrification is a microbially facilitated process of nitrate reduction, which is performed by a large group of heterotrophic facultative anaerobic bacteria. During denitrification, molecular nitrogen (N<sub>2</sub>) is ultimately produced through a series of intermediate gaseous nitrogen oxide products. This respiratory process reduces oxidized forms of nitrogen in response to the oxidation of an electron donor such as organic matter. Throughout the denitrification process, the preferred nitrogen electron acceptors include nitrate (NO<sub>3</sub><sup>-</sup>), nitrite (NO<sub>2</sub><sup>-</sup>), nitric oxide (NO), and nitrous oxide (N<sub>2</sub>O) (in order of most to least thermodynamically favorable). The final product is dinitrogen (N<sub>2</sub>). Denitrifying microbes usually require a very low oxygen concentration, which should be less than 10%, as well as organic carbon for energy. Since denitrification can lower leaching of NO<sub>3</sub> to groundwater, landfill leachate should be treated to remove nitrogen by denitrification after ammonium oxidation. It should be noted that denitrification allows for the production of N<sub>2</sub>O, which is a greenhouse gas that can have a considerable influence on global warming.

The denitrification process is performed primarily by heterotrophic bacteria (such as *Paracoccus denitrificans* and various *pseudomonads*), although autotrophic denitrifiers have also been identified (e.g., *Thiobacillus denitrificans*). Denitrifiers are represented in all main phylogenetic groups. Generally several species of bacteria are involved in the complete reduction of nitrate to molecular nitrogen, and more than one enzymatic pathway has been identified in the reduction process. For this research, the treated leachate after aerated recirculation was introduced to the denitrification column. It was discovered that nitrogen removal by denitrification was a function of input nitrogen and hydraulic loading of the denitrification reactor. For an input nitrate concentration of 96.4 mg/L, 77%, 63% and 55% of nitrogen was removal corresponding to a hydraulic loading of 1, 1.5 and 3 m<sup>3</sup>/(m<sup>2</sup>·hr) (Figure 30). However, for an input nitrate concentration of 246 mg/L, the removal was 85%, 80% and 75%, respectively. Therefore, a higher input nitrogen level displayed a greater removal in the denitrification reactor.



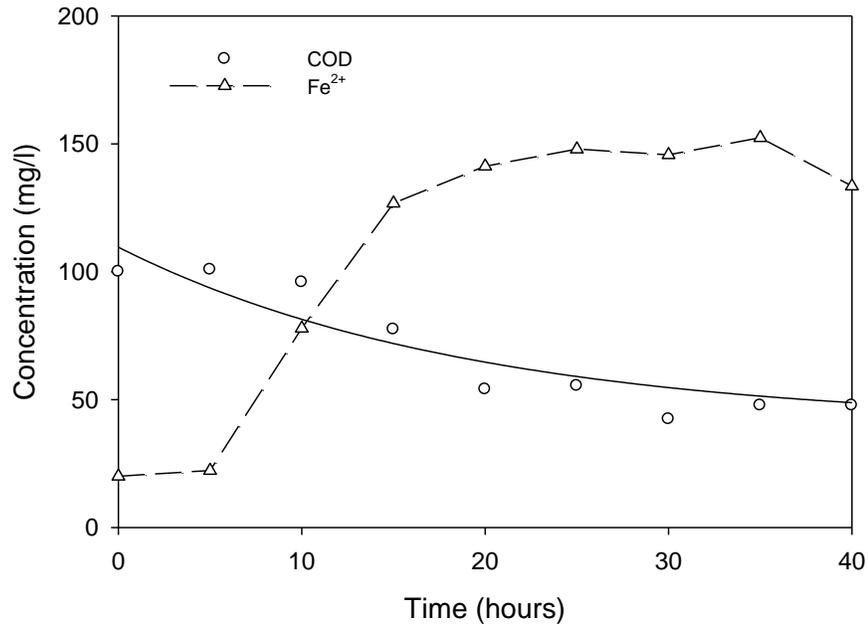
**Figure 30. Nitrogen Removal by Denitrification**

#### 4.6 Iron Reduction and Release

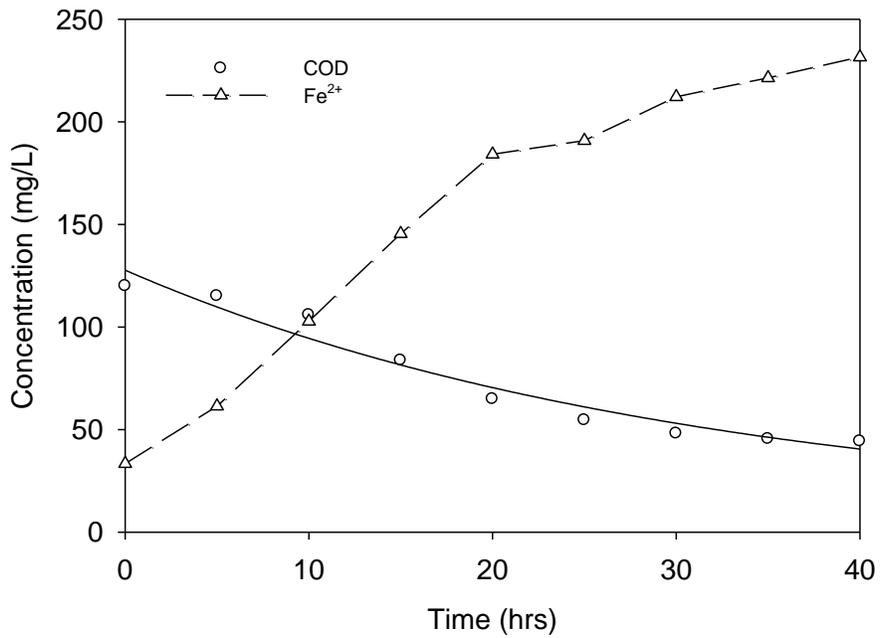
With the ongoing of denitrification, iron oxide in the solid waste and soil would be reduced to ferrous iron and released to the leachate. Metal-reducing bacteria which used solid substrates such as Fe(III) as the terminal electron acceptor for anaerobic respiration must be able to transport the electrons across the outer membrane between large particulate metal oxides (e.g., Fe<sub>2</sub>O<sub>3</sub>) and the electron transport chain in the cytoplasmic membrane (He et al., 2008). Therefore, the bacterial strains that were responsible for iron reduction contained genes encoding cytosolic membrane proteins as well as periplasmic and outer membrane proteins (Ruebush et al., 2006). These proteins were responsible for the inferred path of direct electron transfer from the cytoplasm to an insoluble extracellular substrate. As confirmed by PCR analysis, *S. putrefaciens* was the dominating iron reducing strains in the consortia, which had approximately 80% of the membrane-bound cytochromes localized in its outer membrane (Fornero et al., 2008; Jadhav and Ghangrekar, 2009). The following equation describes iron reduction within the landfill:



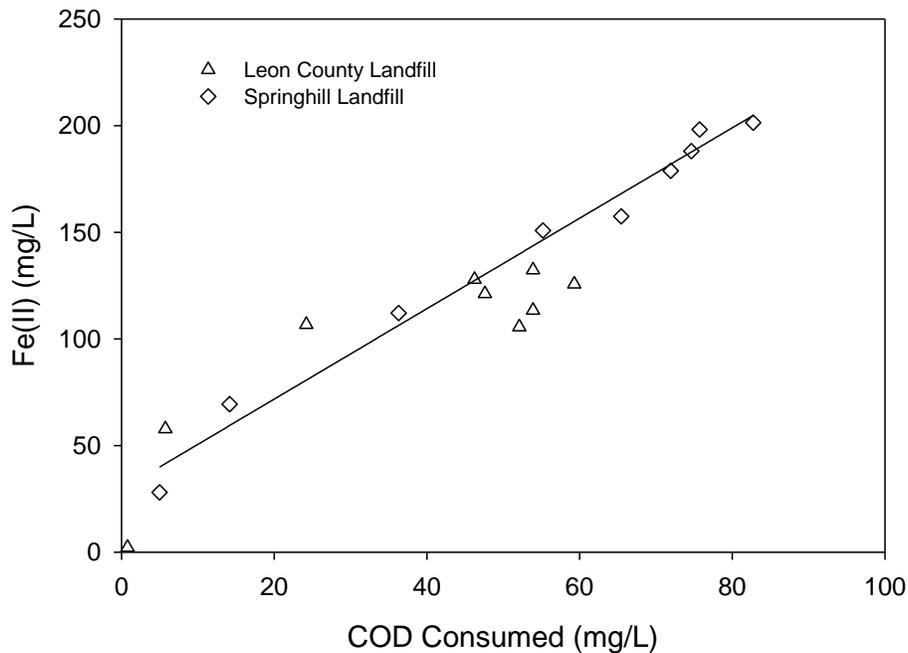
This was evidenced in this research by the fact that organic decomposition and iron released occurred simultaneously (Figure 31 and Figure 32). With the organic decomposition, iron was reduced and subsequent released. As shown in Figure 31 and Figure 32, iron reduction proceeded at much higher rate until 15 to 20 hrs, after which iron reduction became moderate. Compared to Leon County Landfill leachate, Springhill Landfill leachate produced higher iron levels owing to the high organic contents of the treated leachate from prior steps. Although Fe(II) release was observed with the depletion of organic contents, which increased with the proceeding of the experiments, the specific relationship of organic decomposition with iron release was not clearly presented in Figures 31 and Figure 32. To directly illustrate the direct relationship of iron release and organic decomposition, iron release was plotted against organic decomposition. As shown in Figure 33, iron displayed a linear relationship with respect to organic consumption, indicating organic decomposition was the very direct driving force of iron release during landfill operations.



**Figure 31. Organic Degradation and Iron Release for Leon County Landfill Leachate**



**Figure 32. Organic Degradation and Iron Release for Springhill Landfill Leachate**



**Figure 33. Fe(II) Release as a Function of Organic Decomposition**

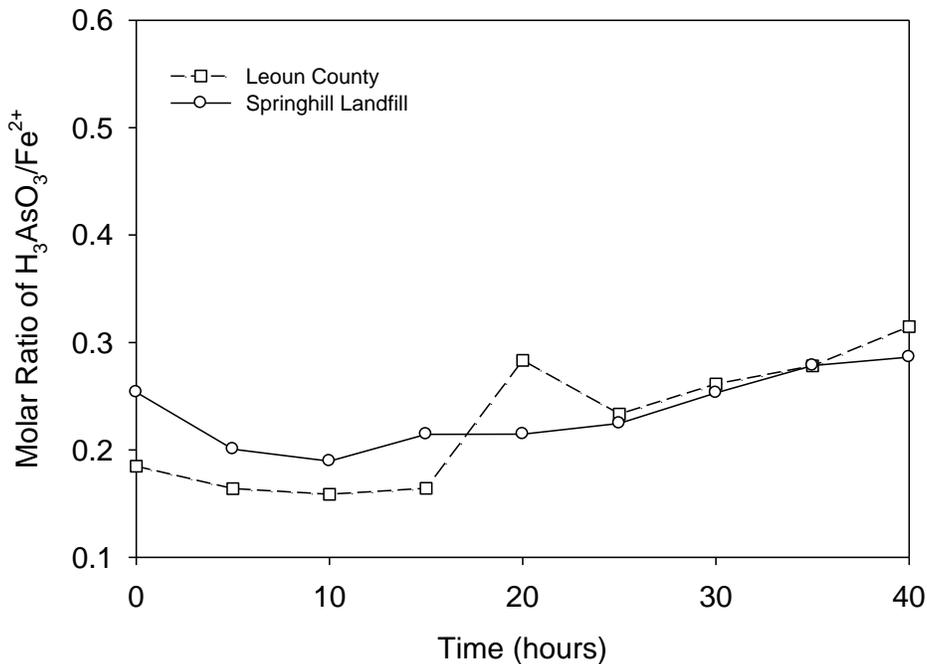
Nearby the landfills in Northwest Florida, arsenic release has been proven to be from unlined construction and demolition debris (C&D) landfills (Wang et al., 2012). When coming out of circulation as construction debris, wood treated with chromated copper arsenate (CCA) for protection from fungus, water damage and termites is primarily disposed within these unlined C&D landfills (Lee et al., 2006; Subramaniam et al., 2010). In the subsurface soil, As(V) and As(III) are the most commonly found arsenic species (Lee et al., 2006). Thermodynamic calculations and experimental results indicate that at high redox levels ( $pe + pH > 10$ ), As(V) is the predominant arsenic species; while under moderately reduced conditions ( $pe + pH < 8$ ), As(III) is the most abundant form of arsenic (Kim et al., 2005). As(V) adsorbs strongly to Al(III) and Fe(III) oxides in the soil (Perez-Gonzalez et al., 2010). Studies show that 90% of arsenic is closely associated with the iron fraction in the subsurface soil nearby landfills in the form of As(V) (Luckarift et al., 2010; Subramaniam et al., 2010). In Northwest Florida, owing to the high iron content, As(V) exhibits very little tendency to leach. However, As(V) readily undergoes

reduction in anaerobic environments to As(III), which is predominantly driven by microbial mediated biogeochemical interactions (You et al., 2010). After reduction, As(III) mainly exists in the form of  $\text{H}_3\text{AsO}_3$  and is very mobile because of its neutral nature. So far, a handful of microorganisms capable of respiring As(V) have been isolated, which include *Sulfurospirillum*, *Clostridium*, *Caloramator*, *Clostridium*, and *Bacillus*, etc. (Fornero et al., 2008; Jadhav and Ghangrekar, 2009; Strik et al., 2008). In addition, iron reducing bacteria such as *Shewanella* species are also able to reduce As(V) to As (III) (You et al., 2010). As a dissimilatory process, arsenic reduction must be coupled to the oxidation of an energy source, most commonly organic carbon. Nearby landfills, the organic content of landfill leachate can serve as the carbon source (Ishii et al., 2008; Rezaei et al., 2008; Sharma et al., 2008).

Before Fe(III) oxide dissolution, As(V) and Fe(III) in the solution were able to be reduced simultaneously based on the thermodynamic analysis. However, the amount of Fe(III) and As(V) in solution was dependent not only on the extent of reduction of each element but also the extent to which they were adsorbed in the soil. Since Fe(III) reduction was thermodynamically more favorable as compared to As(V) reduction, Fe(III) reduction preceded As(V) reduction. Owing to the strong adsorption of As(V) to Fe(III), it was proposed that iron reduction and associated dissolution eventually led to continued As(III) release and elution. Therefore, As(V) adsorption on Fe(III) oxides played an important role in controlling arsenic mobility. In our research, we found that there was no limitation for iron reduction in the soil samples. To simulate arsenic release,  $\text{KH}_2\text{AsO}_4$  at a concentration of 800 mg/L was introduced to the reactor. Subsequently, for As(V) reduction, As(III) release increased after 20 hrs, attributed to the Fe(III) dissolution and subsequent As(V) release and reduction (Figure 34). Based on the speciation analysis, Fe(II) did not precipitate in the pH range of 5 to 9. Therefore, the effect of precipitation of ferrous iron on As(V) reduction was minimal.

This research also demonstrated that arsenic dissolution can be driven by Fe(III) oxide reduction, which was consistent with the previously described arsenic mobilization mechanisms by dissimilatory iron reducers. In essence, the following processes occurring

simultaneously: (1) Desorption promoted by chemical disequilibrium during pore water replacement; (2) Reduction of Fe(III) oxide by iron reducers; and (3) Reduction of As(V) released from iron reduction by arsenate reducers. It should be noted that although As(V) may be released from Fe(III) reduction, owing to its high adsorption capacity, the released As(V) would still be severely constrained by re-adsorption and cannot be mobile until it was reduced. Arsenic mobilization was only possible after As(V) was reduced to As(III) as facilitated by reductive dissolution of Fe (III) oxides in the iron-rich soil. In general, Fe(III) oxides were the dominating iron in the adsorption of arsenate. As(V) adsorption was also pH dependent. In the near neutral pH range of the subsurface soil, Fe(III) oxides were positively charged while the clay minerals were negatively charged. Therefore, Fe(III) oxides were the important sorption “sinks” for As(V), which mainly existed in the form of negatively charged  $\text{H}_2\text{AsO}_4^-$  or  $\text{HAsO}_4^{2-}$ . However, As(III) primarily existed as neutral  $\text{H}_3\text{AsO}_3$ . Therefore, As(III) was not strongly adsorbed under typical soil conditions.



**Figure 34. Molar Ratio of Released As(III) and Fe(II)**

#### 4.7 Chloride Removal

Besides organic contaminants, nutrients and heavy metals, high concentrations of chloride have also been observed in several landfills. For instance, some small counties that have waste-to-energy plants are often unable to use local wastewater treatment plants to dispose the leachate due to high concentrations of chloride in the leachate. These high concentrations of chloride get to the landfills by ashes. The average chloride concentration in landfill leachate is approximately 600 mg/L and the secondary drinking water standard for chloride is 250 mg/L. The elevated concentrations of chloride pose significant challenges to the beneficial waste-to-energy process. If this issue cannot be resolved, the environmental impact of waste-to-energy technology may outweigh the benefits. Chloride tends to percolate and cause surface salt formation and soil alkalinity increase, thereby resulting in loss of soil (Chan et al., 1980). A variety of techniques have been investigated for the removal of chloride, which include ion exchange, reverse osmosis, and norecure, etc. (Ferreira et al., 2004). However, these techniques, though effective, are not feasible from the cost perspective. Therefore, it is the need of time to come up with novel and low cost treatment methods to remove chloride from landfill leachate. As an innovative technology, the ultra-high lime with aluminum process can remove chloride efficiently (Abdel-Wahab and Batchelor, 2006). For this technology, chloride is removed as calcium chloroaluminate [ $\text{Ca}_4\text{Al}_2\text{Cl}_2(\text{OH})_{12}$ ] through precipitation in the presence of calcium and aluminum at high pH.

It was discovered in this research that chloride removal was a function of pH (Figure 35). With the increase of pH, chloride removal was enhanced accordingly. At pH of 7, around 30% chloride was removed. However, at pH of 8, the removal rate increased to 55%; at pH of 10, the removal reached 95%. Chloride removal through the ultra-high lime with aluminum process was impacted by pH because the hydrolysis of  $\text{Al}(\text{OH})_3$  (Figure 36). Consequently, the solubility product ( $K_{sp}$ ) values were a function of pH, which was the driving force of chloride removal in the form of  $\text{Ca}_4\text{Al}_2\text{Cl}_2(\text{OH})_{12}$  precipitates. Chloride removal was also a function of alum concentration added for the precipitation (Figure 37). Chloride concentration dropped dramatically with the increase of alum concentration until around 20 mg/L, after which the drop became moderate.

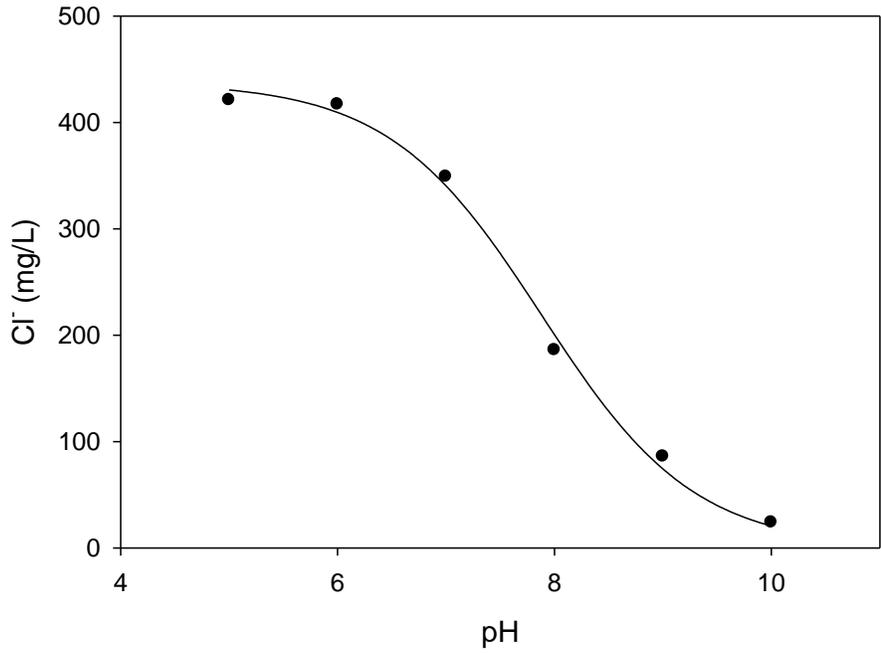


Figure 35. Chloride Removal as a Function of pH

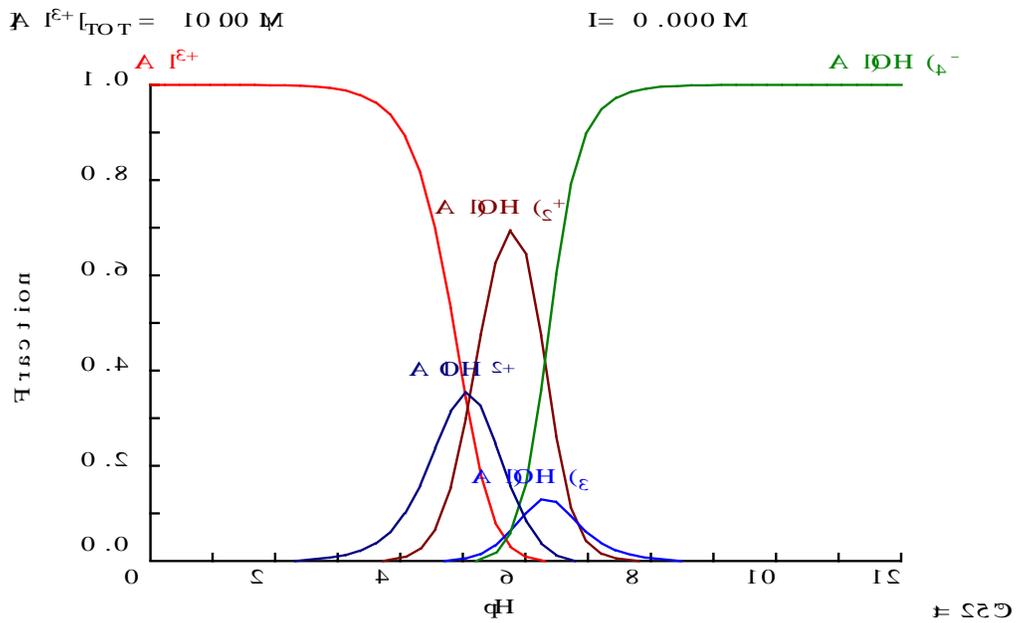
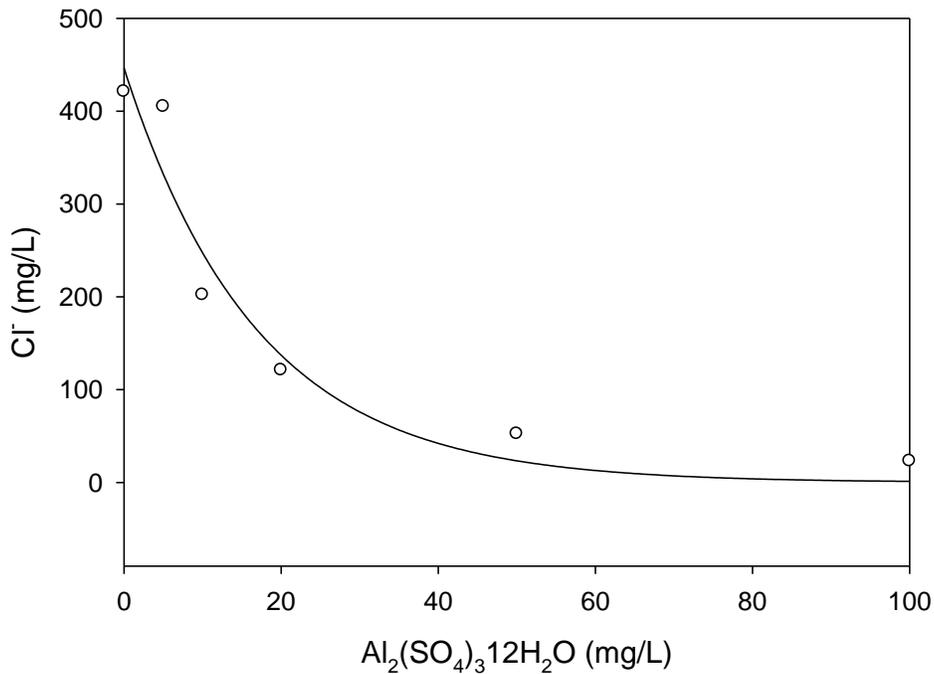


Figure 36. Aluminum Speciation as a Function of pH



**Figure 37. Chloride Removal as a Function of Alum Concentration**

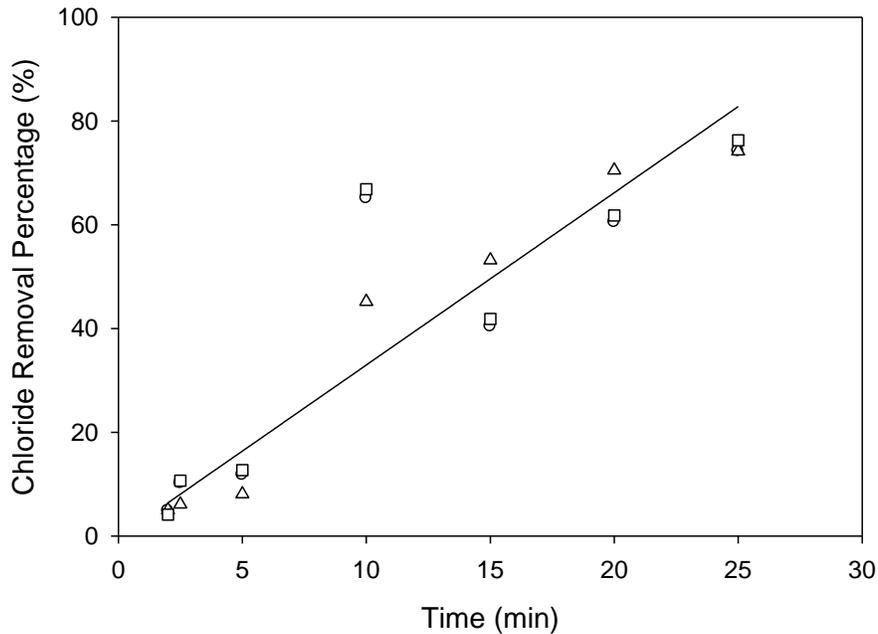
For chloride removal through calcium chloroaluminate precipitation, the chloride removal rate will be modeled as a function of the concentrations of  $\text{Ca}^{2+}$ ,  $\text{Al}^{3+}$  and  $\text{OH}^-$ :

$$\frac{d[\text{Cl}^-]}{dt} = -k[\text{Cl}^-]^e[\text{Ca}^{2+}]^f[\text{Al}^{3+}]^g[\text{OH}^-]^h \quad \text{Equation (9)}$$

where  $k$  is the chloride removal reaction rate coefficient and  $e$ ,  $f$ ,  $g$  and  $h$  are the parameters to be determined. For this case, if we set  $e=0$ ,  $f=0$  and  $h=0$  ( $\text{Ca}^{2+}$  and  $\text{OH}^-$  concentrations did not change), and  $g=1$ , Equation 8 fitted well with our experimental observations (Figure 38).

Considering reducing the chemical costs for the treatment, we tested chloride removal using the alum sludge, a waste of surface water treatment. Alum is commonly utilized to remove color, turbidity, and other impurities during treatment of drinking water. The alum sludge usually contains about 5 percent solids and most states prohibit disposal of any liquid waste containing less than 20 percent solids in landfills. For conditioning and

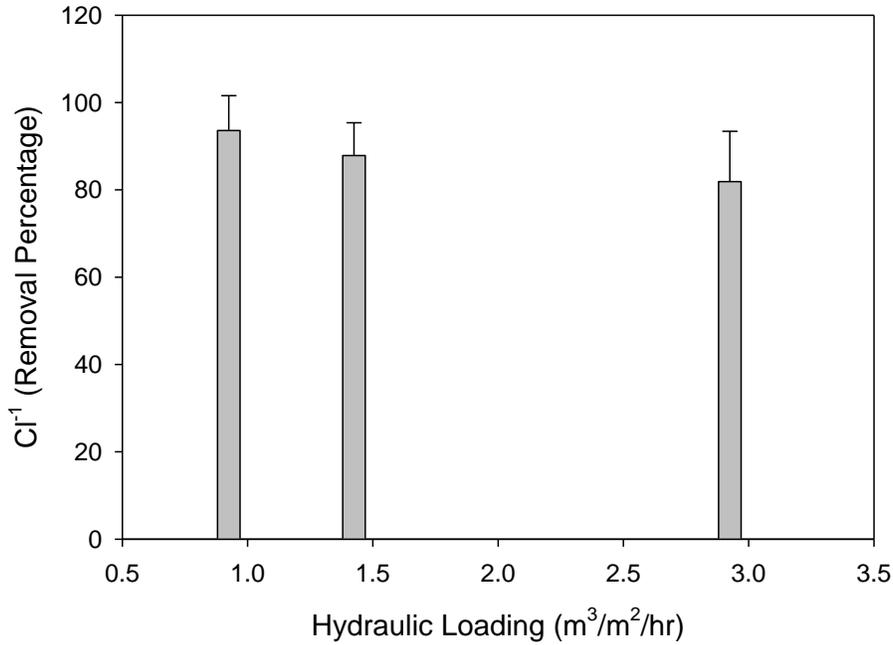
dewatering, lime addition is usually practiced for alum sludge, resulting  $\text{pH} > 12.5$  and making the alum sludge classified as corrosive and can only be deposited in hazardous landfills. Sustainable management of the alum sludge has become an increasing concern in water industry. The beneficial reuse of alum sludge is therefore highly desirable and has attracted considerable research efforts. Most importantly, the high pH and calcium content as a result of dewatering and conditioning with lime addition would promote chloride removal by calcium chloroaluminate precipitation.



**Figure 38. Chloride Removal as a Function of Reaction Time**

This sludge contains approximately 39% aluminum by weight (Huang et al., 2010). The alum sludge was collected from Atlanta-Fulton Water Treatment Plant. After addition of lime and dewatering, the cake-shaped alum sludge had a pH in the range of 12 to 13. The high pH and calcium content of the alum sludge made it possible for chloride to be removed in the form of  $\text{Ca}_4\text{Al}_2\text{Cl}_2(\text{OH})_{12}$ . During chloride removal operation, the most efficient way of using alum sludge is through filtration by using alum sludge as the filtering material. Considering the possible clogging, the alum sludge was bagged before being packed in the filter. A filter with a dimension of 15 cm ID  $\times$  75 cm Length was used. To avoid the flow short-cut inside the filter, the filter was operated as a sequencing

batch reactor. 5 L of the treated leachate after recirculation was introduced into filter at a hydraulic loading of 1.0, 1.5 and 3.0 m<sup>3</sup>/m<sup>2</sup>/hr, after which the leachate was introduced to the pressurized fiber biofilter for further treatment and another 5 L of the treated leachate was introduced. Chloride removal decreased with the increase of hydraulic loading (Figure 39).



**Figure 39. Chloride Removal as a Function of Hydraulic Loading**

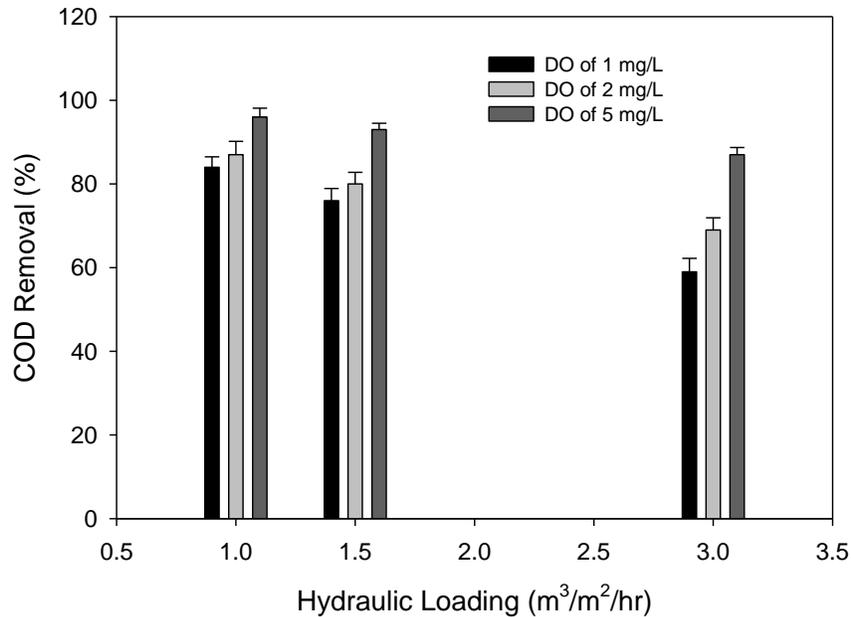
The chloride removal as a function of hydraulic loading can be quantified in terms of removal coefficient,  $K_c$ :

$$\frac{K_c L}{v} = -\ln(1 - fr) \quad \text{Equation (9)}$$

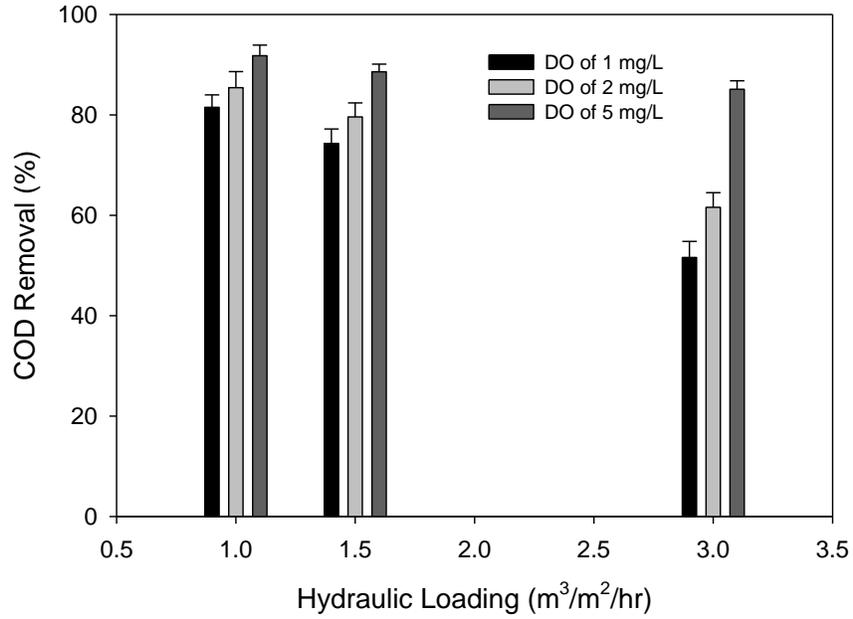
where  $K_c$  is the removal coefficient (min<sup>-1</sup>);  $L$  is the length of the column (cm);  $v$  is the velocity (cm/min); and  $fr$  is the percentage removal (-). The  $K_c$  value was found to be in the range of 1.9 to 4.8 hr<sup>-1</sup>.

#### 4.8 Organic and Iron Removal by Biofiltration

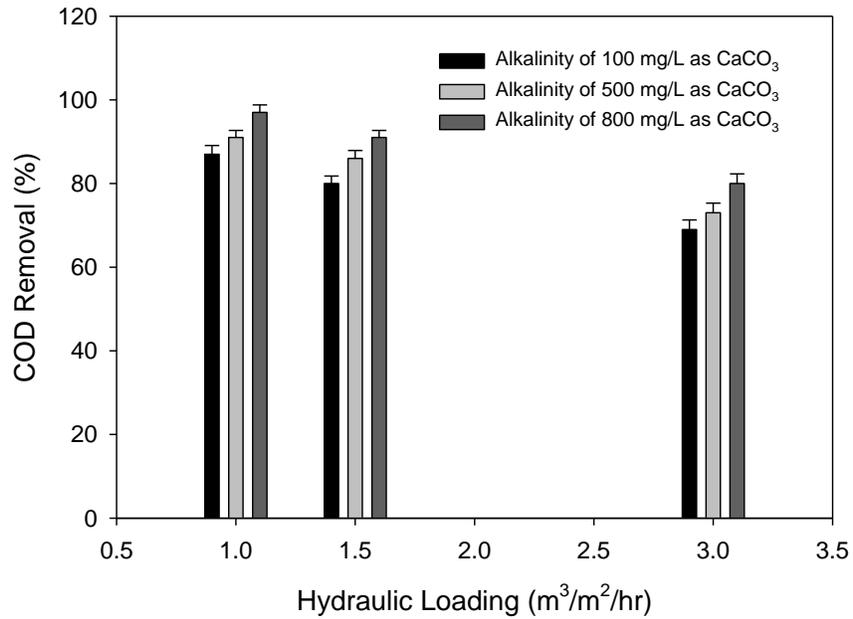
After leachate treatment by aerated recirculation and denitrification, the leachate was introduced to the pressurized biofilter. We monitored the organic decomposition and iron removal during the process and observed efficient organic and iron removal in the biofilter. Both organic removal and iron removal were a function of dissolved oxygen, alkalinity as well as hydraulic loading in the biofilter. Greater dissolved oxygen and alkalinity, lower hydraulic loading favored organic removal. At alkalinity of 100 mg/L as CaCO<sub>3</sub>, 84%, 87% and 96% of COD was removed corresponding to dissolved oxygen of 1, 2 and 5 mg/L with a hydraulic loading of 1.0 m<sup>3</sup>/m<sup>2</sup>/hr for Leon County landfill leachate (Figure 40) and 81%, 85% and 91% for Springhill Landfill leachate (Figure 41). With the increase of alkalinity, COD removal increased accordingly. For Leon County landfill leachate, at dissolved oxygen of 2 mg/L, 87%, 91% and 97% was removed corresponding to alkalinity of 100, 500 and 800 mg/L as CaCO<sub>3</sub> with a hydraulic loading of 1.0 m<sup>3</sup>/m<sup>2</sup>/hr (Figure 42). For Springhill Landfill, these numbers were 85%, 91% and 95% (Figure 43).



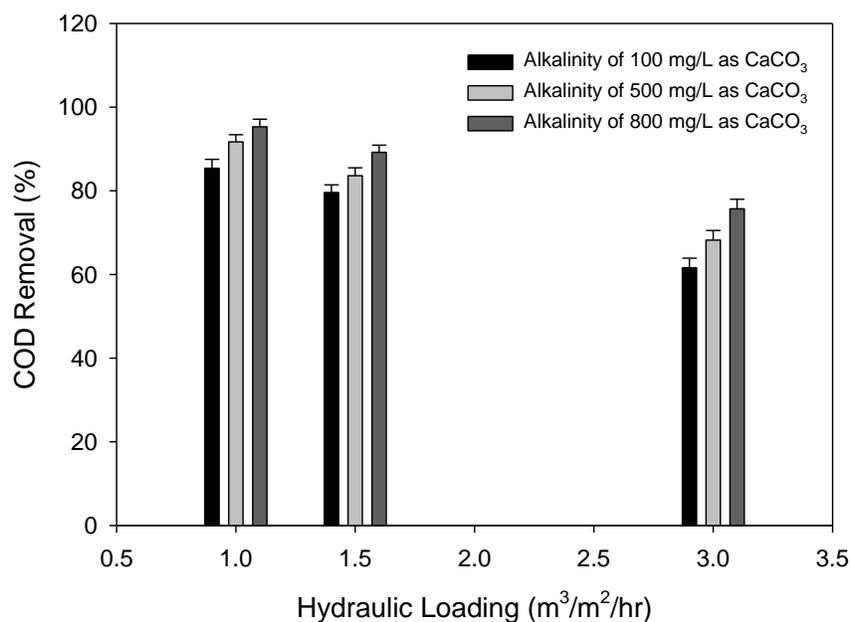
**Figure 40. Organic Removal for Leon County Landfill Leachate as a Function of Dissolved Oxygen**



**Figure 41. Organic Removal for Springhill Landfill Leachate as a Function of Dissolved Oxygen**

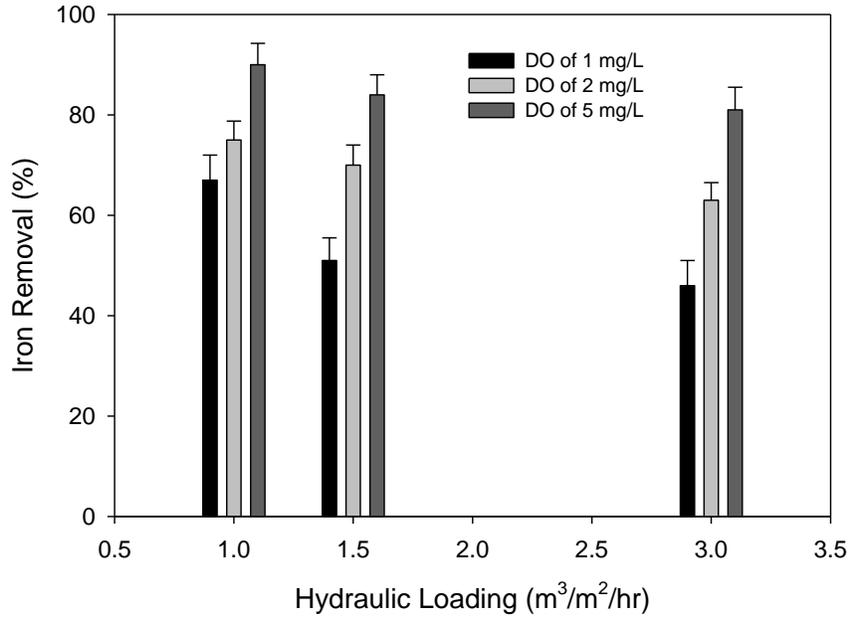


**Figure 42. Organic Removal for Leon County Landfill Leachate as a Function of Alkalinity**

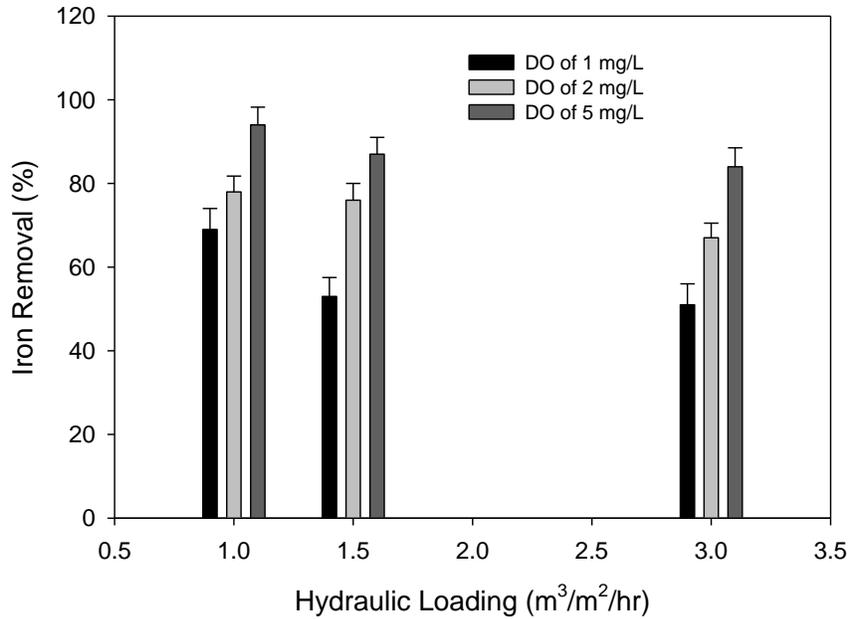


**Figure 43. Organic Removal for Springhill Landfill Leachate as a Function of Alkalinity**

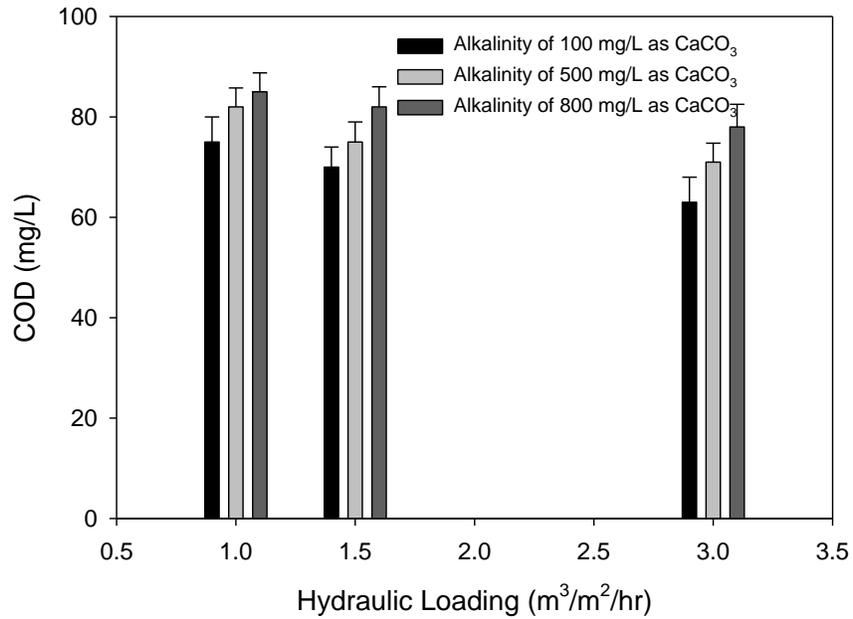
Greater dissolved oxygen and alkalinity, lower hydraulic loading also favored iron removal. At alkalinity of 100 mg/L as CaCO<sub>3</sub>, 67%, 75% and 90% of iron was removed corresponding to dissolved oxygen of 1, 2 and 5 mg/L with a hydraulic loading of 1.0 m<sup>3</sup>/m<sup>2</sup>/hr for Leon County landfill leachate (Figure 44) and 69%, 78% and 94% for Springhill Landfill leachate (Figure 45). With the increase of alkalinity, iron removal increased accordingly. For Leon County landfill leachate, at dissolved oxygen of 2 mg/L, 75%, 82% and 85% was removed corresponding to alkalinity of 100, 500 and 800 mg/L as CaCO<sub>3</sub> with a hydraulic loading of 1.0 m<sup>3</sup>/m<sup>2</sup>/hr (Figure 46). For Springhill Landfill, these numbers were 78%, 86% and 91% (Figure 47).



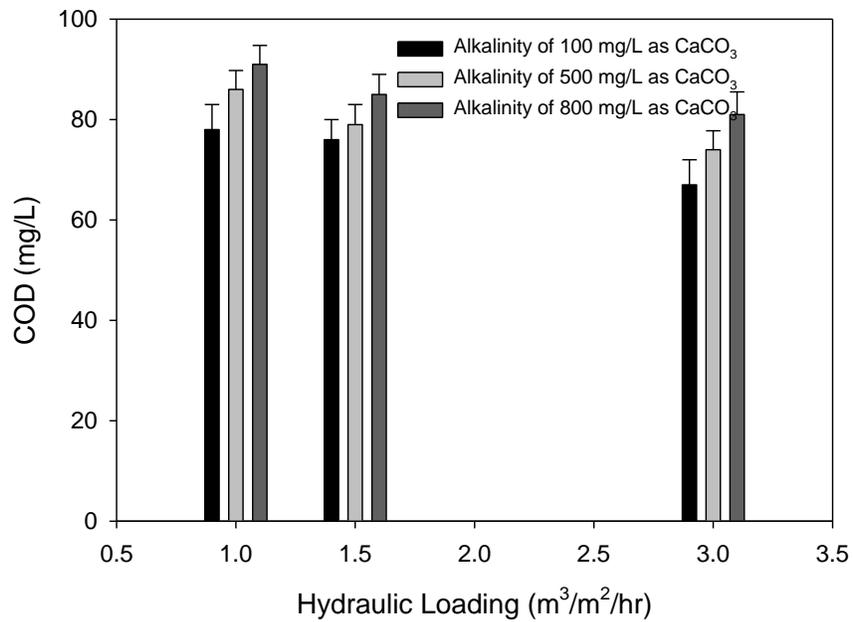
**Figure 44. Iron Removal for Leon County Landfill Leachate as a Function of Dissolved Oxygen**



**Figure 45. Iron Removal for Springhill Landfill Leachate as a Function of Dissolved Oxygen**



**Figure 46. Iron Removal for Leon County Landfill Leachate as a Function of Alkalinity**



**Figure 47. Iron Removal for Springhill Landfill Leachate as a Function of Dissolved Alkalinity**

Iron removal in the pressurized suspended fiber biofilter can be described by:

$$d[\text{Fe}^{2+}]/dt = X_{\text{Fe}^{2+}} \cdot (-\mu_{\text{max}} \cdot [\text{Fe}^{2+}] / ([\text{Fe}^{2+}] + K_{\text{Fe}^{2+}})) / Y_{\text{Fe}^{2+}} \quad \text{Equation (10)}$$

where  $[\text{Fe}^{2+}]$  is the ferrous iron concentration,  $X_{\text{Fe}^{2+}}$  is the iron oxidizing bacteria concentration,  $\mu_{\text{max}}$  is the iron oxidizing bacterial maximal specific growth rate,  $K_{\text{Fe}^{2+}}$  is the Michaelis-Menten constant for ferrous iron oxidation,  $Y_{\text{Fe}^{2+}}$  is the yield coefficient for iron oxidizing bacteria, and  $t$  is time. However, in this research, the iron removal was conducted in the column experiments instead of batch experiments. Without the kinetic iron removal data, Equation 10 cannot be simulated. Instead, we used a general relationship to describe iron removal from the leachate:

$$\frac{C}{C_0} = \frac{1}{1 + k\theta} \quad \text{Equation (11)}$$

where  $C_0$  is input iron concentration to the biofilter (mg/L),  $C_p$  is output iron concentration (mg/L),  $k$  is the reaction rate constant ( $\text{hr}^{-1}$ ), and  $\theta$  is the hydraulic retention time ( $\text{hr}^{-1}$ ).

Based on Equation 11, iron removal rate was found to be  $2.25 \pm 1.40 \text{ hr}^{-1}$  for Leon County Landfill leachate and  $2.41 \pm 1.29 \text{ hr}^{-1}$  for Springhill Landfill leachate.

## 5. Discussion

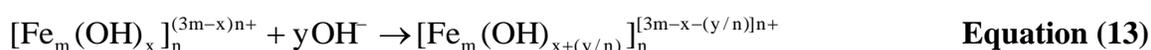
### 5.1 Iron Removal

Iron is one of the most abundant metals of the Earth's crust. It occurs naturally in water in soluble form as the ferrous iron (bivalent iron in dissolved form  $\text{Fe}^{2+}$  or  $\text{Fe}(\text{OH})^+$ ) or complex form like the ferric iron (trivalent iron:  $\text{Fe}^{3+}$  or precipitated as  $\text{Fe}(\text{OH})_3$ ). In general, iron does not present a danger to human health or the environment, but it brings unpleasantness of an aesthetic and organoleptic nature. Indeed, iron gives a rust color to the water, which can stain linen, sanitary facilities or even food industry products. Iron also gives a metallic taste to water, making it unpleasant for consumption. It can also be at the origin of corrosion in drains sewers, due to the development of microorganisms, the *ferrobacteries*.

Ferrous iron is soluble as a cation, while ferric iron is not. Ferrous iron normally can be oxidized to ferric iron in minutes. The redox potential of the water is such as it allows an oxidation of the ferrous iron in ferric iron which precipitates then in iron hydroxide,  $\text{Fe}(\text{OH})_3$ , thus allowing a natural removal of dissolved iron:



Once ferrous iron is oxidized, hydrolysis proceeds:



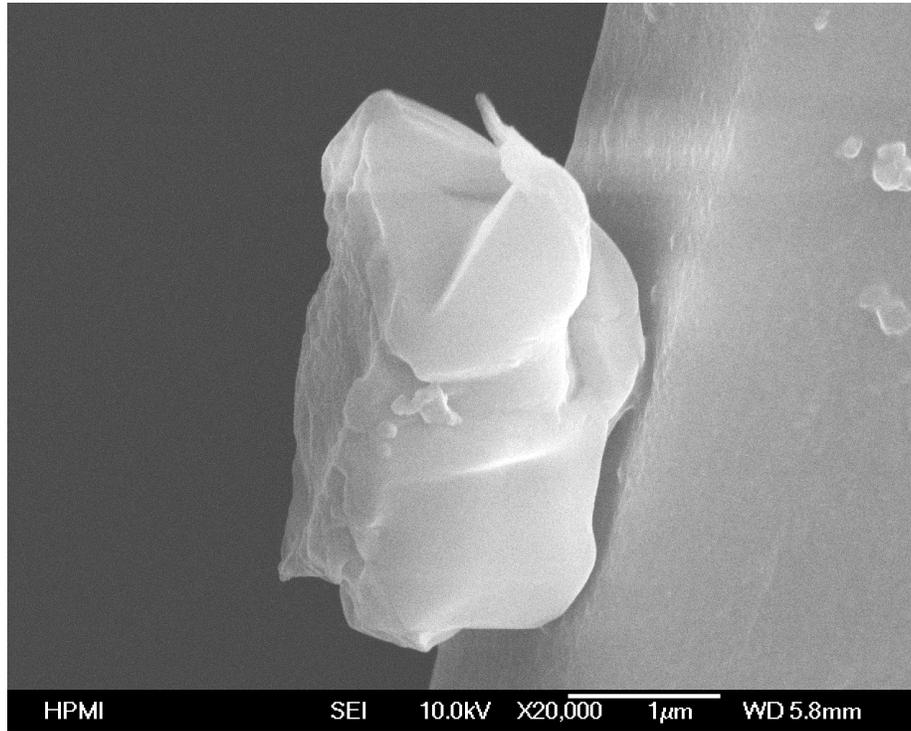
The hydrolysis is primarily related to pH. Amorphous hydrous ferric hydroxide can have a strong sorption capacity to the filter media. Change of solution pH usually accompanies with iron hydrolysis. The change of solution pH occurred because the hydrolysis can consume alkalinity. For landfill leachate with lower alkalinity, pH decreased more obviously with iron hydrolysis. The results of iron removal in the pressurized fiber biofilter as a function of alkalinity further verified the importance of alkalinity on iron removal. It should be noted that alkalinity consumption was also related to the microbial activities.

The oxidation kinetics of ferrous iron are well known to be pH dependent, with the slow oxidation kinetics of ferrous iron at low pH being part of the early basis for considering the importance of microbial iron oxidation and fixation. There are many known iron-oxidizing microorganisms in environments at neutral pH, where the abiotic oxidation of iron is fast enough that the microbes must effectively compete with the abiotic process. Additionally, microbes must compete with each other for the available ferrous iron as substrate, with organisms able to utilize the iron faster in a particular environment making up the predominant part of a community including iron oxidizers. Ferric hydroxide ( $\text{Fe}(\text{OH})_3$ ) is the direct result of ferrous iron oxidation and precipitation. With time, ferric hydroxide is mineralized. The principal forms of mineralized ferric iron include amorphous hydrous ferric oxide ( $\text{Fe}_2\text{O}_3 \cdot \text{XH}_2\text{O}$ ), maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ), lepidocrocite ( $\gamma\text{-FeOOH}$ ), hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ), and goethite ( $\alpha\text{-FeOOH}$ ). The above iron oxides are listed in order of decreasing solubility, which also reflects increasing crystallinity. Amorphous hydrous ferric oxide at neutral pH and oxidizing Eh conditions has a solubility of 0.6  $\mu\text{g/L}$ , which is three orders of magnitude greater than that of goethite.

The elimination of the ferrous iron, by physical-chemical way, is obtained by raising the water redox potential with oxygen. In the case of acid water, the treatment could be supplemented by a correction of the pH. Thus, the ferrous iron is oxidized in ferric iron, which precipitates in iron hydroxide,  $\text{Fe}(\text{OH})_3$ . The precipitate is then separated from the liquid phase phase by sedimentation and filtration. The stage of precipitation by chemical oxidation can also be carried out with the stronger oxidants such as the chlorine dioxide ( $\text{ClO}_2$ ), ozone ( $\text{O}_3$ ) or the potassium permanganate ( $\text{KMnO}_4$ ). Biological iron precipitation has also been practiced, especially for wastewater treatment such as landfill leachate mainly because of the denser structure of biotic iron precipitates compared to the common physicochemical abiotic precipitates. The economic benefit of this method is obvious mainly owing to its low operation costs.

In the current research, biological iron precipitation was practiced in the pressurized fiber biofilter. Using an electronic scanning microscope, crystal structure of iron deposited on

the polypropylene fiber in the pressurized biofilter was captured (Figure 48). The oxidation/precipitation process would be considerably faster in the biological filter than in the filter systems built for physicochemical precipitation with aeration before filtering.



**Figure 48. Crystal Structure of Iron Deposited on Polypropylene Fiber**

## **5.2 Microbial Accumulation**

Biofilters are different from conventional gravity filters and can not only filter suspended solids, but also increase the degradation of organic matter using the fixed film biomass. Inside the biofilter, hydrocarbons provided a carbon source to stimulate aerobic microbial degradation, which consumed the readily available oxygen driving the system anoxic. Therefore, air was continuously provided. Biofilm activity was not proportional to the quantity of fixed biomass, but increased with the depth of biofilter. The biofilm on the top layer became less thick, and then the microbial oxidation and COD removal efficiency were improved which accelerated the start-up operation. Owing to the high organic content in Springhill Landfill leachate, more biomass was produced. This was

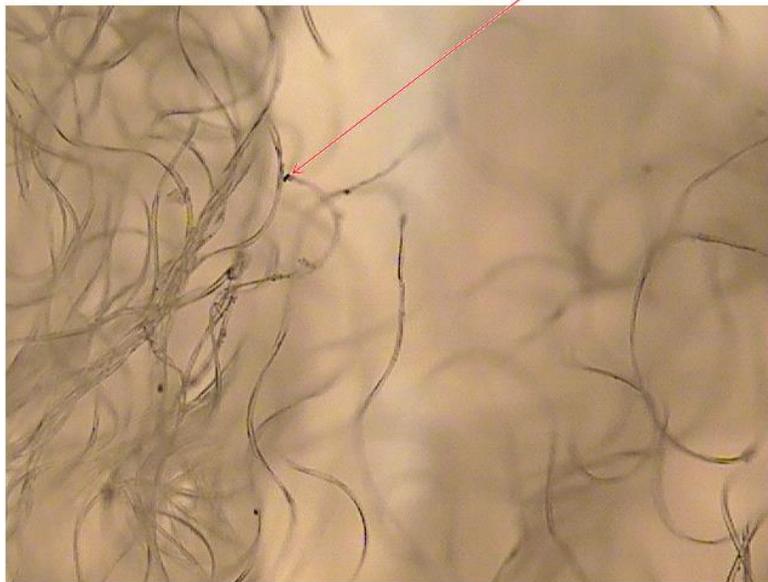
verified by the fiber observations after treatment (Figure 49). The massive biomass ultimately resulted in the progressive clogging of the biofilter, which must then be washed clean. The biofilter without backwashing would become hardened in the operation due to clogging of a large amount of biomass and solids in the bottom layer.



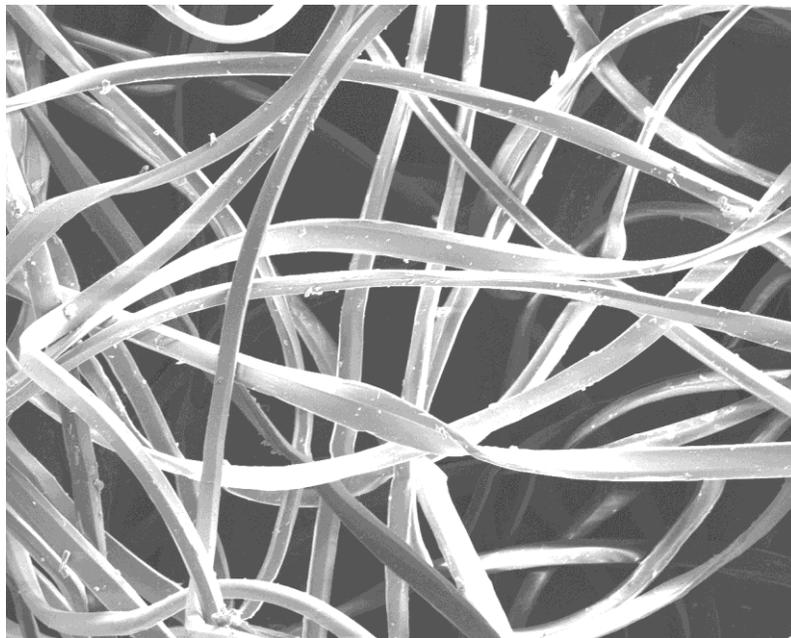
**Figure 49. Polypropylene Fiber after (Left) and before (Right) Usage in the Pressurized Biofilter**

Iron fixation microorganism accumulation on the fiber was evidenced by the observation of fiber under an optical microscope (Figure 50). These strains were further examined under a scanning electronic microscope (Figure 51 and Figure 52). These iron fixation bacterial strains were rod shaped and had the capacity to attach to the fiber. They formed a slimy layer embedded in a polysaccharide matrix known as biofilm (Figure 53). Soluble iron was fixed to the fiber by these iron fixation bacteria when it passed by the fiber with attached iron fixation bacteria. Compared to physicochemical iron oxidation and precipitation, microbial-mediated iron fixation was more efficient besides the benefits of low operation costs.

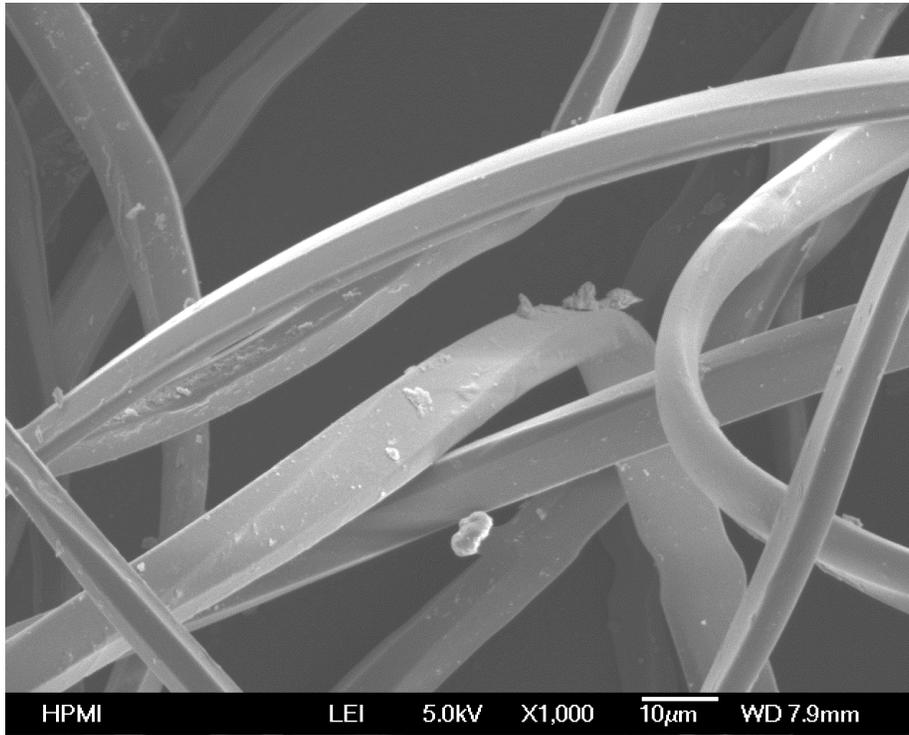
Iron Fixation Bacteria



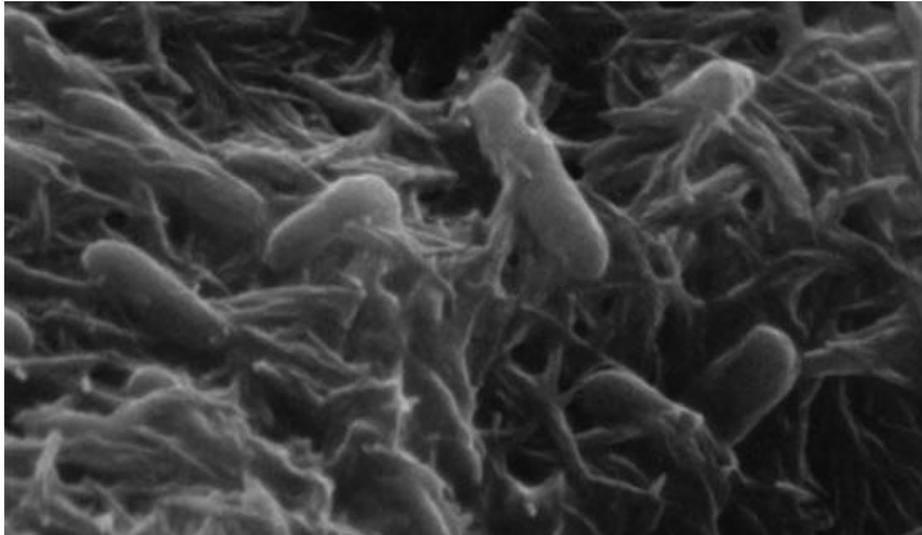
**Figure 50. Iron Fixation Bacteria on Polypropylene Fiber under an Optical Microscope**



**Figure 51. Iron Fixation Bacteria on Polypropylene Fiber under a Scanning Electronic Microscope (I)**



**Figure 52. Iron Fixation Bacteria on Polypropylene Fiber under a Scanning Electronic Microscope (II)**



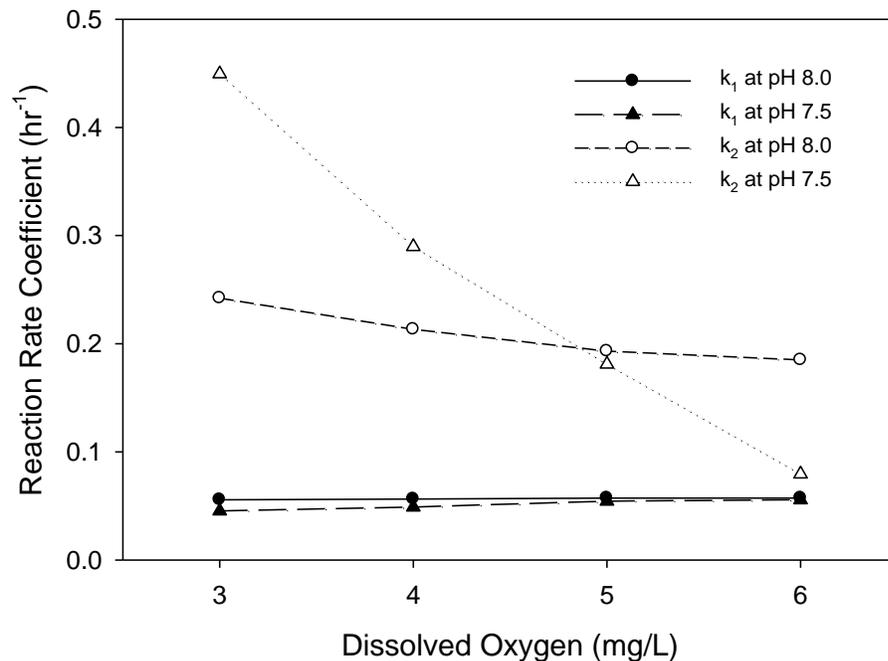
**Figure 53. Iron Fixation Bacterial Strains**

### 5.3 Iron and Organic Removal Quantification

Iron removal and release in the recirculation reactor can be described by the following proposed equation. Iron removal was assumed to follow first order reaction and iron release was to follow exponential function:

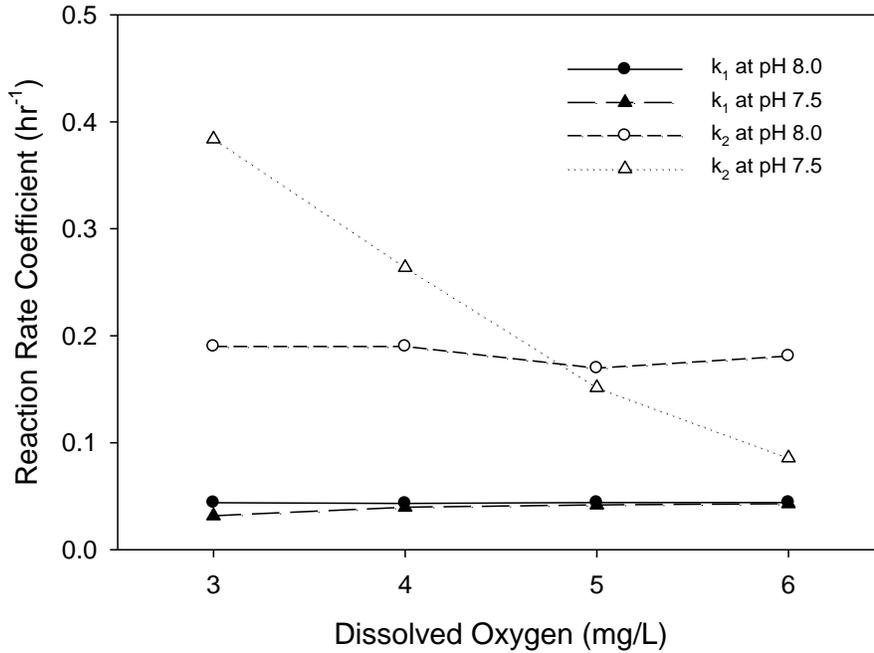
$$\frac{dC}{dt} = -k_1 \cdot C + a \cdot e^{-k_2 C} \quad \text{Equation (14)}$$

where  $k_1$  is the iron removal rate coefficient and  $k_2$  is the iron release rate coefficient, respectively. In above equation, iron release and removal are described in two separate terms, which should well describe the fate of iron in the recirculation reactor. Iron concentrations from the recirculation reactor were simulated against this equation by means of non-linear regression of simplex optimization of least squares. 95% confidence intervals and prognosis intervals were determined for each fitted curve. The simulated iron removal rate coefficients were in the range of  $0.6 \text{ hr}^{-1}$  to  $0.8 \text{ hr}^{-1}$ . On the other hand, the iron release rate coefficients were in the range of  $0.4 \text{ hr}^{-1}$  to  $2.6 \text{ hr}^{-1}$ .



**Figure 54. Iron Release and Removal for Leon Landfill Leachate at pH 7.5 as a Function of Dissolved Oxygen**

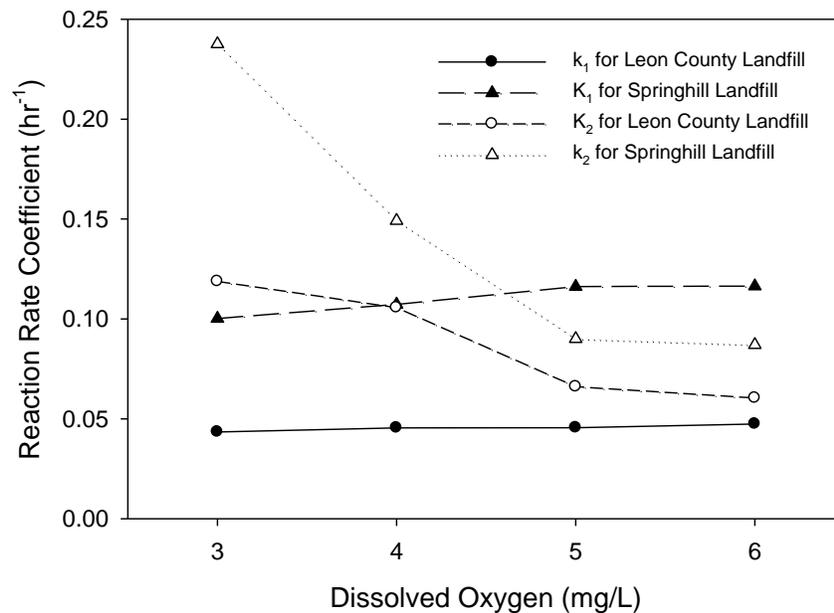
Leon County Landfill had greater iron removal rate coefficients and iron release rate coefficients than that of Springhill Landfill (Figure 54 and Figure 55). For both landfills, the iron removal rate coefficients were higher at pH 8 than that of pH 7.5, which increased with the increase of dissolved oxygen. The iron release rate coefficients decreased with the increase of dissolved oxygen, which was more pronounced at pH 7.5 than that of pH 8.0.



**Figure 55. Iron Release and Removal for Springhill Landfill Leachate at pH 7.5 as a Function of Dissolved Oxygen**

Organic removal in the recirculation reactor was also studied for landfill leachate collected from the Leon County Landfill and Springhill Landfill. During the recirculation process, organic substrates were released from the solid waste owing to the hydrolysis of organic components. The impact of recirculation cycle on organic release and removal was investigated for 10 recirculation cycles at pH 7.5. After 4 to 5 recirculation cycles, the organic removal became stable. Similar to iron release and removal, Equation (14) was used to simulated organic concentrations from the recirculation reactor to obtain

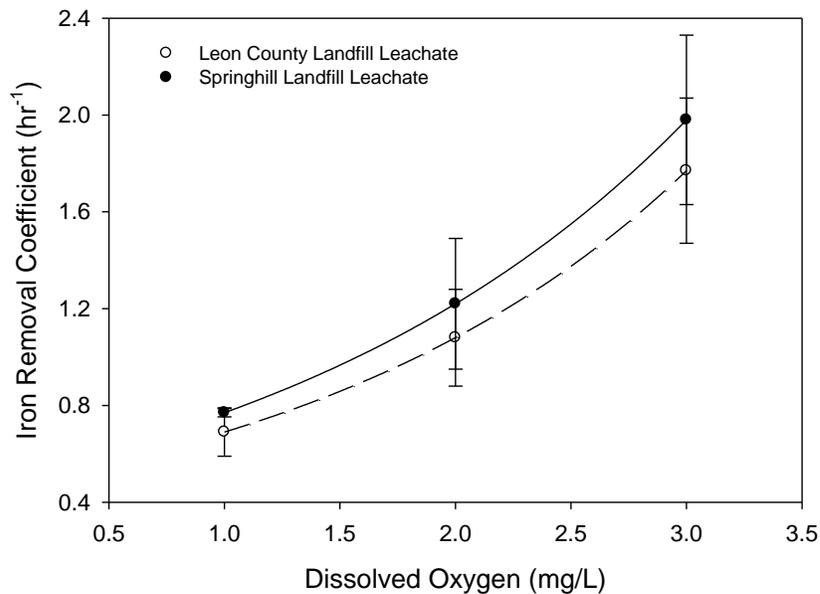
organic release and removal rate coefficients. Compared to Leon County Landfill leachate, leachate collected from Springhill Landfill had higher organic contents. The organic removal reached an average of 70% for Leon County Landfill leachate and 80% for Springhill Landfill leachate when organic removal became stable. Springhill Landfill had greater organic removal rate coefficients than that of Leon County Landfill with organic removal rate coefficients in the range of  $0.043 \text{ hr}^{-1}$  to  $0.047 \text{ hr}^{-1}$  as compared to  $0.10 \text{ hr}^{-1}$  to  $0.12 \text{ hr}^{-1}$ . For both Leon County Landfill and Springhill Landfill, the organic removal rate coefficients decreased with the increase of dissolved oxygen, which was more pronounced for Springhill Landfill (Figure 56). Springhill Landfill also had greater organic release rate coefficients than that of Leon County Landfill ( $0.24 \text{ hr}^{-1}$  to  $0.08 \text{ hr}^{-1}$  as compared to  $0.12 \text{ hr}^{-1}$  to  $0.06 \text{ hr}^{-1}$ ). Leon County Landfill stopped accepting domestic wastes and most of the domestic wastes from Leon County were deposited in Springhill Landfill currently. Therefore, Springhill Landfill contained more easily decomposable organic contents, resulting release and removal rate coefficients. For both Leon County Landfill and Springhill Landfill, the organic release rate coefficients decreased with the increase of dissolved oxygen.



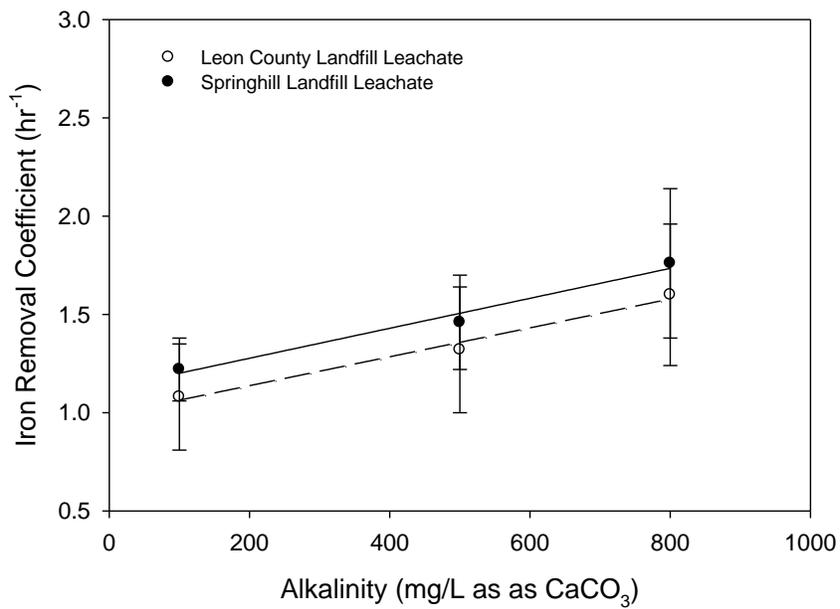
**Figure 56. Organic Release and Removal as a Function of Dissolved Oxygen**

After treatment in the aerated recirculation reactor, the treated leachate was introduced to the pressurized fiber biofilter. Within the pressurized fiber biofilter, iron removal and organic decomposition were monitored, which were a function of dissolved oxygen and alkalinity. Iron and organic removal in the pressurized fiber biofilter was quantified in terms of removal coefficient,  $k_c$  as described in Equation (9).

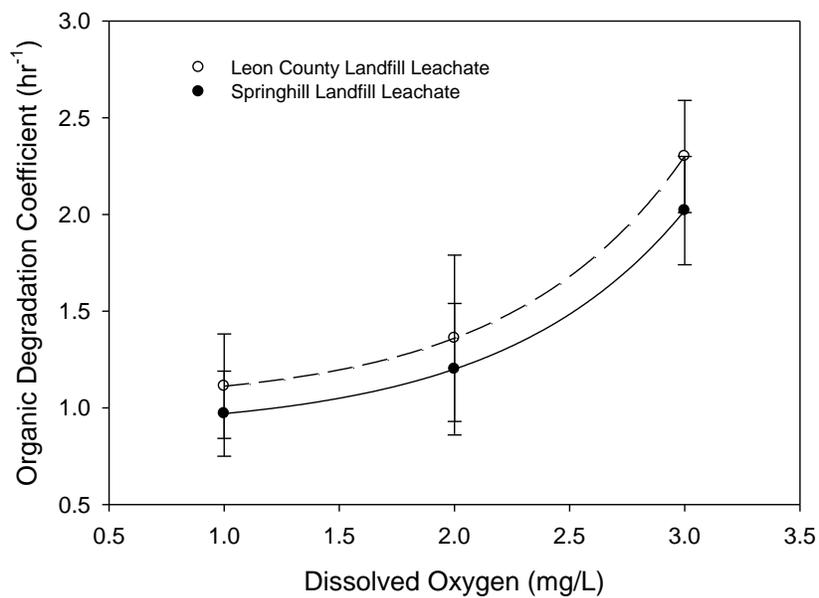
At alkalinity of 100 mg/L as  $\text{CaCO}_3$  and dissolved oxygen of 1 mg/L, the iron removal coefficient was  $0.69 \text{ hr}^{-1}$  for Leon County landfill leachate and  $0.78 \text{ hr}^{-1}$  for Springhill Landfill leachate (Figure 57). With the increase of dissolved oxygen, iron removal coefficients increased exponentially, but linearly increased with the increase of alkalinity (Figure 57 and Figure 58). Organic removal had similar observations as iron removal. With the increase dissolved oxygen from 1 mg/L to 3 mg/L, organic removal coefficient increased exponentially from  $1.1 \text{ hr}^{-1}$  to  $2.3 \text{ hr}^{-1}$  for Leon County Landfill and  $0.98 \text{ hr}^{-1}$  to  $2.0 \text{ hr}^{-1}$  for Springhill Landfill; while with the increase of alkalinity from 100 mg/L as  $\text{CaCO}_3$  to 800 mg/L as  $\text{CaCO}_3$ , organic removal coefficient increased linearly from  $1.35 \text{ hr}^{-1}$  to  $1.98 \text{ hr}^{-1}$  for Leon County landfill and  $1.20 \text{ hr}^{-1}$  to  $1.78 \text{ hr}^{-1}$  for Springhill Landfill (Figure 59 and Figure 60).



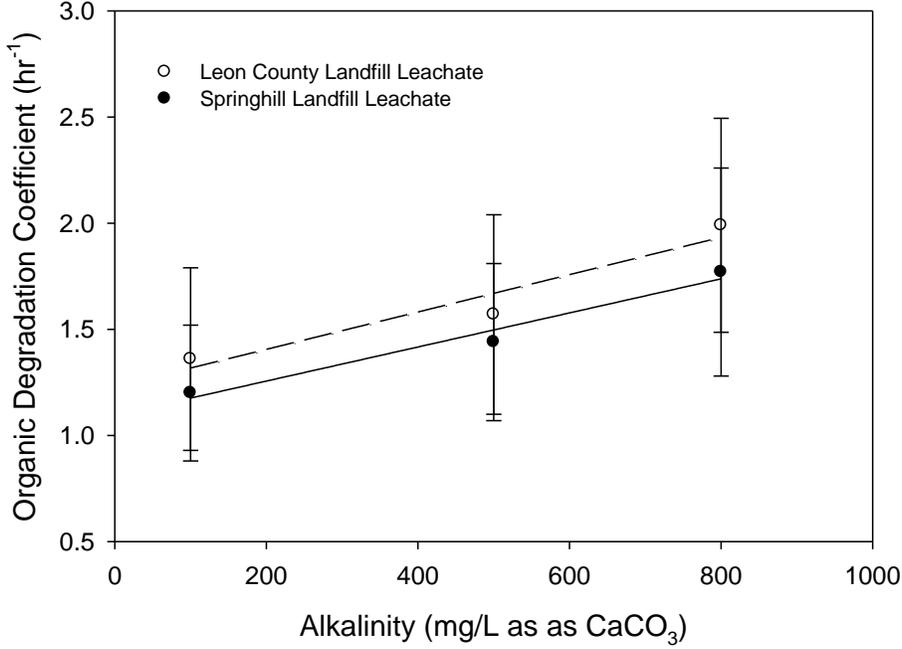
**Figure 57. Iron Removal in Pressurized Fiber Biofilter as a Function of Dissolved Oxygen**



**Figure 58. Iron Removal in Pressurized Fiber Biofilter as a Function of Alkalinity**



**Figure 59. Organic Removal in Pressurized Fiber Biofilter as a Function of Dissolved Oxygen**



**Figure 60. Organic Removal in Pressurized Fiber Biofilter as a Function of Alkalinity**

#### 5.4 Correlation and Sensitivity Study

Organic and iron removal might be correlated since they both occurred in the biofilter. The correlation can be described by the Pearson product-moment correlation coefficient, or “Pearson’s correlation”, which was obtained by dividing the covariance of the two variables by the product of their standard deviations (Chaudhuri and Lovley, 2003):

$$\rho_{x,y} = \frac{\sum_{i=1}^n (x_i - \bar{x})(y_i - \bar{y})}{(n-1)S_x S_y} = \frac{\sum_{i=1}^n (x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum_{i=1}^n (x_i - \bar{x})^2 \sum_{i=1}^n (y_i - \bar{y})^2}} \quad \text{Equation (15)}$$

where  $\bar{x}$  and  $\bar{y}$  denote the means of  $\frac{d[\text{COD}]}{dt}$  and  $\frac{d[\text{Fe}^{2+}]}{dt}$  and  $S_x$  and  $S_y$  denote the standard deviations of  $\frac{d[\text{COD}]}{dt}$  and  $\frac{d[\text{Fe}^{2+}]}{dt}$ . The results indicated that the strength of

association between the organic decomposition and iron removal was low ( $r = 0.36$ ), and that the correlation coefficient was not very highly significantly different from zero.

## 5.5 Cost Analysis

Besides the space saving by using the pressurized biofiltration, operation cost was also obvious as compared to the traditional treatment processes. The cost analysis is summarized in Table 4.

**Table 4. Comparison of Pressurized Fiber Biofilter with Traditional Biological Leachate Treatment**

	Pressurized Fiber Biofilter	Aeration and Sedimentation	Treatment Cost Saving
Aeration	Medium	High	Around 50% Electric Power
Sludge Production	Low	High	Around 60% for Sludge Treatment
Chemical for Iron Removal	None	High	100% Chemical Costs
Operation Costs	High	Average	Extra Costs for Pressure

The proposed treatment system can efficiently removal organic, nitrogen, chloride and iron from landfill leachate. The benefits of aerated recirculation have documented before. Here the comparison of pressurized fiber biofilter with traditional biological landfill leachate is emphasized. Compared to traditional biological system, medium aeration is required for the pressurized system. Consequently, around 50% of electric power that is required for aeration is saved. In addition, owing to the low sludge production, around 60% of sludge handling costs can also be saved. Most importantly, since there are no chemical requirements for iron removal in the pressurized fiber biofilter, no chemical costs are incurred for iron removal. The disadvantage of the pressurized fiber biofilter is the high operation costs, which attribute to the pressure requirements of the operation.

## 6. Conclusions

From this research, it is demonstrated that landfill leachate can be treated by aerated recirculation, denitrification, the ultra-high lime with aluminum process, and suspended fiber biofiltration to remove organics, nitrogen, chloride and iron. This treatment process start with aerated recirculation, which can improve the leachate quality and shorten the time required for landfill stabilization. During aerated recirculation, ammonium in the landfill leachate is oxidized to nitrate and is removed in the denitrification reactor following aerated recirculation. A dissolved oxygen level of 5.0 mg/L is recommended to ensure a complete nitrification. For chloride removal, pH plays an very important role. With the increase of pH, chloride removal efficiency increases accordingly. At pH of 7, around 30% chloride can be removed. However, at pH of 8, the removal rate increases to 55%; at pH of 10, the removal reaches 95%. The suspended fiber biofilter is designed and operated under pressurized aeration to achieve biological contact oxidation, which can removal organic compounds and iron more efficiently than conventional biological methods through biological contact oxidation. Especially, the biological contact oxidation has extreme advantages in iron removal by fixing iron onto the filter media. Consequently, there is minimal ferric iron suspending in the solution that can escape the filter. After treatment by the combined aerated leachate recirculation and pressurized suspended fiber biofiltration, together with denitrification and the ultra-high lime with aluminum process, the COD of the treated landfill leachate can achieve as low as 8 mg/L and iron can be as low as 0.02 mg/L. This treatment preprocess provides a new alternative means for the treatment of landfill leachate with high organic, nitrogen, chloride and iron contents.

At the end of this research, the best operation parameters are identified for aerated leachate recirculation, denitrification, the ultra-high lime with aluminum process, and pressurized suspended fiber biofiltration and presented in the recommendation section. Cost saving is conducted and compared with that of conventional treatment processes.

## 7. Recommendation

For the treatment of landfill leachate using the combined aerated recirculation and suspended fiber biofiltration, together with denitrification and the ultra-high lime with aluminum process to remove organics, nitrogen, chloride and iron, the following operation parameters are recommended:

### Aerated Recirculation:

Aeration: Dissolved oxygen of 5.0 mg/L is required to ensure a through nitrification and iron oxidation and removal by precipitation at pH 7.5.

Recirculation Cycle: A recirculation cycle of 4 is recommended for the leachate with a neutral pH i.e., 7.5.

Recirculation Ratio: 50% recirculation ratio would produce reasonable organic and iron removal results.

### Denitrification:

A hydraulic loading of  $1 \text{ m}^3/\text{m}^2/\text{hr}$  is recommended for the denitrification reactor.

### Ultra-High Lime with Aluminum Process:

pH 10 and alum dose of at least 20 mg/L are recommended.

Suggestion: Alum sludge from surface water treatment, which contains 39% aluminum by weight and maintains a pH > 12.5

### Pressurized Fiber Bifilter:

Alkalinity of 500 mg/L as  $\text{CaCO}_3$  and dissolved oxygen of 2 mg/L with a hydraulic loading of  $1.0 \text{ m}^3/\text{m}^2/\text{hr}$

## 8. Future Work

In the pressurized suspended fiber biofilter, iron is oxidized by contact oxidation and removed as iron oxides, which have high binding strength for phosphorus. This makes the pressurized suspended fiber biofilter have the potential implications of phosphorus removal for landfill leachate. The prominent correlation between phosphorus and iron oxides has led to numerous examinations of phosphorous adsorption capacities and mechanisms by iron oxides. The mechanism of phosphorous adsorption onto ferric oxides is generally dominated by ligand exchange in which two singly coordinated hydroxyl groups or water molecules are replaced by a single phosphate anion, resulting in the formation of a bidentate, binuclear complex. The phosphate surface complexes are very stable, resulting in slow exchange rates and an apparent irreversibility (hysteresis) of phosphorus adsorption. Phosphorous adsorption on hematite has been investigated by IR spectroscopy, which suggests that monodentate inner-sphere complexation is the primary adsorption mechanism. It has also been demonstrated that phosphorous adsorption by synthetic and naturally occurring iron oxides can be described by Langmuir and Freundlich isotherms, although limitations exist for both of them. In our prior research, we have also demonstrated that phosphorus is able to adsorb to iron species, during which phosphate replaces singly coordinated OH<sup>-</sup> groups and then reorganizes into a very stable binuclear bridge between the cations. This chemisorption process is coupled with the release of OH<sup>-</sup> ions, thus this process is favored by low pH values. Since the pressurized suspended fiber biofilter has dramatically increased surface areas, phosphorous removal can thus achieve a significant efficiency.

In addition, a kinetic process of iron removal can be further investigated:

$$-\frac{d[\text{Fe}^{2+}]}{dt} = k[\text{OH}^{-}]^2 P_{\text{O}_2} [\text{Fe}^{2+}] \quad \text{Equation (16)}$$

where  $k$  is the removal constant,  $[\text{Fe}^{2+}]$  and  $[\text{OH}^{-}]$  are concentrations of  $\text{Fe}^{2+}$  and  $\text{OH}^{-}$ , respectively, and  $P_{\text{O}_2}$  is the partial pressure of oxygen. By keeping  $P_{\text{O}_2}$  and  $[\text{OH}^{-}]$  as constants, which is often the case during operations, a pseudo-first order equation can be obtained:

$$-\frac{d[\text{Fe}^{2+}]}{dt} = k^*[\text{Fe}^{2+}] \quad \text{Equation (17)}$$

where  $k^* = k[\text{OH}^-]^2\text{P}_{\text{O}_2}$ .

This equation can be integrated to give:

$$\text{Ln} \frac{[\text{Fe}^{2+}]_0}{[\text{Fe}^{2+}]} = k^* t \quad \text{Equation (18)}$$

where  $[\text{Fe}^{2+}]_0$  is the input  $\text{Fe}^{2+}$  concentration and  $t$  is the residence time of leachate in the biofilter, which can be estimated by:

$$t = \frac{V}{Q} \quad \text{Equation (19)}$$

The sensitivities of above equation in describing  $\text{Fe}^{2+}$  removal can also be examined. Specifically, the input  $\text{Fe}^{2+}$  concentration will be increased to 40% with other parameters being fixed. The sensitive index  $\beta$  is thus calculated based on the formula given by Friend et al. (Li and Zhao, 2003):

$$\beta_{\text{Fe}^{2+}} = \frac{\left(\left(\frac{d[\text{Fe}^{2+}]}{dt}\right)_1 - \left(\frac{d[\text{Fe}^{2+}]}{dt}\right)_0\right) \cdot \left(\frac{d[\text{Fe}^{2+}]}{dt}\right)_0}{([\text{Fe}^{2+}]_1 - [\text{Fe}^{2+}]_0) \cdot [\text{Fe}^{2+}]_0} \quad \text{Equation (20)}$$

In above equations,  $\left(\frac{d[\text{Fe}^{2+}]}{dt}\right)_1$  denote  $\text{Fe}^{2+}$  removal rate in response to  $\text{Fe}^{2+}$  input increase and  $\left(\frac{d[\text{Fe}^{2+}]}{dt}\right)_0$  denote  $\text{Fe}^{2+}$  removal rate of original  $\text{Fe}^{2+}$  inputs. The distance of  $\beta$  value from zero is proportional to the sensitivity and the sign of  $\beta$  indicates if the correlation is positive or negative.

In the pressurized suspended fiber biofilter, the oxygen transfer to the biofilm plays the key role and the following diffusion/reaction model can be used to describe the oxygen consumption in the biofilm, focusing on the limiting substrate oxygen (Li et al., 1999):

$$D_{\text{O}_2, \text{f}} \frac{d^2 C_{\text{O}_2, \text{f}}}{dZ^2} = V_{\text{m}, \text{O}_2} \frac{C_{\text{O}_2, \text{f}}}{K_{\text{O}_2} + C_{\text{O}_2, \text{f}}} \quad \text{Equation (21)}$$

where  $D_{O_2,f}$  is the oxygen diffusivity within the film,  $C_{O_2,f}$  is the oxygen concentration in the biofilm,  $Z$  is the depth from the biofilm substratum,  $V_{m,O_2}$  is the maximum volumetric oxygen reaction rate, and  $K_{O_2}$  is the Michaelis-Menten constant for  $O_2$  utilization. This model assumes that the biofilm is planar and within the film, oxygen diffusion and organic depletion reaction occurring at steady state. Under conditions where oxygen concentration decreases to zero within the biofilm, the system can be modeled as a deep biofilm and Equation (10) thus has an analytical solution:

$$-J_{O_2,s} = \sqrt{2V_m D_{O_2,f} [C_{O_2,s} - K_{O_2} \ln(\frac{K_{O_2} + C_{O_2,s}}{K_{O_2}})]} \quad \text{Equation (22)}$$

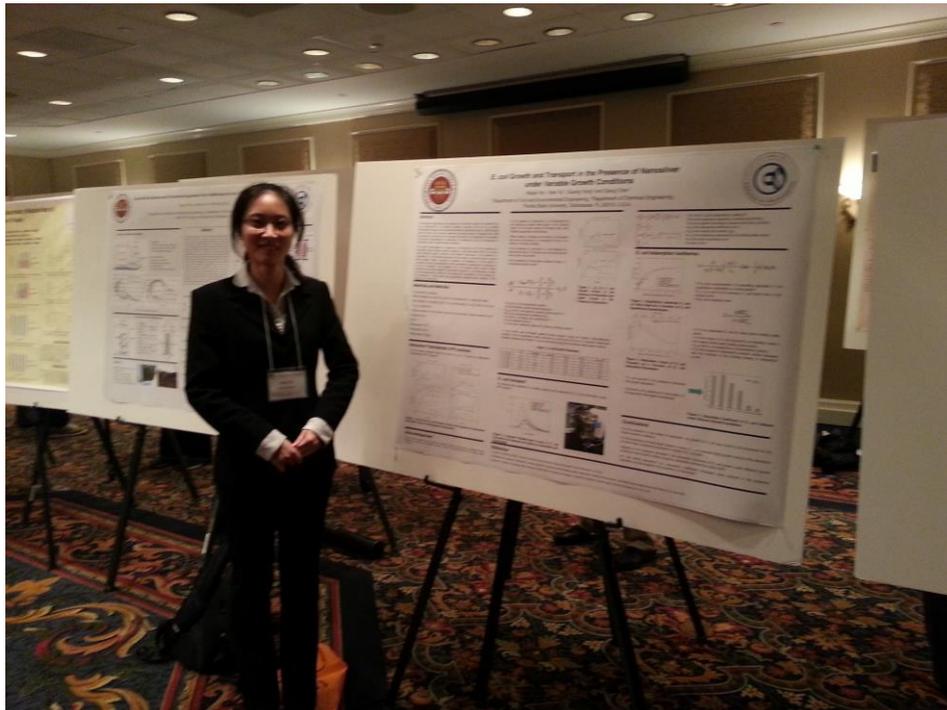
where  $J_{O_2,s}$  is oxygen biofilm flux at the biofilm surface and  $C_{O_2,s}$  is the oxygen concentration at the biofilm surface. At the biofilm–liquid interface, the substrate oxygen flux is equal to the external mass transfer rate between the liquid and biofilm, which can be calculated from:

$$-J_{O_2,s} = K_{L,O_2} (C_{O_2,b} - C_{O_2,s}) \quad \text{Equation (23)}$$

where  $K_L$  is the external mass transfer coefficient and  $C_{O_2,b}$  is the oxygen concentration in the bulk liquid phase.

## 9. Student Training

Three graduate students, Weijie Xie, Kien Vu and Boya Wang were involved in this project. Weijie Xie and Kien Vu successfully defended their master theses in Spring 2014. Kien Vu is currently pursuing his Ph.D. in our laboratory. Boya Wang joined our group in August 2014 as a new master student. He picked up the research of this project after Weijie Xie's graduation. All of these three students were very active and productive in their research. So far, they have published four technical journal papers in leading professional journals based on the work sponsored by the Hinkley Center for Solid and Hazardous Waste management. In addition, they have presented two times in national conferences. The following images were taken when Weijie Xie and Kien Vu presented their work at 99th Annual American Society of Microbiology Southeastern Branch Conference, Auburn, AL and Boya Wang conducted the research of this project in our laboratory.





## 10. Acknowledgements

The work was supported by the Hinkley Center for Solid and Hazardous Waste Management through Grant UF-EIES-1332025-FSU to Florida State University. We thank Peter Grasel, Gary Millington, John Hallas, Brian Lee Moody, Hafiz Ahmad and Tarek Abichou for serving on the TAG committee. They provided invaluable advice on improving the laboratory design and data analysis.

### 10.1 Peer-Reviewed Journal Paper Publication:

1. Wang, B., Grasel, P., Millington, G., Hallas, J., Ahmad, H. and Chen, G., *Aerated Recirculation and Pressurized Suspended Fiber Biofiltration for the Treatment of Landfill Leachate*, Environmental Technology, to be submitted.

### 10.2 Conference Presentation:

1. Yang, G., Lee, Y. and Chen, G. (Presented 2013, November) *Aerated Recirculation and Pressurized Suspended Fiber Biofiltration for the Treatment of Landfill Leachate*. Poster presentation at 99th Annual American Society of Microbiology Southeastern Branch Conference, Auburn, AL: American Society of Microbiology Southeastern Branch.

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