Design and Testing of a Multifunctional Energy- and Space-Saving Reactor for the Treatment of Landfill Leachate

December, 2015

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FINAL REPORT

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ABSTRACT (1 page only)

In our prior research, we have demonstrated that aerated leachate recirculation can effectively remove the organics from landfill leachate. In this research, a novel and energy- and space-saving reactor was designed and tested for further on-site treatment of landfill leachate to remove ammonium, chloride, phosphorous and heavy metals. The multifunctional reactor was designed to enhance chemical reactions and physical separation and to demonstrate the ability to achieve multifunctional landfill leachate treatment goals depending on the treatment requirements, i.e., struvite recovery, chloride removal, phosphorous removal, and iron removal. The hydraulic parameters were characterized and the reactor was optimized to achieve the desired mixing for the reaction and sedimentation for the separation. In addition, operational factors that impacted the treatment results were also investigated. In this research, the multifunctional reactor operational factors were optimized based on the treatment results and operation costs. This technology makes the on-site leachate treatment possible, which may reduce the current high costs of off-site leachate disposal by means such as transporting landfill leachate via tanker trucks to local wastewater treatment plants. This efficient, low-maintenance and cost-saving multifunctional reactor can be recommended for the treatment of landfill leachate with variable compositions at landfill sites where current leachate disposal costs are high and space- and environmental concerns limit other long-term options.

Metrics:

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

Last name, first name	Rank	Department	Professor	Institution
Houzhen Wei	Postdoctoral Researcher	Civil and Environmental Engineering	Gang Chen	Florida State University
Kien Vu	Ph.D.	Civil and Environmental Engineering	Gang Chen	Florida State University
Boya Wang	M.S.	Civil and Environmental Engineering	Gang Chen	Florida State University

2. List undergraduate researchers working on this Hinkley Center project

Last name, first name	Department	Professor	Institution
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. "Chloride removal from landfill leachate by the ultra-high lime with aluminum process", J. Urban Environ. Engr. Under review (2015).

Wang, B., Grasel, P., Millington, G., Hallas, J., Ahmad, H. and Chen, G. "Landfill Leachate Treatment by Aerated Recirculation and Pressurized Suspended Fiber Biofiltration", Frontier in Environmental Engineering, 2015, 4 (1) 7-18.

4. List research presentations resulting from this Hinkley Center project

Wang, B. and Chen, G. "Multifunctional Energy- and Space-Saving Reactor for the Treatment of Landfill Leachate". 101th Annual American Society of Microbiology Southeastern Branch Conference, Kennesaw, GA. Nov 13-15, 2015.

Chen, G., Wang, B. and Tawfiq, K. "Design and Testing of a Multifunctional Energy- and Space-Saving Reactor for the Treatment of Landfill Leachate", South Carolina Environmental Conference, Myrtle Beach, SC, March 14 to March 17, 2015.

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

Current research has been submitted to Journal of Urban and Environmental Engineering and currently is under review. Following is the information of citation of recently finished projects:

Power generation and nitrogen removal of landfill leachate using microbial fuel cell technology

Lee, Y., L. Martin, P. Grasel, K. Tawfiq and G. Chen*, 2013, Power generation and nitrogen removal of landfill leachate using microbial fuel cell technology, Environmental Technology, 34, 2727-2736.

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6. How have the research results from this Hinkley Center project been leveraged to secure additional research funding?
"Electromagnetic Waves-Induced Heavy Metal Removal for Biosolids" by Gang Chen and Youneng Tang will be 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.

7. 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. In addition, we have been contacted by Jeffrey Cunningham from University of South Florida and requested for collaboration through an EPA-funded research center (http://usf-reclaim.org/). They are interested in investigating the removal and recovery of nutrients (nitrogen and phosphorus) at centralized wastewater treatment plants. They are currently conducting research on recovery and removal of N and P through a combination of engineered struvite precipitation and microbial fuel cells, which we have investigated through the projects sponsored by the Hinkley Center. They learned about our research through our web sites and requested for collaboration. Other people involved in the collaboration include Daniel Yeh (USF), Treavor Boyer (UF), and Jim Mihelcic (USF).

8. 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 presented our research at Leon County Landfill and Springhill Regional Landfill. Leon County Solid Waste Management Director, Leon County Solid Waste Superintendent, District Manager of Waste Management at Springhill, Market Area Engineer of Waste Management, Inc. and Environmental Protection Manager of Waste Management, Inc., etc. attended the presentation. The technical achievement of this project was discussed and suggestions were provided for further research. We also shared 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 discussed the results with Talquin Electric Cooperative, Inc., which operates seven wastewater treatment plants.

EXECUTIVE SUMMARY

December 1, 2014 to November 30, 2015

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PROJECT TAG MEMBERS: Peter Grasel, Gary Millington, John Hallas, Chen Lin, Hafiz Ahmad and Matthew Hendrix

COMPLETION DATE: November 30, 2015

Objective:
Nitrogen, chloride, iron and phosphorus may exist separately or co-exist in the landfill leachate. In order to efficiently treat the landfill leachate at the landfill sites, a multifunctional energy- and space-saving reactor is desirable, which can remove either one or all of these four contaminants. In our prior research, we have demonstrated that aerated leachate recirculation can effectively remove the organics from landfill leachate. In this research, a novel and energy- and space-saving reactor was designed and tested for further on-site treatment of landfill leachate to remove ammonium, chloride, phosphorous and heavy metals. In this project, the designed reactor exhibited multiple functions of landfill leachate treatment depending on the treatment requirements, i.e., struvite recovery, chloride removal, phosphorous removal, or iron removal. This technology makes the on-site leachate treatment possible, which can reduce the current high costs of off-site leachate disposal means such as transporting landfill leachate via tanker trucks to local wastewater treatment plants. The efficient, low-maintenance and cost-saving multifunctional reactor can be recommended for the treatment of landfill leachate with variable compositions at landfill sites where current leachate disposal costs are high and space- and environmental concerns limit other long-term options. Specific objectives achieved in this research included:

1. Multifunctional Reactor Design, Setup and Parameter Characterization. The multifunctional reactor was designed to enhance chemical reactions and physical separation. The hydraulic parameters were characterized and the design of the reactor was optimized to achieve the desired mixing for the reaction and sedimentation for the separation.

2. Testing of the Multifunction Reactor for Struvite Recovery, and Chloride, Iron and Phosphorous Removal. Operational factors such as pH, alkalinity, and dissolved oxygen that impacted the treatment results were investigated.

3. System Optimization and Cost Analysis. The multifunctional reactor operational factors were optimized based on the treatment results and operation costs. Cost analysis of the optimized operations was conducted and compared with that of off-site treatment.

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. There is an evident need for cost- and space-saving technologies for the treatment of landfill leachate, especially with high ammonium, chloride, phosphorous and heavy metal contents. This research provided an efficient and energy- and space-saving means of on-site management of landfill leachate. In this research, a multifunctional reactor was designed and tested for ammonium removal by struvite precipitation, chloride removal by the ultra-high lime with aluminum process, phosphorous removal by adsorption and precipitation with coagulant addition, and iron removal by iron hydroxide precipitation.

Results:

From this research, it is demonstrated that landfill leachate can be treated in the multifunctional reactor for struvite recovery, chloride removal, iron removal and phosphorous removal after aerated recirculation. Aerated recirculation can remove organics and solid components from the landfill leachate. Through aerated recirculation, the organic removal reached an average of 84% for Leon County Landfill leachate and 87% for Springhill Landfill leachate when organic removal became stable at dissolved oxygen of 2 mg/L. Chloride removal in the multifunctional reactor was a function of both pH and alum concentration. With the increase of pH, obviously more chloride was removed. For struvite recovery, the stoichiometry of $NH_4^+/Mg^{2+}/PO_4^{3-}$ molar ratio should be maintained at 1:0.75:0.75. For Leon County Landfill leachate with ammonium content of 384 mg/L, 98% of ammonium can be recovered with 20 mg/L of alum addition at pH 10. Also, in the presence of 20 mg/L of alum at pH 10.0, around 95% of iron was removed. For phosphorous removal, alum had obvious better removal efficiency than that of ferric chloride. At 20 mg/L of alum, 85% phosphorous can be removed at pH 7.

This technology had potential markets for small landfills that serve low population areas and landfills that are at a distance from sewage treatment systems. It provides a sustainable and profitable solution for landfill managers to handle landfill leachate with high organic, ammonium, chloride, phosphorous and heavy metal contents at the landfill sites. Besides being practical, this treatment process also has the benefits of lowering the treatment costs. Struvite, a marketable commodity can be recovered during the treatment. The commercialization of struvite may offset the high chemical costs of the treatment.

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1. Introduction

1.1 Contaminant Concerns of Landfill Leachate

Landfilling is widely adopted as one of the most economical processes for solid waste disposal. At the same time, landfill leachate is also 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 of the bottom of the landfill cell into the leachate collection system. Landfill leachate characteristics present a high variation due to several factors such as the composition of the solid waste, waste age, site hydrology, landfill design and operation, sampling procedure, and interactions of leachate with the environment, etc. (Jia et al., 2010; Wu et al., 2014). Besides organic contaminants, ammonium is drawing more and more attention. A recent study has demonstrated that ammonium in landfill leachate can be removed by means of magnesium ammonium phosphate ($MgNH_4PO_4 \cdot 6H_2O$ or struvite) precipitation, which is a potential valuable commodity that can be recovered (Di Iaconi et al., 2010). This technology was first discovered as a precipitate in sewer pipes and since then has been widely studied (Booker et al., 1999; Kabdasli et al., 2000; de-Bashan and Bashan, 2004; Shu et al., 2006; Barnes et al., 2007; Turker and Celen, 2007). Struvite is a white crystalline substance consisting of magnesium, ammonium and phosphate in equal molar concentrations (Zhang et al., 2014). Recovered struvite can be used as a fertilizer and the commercialization of the purified struvite may offset the operation and chemical costs of rececovery (Schuiling and Andrade, 1998). The fertilizing property of struvite has been demonstrated in the 1960s in Germany and the United States. Struvite is only slightly soluble in water and soil solutions, and slow-release struvite has been found to be a highly effective source of phosphorus, nitrogen and magnesium for plants through both foliar and soil applications. Especially, the usage of struvite may be particularly advantageous when soluble fertilizers are inefficient, low soluble salts are required in the root zone, or a long residual effect is required. In addition, when properly granulated, struvite can be applied to the soil at rates greatly exceeding those of conventional fertilizers without the danger of burning plant roots (Ponce and De Sa, 2007). Struvite also has the potential to be used for container plants as well as turf, tree seedlings, ornamentals, vegetables and flower boards since less frequent applications of struvite are required. Improved growth of grass, fruit and various high-value crops has been observed when they are fertilized with struvite as compared with conventional soluble fertilizers.

Recently, high concentrations of chloride have also been observed in several landfills, especially with waste-to-energy applications (Yong and Sheremata, 1991; Tzoupanos et al., 2008). Chloride tends to percolate and cause surface salt formation and soil alkalinity increase, thereby resulting in loss of soil (Clarke et al., 2009). However, 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. A variety of techniques have been investigated for the removal of chloride, which include ion exchange, reverse osmosis, NORCURE, 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 cost- and space-saving 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 [$Ca_4Al_2Cl_2(OH)_{12}$] through precipitation in the presence of calcium and aluminum at high pH.

In Northwest Florida, high concentrations of iron are commonly detected in landfill leachate. It is believed that iron is released from iron-rich soil owing to changes in pH and redox conditions. Especially, decomposition of organic waste may lead to reducing conditions, favoring iron reduction and release. In our prior research, we have investigated the geomicrobial iron reduction processes and have quantified the possible iron reduction and release under conditions of landfills. Northwest Florida soil has a high iron content, ranging from 10 mg to 100 mg per gram of soil (Williams et al., 2012). During landfill operations, top soil is used to cover the municipal solid waste to block the odor and fliers. Subsequently, iron is reduced and released to the landfill leachate. In order to remove iron from landfill leachate, different methods have been practiced, among which oxidation and precipitation is the most commonly utilized one.

1.2 Multifunctional Reactor Design

Multifunctional reactors integrate physicochemical reactions and separation operations in one apparatus. The integration of reaction and separation processes offers the additional degrees of freedom in the unit design as well as the possibility to tailor the concentration profiles inside the unit in order to achieve better process performance (e.g. higher selectivity and higher yield) (Kienle et al., 2005). Especially, the in-situ separation results in continuous removal of product, which not only generally overcomes the limitation of chemical equilibrium but also suppresses the side reactions for many cases (Santoro et al., 2013). Therefore, the integration gives rise to synergetic effects, which may enhance the performance of the whole system. With suitable process design, an efficient and environmental friendly process operation can be achieved, the general benefits of which include higher productivity, higher selectivity, reduced capital investment and energy consumption, improved operational safety, and improved ecological harmlessness. The most important advantage is realized by using reaction to improve separation, e.g. reacting away contaminants. Another advantage is realized by improved reaction efficiency, e.g. overcoming the reaction equilibrium limitation. The potential is greatest when both aspects are achieved. Moreover, multifunctional reactors are found in some areas to meet the requirements of space limitation, green engineering, and sustainable development with safe and environmental friendly processing. Though multifunctional reactors are promising and even many processes have been successfully applied, the process behaviors are very complicated due to the interaction of different effects in a single unit. Suitable method for the process design and control therefore must be developed and applied. In addition, experimental work should be carried out to ensure optimal and safe operations of the integrated process.

1.2.1 Mixing

Physicochemical reactions rely on efficient mixing. The continuous flow stirred-tank reactor (CSTR), also known as vat- or back-mix reactor, is a common ideal reactor type in engineering applications for mixing (Figure 1). Mathematic models have been developed to estimate the key unit operation variables when using a CSTR to reach a specified output, which work for all fluids: liquids, gases, and slurries (Hlavacova and Sevcik, 1994). These models are approximated or calculated assuming perfect mixing performance. In a perfectly mixed reactor, the output composition is identical to composition of the material inside the reactor, which is a function of residence time and rate of reaction. Because the compositions of mixtures leaving a CSTR are those within the reactor, the reaction driving forces, usually the reactant concentrations, are necessarily low (Heny et al., 2000). Therefore, except for zero and negative reaction orders, a CSTR requires the largest volume of the reactor types to obtain desired conversions. However, the low driving force makes possible better control of rapid exothermic and endothermic reactions. When high conversions of reactants are needed, several CSTRs in series can be used. Equally good results can be obtained by dividing a single vessel into compartments while minimizing back-mixing and short-circuiting.

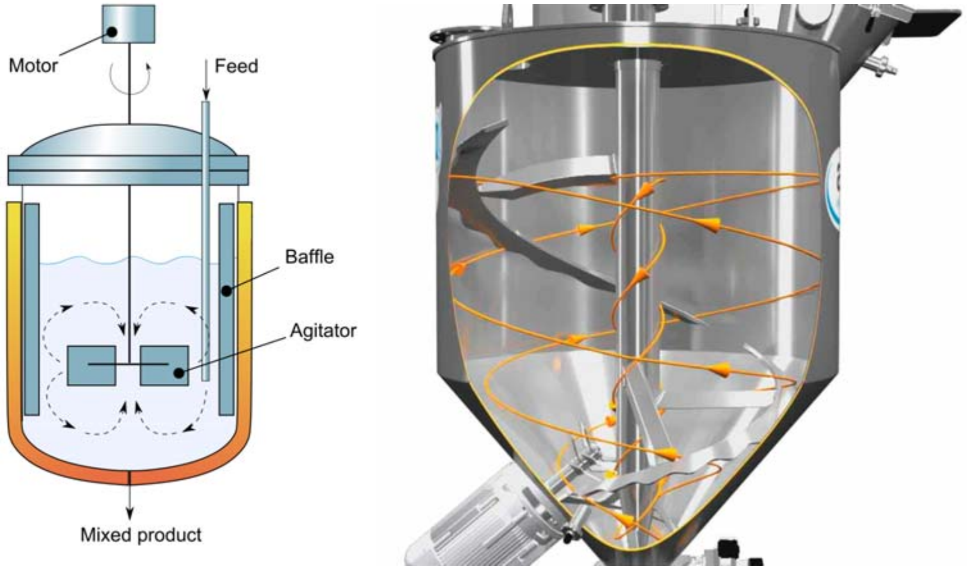


Figure 1. Illustration of a CSTR Reactor (Left) and a Conical Batch Screw Mixing Reactor (Right)

The larger the number of CSTR stages, the closer the performance approaches that of a tubular plug-flow reactor. CSTRs in series are simpler and easier to design for isothermal operation than are tubular reactors. Reactions with narrow operating temperature ranges or those requiring close control of reactant concentrations for optimum selectivity benefit from series arrangements. If severe heat-transfer requirements are imposed, heating or cooling zones can be incorporated within or external to the CSTR. Mixing has been advanced by the introduction of conical batch screw mixer (Figure 1). Inside a conical batch screw mixer, the flow is split into two channels (Maric and Macosko, 2001). The combination of pressure flow up the channel and perpendicular drag flow produces an elongating flow. It is well known that elongational forces are more effective for dispersive mixing than shear mixing.

1.2.2 Sedimentation

Following reaction, precipitates are separated from the liquid phase in a sedimentation tank. The efficiency of removal of particles is governed by the area available for settlement. To improve the settling efficiency and capacity, inclined settling tubes have been introduced to the sedimentation process (Figure 2). In a conventional clarifier or sedimentation basin, the available settling area is limited to the surface area. The inclined tube principle utilizes a series of inclined tubes mounted together in a pack. With this principle, the available settling area becomes the total area of the tubes projected on a horizontal surface (Adelman et al., 2013). It should be remembered that in a conventional settling basin, the sludge particle often has a considerable distance to traverse before reaching the bottom. In an inclined tube sedimentation tank, this settling distance is something less than 1¼”. The inclined tubes are usually constructed with lightweight material in modular form which can be easily positioned in a concrete or steel tank. Flow between such inclined tubes can be co-current or counter-current. In the co-current arrangement, the water flows downward in the tubes in the direction of particle settlement. In the counter-current arrangement, the water flows upward in the tubes against the direction of particle settlement. With inclined tube applications, cross-flow or horizontal flow is prohibited to avoid turbulence which interferes with particle settling. Counter-current arrangement is usually practiced during which flow enters the tubes through specially sized feed openings located in the lower sides of the tubes. The solids then settle on the surface of the tubes while effluent is discharged from the top of the tubes. The heavier particles, which have settled on the inclined tubes, slide down the tubes while the lighter material accumulates on the tubes. The lighter material continues to accumulate on the tubes until a critical mass is reached at which point gravity causes the solids to slide down into the sludge storage/thickening area below. Since the inclined tubes are mounted at a 60-degree angle to the horizontal, the settling sludge can easily slide down the tubes for collection. The inclined tube method removes the densest sludge by eliminating the requirement for supplemental expensive thickening equipment.

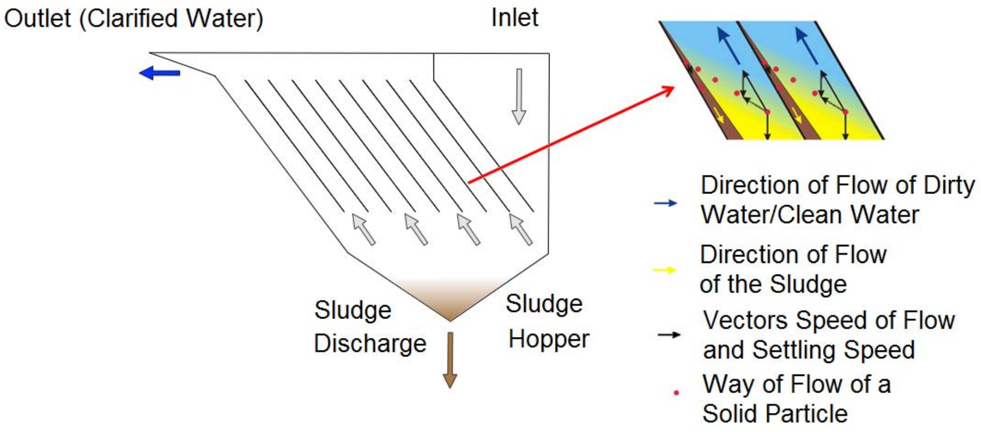


Figure 2. Sedimentation Tank with Inclined Pipes

1.2.3 Sludge Handling

After sedimentation, the sludge still contains large amount of water. The sludge must be dewatered before being discharged. Continuous belt filter pressing, pressure filtration and centrifugation are commonly utilized methods for dewatering. The continuous belt filter press combines sludge conditioning, gravity dewatering and pressure dewatering to increase the solid content of the sludge (Mathewson et al., 2006) (Figure 3). During operation, the in-feed sludge will be placed onto a moving porous belt or screen. Dewatering occurs as the sludge moves through a series of rollers which squeeze the sludge to the belt or squeeze the sludge between two belts. The cake formed is then discharged from the belt by a scraper mechanism. There are basically three processing zones which occur along the length of the unit. These are: the initial drainage zone, which is analogous to the action of a drying bed; the press zone, which involves application of pressure; and a shear zone, in which shear is applied to the partially dewatered cake

(Olivier and Vaxelaire, 2005). Shearing action is accomplished by positioning the support rollers of the filter belt and the pressure rollers of the pressure belt in such a way that the belts and the sludge between them describe an S-shape curve. This condition creates a parallel displacement of the belts relative to each other due to the difference in radius. In the initial stage, gravity drainage occurs on a continuous belt of pockets formed by folding a rectangular piece of filter media. After this initial gravity drainage (thickening), the sludge is transferred to a different belt which passes over another drainage tray before being transferred to yet another belt where a small amount of pressure is applied via small diameter rollers. The sludge is then subjected to a slightly greater pressure before entering the medium pressure stage. While passing over the medium pressure rolls, which are adjustable for pressure optimization, the cake sandwiched between the belts is flexed from one side to the other. Each of the larger drums has smaller diameter rolls which apply pressure as the sandwich passes over the drum. The sludge cake then enters the high pressure stage where pressure is applied by upright belts.

Figure 3. Continuous Belt Filter Press

Of the several types of pressure filters available, the most widely used pressure filter consists of a series of vertical plates held ridgedly in a frame which are pressed together between a fixed and moving end (Rencken and Buckley, 1992) (Figure 4). Mounted on the face of each individual plate is a filter cloth to support and contain the cake produced. Pressure filters do not produce a cake by pressing and squeezing. Instead, sludge is fed into the press "batch mode" through feed holes in trays along the length of the press. Pressures up to 225 psi (16 kg/cm^2) are applied to the sludge, forcing water to pass through the cloth while the solids are retained to form a cake on the surface of the filter cloth. Sludge feed is stopped when the chambers between the trays are completely filled. Drainage ports are provided at the bottom of each chamber where the filtrate is collected and discharged. The dewatering phase is complete when the flow of filtrate through the filter cloth nears zero. At this point, the sludge feed pump is stopped and any back pressure in the piping is released. Each plate is then turned over the gap between the plates and the moving end to allow for cake removal. Filter cake usually drops below onto a conveyor for further removal. After each plate has released its cake, the plates are pushed back together and the dewatering cycle restarts. In most applications, filter presses require a pre-coat material to aid in solid retention on the cloth and cake release.

Figure 4. Pressure Filter

A centrifuge is essentially a sedimentation device in which the solids-liquid separation is enhanced by the use of centrifugal force. This is accomplished by rotating the liquid at high speeds to subject the sludge to increased gravitational forces. The commonly used decanter centrifuge consists of two principal elements: a horizontal cylindrical bowl rotating at a high speed and a helical extraction screw placed coaxially (Bishop et al., 1991) (Figure 5). The screw perfectly fits the internal contour of the bowl, only allowing clearance between the bowl and the scroll. The differential speed between screw and scroll provides the conveying motion to collect and remove the solids, which accumulate at the bowl wall. Sludge enters the rotating bowl through a stationary feed pipe extending into the hollow shaft of the rotating screw conveyor and is distributed through ports into a pool within the bowl. As the bowl rotates, centrifugal force causes the slurry to form an annular pool, the depth of which is determined by the effluent fluent weirs. The rotating screw conveyor continuously moves the sludge solids across the bowl, up the beaching incline to outlet ports and then to a discharge hopper for ultimate removal. As the liquid sludge flows through the bowl towards the overflow weirs, progressively finer solids are forced to the rotating bowls wall. The water (centrate) drains from the solids and then discharged through ports at the end where the effluent weirs are located. Most solid bowl centrifuges are of the "counter-current" type employing a countercurrent flow of liquid and solids. Recently a "con-current" centrifuge has been introduced in which the incoming sludge is carried by the feed pipe to the end of the bowl opposite the discharge. As a result, settled solids are not disturbed by the incoming feed. Turbulence is reduced substantially as both the solids and liquid pass through the bowl in smooth parallel flow patterns.

Figure 5. Dewatering Centrifuge

Polymer (especially cationic polymer) addition is often practiced for sludge dewatering (Garcia et al., 2007). Cationic polymer not only facilitates solid removal, but also unexpectedly facilitates precipitation/recovery of certain nutrients, such as phosphate and nitrogen, during the solid-liquid separation process. The NH_4^+ and PO_4^{3-} concentrations in the polymer-assisted centrifuged samples are usually 20% and 50% lower than those in the polymer-free centrifugation sample (Lai and Liu, 2004). With polymer addition, the solid removal is more obvious. For instance, the total suspended solids (TSS) content is about 7.0% in the raw digested sample, about 2.2% in the liquid portion of the sample centrifuged without polymer addition, and only about 0.6% in the liquid portion of the sample after polymer-assisted centrifugation (Lai and Liu, 2004). Furthermore, polymer addition also helps the reducing of total dissolved solid (TDS) content. Overall, polymer addition can significantly improve solid-liquid separation and reduce total suspended solids (TSS) and total dissolved solids (TDS) in effluents. Polymer-assisted solid-liquid separation is commonly combined with lime treatment.

1.3 Objectives

Nitrogen, chloride, iron and phosphorus may exist separately or co-exist in the landfill leachate. In order to efficiently treat the landfill leachate, a multifunctional energy- and space-saving reactor is desirable, which should remove either one or all of these four contaminants. From our last project, we have demonstrated that aerated leachate recirculation can effectively remove the organics from landfill leachate. In this research, a novel and energy- and space-saving reactor was designed and tested for the further on-site treatment of landfill leachate in terms of ammonium, chloride, phosphorous and heavy metal removal. The overall goal of this project was to demonstrate that the designed reactor could achieve multiple functions of landfill leachate treatment depending on the treatment requirements, i.e., struvite recovery, chloride removal, phosphorous removal, or iron removal. This technology makes the on-site leachate treatment possible and thus reduces the current high costs of off-site leachate disposal means such as transporting landfill leachate via tanker trucks to local wastewater treatment plants. From this research, the efficient, low-maintenance and cost-saving multifunctional reactor can be recommended for the treatment of landfill leachate with variable compositions at landfill sites where current leachate disposal costs are high and space and environmental concerns limit other long-term options. Specific objectives achieved in this research include:

1. Multifunctional Reactor Design, Setup and Parameter Characterization. The multifunctional reactor was designed to enhance chemical reactions and physical separation. The hydraulic parameters were characterized and the design of the reactor was optimized to achieve the desired mixing for the reaction and sedimentation for the separation.

2. Testing of the Multifunction Reactor for Struvite Recovery, and Chloride, Iron and Phosphorous Removal. Operational factors such as pH, alkalinity, and dissolved oxygen were investigated.

3. System Optimization and Cost Analysis. The multifunctional reactor operational factors were optimized based on the treatment results and costs. Cost analysis of the optimized operations was conducted and compared with that of off-site treatment.

2. Background

Landfilling is the chief method for municipal solid waste (MSW) disposal. Landfill leachate treatment is subsequently one of the major challenges of landfill management. Landfill leachate contains organic and inorganic compounds generated during the decomposition of the waste in the landfill. Typically, landfill leachate has high concentrations of organics, ammonium, inorganic salts, and in some cases, heavy metals (Karnchanawong et al., 1995; Park et al., 1999; Yusmartini et al., 2013). The organic compounds in the landfill leachate may include alkenes, aromatic hydrocarbons, acids, esters, alcohols, hydroxybenzene, aldehydes, ketones, and amides, etc. (do Nascimento et al., 2001; Liu et al., 2011). In addition, landfill leachate usually has strong color and bad odor. Leachate characteristics depend upon many factors including landfill operation (i.e., compaction of waste, operation method, daily cover material, superficial drainage, and infiltration, etc.), solid waste characteristics (i.e., type and original moisture content, and water-holding capacity, etc.), and climatic conditions (i.e., rainfall, humidity, ambient temperature, evaporation, and evapotranspiration) (Zhang et al., 2013). Treatment of landfill leachates presents unique challenges from engineering point of view mainly because of high organic and ammonia nitrogen contents (Im et al., 2001; Sun et al., 2015). Many different methods are currently in use to treat the landfill leachate. Most of these methods are adapted from wastewater treatment processing and can be divided into two main categories: biological treatments and physical/chemical treatment.

2.1 Biological Treatment

2.1.1 Organic Removal

High COD contents as well as the high COD/BOD ratio of the landfill leachate makes anaerobic treatment more advantageous as compared to the aerobic process for the treatment of landfill leachate (Li et al., 2012). Prior research has demonstrated that up to 92% of COD removal can be achieved by anaerobic treatment (Bilgili et al., 2008; Chen et al., 2008). Current research has also demonstrated that combined anaerobic and aerobic systems for the removal of organics and ammonia nitrogen may be the most suitable one for the treatment of landfill leachate (Im et al., 2001; Li et al., 2012; Sun et al., 2015). In conventional biological systems, anaerobic and aerobic conditions are separated, or temporarily separated in phases such as sequencing batch reactors (SBR). A combination of aerobic and anaerobic degradation pathways in a single reactor can also be used to improve the overall degradation efficiency (Im et al., 2001; Li et al., 2012; Sun et al., 2015). The combined system is a good strategy since both reductive and oxidative bio-transformations might occur concomitantly to complete the mineralization of highly substituted compounds under micro-aeration conditions. Under oxygen-limited conditions, simultaneous aerobic and anaerobic processes occur as a result of dissolved oxygen concentration gradients arising from diffusion limitations (Im et al., 2001).

2.1.2 Ammonia Removal

Ammonia deserves special attention in the treatment of landfill leachate as it constitutes a critical long term pollutant (Purcell et al., 1999; Berge et al., 2006; Huang et al., 2009). Traditional biological nitrogen removal is nonreversible and is carried out in two stages: aerobic nitrification of ammonium via hydroxylamine and nitrite to nitrate, and, subsequently, anoxic denitrification of nitrate via intermediate stages to nitrogen gas (Chang et al., 2006; Ishii et al., 2008; Trinh et al., 2009). Practically, suspended processes have been applied in full scale for nitrification and denitrification of high nitrogen content wastewater as a means of nitrogen removal (Agdag and Sponza, 2008; Huo et al., 2008). For the treatment of high ammonium content landfill leachate, a 4-stage Bardenpho process, which consists of a sequence of anoxic and aerobic zones with capacities of nitrification with pre- and post-denitrification biological processes has been proposed (Ilies and Mavinic, 2001). Recently, a novel process called anaerobic ammonium oxidation (ANAMMOX) has been proposed to treat municipal landfill leachate with high concentrations of ammonium (Baron et al., 2009). ANAMMOX is a microbiological mediated exergonic process during which ammonium is converted to nitrogen gas under anaerobic conditions with nitrite serving as the electron acceptor (Ganigue et al., 2007; Ishii et al., 2008).

2.2 Physicochemical Treatment

Besides being treated by various biological processes, landfill leachate can also be treated in physicochemical ways, which include coagulation-flocculation, carbon adsorption, ion exchange, chemical precipitation, chemical oxidation, and membrane filtration (Trebouet et al., 2001b).

2.2.1 Coagulation-Flocculation

During physicochemical treatment, the separation of suspended particles from the liquid phase is usually accomplished by coagulation, flocculation and sedimentation (Farley and Morel, 1986; Smoczynski et al., 2009). Specifically, coagulation-flocculation has been used for the removal of non-biodegradable organic compounds and heavy metals from landfill leachate (Abood et al., 2014). The coagulant addition is usually accompanied with pH adjustment. The selection of the optimum coagulant, or mixture of coagulants, is essential for the process to succeed (Adlan et al., 2011). Leachate characteristics such as pH, alkalinity, suspended solids, electric charge of suspended particles, and interactions of solid particles are important parameters that influence the aggregation and subsequent solid organic removal (Wang et al., 2002; Labanowski et al., 2010). For coagulation-flocculation treatment of landfill leachate, coagulants play the most important role in controlling the quality of treated leachate. Metallic salts (aluminum sulfate, aluminum chloride, ferric sulfate, ferric chloride, and poly-ferric chloride, etc.) and some synthetic organic substances such as polyelectrolytes are the most commonly utilized coagulants (Skvarla, 2013). There are a lot of commercial polyelectrolytes available, grouped in cationic, anionic and nonionic. In water and wastewater treatment, aluminum sulfate (or alum) and ferric chloride are most commonly practiced. The subsequent coagulation results depend on the presence of Al^{3+} and Fe^{3+} cations in equilibrium with an amorphous $Al(OH)_3$ and $Fe(OH)_3$ (Jarvis et al., 2012). Table 1 summarizes the aluminum and iron equilibria (Jiang and Graham, 1998). Speciciation of iron and aluminum as a function of solution pH is illustrated in Figure 6.

Landfill leachate contains inorganic particles in large quantities, including clay, iron oxides, silicates, calcites, aluminium oxides and many other minerals. All these particles show similar electrochemical behavior, since their surfaces are generally covered with surface hydroxyl (OH-) groups (Zigah et al., 2012). Depending of the solution pH, the charges of these hydroxyl groups may be positive or negative, which impact the particle aggregation dramatically (Tuller, 1946). Similarly, organic particles may have similar surfaces. For inorganic and organic particles that are negatively charged, they can be effectively destabilized by the neutralization of their surface charges by positively charged coagulant species such as alum and ferric chloride (Tuller, 1946). For inorganic and organic particles that are positively charged or neutrally charged, anionic and nonionic polyelectrolytes are recommended to be used.

Table 1. Aluminum and Iron Equilibria at 25°C

Reaction	LogK (25°C)
$Al^{3+} + H_2O \rightleftharpoons AlOH^{2+} + H^+$	-4.97
$AlOH^{2+} + H_2O \rightleftharpoons Al(OH)_2^+ + H^+$	-4.3
$Al(OH)_2^+ + H_2O \rightleftharpoons Al(OH)_3 + H^+$	-5.7
$Al(OH)_3 + H_2O \rightleftharpoons Al(OH)_4^- + H^+$	-8.0
$2Al^{3+} + 2H_2O \rightleftharpoons Al_2(OH)_2^{4+} + 2H^+$	-7.7
$3Al^{3+} + 4H_2O \rightleftharpoons Al_3(OH)_4^{5+} + 4H^+$	-13.97
$13Al^{3+} + 28H_2O \rightleftharpoons Al_{13}O_4(OH)_{24}^{7+} + 32H^+$	-98.73
$Al(OH)_s\ (am) \rightleftharpoons Al^{3+} + 3OH^-$	-31.5
$Fe^{3+} + H_2O \rightleftharpoons FeOH^{2+} + H^+$	-2.2
$FeOH^{2+} + H_2O \rightleftharpoons Fe(OH)_2^+ + H^+$	-3.5
$Fe(OH)_2^{2+} + H_2O \rightleftharpoons Fe(OH)_{3+} + H^+$	-6
$Fe(OH)_3 + H_2O \rightleftharpoons Fe(OH)_4^- + H^+$	-10
$2Fe^{3+} + 2H_2O \rightleftharpoons Fe_2(OH)_2^{4+} + 2H^+$	-2.9
$3Fe^{3+} + 4H_2O \rightleftharpoons Fe_3(OH)_4^{5+} + 4\ H^+$	-6.3
$Fe(OH)_s\ (am) \rightleftharpoons Fe^{3+} + 3OH^-$	-38.7
$A\text{-}FeOOH(c) + H_2O \rightleftharpoons Fe^{3+} + 3OH^-$	-41.7

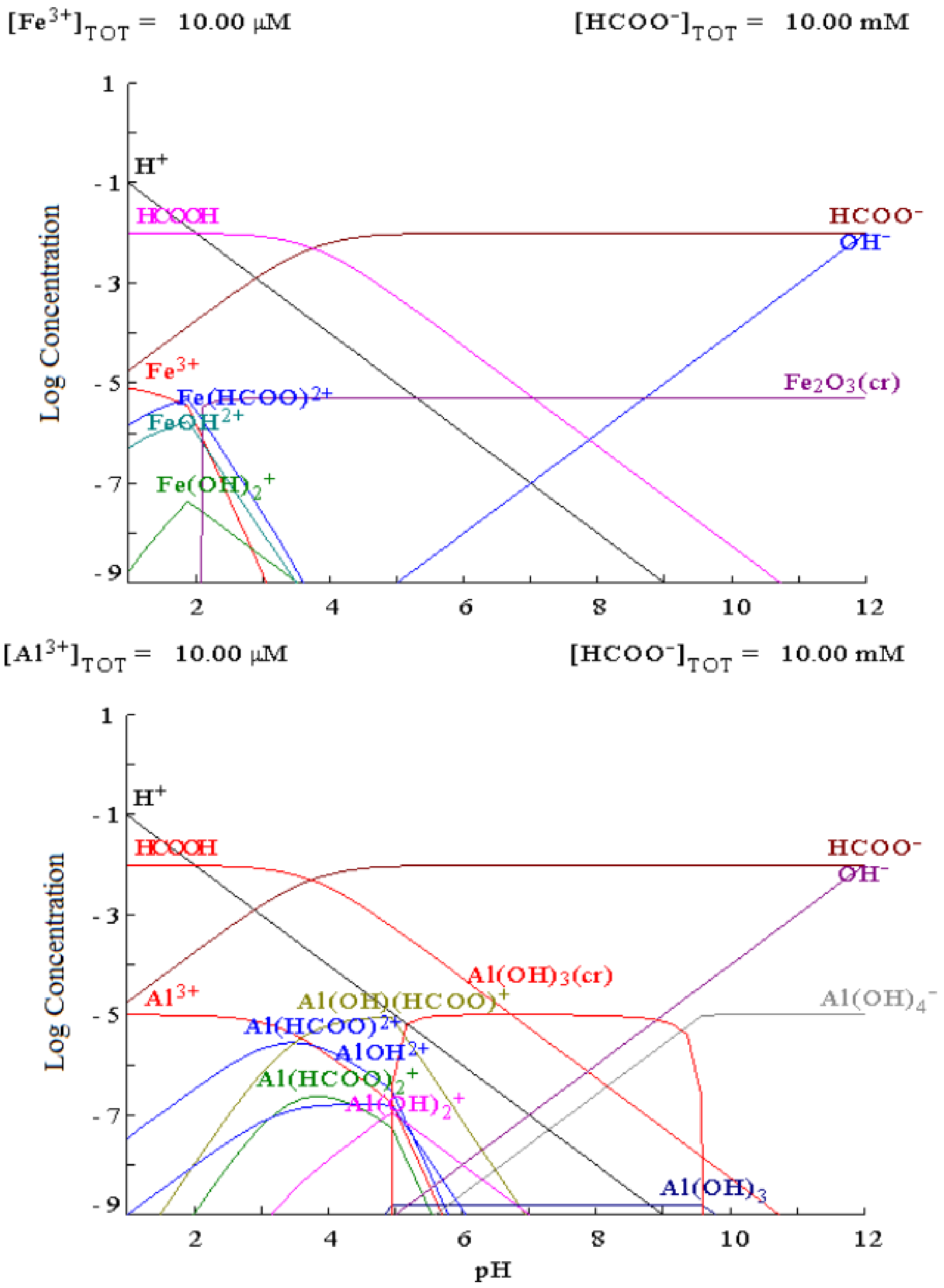


Figure 6. Iron and Aluminum Speciation as a Function of Solution pH

2.2.2 Carbon Adsorption

Adsorption is the most widely used technique for the removal of recalcitrant organic compounds from landfill leachate (Kurniawan et al., 2006; Foo and Hameed, 2009; Papastavrou et al., 2009; Gandhimathi et al., 2013). Fundamentally, adsorption is a mass transfer process by which a substance is transferred from the liquid phase to the surface of a solid, and becomes bound by physical and/or chemical interactions (Wang et al., 2013). Accordingly, film diffusion and internal surface diffusion have been demonstrated to play a key role in determining the adsorption kinetics (Sonetaka et al., 2009). Especially, activated carbon adsorption has been popularly utilized because of its large porous surface area, controllable pore structure, thermo-stability and low acid/base reactivity (Foo and Hameed, 2009). Activated carbon has superior ability for the removal of a wide variety of organic and inorganic pollutants dissolved in aqueous media, even from gaseous environment. The main drawback is the need for frequent regeneration.

For landfill leachate treatment, activated carbon is commonly used for the reduction of non-biodegradable organics from landfill leachate (Foo and Hameed, 2009). Therefore, biodegradable organics are usually reduced to acceptable levels by biological treatment before activated carbon adsorption applications. A substantial amount of simultaneous biological treatment and activated carbon adsorption have been practiced, offering a number of advantages, including the removal of refractory organic compounds (Kargi and Pamukoglu, 2003). Under the co-treatment processes, the existence of activated carbons is believed to contribute a synergy effect for providing an attachment surface for microorganisms that are responsible for the organic decomposition.

2.2.3 Ion Exchange

Ion exchange is a reversible interchange of ions between the solid and liquid phases where there is no permanent change in the structure of the solid (Bashir et al., 2010). The removal of total dissolved solids from landfill leachate can be achieved through the application of ion exchange. Prior to ion exchange, the leachate should first be subjected to a biological treatment to remove organic compounds. The solid ion exchange resins used in ion exchange can be classified as natural inorganic particles (zeolites) and synthetic organic resins (Allen et al., 1993). The synthetic organic resins are usually developed from high-molecular-weight polyelectrolytes. Depending on the characteristics of the ion exchange resins, they can be utilized in a variable of ion removal applications. The prominent benefits of ion exchange technique applications are its capacity to handle shock loadings and operate over a wider range of temperatures.

For landfill leachate treatment, ion exchange is mainly used for ammonia and phosphate removal to near-zero levels (Primo et al., 2009; Ye et al., 2015). For these applications, zeolites are most widely used, which consist of an aluminosilicate molecular structure with weak cationic bonding sites. In addition, zeolites are cost effective and are amenable to efficient regeneration and reuse. Ion exchange can also be combined with activated carbon adsorption as post-treatment to the biological treatment process to achieve very high degree of clarification.

2.2.4 Chemical Precipitation

The chemical precipitation is generally used as pre-treatment to remove high concentrations of ammonium nitrogen (NH_4^+-N) by means of magnesium ammonium phosphate (MAP, $MgNH_4PO_4 \cdot 6H_2O$ or struvite) precipitation during landfill leachate treatment (Tunay et al., 2004; Kline et al., 2010). In addition to ammonium removal, MAP precipitation also helps the removal of some other pollutants such as suspended solids and heavy metals. Since suspended solids attribute greatly to the organic load of landfill leachate, struvite precipitation can thus remove organic matter by means of co-precipitation of suspended solids. Landfill leachate may also have high phosphorous contents, magnesium salts are therefore a major economic constraint for struvite precipitation applications (Giesen, 1999; Lee et al., 2003). In order to reduce the cost, struvite may be used as a recycling material for the removal-recovery of ammonium (Stefanowicz et al., 1992a, b). Most importantly, the purity of precipitated struvite can be high, which makes it possible for the precipitated struvite to be recovered.

In Northwest Florida, high iron content is a common problem associated with landfill leachate, which can also be removed from landfill leachate through oxidation and precipitation. pH, alkalinity and dissolved oxygen are the major impact factors for iron precipitation and removal since these parameters affect the solubility of iron precipitate and the kinetics of the oxidation. Other inorganic contaminants, such as heavy metals, may also be precipitated with iron precipitation. Table 2 summarizes the equilibria related to the solubility of phosphate and iron precipitates.

Table 2. Equilibria Related to Solubility of Phosphates of Fe^{3+}, Al^{3+}, Ca^{2+}, and Mg^{2+}

Reaction	LogK (25°C), I = 0
$FePO_4 \cdot 2H_2O(s)$ (strengite) $\rightleftharpoons Fe^{3+} + PO_4^{3-} + 2H_2O$	-26
$AlPO_4 \cdot 2H_2O(s)$ (varsitite) $\rightleftharpoons Al^{3+} + PO_4^{3-} + 2H_2O$	-21
$CaHPO_4(s) \rightleftharpoons Ca^{2+} + HPO_4^{2-}$	-6.6
$Ca_4H(PO_4)_3(s) \rightleftharpoons 4Ca^{2+} + 3PO_4^{3-} + H^+$	-46.9
$Ca_{10}(PO_4)_6(OH)_2(s) \rightleftharpoons 10Ca^{2+} + 6PO_4^{3-} + 2OH^-$	-114
$Ca_{10}(PO_4)_6(F)_2(s) \rightleftharpoons 10Ca^{2+} + 6PO_4^{3-} + 2F^-$	-118
$Ca_{10}(PO_4)_6(OH)_2(s) + 6H_2O \rightleftharpoons 4[Ca_2(HPO_4)(OH)_2] + 2Ca^{2+} + 2HPO_4^{2-}$	-17
$CaHAl(PO_4)_2(s) \rightleftharpoons Ca^{2+} + Al^{3+} + H^+ + 2HPO_4^{2-}$	-39
$CaF_2(s) \rightleftharpoons Ca^{2+} + 2F^-$	-10.4
$MgNH_4PO_4(s) \rightleftharpoons Mg^{2+} + NH_4^+ + PO_4^{3-}$	-12.6
$FeNH_4PO_4(s) \rightleftharpoons Fe^{2+} + NH_4^+ + PO_4^{3-}$	-13
$Fe_3(PO_4)_2(s) \rightleftharpoons 3Fe^{2+} + 2PO_4^{3-}$	-32
$FeOH^{2+} + H_2O \rightleftharpoons Fe(OH)_2^+ + H^+$	-3.5
$Fe(OH)_2^{2+} + H_2O \rightleftharpoons Fe(OH)_{3+} + H^+$	-6
$Fe(OH)_3 + H_2O \rightleftharpoons Fe(OH)_4^- + H^+$	-10
$2Fe^{3+} + 2H_2O \rightleftharpoons Fe_2(OH)_2^{4+} + 2H^+$	-2.9
$3Fe^{3+} + 4H_2O \rightleftharpoons Fe_3(OH)_4^{5+} + 4H^+$	-6.3
$Fe(OH)_s$ (am) $\rightleftharpoons Fe^{3+} + 3OH^-$	-38.7
A-$FeOOH(c) + H_2O \rightleftharpoons Fe^{3+} + 3OH^-$	-41.7

2.2.5 Chemical Oxidation

The advanced oxidation process has evoked interest during the last couple of years, which mainly involves the use of O_3, H_2O_2, UV light and other oxidizing compounds to degrade recalcitrant organic compounds (Gulyas, 1997; Wang and Xu, 2012). Most of these oxidizing agents can produce free radicals, which indiscriminately destroy organic matter. These radicals can be initiated into the water by means of a certain type of substance (activator). The most difficult problem in the practical applications of advanced oxidation is the choice or design of the most efficient oxidation system for the given pollutants. Prior studies have demonstrated the existence of severe limitations of the applications of single oxidizing compound for the treatment of certain pollutants (Tong et al., 2005; Diya'uddeen et al., 2012). It is, therefore, recommended oxidizing compounds be combined to treat recalcitrant chemicals. For xenobiotic degradation, O_3 combined with H_2O_2, or O_3 with UV radiation, or H_2O_2 with UV radiation, or O_3 with H_2O_2 and UV radiation can be utilized (Horsch et al., 2003; Lafi and Al-Qodah, 2006). Table 3 illustrates the reactions that can lead to the generation of hydroxyl radicals of ($^{\bullet}OH$), which possesses a very high electronic potential and can oxidize a variety of organic compounds (Tizaoui et al., 2007; Keen et al., 2015). It should be noted that although both H_2O_2 and O_3 have the potential to release $^{\bullet}OH$ radicals, the $^{\bullet}OH$ radicals produced per incident photon are different (Table 3).

Table 3. Formation of •OH Radicals from H_2O_2 and O_3

Oxidant	$\varepsilon_{254\ nm}$ ($M^{-1}\ cm^{-1}$)	Stoichiometry	$^{\bullet}OH$ Formed per Incident Photon
H_2O_2	20	$H_2O_2 \rightarrow 2^{\bullet}OH$	0.09
O_3	3300	$3O_3 \rightarrow 2^{\bullet}OH$	2.00

As one of chemical oxidation means, Fenton oxidation has been widely studied in recent years and the analysis indicates that Fenton process is one of the most cost-effective alternatives among potential physicochemical technologies for landfill leachate treatment (Rivas et al., 2003; Singh et al., 2013; He et al., 2015). Fenton oxidation refers to the process of the usage of the mixture of H_2O_2 and ferrous salts to generate aggressive hydroxyl radicals at ambient temperature. Fenton oxidation is high efficiency because it can oxidize a wide range of chemicals in aquatic media, theoretically all organic compounds containing hydrogen (Deng and Englehardt, 2006). Specifically, Fenton oxidation can achieve two alternative goals: (1) exploiting the strong oxidation potential of •OH to mineralize recalcitrant contaminants and (2) promotion of the biodegradability of treated effluents to make the subsequent biological treatment possible. Fenton oxidation is effective in achieving not only good oxidation of organics but also coagulation and precipitation of particle contaminants owing to the presence of ferrous salts (Yoo et al., 2001; Badawy and Ali, 2006). Commonly, Fenton oxidation is composed of following steps: pH adjustment, oxidation reaction, neutralization, coagulation and solid-liquid separation (Deng and Englehardt, 2006). Under acidic conditions, the organic substances are degraded by reactive free radicals •OH produced in the H_2O_2/Fe^{2+} mixture, and removed by means of coagulation with the formation of ferric hydroxyl complexes after neutralization. Both oxidation and coagulation play vital roles in the removal of organics.

2.2.6 Membrane Filtration

A membrane can be defined as a material that creates a thin barrier capable of selectively resisting the move of different constituents of a fluid and therefore affecting separation of the constituents. Different membrane filtration techniques including microfiltration, ultrafiltration, nanofiltration, and reverse osmosis can be used in landfill leachate treatment (Chaudhari and Murthy, 2010; Amaral et al., 2015). Pressure-driven membrane techniques have also been introduced to biological treated landfill leachate. Recently, several hybrid processes such as activated sludge-chemical oxidation, activated sludge-ultrafiltration-chemical oxidation and activated sludge-ultrafiltration-reverse osmosis have been practiced for landfill leachate treatment (Aloui et al., 2009; Castrillon et al., 2010; Insel et al., 2013; Moravia et al., 2013; Amaral et al., 2015).

Microfiltration (pore sizes of 0.05 to 10 microns) is employed to capture microbial cells, small particles and large colloids. This method is not suitable to be used alone for the treatment of landfill leachate. It is recommended that microfiltration be used as a pretreatment or combined with chemical treatment processes to remove suspended solids and colloids (Amaral et al., 2015). Ultrafiltration is a pressurized selective process (up to 10 bars). This technique is efficient to remove suspended solids either by direct filtration or with biological treatment (Insel et al., 2013). It can be employed to eliminate the larger molecular weight components in the landfill leachate that tend to foul reverse osmosis membranes. Nanofiltration is used for the removal of recalcitrant organic compounds and heavy metals from landfill leachate because of its unique properties between ultrafiltration and reverse osmosis membranes (Trebouet et al., 2001a; Amaral et al., 2015). It has the ability to remove particles with a molecular weight higher than 300 Da. Nanofiltration is also able to remove inorganic substances through electrostatic interactions between the ions and membranes, allowing charged solutes smaller than the membrane pores to be rejected, along with bigger neutral solutes and salts. In addition, nanofiltration is also effective for the removal of heavy metals because of the negatively charged functional groups on the membrane. Reverse osmosis can also be used to remove total dissolved solids (i.e., cations and anions) from the landfill leachate (Hasbach, 1995; Chianese et al., 1999; Talalaj, 2015).

In recent years, electrochemical methods are used for the treatment of organic materials having high toxicity and low biological degradability. Consequently, electrochemical methods such as electrocoagulation, electrooxidation and electro-photooxidation have been introduced to the treatment of landfill leachate (Deng and Englehardt, 2007; Panizza et al., 2010; Moreira et al., 2015; Silveira et al., 2015). Especially, the electrochemical oxidation process has shown to be promising for its effectiveness and easy operation (Deng and Englehardt, 2007; Bashir et al., 2009). This process has a great efficacy for the destruction of refractory pollutants including cyanide, EDTA and aniline besides color removal. Combination of physical, chemical and biological methods may be the future trend of effective treatment of landfill leachate since it is difficult to obtain satisfactory results by using anyone of those methods alone (Gao et al., 2015).

3. Materials and Methods

3.1 Landfill Leachate and Soil Sample Collection

Landfill leachate and solid waste were collected from the Leon County Landfill, located in Tallahassee, Florida and Springhill Landfill, located in Campbellton, Florida. 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 stryofoam TM (packaging foam only), etc. Owing to the contract with Marpan Recycling to process and recycle construction debris and packaging materials, over 50% of these materials are now being recycled rather than buried in the 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 and demolition debris, drum management-liquids, drum management-solids, industrial and 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 treatment. BOD_5, COD, phosphorus and chloride were characterized in our laboratory following the standard methods. NH_4^+-N and NO_3^- concentrations were quantified colorimetrically by means of spectrophotometry

(Mccrady, 1966). Dissolved oxygen concentration was measured directly by a dissolved oxygen meter (WTW Oxi 315i, Cellox 325, Germany).

3.2 Leachate Treatment Process

A laboratory scale recirculation bioreactor followed by a multifunctional reactor was set up for this research (Figure 7 and Figure 8). The custom-made recirculation bioreactor had a working volume of 26 L with a height to diameter ratio of 10:1 (height = 150 cm and diameter = 15 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_2 was expected to be produced especially after aerated recirculation. Through leachate recirculation, most organics and solid components can be removed. The following multifunctional reactor was designed for the removal of chloride, ammonia, phosphorous and iron. For the multifunctional reactor, a series of continuous-mixing tube reactors were utilized and the energy that carried the flow into the reactors was fully utilized. Since physicochemical means was applied for the efficient removal of the contaminants of concern, rapid reaction and effective separation were the keys to the success of the multifunctional reactor. The reactor diameter and the subsequent volume increased incrementally, therefore, the velocity gradient decreased accordingly, allowing precipitates to aggregate to settle in the sedimentation tank.

Chemicals including coagulants were added after leachate existed from the recirculation bioreactor and before being introduced to the multifunctional reactor. Depending on the function of the multifunctional reactor in terms of ammonium, chloride, phosphorous and heavy metal removal, magnesium, calcium and phosphate were added together with aluminum sulfate or ferric chloride. All the chemicals and coagulants were added under flash-mixing conditions. After sedimentation, the settled solids were further processed for dewatering by centrifugation. The centrifugation speed was calculated following the Stokes' Law.

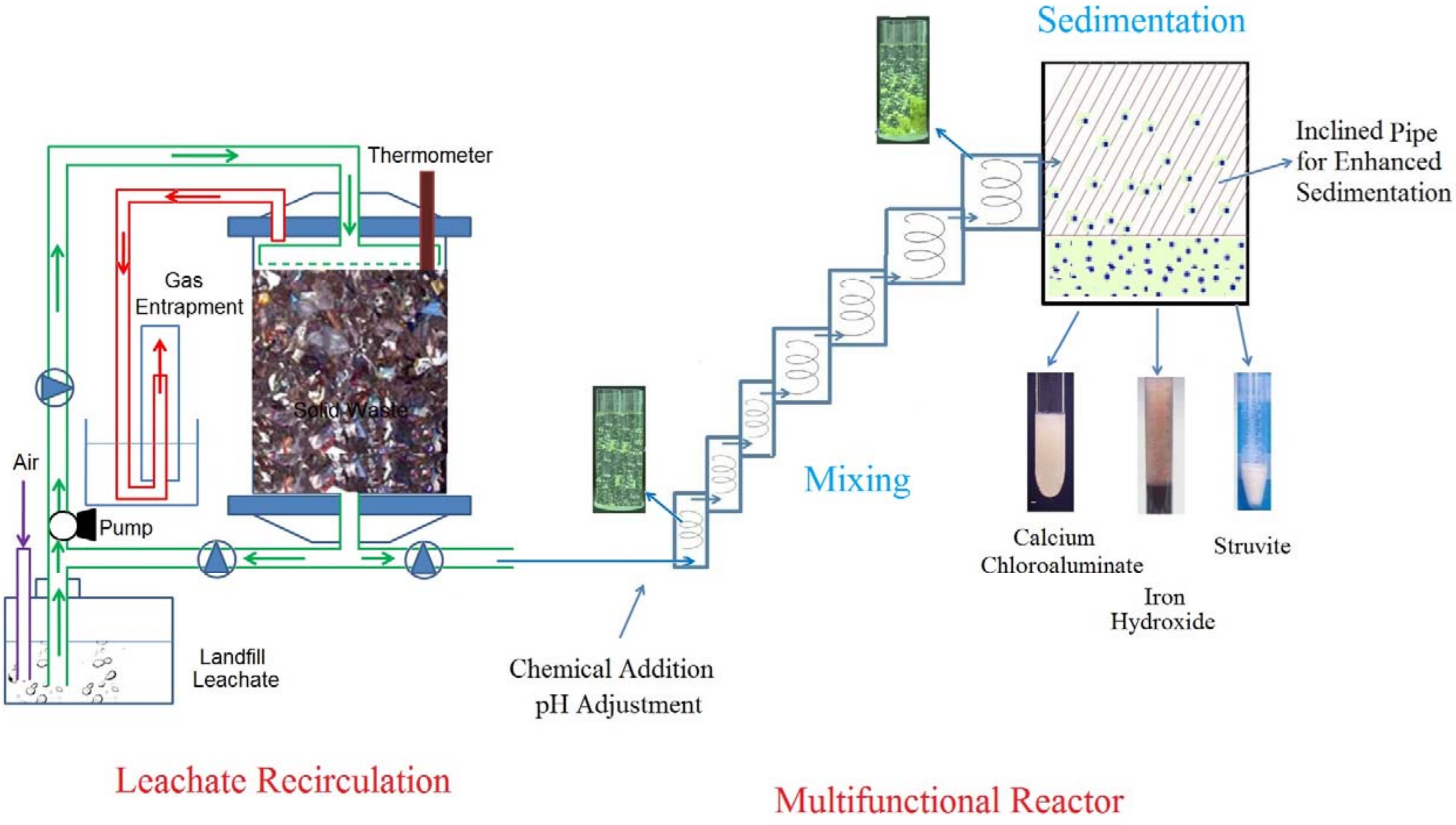


Figure 7. Leachate Recirculation Followed by Treatment in a Multifunctional Reactor ---- Process Illustration

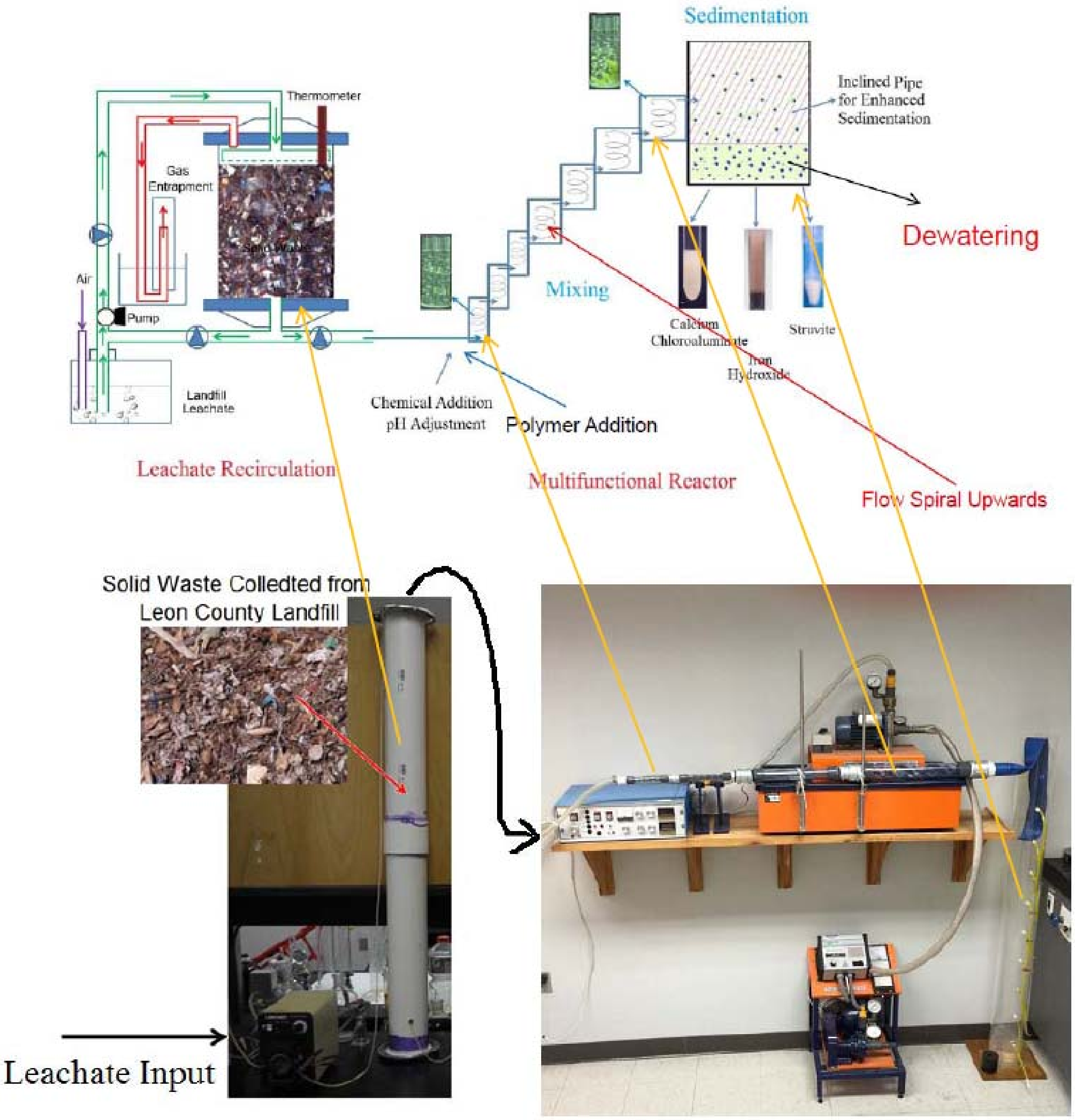


Figure 8. Leachate Recirculation Followed by Treatment in a Multifunctional Reactor ---- Experimental Setup

3.2.1 Aerated Leachate Recirculation

Through aerated leachate recirculation, organic contents were significantly reduced. During this process, solid components were removed at the same time. The leachate recirculation not only improved the leachate quality, but also shortened the time required for landfill stabilization. For this research, aerated recirculation reactor was set up with a dimension of 15 cm ID × 150 cm Length (Figure 9). The solid waste collected from the Leon County Landfill or Springhill Landfill was ground and sieved before introduced into the recirculation reactor. The corresponding leachate was first aerated, after which the leachate 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 2 mg/L to 6 mg/L). Considering the possible organic leaching from the solid waste in the bioreactor, the leachate was re-circulated 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 re-circulated. 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 (DO), pH, oxidation/reduction potential (ORP), BOD_5, ammonium, chloride, phosphorous and iron concentrations were monitored for the leachate before re-circulation into the bioreactor and after getting out of the bioreactor.

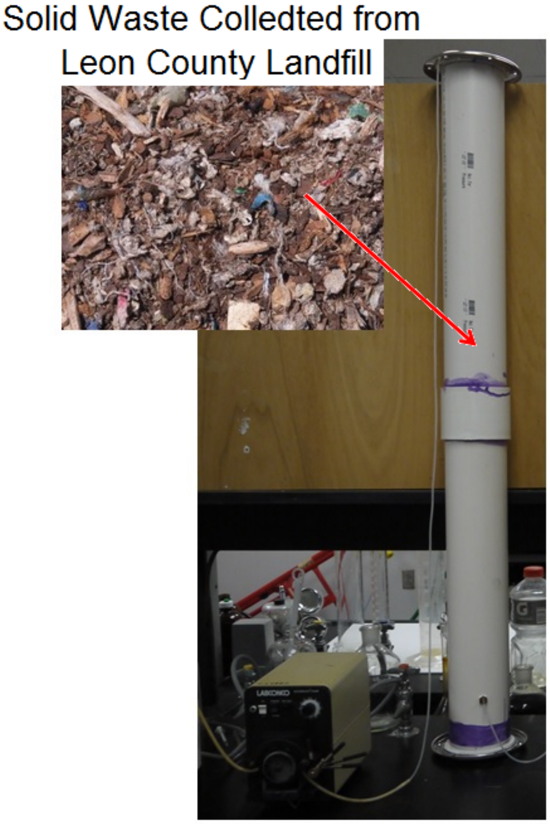


Figure 9. Recirculation Reactor

3.2.2 Multifunctional Reactor Design, Setup and Parameter Characterization

For chloride, iron, phosphorous removal and struvite recovery through precipitation, chemical addition was required. After chemical addition, mixing was the most important process to facilitate a quick reaction. During this process, a more homogenous mixing was desired. Well-mixing operations tended to decrease the chemical demand for an efficient chloride, iron and phosphorous removal as well as struvite recovery. For the multifunctional reactor, a series of static mixing reactors was utilized (Figure 10), followed by a sedimentation reactor (Figure 11). The design of the multifunctional reactor fully utilized the energy that transported the fluid into the reactor. During operation, the aliquot of treated landfill leachate from aerated recirculation was applied with a rate 600 mL/min to the multifunctional reactor. Chemicals were added before the leachate was introduced to the multifunction reactor.

Figure 10. Static Mixers of the Multifunctional Reactor

With the increase of reactor diameter and the subsequent volume, the velocity gradient decreased accordingly, allowing precipitates to aggregate and getting ready to settle in the sedimentation tank. The velocity gradient was related to the imparted energy following:

$$G = \sqrt{\frac{P}{\mu V}} \qquad \textbf{Equation (1)}$$

where G is the velocity gradient; P is the power imparted to the reactor; μ is the viscosity; and V is the reactor volume.

3.2.3 Chloride Removal

For the multifunctional reactor, chloride, iron, phosphorous removal and struvite recovery were conducted separately. Depending on the purposes, the multifunctional reactor proceeded accordingly. For chloride removal, chloride was removed as calcium chloroaluminate [$Ca_4Al_2Cl_2(OH)_{12}$] through precipitation in the presence of calcium and aluminum at high pH. $Al_2(SO_4)_3 \cdot 12H_2O$ at a concentration up to 100 mg/L was added to the landfill leachate with pH adjusted with lime. Considering reducing the chemical costs for the treatment, chloride removal was also tested using the alum sludge, a waste from surface water treatment.

For drinking water treatment, alum was utilized to remove color, turbidity, and other impurities. The subsequent alum sludge was conditioned and dewatered with lime addition. The lime addition resulted pH > 12.5, which made the sludge classified as corrosive and can only be deposited in hazardous landfills. The alum sludge was collected from Atlanta-Fulton Water Treatment Plant (Figure 12) and contained approximately 39% aluminum by weight. The cake-shaped alum sludge had a pH in the range of 12 to 13. The high pH and high calcium content of the alum sludge made it possible to be used for chloride removal by calcium chloroaluminate precipitation. With the alum sludge addition, chloride interacted with alum and precipitated in the sedimentation tank.

Figure 11. Sedimentation Reactor

Figure 12. Alum Sludge Collected from Atlanta-Fulton Water Treatment Plant

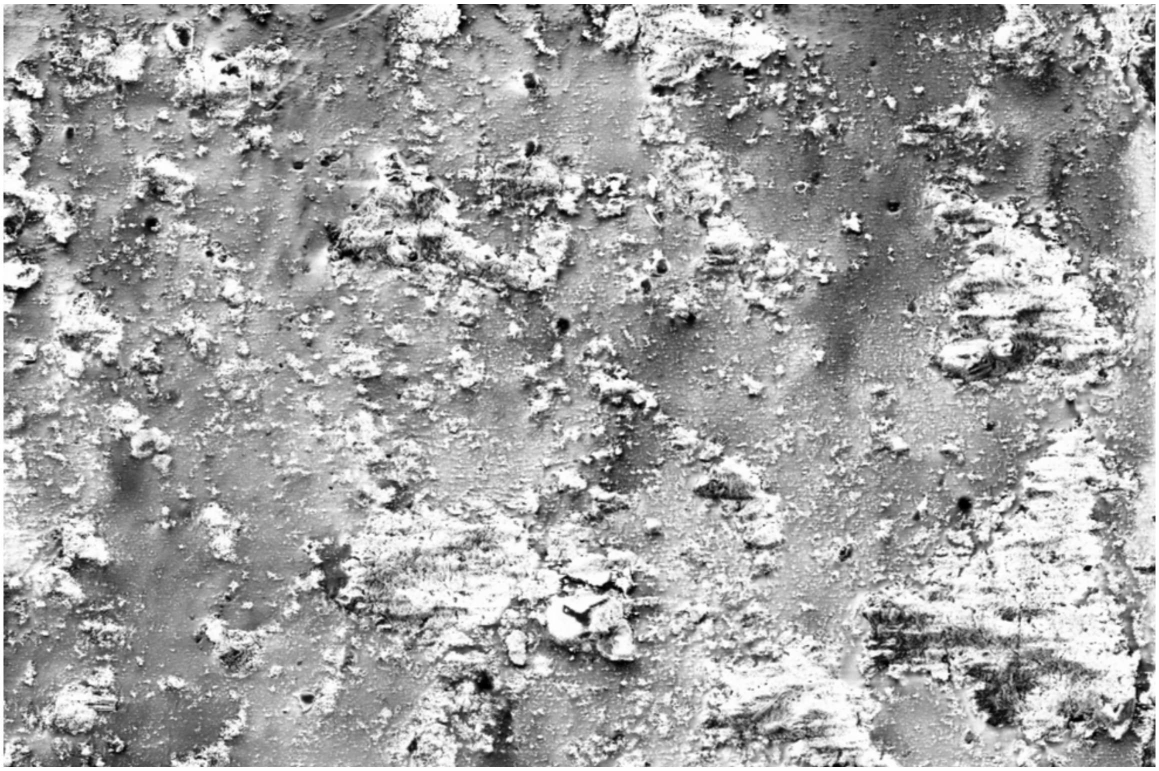


Figure 13. Scanning Electron Microscopy Image of Alum Sludge

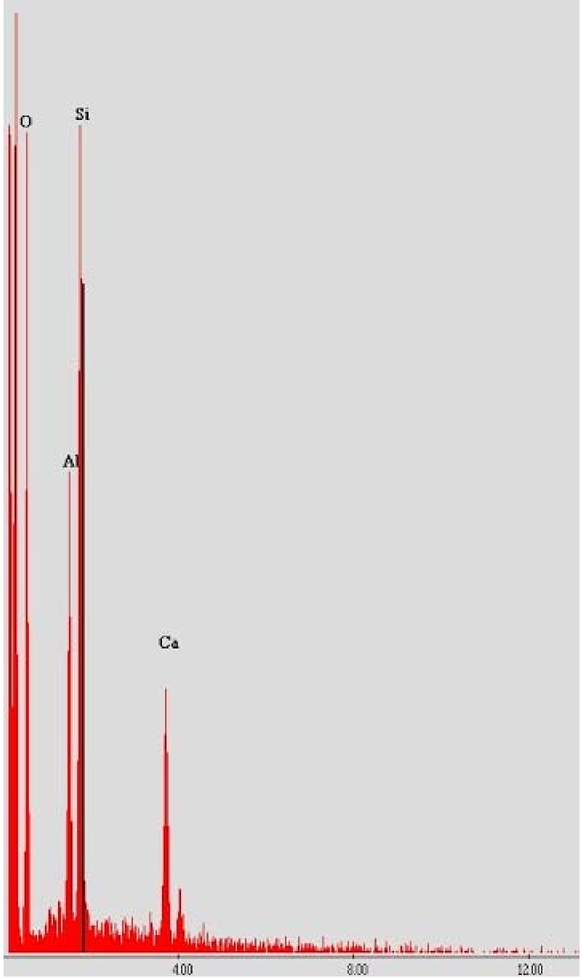


Figure 14. Composition Analysis of Alum Sludge by Scanning Electron Microscopy

The alum sludge was analyzed by scanning electron microscopy (Figure 13), which showed SiO_2, aluminum and calcium were the major components of the sludge (Figure 14). For this research, both alum sludge suspension and the supernatant of alum sludge were tested for their roles in removing chloride (Figure 15). The collected sludge was added to de-ionized water and the supernatant of alum sludge was further characterized. Specifically, 100 mL distilled water was added to a 250-mL Erlenmeyer flask containing 100 g dry sludge. The suspension was stirred using a multiple position magnetic stirring plate. The effect of pH and reaction time on aluminum extraction was investigated. The pH was adjusted either using 1 M H_2SO_4 to solubilize Al as Al^{3+} or 1 M NaOH to extract Al as $Al(OH)_4^-$. Based on the stoichiometry of calcium, aluminum and chloride on calcium chloroaluminate precipitation, both the alum sludge suspension and supernatant were tested for their roles in chloride removal through calcium chloroaluminate precipitation with proper pH adjustment. Depending on the water chemistry of the leachate after alum sludge addition, pH and alkalinity were adjusted with lime and $NaHCO_3$ for better chloride removal results.

Figure 15. Alum Sludge Suspension and Supernatant

3.2.4 Struvite Recovery

For struvite recovery, pH played an important role since pH affected the solubility and the kinetics of the reaction. In our prior research, we had investigated the impact of pH, alkalinity, stoichiometry of precipitating ions, and reaction and settling time on struvite recovery. Among these factors, pH was found to be the most important factor. pH also affected the mechanism and the extent of interference of some cations such as calcium and iron. It also should be noted that the transformation of ammonium to ammonia at high pH would prevent struvite precipitation since ammonium might react with OH^- to release ammonia and deteriorate the formation of struvite. Stoichiometry of magnesium, phosphate and ammonium was important from the standpoint of struvite solubility. It was discovered that $NH_4^+/Mg^{2+}/PO_4^{3-}$ molar ratio of 1:0.75:0.75 would result in the optimum precipitating ion concentration for which struvite precipitation could be maximized. For this research, the aliquot of leachate after aerated recirculation was introduced to the multifunctional reactor at a rate of 600 mL/min. The $NH_4^+/Mg^{2+}/PO_4^{3-}$ molar ratios were maintained at 1:0.75:0.75. For the case that the phosphorous content was not enough, both phosphorous and magnesium were added. Phosphorous was added in the form of $Na_2HPO_4 \cdot 12H_2O$ and magnesium was added as $MgCl_2 \cdot 6H_2O$. The pH adjustment was achieved by the addition of lime to 10, which had also been demonstrated to have a better result than that of pre-aeration (Battistoni et al., 1998). $MgCl_2 \cdot 6H_2O$, $Na_2HPO_4 \cdot 12H_2O$ and lime were added under flash-mixing conditions.

From our prior research, we discovered that the low struvite recovery for low ammonium-content leachate was owing to the poor settling of micro-sized struvite. In the laboratory test at pH 7.6, only leachate with ammonium content greater than 100 mg/L had obvious struvite precipitation observations. In prior research, it was demonstrated that the most struvite would be formed at pH 10. For this research, we therefore raised the pH to 10 for better struvite formation. In addition, in order for the micro-sized struvite to precipitate, coagulant was added to enhance struvite precipitation. After the treatment, the pH of the effluent was adjusted with sulfuric acid if necessary before being discharged.

3.2.5 Iron Removal

For iron removal through iron oxidation and precipitation, lime was added. For this process, pH and dissolved oxygen were the major impact factors for iron precipitation and removal, since these parameters affected the solubility of iron precipitate and the kinetics of the oxidation and hydrolysis processes. Inorganic contaminants, such as heavy metals, may also be co-precipitated with iron. The pH adjustment was achieved by the addition of lime.

After aerated leachate recirculation, the dissolved oxygen of the leachate was above 2 mg/L. Under these conditions, iron started to precipitated when pH was greater than 8.5. For a better iron removal, pH was adjusted to 10 with lime addition before the leachate was introduced to the reactor. Similarly, removal of micro-sized iron hydroxide can be enhanced with coagulation. After the treatment, the pH of the effluent was adjusted with sulfuric acid if necessary before being discharged.

3.2.6 Phosphorous Removal

For phosphorus chemical precipitation by means of coagulation, pH, temperature, and ionic strength were the major impact factors (Takacs et al., 2005). Aluminum and iron coagulants had advantages over calcium salts since they were not sensitive to pH. In addition, aluminum and iron coagulants produced much less sludge (van der Houwen and Vaisami-Jones, 2001). Using ferric salts as a model chemical for phosphorus removal, a model has been developed to describe the single-phase precipitation and two-phase co-precipitation of phosphorus (Fytianos et al., 1998). Based on this model, it was concluded that pH was the most important factor for phosphorus removal and the optimum pH for phosphorus removal was 4.5. Recently, it was demonstrated that phosphorus was removed by adsorption to the aluminum or iron hydroxide rather than by precipitation (Peak et al., 2002). However, the most acceptable mechanism assumed that phosphorus removal was a continuous sequence of adsorption and precipitation, which consisted of two processes: reversible adsorption process and irreversible precipitation process (Arias et al., 2006). The adsorption process was relatively fast and the precipitation process was relatively slow and practically, it was very difficult to distinguish between these two processes.

For this proposed research, phosphorous removal was tested in the multifunctional reactor by using commercially available metal salt coagulants, including aluminum sulfate ($Al_2(SO_4)_3 \cdot 18H_2O$) and ferric chloride ($FeCl_3 \cdot 6H_2O$). Depending on the water chemistry of the leachate after coagulant addition, pH and alkalinity were adjusted with hydrochloric acid or lime and $NaHCO_3$ for better phosphorus removal results. With the addition of the coagulants, solution pH decreased according. The decrease of solution pH was attributed to the alkalinity consumption during coagulant hydration. In the case of Al^{3+} and Fe^{3+}, there was a primary hydration shell with six octahedrally coordinated water molecules, e.g., $Al(H_2O)_6^{3+}$ and $Fe(H_2O)_6^{3+}$ (Sarparastzadeh et al., 2007). Hydrolysis of $Al(H_2O)_6^{3+}$ and $Fe(H_2O)_6^{3+}$ was a sequential replacement of the water molecules with hydroxide ions, the progressive of which involved in many competing reactions. These reactions of the de-protonation were functions of the reaction equilibrium constants and solution pH. Compared to Al^{3+}, Fe^{3+} reacted slowly with the natural alkalinity, and consequently, iron salt coagulants encountered less pH decrease.

3.2.7 Sludge Dewatering

The sludge or struvite produced from above reactions was dewatered before discharged or re-used. The dewatering process was carried out in the laboratory by centrifugation. Specifically, the sludge or struvite solution was placed in 250 mL centrifuge tubes. A mark 7 cm from the bottom and a mark 0.2 cm were put on the tubes. These marks corresponded to S =10.5 cm and R = 17.3 cm as shown in Figure 16.

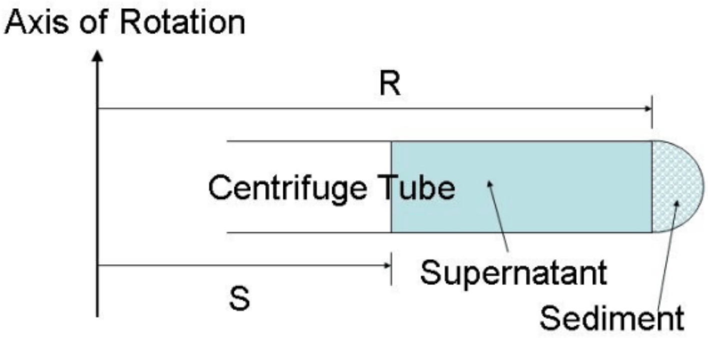


Figure 16. Illustration of Sludge Centrifugation

The centrifuge tubes were placed in Sorvall RC-5C Centrifuge (Block Scientific, Inc.) and centrifuged at room temperature. By using centrifugation, all particles in the solution were graded. The separation was based on the Stokes' Law, which was a formula for determining the rate of sedimentation. For the same density particle, the sedimentation rate was a function of particle size. For this research, the method developed by M. L. Jackson was used (Jia et al., 2010):

$$T_m = \frac{63.0 \cdot 10^8 \eta \log_{10}[\frac{R}{S}]}{N^2 D^2 \Delta s} \qquad \textbf{Equation (2)}$$

where Tm is the time for sedimentation in minutes; η is the viscosity in poise at the existing temperature (0.01111 poise for water); R is the radius in centimeters from the axis of rotation to the top of the sediment in the centrifuge tube or bottle; S is the radius in centimeters from the axis of rotation to the surface of the suspension in the centrifuge tube or bottle; N is the revolutions per minute (rpm); D is the particle diameter in microns; and Δs is the difference in specific gravity between the solvated particle and the suspension liquid.

3.2.8 System Optimization and Cost Analysis

The operation parameters of aerated leachate recirculation and multifunctional reactor were optimized based on overall treatment results, which included aeration ratio, recirculation ratio as well as pH, alkalinity, and chemical addition for specific removal or recovery purpose, etc. Cost benefits and space-saving were analyzed and compared with that of off-site treatment processes and reported in this research.

4. Results

4.1 Landfill Leachate Characterization

The landfill leachate collected from Leon County Landfill had a BOD_5 of 221 mg/L, COD of 961 mg/L, NH_4^+-N of 314 mg/L and chloride of 384 mg/L. The Springhill Landfill leachate had a BOD_5 of 421 mg/L, COD of 1,532 mg/L, NH_4^+-N of 526 mg/L and chloride of 527 mg/L. It should be noted that these measurements were based on the supernatant of the collected samples. Compared to Springhill Landfill leachate, the Leon County Landfill leachate had a darker color and obvious solid precipitation after settling over 24 hours (Figure 17). These solid precipitates also contained high organics (Figure 18). To analyze the components of the solid precipitates, EDX analysis was conducted (Figure 19 and Figure 20). The results showed that the Leon County Landfill leachate solid precipitate had 78% C, 12% O, 7% Si, and 3% Fe (Table 4). For comparison, Springhill Landfill Leachate was centrifuged to obtain solid precipitate, which had 74% C, 16% O, 9% Si and 1% Fe (Figure 20 and Table 4).

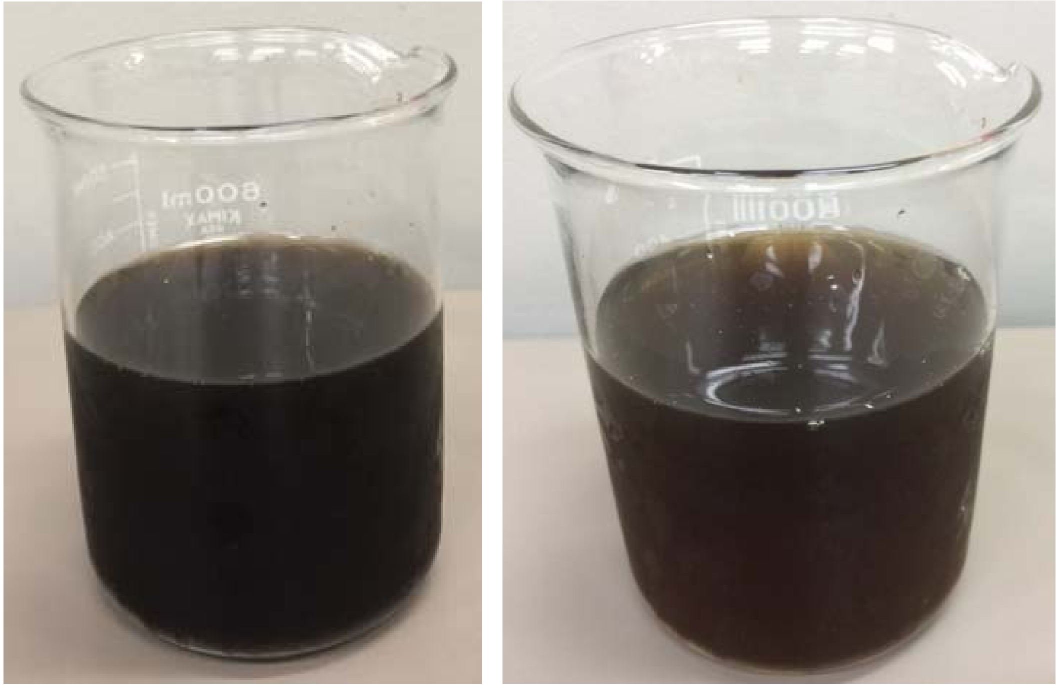


Figure 17. Landfill Leachate Collected from Leon County Landfill (Left) and Springhill Landfill (Right)

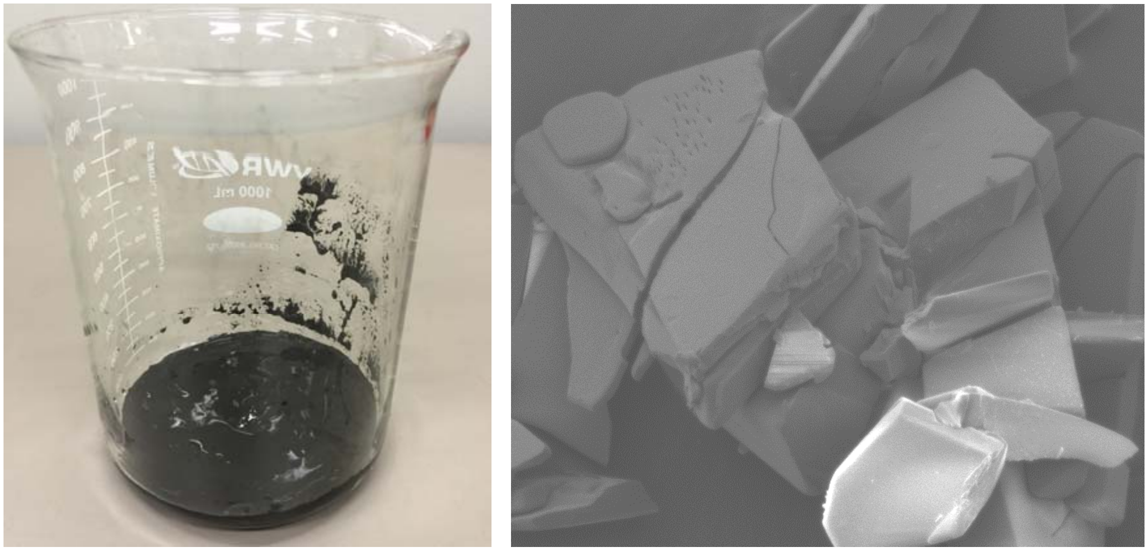


Figure 18. Leon County Landfill Leachate Precipitate and Scanning Electron Microscopy Image

Table 4. Composition of Landfill Leachate Precipitate

Element	[a]Wt%	[b]Wt%
C	77.96	73.73
O	11.70	16.06
Si	7.33	9.01
Fe	2.65	1.20
Ca	0.06	0.00

[a] Leon County Landfill Leachate

[b] Springhill Landfill Leachate

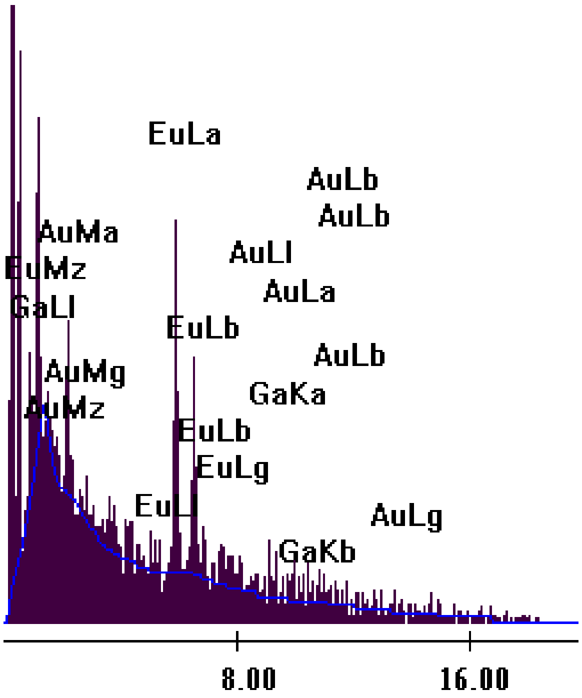


Figure 19. Composition Analysis of Leon County Landfill Leachate

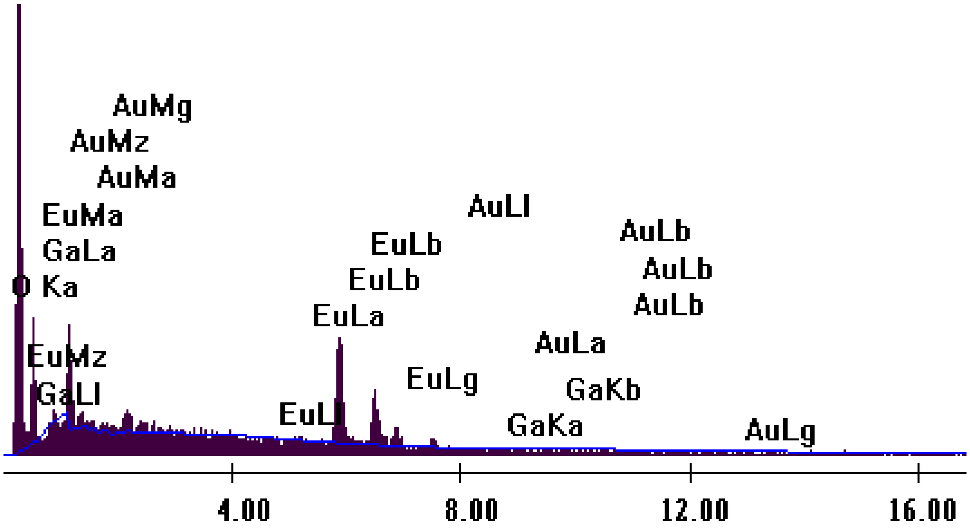


Figure 20. Composition Analysis of Springhill Landfill Leachate

4.2 Aerated Leachate Recirculation

Organic removal from the landfill leachate collected from the Leon County Landfill and Springhill Landfill was investigated in the laboratory. It was discovered that after 4 to 5 recirculation cycles, the organic removal became stable (Figure 21 and Figure 22). Compared to Leon County Landfill leachate, leachate collected from Springhill Landfill had higher organic contents. The organic removal reached an average of 84% for Leon County Landfill leachate and 87% for Springhill Landfill leachate when organic removal became stable at dissolved oxygen of 2 mg/L. At a recirculation cycle of 4, 50% of the treated leachate was introduced to the next treatment step and 50% fresh leachate was added.

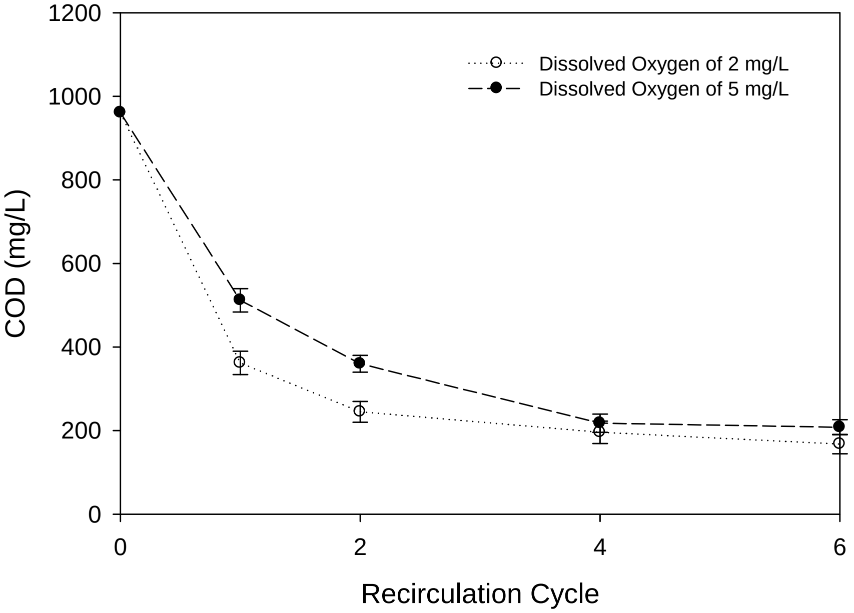


Figure 21. COD Removal as a Function of Recirculation Cycle for Leon County Landfill Leachate

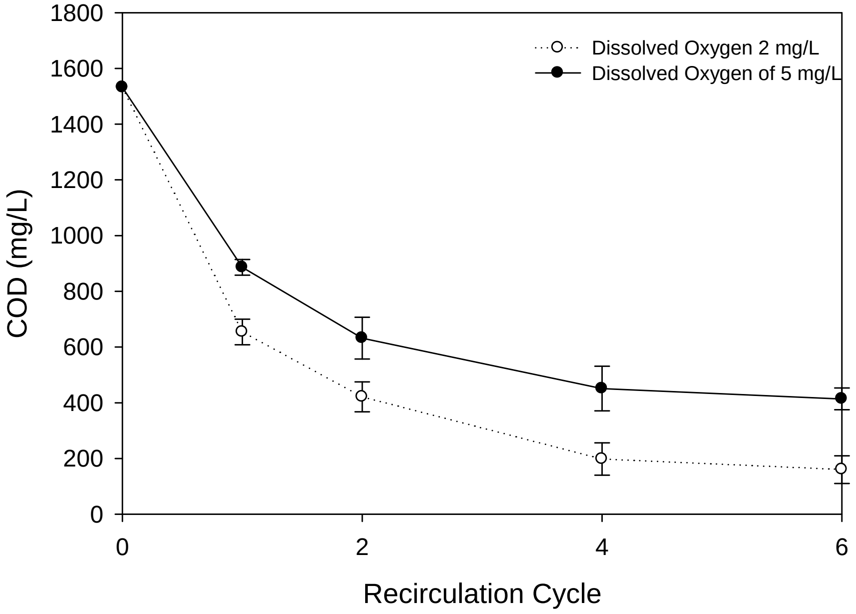


Figure 22. COD Removal as a Function of Recirculation Cycle for Springhill Landfill Leachate

4.3 Chloride Removal

Besides organic contaminants, nutrients and heavy metals, high concentrations of chloride have also been observed in several landfills, especially those where waste-to-energy ash is co-disposed with municipal solid waste. Chloride has been demonstrated to be the major contribution of total dissolved solids in the landfill leachate and the elevated concentrations of chloride pose significant challenges to the beneficial waste-to-energy processes. Since the secondary drinking water standard for chloride is 250 mg/L, chloride removal is drawing more and more attention. From this research, the chloride concentration was found to be 384 mg/L for Leon County Landfill leachate and 527 mg/L for Springhill Landfill leachate. Chloride removal was tested by the ultra-high lime with aluminum process, during which chloride was removed as calcium chloroaluminate [$Ca_4Al_2Cl_2(OH)_{12}$] through precipitation in the presence of calcium and aluminum at high pH in the multifunctional reactor.

Chloride removal in the multifunctional reactor was a function of both pH and alum concentration (Figure 23 and Figure 24). With the increase of pH, obviously more chloride was removed. Chloride removal increased with the increase of alum addition until 20 mg/L, after which the chloride removal became moderate. It is therefore recommended that alum of 20 mg/L be used for chloride removal during leachate treatment.

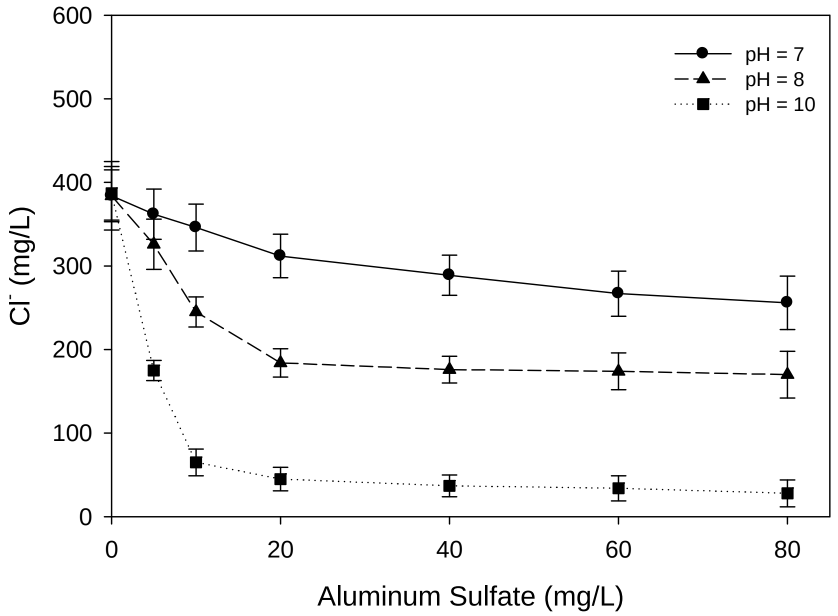


Figure 23. Chloride Removal as a Function of Alum Concentration for Leon County Landfill Leachate

Chloride removal as a function of pH when alum was applied at 20 mg/L is illustrated in Figure 25. For both Leon County Landfill leachate and Springhill Landfill leachate, chloride removal decreased linearly with the increase of pH. However, the decrease with the increase of pH was more pronounced for the Springhill Landfill leachate and less pronounced for Leon County Landfill leachate. This was mainly because Springhill Landfill had a high chloride concentration than that of Leon County Landfill (527 mg/L as compared to 384 mg/L).

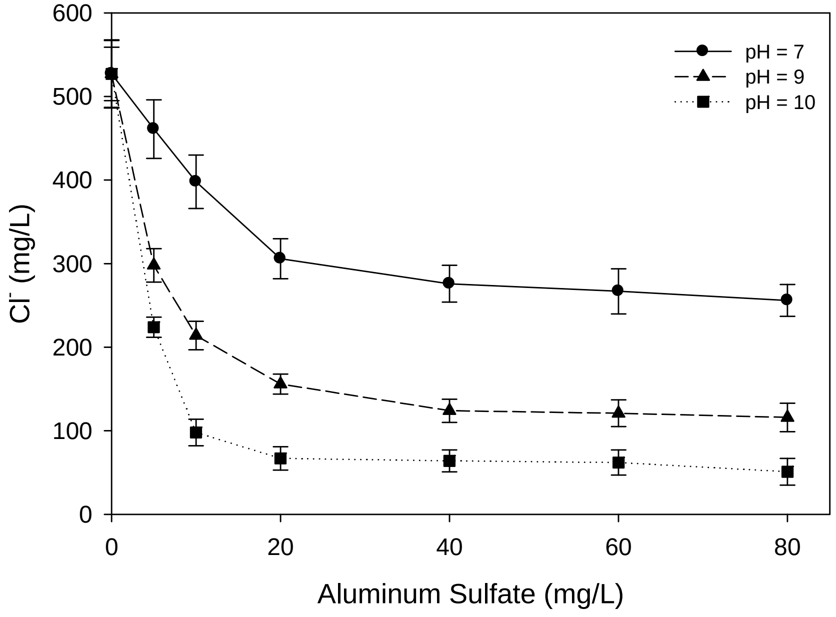


Figure 24. Chloride Removal as a Function of Alum Concentration for Springhill Landfill Leachate

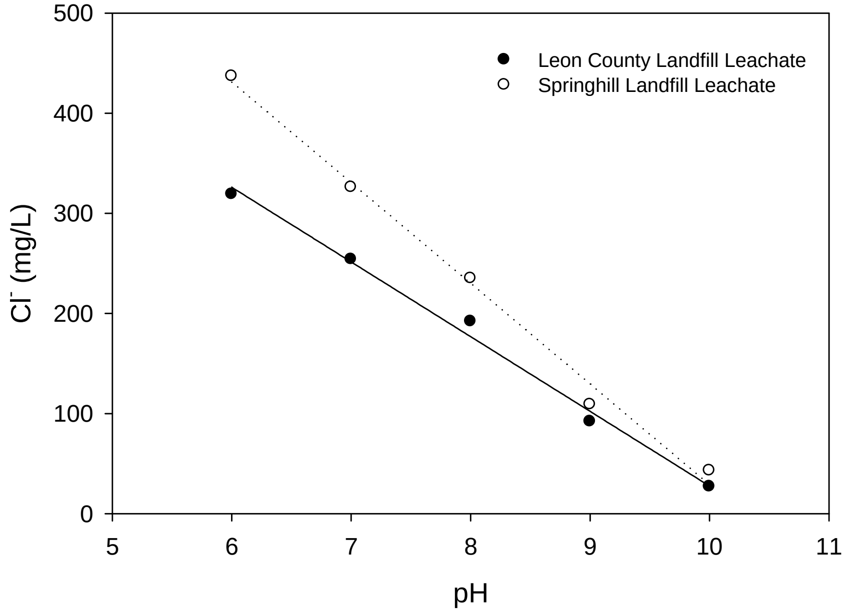


Figure 25. Residual Chloride Concentration as a Function of pH

With the increase of pH, chloride removal was enhanced accordingly. At pH of 7, around 20% chloride was removed for Leon County Landfill leachate and 40% for Springhill Landfill leachate. At pH of 8, the removal rate increased to 40% and 55%. At pH of 10, the removal reached 92% and 95%.

Considering reducing the chemical costs for the treatment, we tested chloride removal using the alum sludge, a waste from 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 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 drinking water treatment. The beneficial reuse of alum sludge is therefore highly desirable and has attracted considerable research efforts. Most importantly, the high pH and high calcium content as a result of dewatering and conditioning with lime addition would promote chloride removal by calcium chloroaluminate precipitation. This sludge contains approximately 39% aluminum by weight (Huang et al., 2010). The alum sludge used in this research 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 high calcium content of the alum sludge made it possible for chloride to be removed in the form of $Ca_4Al_2Cl_2(OH)_{12}$.

Both powdered alum sludge and the supernatant of alum sludge suspension were tested for their roles in removing chloride (Figure 26 and Figure 27). Although the chloride removal was not as efficient as alum, the results were still acceptable, especially considering the significant savings of chemical costs. Compared to the powdered alum sludge, the supernatant of alum sludge suspension had better chloride removal observation, which was very close to that of alum. The supernatant of alum sludge suspension had minimal clay minerals and the aluminum cations existed either in the soluble format or amorphous $Al(OH)_3$ format.

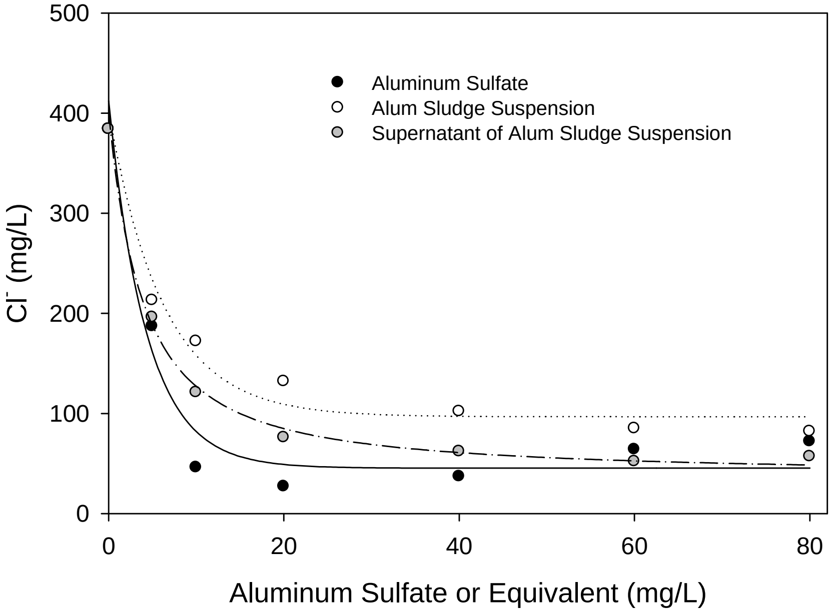


Figure 26. Chloride Removal as a Function of Alum Concentration for Leon County Landfill Leachate

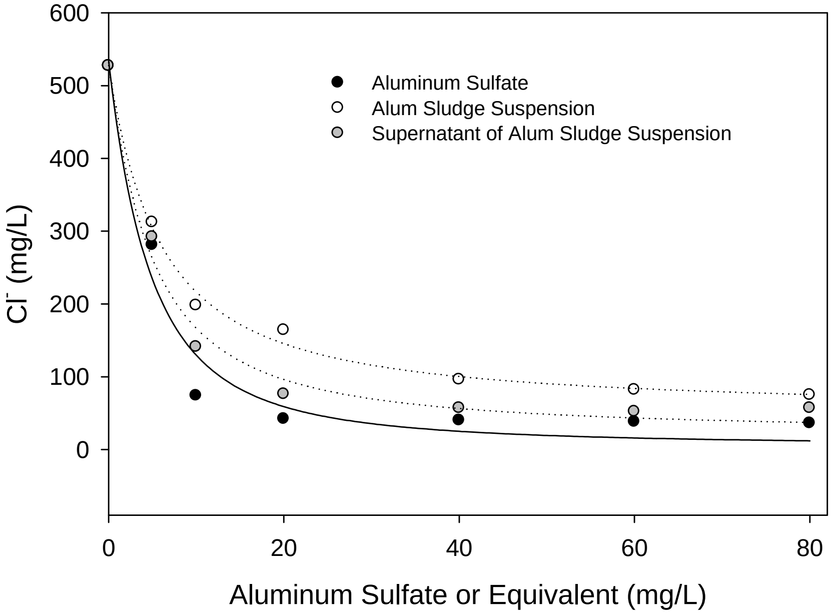


Figure 27. Chloride Removal as a Function of Alum Concentration for Springhill Landfill Leachate

4.4 Struvite Recovery

Struvite can precipitate ammonium and phosphorous from landfill leachate. However, the efficiency was not satisfactory for ammonium removal, especially for landfill leachate with low initial ammonium content. The low ammonium removal efficiency through struvite precipitation and sedimentation was attributed to the fact that micro-scale struvite cannot settle efficiently. To further improve ammonium removal by struvite precipitation, alum was added in the multifunction reactor. The stoichiometry of $NH_4^+/Mg^{2+}/PO_4^{3-}$ molar ratio was maintained at 1:0.75:0.75. With the application of alum at a concentration of 20 mg/L, ammonium removal by struvite precipitation was dramatically enhanced (Figure 28). At pH of 8.0, the ammonium removal efficiency increased from 47% to 90% for initial ammonium concentration of 300 mg/L when alum was added at 20 mg/L. Ammonia removal linearly increased with the increase of initial ammonia concentration. The higher ammonia removal efficiency was attributed to the fact that the formed struvite that cannot settle was removed with alum flocs.

The pH had a great influence on landfill leachate ammonium removal, i.e., ammonium removal increased with the increase of pH until pH 10, after which, ammonium removal decreased with the increase of pH (Figure 29 and Figure 30). For Leon County Landfill leachate with ammonium content of 384 mg/L, the maximum ammonium removal achieved 85% after without alum addition and 98% with alum addition at pH 10 (Figure 29). pH impacted ammonium removal since it determined struvite solubility. Although H^+ concentration did not directly enter the ion-activity product equation, $MgNH_4PO_4{\cdot}6H_2O$ precipitation was highly pH dependent because the activities of both NH_4^+ and PO_4^{3-} were pH dependent (Nelson et al., 2003). Some research reported that the struvite solubility decreased with the increase of pH (Marti et al., 2008). The decrease of solution product with the increase of pH was attributed to the fact that activities of both NH_4^+ and PO_4^{3-} were pH dependent. Based on the theoretical calculation, struvite solubility product decreased with the increase of pH until pH reached 10.2, after which struvite solubility product increased with the continuing increase of pH. At pH 10.2, struvite had the minimum solubility product of 3×10^{-10}.

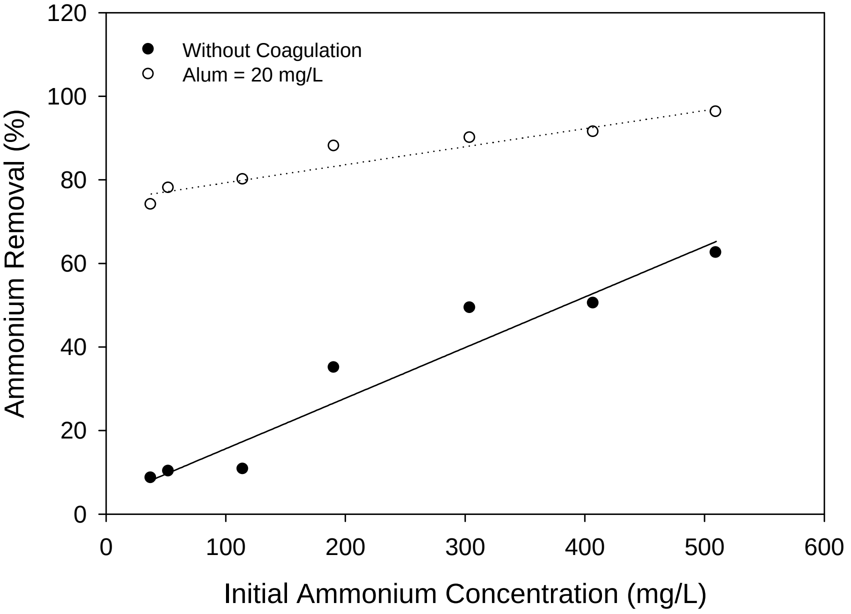


Figure 28. Ammonium Removal as Function of Initial Ammonium Concentration

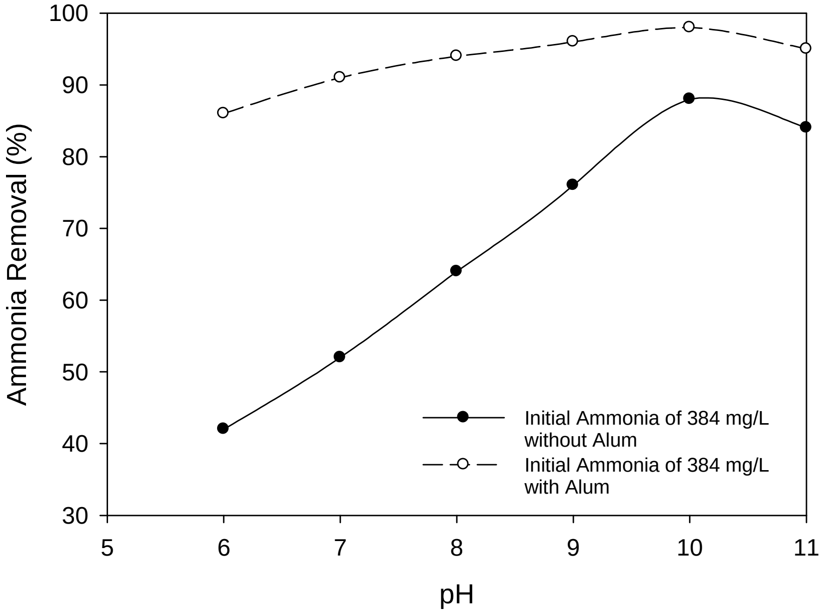


Figure 29. Ammonium Removal as Function of pH for Leon County Landfill Leachate

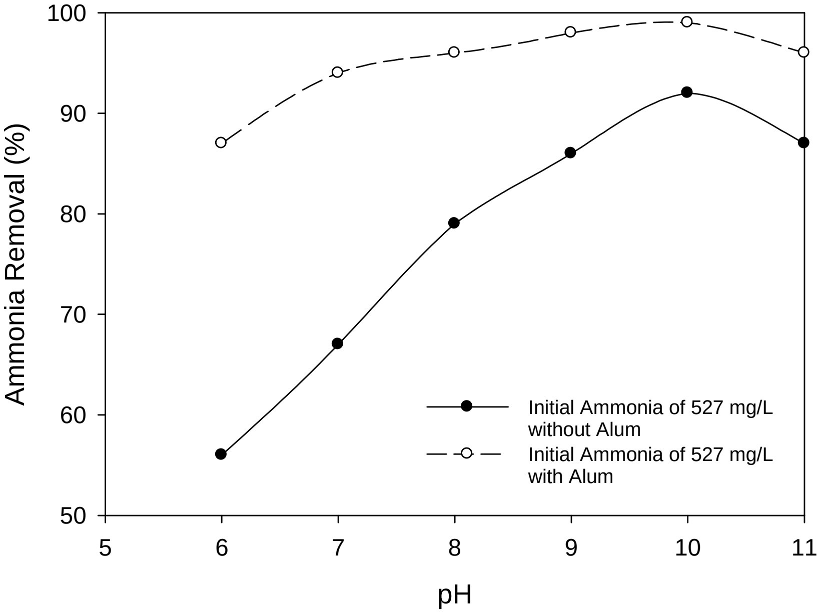


Figure 30. Ammonium Removal as a Function of pH for Springhill Landfill Leachate

4.5 Iron Removal

Iron removal is very important for the landfill leachate treatment in Northwest Florida owing to the high iron content in the soil. During landfill operation, ferric iron (Fe^{+3}) is reduced to ferrous iron (Fe^{+2}) and released to the leachate. Ferrous iron can be removed by oxidation and precipitation, which is pH dependent. Batch experiment was conducted first to evaluate ferrous iron oxidation as a function of pH. High pH favored ferrous iron oxidation as shown in Figure 31 and Figure 32. Ferrous oxidation was also a function of reaction time. From our experiments, it was discovered that at least 10 minutes was required before stable oxidation could be reached. With dissolved oxygen of 2 mg/L, around 97% of iron existed in the form of ferric iron after 10 minutes of oxidation at pH 8.0. It was demonstrated that pH of 8.0 and above was required for efficient iron oxidation. However, the separation of ferric iron as ferric hydroxide ($Fe(OH)_3$) from water was difficult owing to the micro-sized precipitate. The presence of clay minerals might help micro-sized ferric hydroxide ($Fe(OH)_3$) precipitation.

Figure 31. Ferrous Iron Transformation

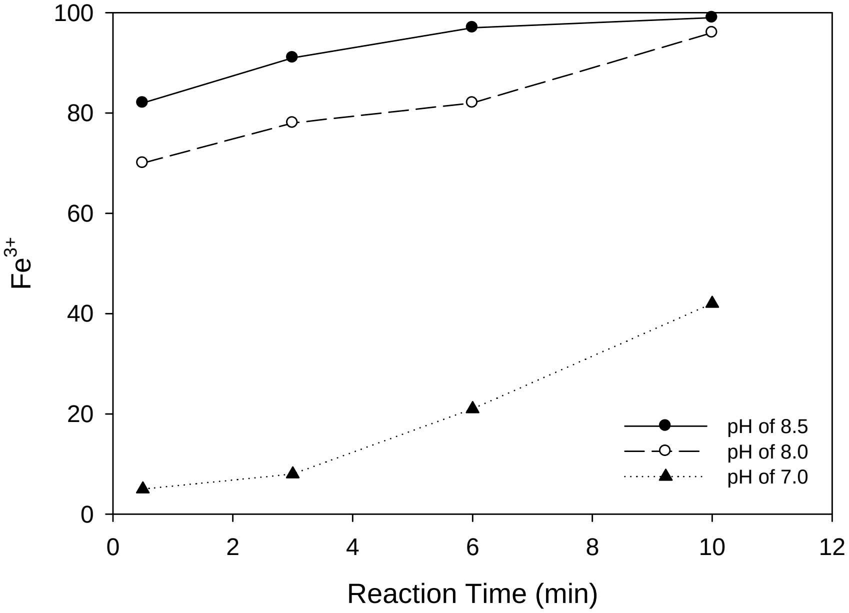


Figure 32. Ferrous Iron Oxidation as a Function of pH and Reaction Time

In the presence of alum, iron removal increased accordingly. Around 95% of iron was removed when the in the presence of 20 mg/L alum at pH 10.0 (Figure 33). For pH 7 and 8, around 91% and 87% were removed. It seemed that alum addition at a concentration of

20 mg/L was enough for the precipitate to settle from water. The further addition of alum did not contribute more to iron removal. Again, iron removal was a function of pH. The higher the pH, more iron was removed.

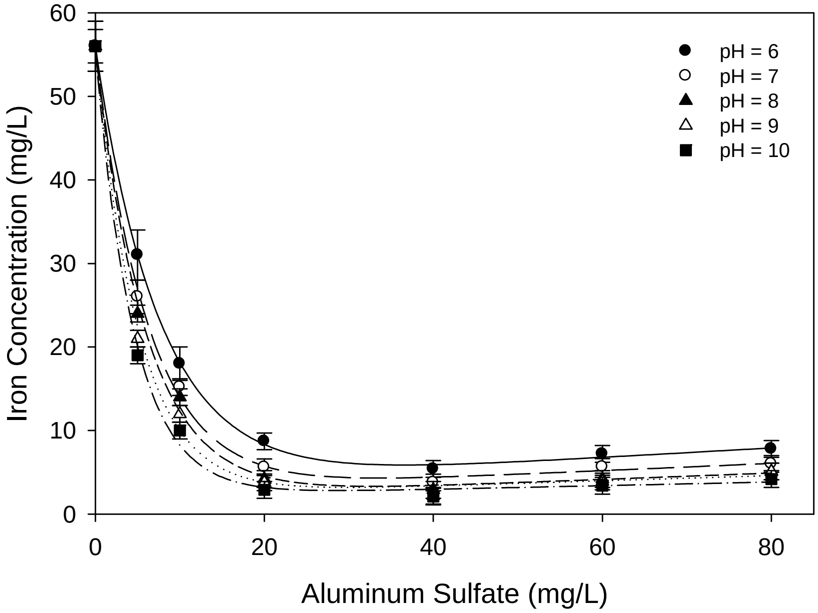


Figure 33. Iron Removal as a Function of Alum Concentration

4.6 Phosphorous Removal

For phosphorous removal, alum had obvious better removal efficiency than that of ferric chloride (Figure 34). When applied in water, the coagulants, aluminum and ferric salts formed a series of products including monomers, oligomers, and polymeric hydroxyl complexes, depending on the pH of the solution. For the pH range of 6 to 7, $AlOH^{2+}$, $Al(OH)_2^+$, and $Al(OH)_3$ co-existed for aluminum salt coagulants and $Fe(OH)^+$ and $Fe(OH)_3$ co-existed for iron salt coagulants. The amorphous $Al(OH)_3$ and $Fe(OH)_3$ were the species that are responsible for phosphorus precipitation (Yang et al., 2010) and $AlOH^{2+}$, $Al(OH)_2^+$ and $Fe(OH)^+$ were the species for the adsorption of phosphorus. For phosphorus to adsorb to $Fe(OH)^+$, $AlOH^{2+}$, and $Al(OH)_2^+$, phosphorus replaced singly coordinated OH^- groups and then reorganized into a very stable binuclear bridge between the cations. This sorption process was coupled with the release of OH^- ions, thus this process was favored by low pH values (Luk, 1999). Since these species co-existed, adsorption and precipitation of phosphorus were functioning at the same time. However, it has been suggested that adsorption should play a more important role in phosphorus removal, which is consistent with prior research (Peak et al., 2002). In the pH range of 6 to 7, $AlOH^{2+}$ and $Al(OH)_2^+$ were abundant while $Fe(OH)^+$ was not, subsequently aluminum salt coagulants had a better phosphorus removal result. This was because phosphorous sorption process released OH^-, increasing the solution pH, which prevented Fe^{3+} hydrolysis process that also preferred low pH. At 20 mg/L of alum, 85% phosphorous can be removed efficiently.

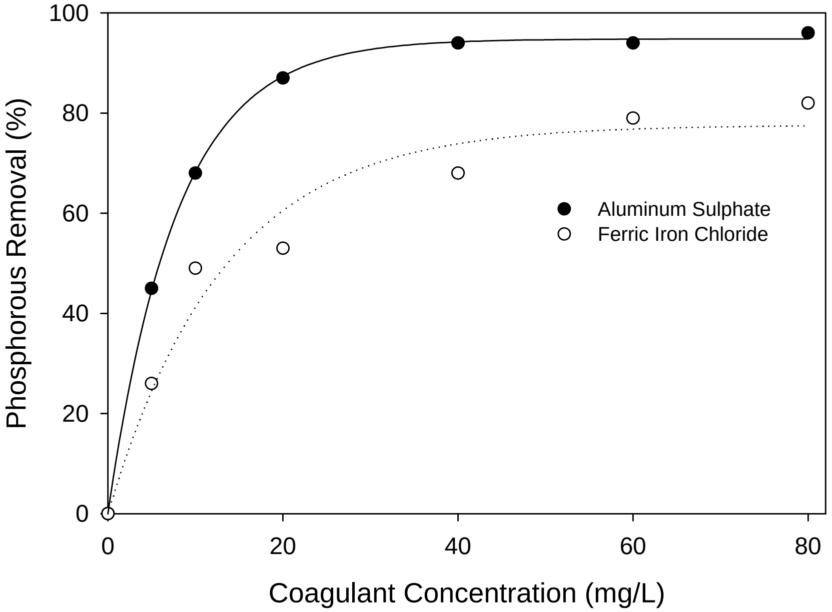


Figure 34. Phosphorous Removal as a Function of Coagulant Dosage

4.7 Sludge Dewatering

Based on the Stokes' Law, the time requirements for the fines of this research are calculated in Table 5. By centrifugation at 100 rpm for 12 minutes, 75 μm particles were separated from the liquid phase. In contrast, the 600 μm particles required only 1.5 minutes.

Table 5. Sedimentation Time for Variable Particle Sizes

Particle Size	Sedimentation Time at 100 rpm (Minutes)
600 µm (Sieve No. 30)	1.5
300 µm (Sieve No. 50)	3.0
150 µm (Sieve No. 100)	6.0
75 µm (Sieve No. 200)	12.0

With centrifugation, it was the centrifugal force instead of gravity that was responsible for the solid/liquid separation, which was created in a conical-cylinder bowl that rotated at high speeds. The sludge particles were pressed against the bowl and conveyed out of the centrifuge by a screw that rotated at a slightly different speed than the bowl. To enhance solid dewatering, lime addition was required. The dry solid percentage increased with the lime dose increase (Figure 35).

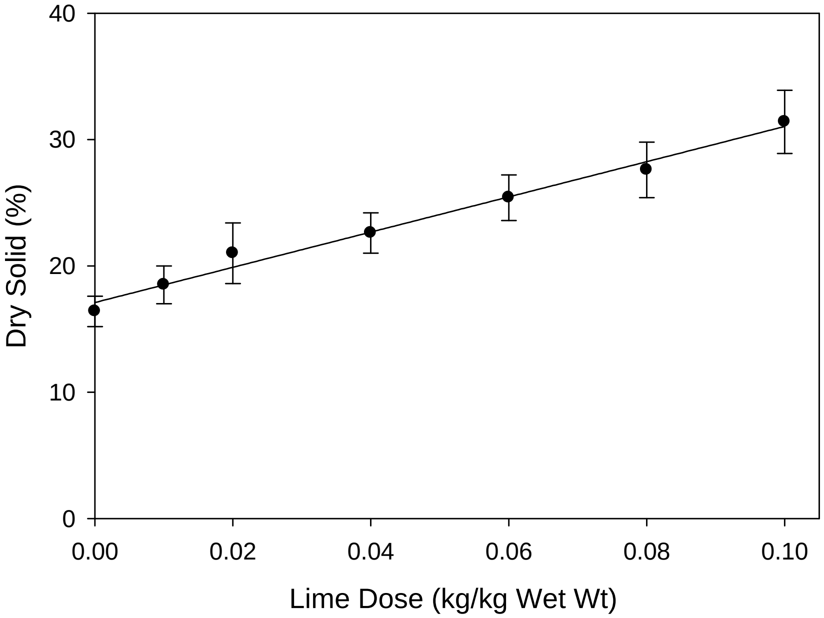


Figure 35. Dry Solid Percentage as a Function of Lime Addition

5. Discussion

5.1 Organic Removal by Coagulation

Organic matter, especially solid organics or organic compounds coated on the clay mineral surfaces can combine with coagulants, aluminum or ferric ions, to form a complex and precipitate in regions of pH where aluminum hydroxide or ferric hydroxide precipitation is minimal. Using aluminum coagulant as an example, four processes, i.e., A. enmeshment, B. charge neutralization, C. adsorption, and D. precipitation are involved in contaminant removal by means of coagulation (Figure 36 and Figure 37). Cationic aluminum can electrotastically interact with anionic organic matter to form insoluble charge-neutral products (pathway B). Secondly, at high coagulant doses, the insoluble aluminum hydroxyl can be removed by enmeshment or surface adsorption (pathways A and C). The concentration of coagulant has to be high to ensure rapid precipitation of $Al(OH)_3$. Colloidal organic matter can act as nuclei for precipitate formation or can become entrapped during floc aggregation.

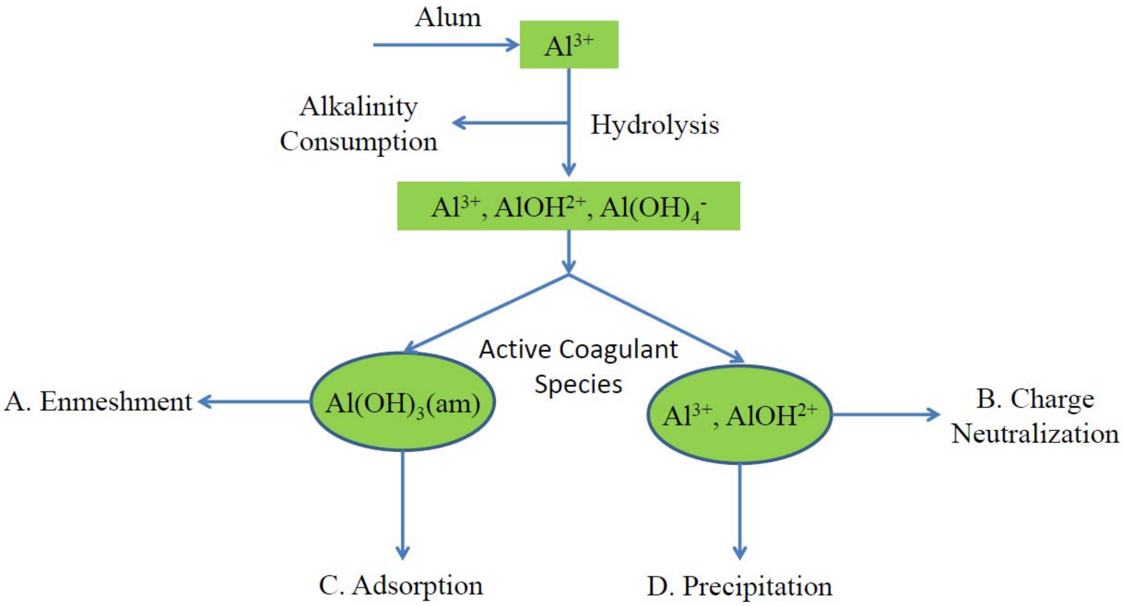


Figure 36. Organic Removal Mechanisms by Coagulation

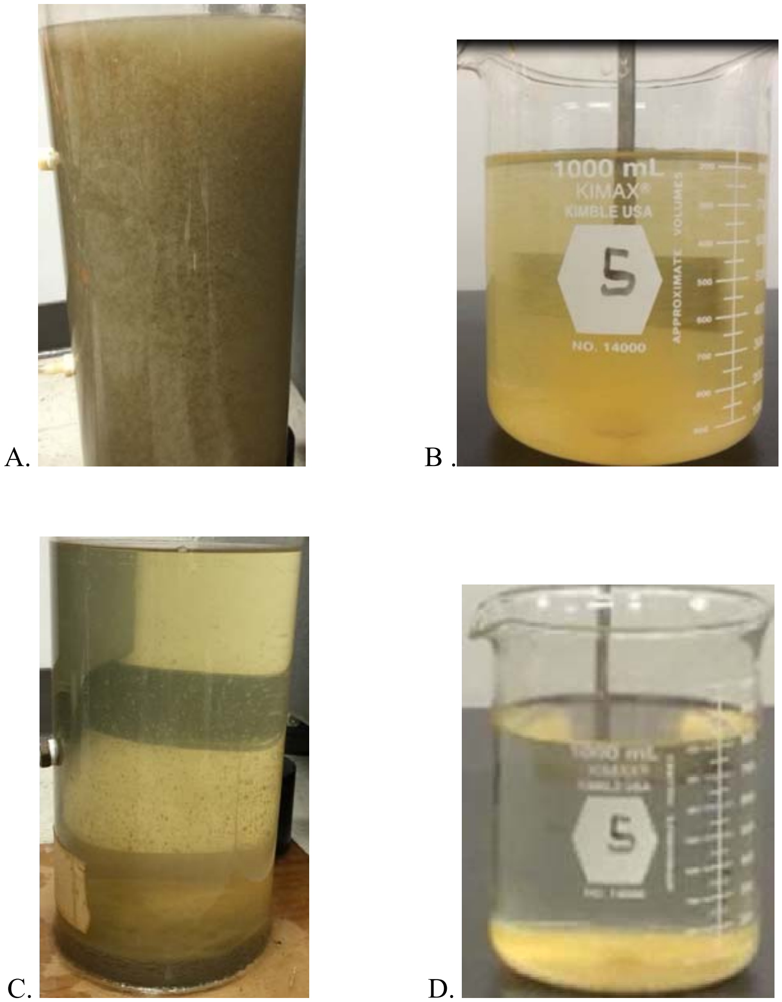


Figure 37. Organic Removal Observations by Coagulation

In this research, organics contained in the solid particles of the landfill leachate were removed by coagulation. This is especially the case of Leon County Landfill leachate owing to its high clay mineral contents.

Amino-acids, carbohydrates, and carboxylic acids which were generally present in landfill leachate may coat clay minerals and exit in the solid form in the landfill leachate. Because of leachate's heterogeneous and undefined character, the amount of organics was measured through surrogate parameters as total organic carbon (TOC). Rapid removal of TOC was observed in the current work, especially during sweep coagulation.

Sweep coagulation, nevertheless, may proceed at moderate bulk concentrations by virtue of exceeding super-saturation locally as a consequence of concentrating the coagulants through interactions with functional groups on the contaminant or colloidal particles. TOC removal decreased with the increase of equivalent ratio of coagulant to TOC (Figure 38). This decrease was obvious before the equivalent ratio reached 0.1. After that, the decrease was moderate. It seemed that super-saturation was possible once the equivalent mass ratio of the coagulant to TOC reached 0.1. However, no obvious difference was observed for TOC removal by alum and ferric chloride.

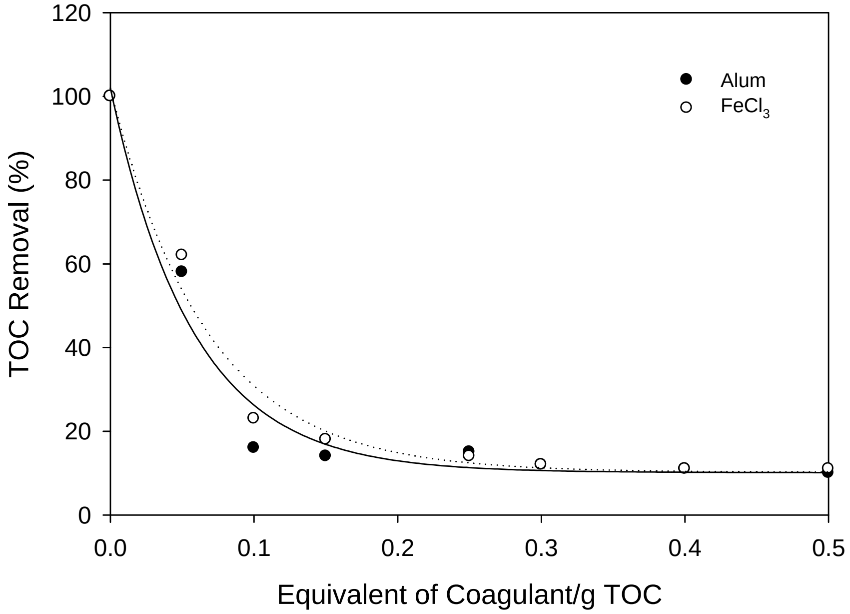


Figure 38. Organic Removal as a Function of Coagulant Dosage

The hydrolyzed metal species had a higher tendency toward adsorption than the metal ions, and this may explain the stronger interactions with TOC during coagulation. With the ongoing of coagulation, Al^{3+} or Fe^{3+} and their hydrolysis products formed more stable and less water soluble complexes with TOC. High coagulant concentrations resulted in low pH. Subsequently, polymeric hydrolysis species such as $Fe_2(OH)_{24}^+$ and $Fe_3(OH)_{45}^+$ were predominant and were responsible for charge reversal and the formation of low water soluble complexes upon interactions with the functional groups of the TOC. In addition, the dominating polymeric species increased with the increase of coagulant dose.

For example, the penta-positive dimeric species, $Fe_3(OH)_4^{5+}$ was the most important hydrolysis species when Fe(III) was greater than 1 mM. It should be noted that interactions of polymeric hydrolysis species with TOC may yield an overall positively charged complex, which may lead to re-stabilization through charge reversal.

5.2 Zeta Potential

Zeta (ζ)-potential played the most important role during coagulation. In this research, ζ-potential was quantified in parallel during the experiments by means of microelectrophoresis in terms of electrophoretic mobility through dynamic light scanning (Zetasizer 3000HAS, Malvern Instruments Ltd., Malvern, UK). During the measurement, a laser beam passed through the electrophoresis cell, irradiating the particles dispersed in the solution. The scattered light was then detected by a photo-multiplier after passing through the electrophoresis cell. ζ-potential was related to the electrophoretic mobility by the following equation:

$$U_E = \frac{\varepsilon_r \varepsilon_0 \zeta}{\eta} \qquad \textbf{Equation (3)}$$

where U_E is the electrophoretic mobility; ε_r and ε_0 are the relative dielectric permittivities of the dispersion medium and the permittivity of vacuum, respectively; and η is the viscosity. Each test was repeated 6 times and the average value was reported.

ζ-potential of the solution increased with the increase of coagulant concentration. The increase was more pronounced before the coagulant concentration reached 20 mg/L. After 20 mg/L, the increase of ζ-potential with the increase of coagulant concentration became moderate (Figure 39). With the increase of coagulant concentration, solution pH decreased accordingly (Figure 40). ζ-potential subsequently decreased with the increase of solution pH (Figure 41). The decrease was moderate until pH of 6.8. Between 6.8 and 7, there was a sharp decrease of ζ-potential. Compared to iron salts, the decrease for aluminum salts was more obvious. Contaminant removal was closely related to the ζ-potential of the solution, resulted from the accumulation of $Fe(OH)^+$, $AlOH^{2+}$, and $Al(OH)_2^+$, etc. These species were responsible for the adsorption of contaminants. For the same concentration, aluminum salt coagulants had greater removal efficiency than iron salt coagulants since they resulted in greater ζ-potential increase.

A ζ-potential close to zero was the point for best coagulation results. Therefore, coagulant concentrations between 10 mg/L to 20 mg/L were preferred. At this point, the maximum amount of coagulant was converted to solid-phase floc particles. At pH values higher or lower than this range, dissolved Al and ferric levels in the solution increased. For instance, at lower pH ranges, the charged Al^{+3}, and $Al(OH)_4^-$ species were the most prevalent dissolved species. The amorphous solid phase formed upon precipitation $[Al(OH)_3(am)]$ had a surface charge that was dependent on the pH, due to the hydroxyl groups present. For both inorganic and organic matters, the surface charge was more positive at lower pH. This had implications for the adsorption of organic matter onto the floc surface.

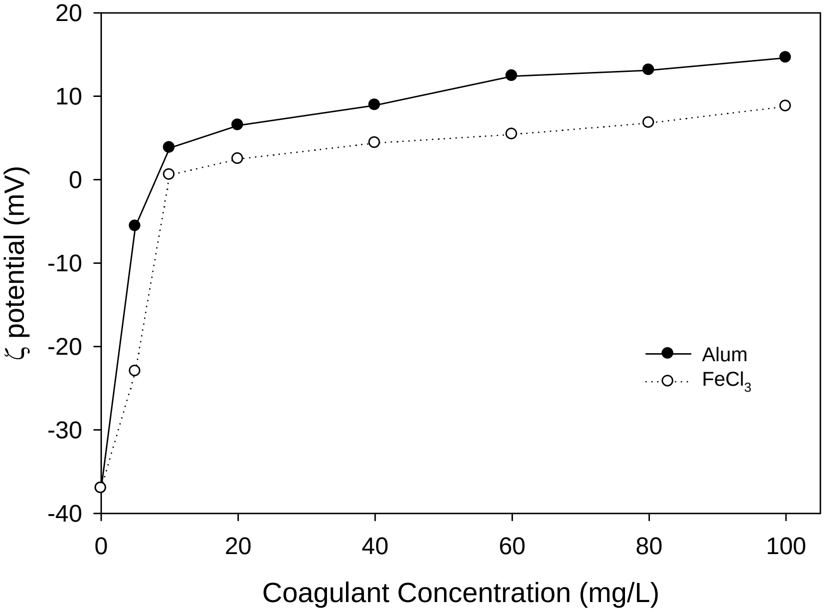


Figure 39. ζ potential as a Function of Coagulant Dosage

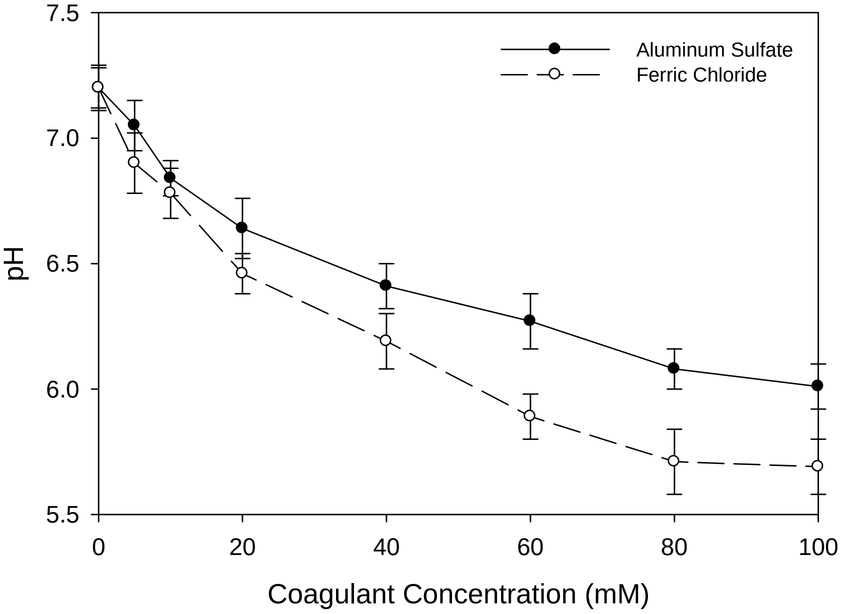


Figure 40. pH as a Function of Coagulant Dosage

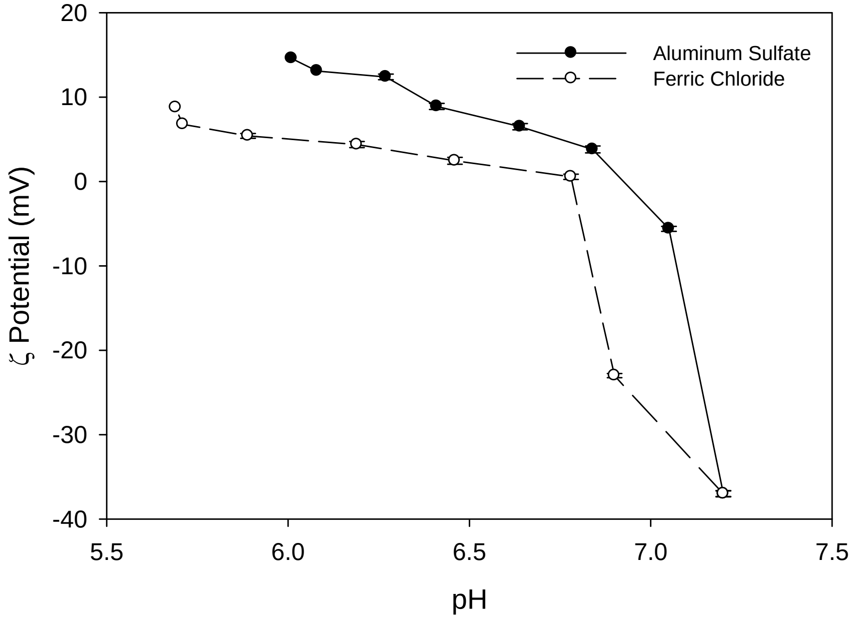


Figure 41. ζ potential as a Function of pH

5.3 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 Fe^{2+} or $Fe(OH)^{+}$) or complex form like the ferric iron (trivalent iron of Fe^{3+} or precipitated as $Fe(OH)_3$). Nearby landfills in Northwest Florida, owing to the high iron contents in the soil, elevated iron concentrations are commonly observed. 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 drain sewers, due to the development of microorganisms, the *ferrobacteries*. However, treated leachate must meet the drinking water standard of 0.3 mg/L total iron before being discharged to the receiving water bodies. Coagulation can reduce the iron level by different pathways.

Ferrous iron is soluble as a cation, while ferric iron is not. Ferrous iron normally can be oxidized to ferric iron in minutes. For the natural removal of dissolved iron, the redox potential of the water promotes the oxidation of ferrous iron to ferric iron, which can precipitate in the form of ferric iron hydroxide, $Fe(OH)_3$:

$$Fe^{2+} \xrightarrow{\text{Oxidation}} Fe^{3+} \xrightarrow{\text{Precipitation}} Fe(OH)_3 \qquad \textbf{Equation (4)}$$

Once ferrous iron is oxidized, hydrolysis proceeds:

$$[Fe_m(OH)_x]_n^{(3m-x)n+} + yOH^- \rightarrow [Fe_m(OH)_{x+(y/n)}]_n^{[3m-x-(y/n)]n+} \textbf{ Equation (5)}$$

The hydrolysis rate is primarily related to pH. Increase of solution pH usually enhances iron hydrolysis. During hydrolysis, solution pH changes because the hydrolysis can consume alkalinity. For landfill leachate with low alkalinity, pH decreases obviously with iron hydrolysis. It should be noted that amorphous hydrous ferric hydroxide cannot settle efficiently by itself. Efficient iron removal is commonly achieved with the addition of coagulants. Therefore, coagulant applications play a very important role in trace iron removal.

The oxidation kinetics of ferrous iron is well known to be pH dependent, with the slow oxidation kinetics of ferrous iron at low pH. This is important for microbial-mediated iron oxidation and fixation. Many known iron-oxidizing microorganisms in the environment can also oxidize ferrous iron at neutral pH. Since the abiotic oxidation of iron is very fast, these microbes must compete effectively with the abiotic process. Additionally, microbes must compete with each other for the available ferrous iron. The organisms that are able to utilize the iron faster in the particular environment make up the predominant part of the iron oxidizing community. Ferric hydroxide ($Fe(OH)_3$) 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 ($Fe_2O_3 \cdot XH_2O$), maghemite (gamma-Fe_2O_3), lepidocrocite (gamma-FeOOH), hematite (alpha-Fe_2O_3), and goethite (alpha-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 redox conditions has a solubility of 0.6 μg/L, which is three orders of magnitude greater than that of goethite. After coagulation, residual iron content was found to be a function of coagulant concentration. The higher the coagulant concentration, the lower the residual iron was achieved (Figure 42). However, meeting the drinking water stardard of 0.3 mg/L of total iron was not an easy task to be achieved.

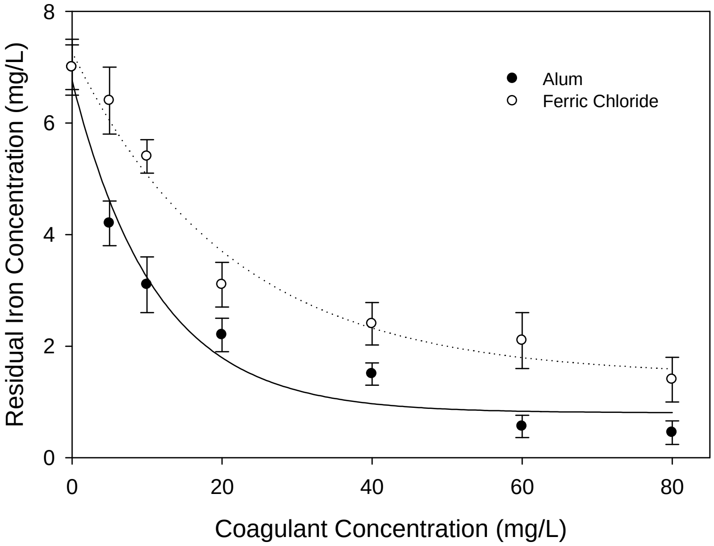


Figure 42. Iron Removal as a Function of Coagulant Dosage

5.4 Chloride Removal

The essential part of the ultra-high lime process is the addition of high doses of lime to maintain a high pH and calcium concentration. With aluminum addition, the ultra-high lime with aluminum process has been practiced to promote removal of sulfate as calcium sulfoaluminate ($Ca_6A_{l2}(SO_4)_3(OH)_{12}$), which has demonstrated the ability to achieve high sulfate removal efficiency (Zhou et al., 2006; Qian et al., 2008). The ultra-high lime with aluminum process has also been further expanded to remove chloride by precipitation as calcium chloroaluminate ($Ca_4A_{l2}C_{l2}(OH)_{12}$). Calcium chloroaluminate is a layered double hydroxide, also known as the Friedel's salt (Abdel-Wahab and Batchelor, 2006, 2007). The interlayer anions of layered double hydroxides can be exchanged with various organic and inorganic charged compounds including chloride. The ultra-high lime with aluminum process is attractive economically because of the less expensive chemicals in addition to the easy operation.

Considering reducing the chemical costs for the treatment, chloride removal was also tested using the alum drinking water treatment sludge, a residual waste material from surface water treatment. The mechanisms for alum sludge suspension and supernatant in chloride removal by means of calcium chloroaluminate precipitation are different. Within the alum sludge, octahedral sheets of $Ca(OH)_2$ are substituted with Al^{3+} and the charge is neutralized by interlayer anions such as CO_3^{2-}, SO_4^{2-}, OH^-, and SiO_4^{4-}, Cl^-, Br^-, I^-, etc. When alum sludge suspension was added to the landfill leachate, the bulk Cl^- ions present in the solution diffused into the interlayers of the principal layers, $[Ca_2Al(OH^-)_6{\cdot}2H_2O]^+$ by anion-exchange. The formed calcium chloroaluminate contained two metallic cations in the main layers with interlayer domains containing anionic species and water molecules (Abdel-Wahab and Batchelor, 2006). The exchange of chloride with the interlayer anions of the layered double hydroxides removed chloride from the solution. Once chloride was exchanged into the interlayers, calcium chloroaluminate was composed of positively charged main layers of composition $[Ca_2Al(OH)_6]^+$ and negatively charged interlayers of composition [Cl^- and $2H_2O$] (Rapin et al., 1999). The chloride anions were surrounded by 10 hydrogen atoms, of which six belonged to hydroxyl groups and four belonged to water molecules (Glasser et al., 1999; Rapin et al., 2002). Chloride removal through inter-ionic exchange was possible because the interlayer anions were loosely held by electrostatic forces.

For alum sludge supernatant, chloride was removed by calcium chloroaluminate precipitation according to the followed reaction,

$$4Ca^{2+} + 2Al(OH)_4^- + 2Cl^- + 4OH^- \rightarrow Ca_4Al_2Cl_2(OH)_{12}(s) \quad \textbf{Equation (6)}$$

By analyzing the supernatant of the alum sludge suspension, it was discovered that 57% of aluminum was in the form of aluminate (AlO_4^-). To investigate the impact of pH on the speciation, the solution pH was adjusted with sulfuric acid and sodium hydroxide. Aluminate content was found to exhibit an exponential function of pH. Higher aluminate content was obtained if pH was further increased (Figure 43). According to Equation 1, high pH, calcium and aluminate contents fovered chloride removal by calcium chloroaluminate precipitation. Chloride removal results showed that the supernatant of the alum sludge was more efficient than that of alum sludge suspension in chloride removal (Figure 26 and Figure 27). It is therefore recommended that the supernatant of the alum sludge be used for chloride removal from landfill leachate to save the operation chemical costs.

For chloride removal in terms of $Ca_4Al_2Cl_2(OH)_{12}$, chloride, aluminum, calcium and hydroxide concentrations played the key roles based on Equation 1. Chloride removal was thus modeled as a function of the concentrations of Ca^{2+}, Cl^-, $Al(OH)_4^-$ and OH^-:

$$\frac{d[Cl^-]}{dt} = k[Ca^{2+}]^a[Cl^-]^b[Al(OH)_4^-]^c[OH^-]^d \qquad \textbf{Equation (7)}$$

where k is the chloride removal reaction rate coefficient and a, b, c and d are the parameters to be determined. Based on the evaluation of these impact factors, chloride removal was described as:

$$\frac{d[Cl^-]}{dt} = 0.338 \cdot [Ca^{2+}][Cl^-]^{0.5}[Al(OH)_4^-]^{0.25} \log[OH^-] \quad \textbf{Equation (8)}$$

The simulation fitting against the observed data is illustrated in Figure 44.

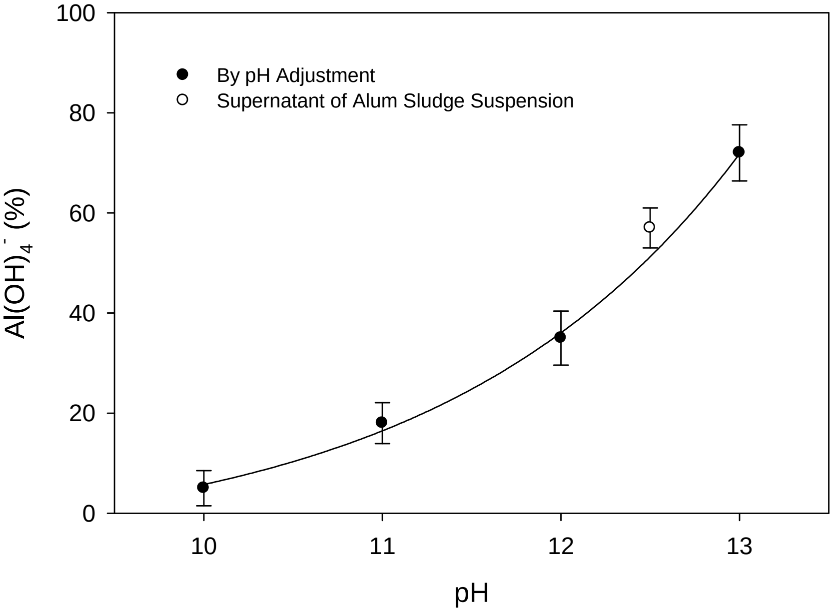


Figure 43. Aluminate as a Function of pH

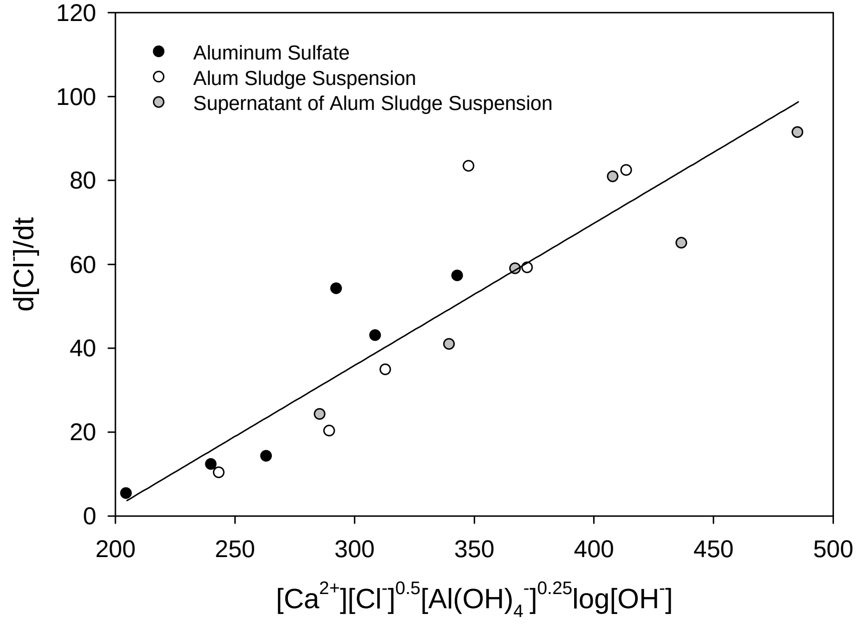


Figure 44. Chloride Removal Efficiency as Reflected by Equation 8

5.5 Struvite Coagulation

To improve the harvesting of struvite fine particles, the possibility of struvite agglomeration by adding cationic coagulants such as metal salts and synthetic polymers was investigated. The results revealed that the quaternary ammonium polymer, poly(diallyldimethyl ammonium chloride) (Poly-DADMAC), had much greater potential in agglomerating struvite crystals than positively charged metal salts (Fe^{3+} and Al^{3+}) that were commonly used in wastewater treatment. However, the use of synthetic cationic polymers including Poly-DADMAC has been restricted in many cases due to their possible toxicity under some conditions. For example, countries such as Germany, The Netherlands and Japan have abandoned the use of many synthetic polymers for the treatment of drinking water. Apart from the potential toxicity of synthetic polymers, their poor biodegradability and high costs negatively affect their wider applications.

In recent years, there has been an increasing interest in the use of natural polymers and their derivatives as coagulants to replace the existing synthetic polymers for the treatment of water and wastewater. The main advantages of these biopolymers are that they are non-toxic, biodegradable and are often abundant in nature. Some of these biological polymers reported in literature include chitosan, alginate, starch, Nirmali (Strychnos potatorum) seed extracts, tannin, *Moringa oleifera* seed extract and extracellular biopolymers. However, these natural polymers have been tested in struvite recovery in comparison with other coagulants commonly used in wastewater treatment, including alum, cationic polyamine and anionic polyacrylamide. The results showed no significant improvement in struvite recovery. Considering the costs and ease of application, it is therefore highly recommended that metal salts coagulants be used for struvite harvesting.

The difficulty of struvite settling is the micro-sized struvite particles. As shown in Figure 45, the major portion of the struvite formed was in the range of 100 μm, which made the struvite hard to settle.

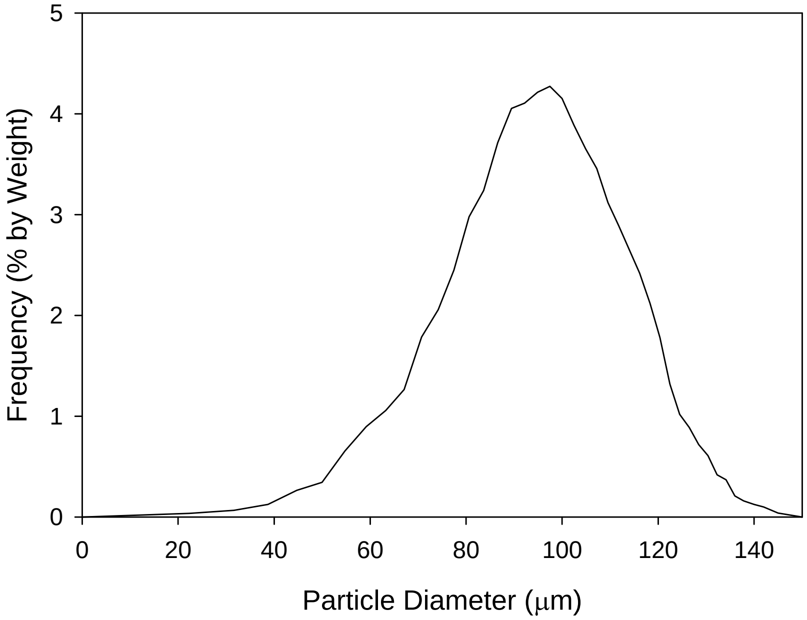


Figure 45. Strvite Particle Size Distribution

After coagulation, the formed struvite particles were able to diffuse. The effective diffusion coefficient was measured in this research. Specifically, the struvite diffusion was described by the following equation (Sacco et al., 1995):

$$\frac{\partial C}{\partial t} = D_{eff} \frac{\partial^2 C}{\partial r^2} \qquad \textbf{Equation (9)}$$

where C is the concentration of struvite in solution; t is the time; D_{eff} is the effective diffusion coefficient; and r is the radius of the diffusion process. The initial and boundary conditions were as follows:

$$C(r, t = 0) = \{ \begin{matrix} C_0 & \text{for } r = 0 \\ 0 & \text{for } r > 0 \end{matrix} \qquad \textbf{Equation (10)}$$

$$\left.\frac{\partial C}{\partial z}\right|_{z=L} = 0 \qquad \textbf{Equation (11)}$$

where C_0 is initial struvite concentration and L is the radius of the reactor. The analytical solution of the diffusion equation is given as (Sacco et al., 1995):

$$C(x, t) = \frac{M}{\sqrt{4\pi Dt}} \exp(-\frac{x^2}{4Dt}) \qquad \textbf{Equation (12)}$$

The D_{eff} was then estimated by fitting the experimental data to above equation based on the least-square minimization following the Powell's method (Shatalin and Neyfakh, 2005).

The analysis of the diffusion indicated that the characteristic time scale of struvite diffusion was in the order of a few minutes. Based on this result, only the first 2 minutes of data were used to estimate the diffusion coefficient. By and large, the diffusion process could be well described with equation (11) and the estimated D_{eff} of struvite was in the order of 10^{-9} m^2/s. The estimated diffusion coefficient can present useful knowledge about struvute settling in the sedimentation tank. Since the characteristic time scale of struvite was found to be in the order of a few minutes, the spreading of struvite does not interfere with struvite settling.

5.6 Pre-Oxidation

The elimination of organic matter, by physical-chemical means, can be obtained by coagulation. Together with coagulation, heavy metals can be removed. Especially, ferrous iron is oxidized to ferric iron, which precipitates in the form of iron hydroxide, $Fe(OH)_3$, whose precipitation can help the co-removal of other contaminants. The removal of organic matter can also achieved by chemical oxidation, especially for those coating the clay minerals, with strong oxidants such as chlorine dioxide (ClO_2), ozone (O_3) and potassium permanganate ($KMnO_4$).

This oxidation process can be used as pre-treatment for landfill leachate, especially for landfill leachate with high organic contents. Oxidation can remove the organic coverage of clay minerals, promoting the subsequent coagulation and flocculation. Therefore, pre-oxidation is recommended for leachate with high organic contents to improve coagulation. Ozonation has become a preferential pre-oxidation method prior to coagulation. The amount of ozone to be used during pre-ozonation is closely related to the organic coating characteristics and basic properties of leachate to be treated. At lower ozone dosage, ozone produced some hydrophobic neutral and intermediate organic compounds, which can be removed efficiently in the following coagulation process. On the contrary, at higher ozone doses, the organics may be oxidized further into more hydrophilic and low molecular-sized compounds, which are more difficult to coagulate. The beneficial effect of ozonation towards better coagulation of non-humic fraction has also been observed. Pre-oxidation prior to coagulation is noted to increase coagulation efficiency by 15%, most likely because the oxidation changes the characteristics of organics and degrades organic molecules towards lower MW compounds. The organics coated clay mineral particles have been proven to interfere with clay mineral coagulation because most organics are non-charged. Oxidation seems to be the best option for the removal of the organics that coat the mineral clays. In this research, pre-ozonation was investigated for the treatment of Springhill Landfill leachate. The color became obviously lighter with ozonation at increased dosage (Figure 47). COD removal increased accordingly with the increase of ozone dosage/COD molar ratio.

Pre-oxidation also encourages ferrous iron oxidation and subsequent ferric iron hydrolysis and precipitation. Pre-oxidation produces denser structure of iron precipitates compared to that of no pre-oxidation.

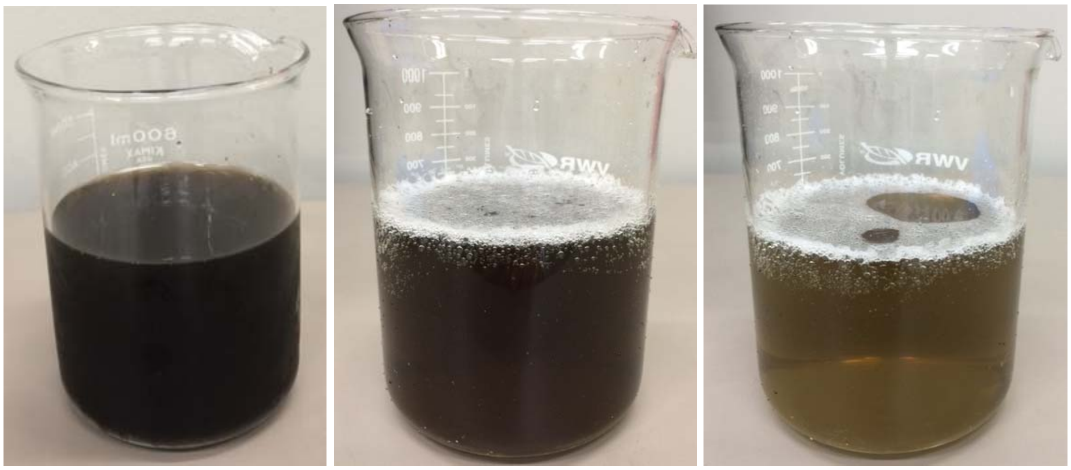


Figure 46. Organic Degradation by Pre-Ozonation for Springhill Landfill Leachate

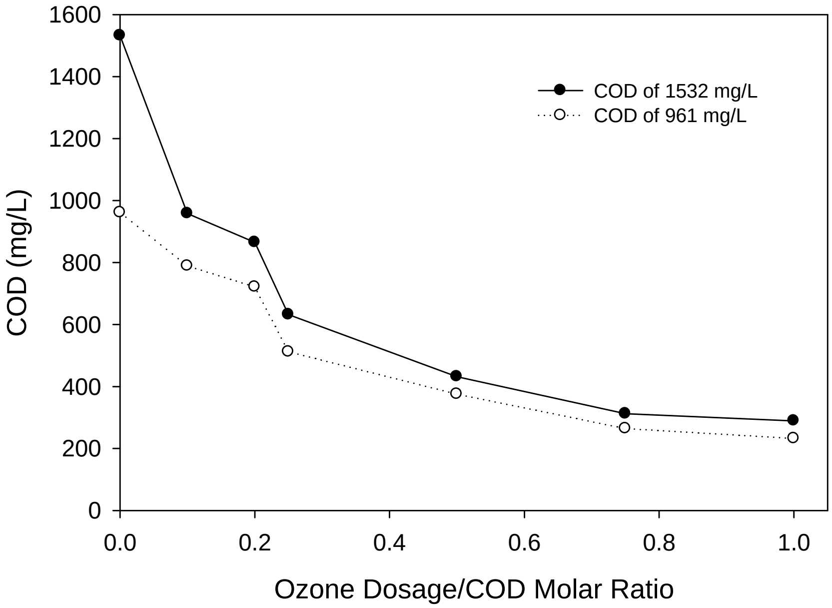


Figure 47. COD Removal as a Function of Ozone Dosage/COD Molar Ration for Springhill Landfill Leachate

5.7 Cost Analysis

The major costs of the multifunctional reactor are the chemical costs. Since aeration is included in aerated recirculation, only low aeration is required during the multifunctional reactor treatment. Subsequently, electric costs can be saved as compared to the biological treatment process. In addition, compared to traditional biological system, this treatment produces less sludge and around 50% of sludge handling costs can be saved. The multifunctional reactor can achieve multiple functions depending on the treatment requirements, including struvite recovery, chloride removal, iron removal and phosphorous removal from landfill leachate and the benefit of space saving is obvious. The infrastructure costs are thereby reduced. The cost analysis is summarized in Table 6. Although high chemical costs are associated with the usage of mutifuctional reactor for the treatment of landfill leachate, this treatment technology has obvious advantages. For instance, currently there is no available biological removal option for chloride removal. Physicochemical means such as precipitation that are adopted in the multifunctional reactor are the only options.

Table 6. Treatment Cost Comparison with Traditional Biological Leachate Treatment

	Multifunctional Reactor Treatment	Biological Treatment	Treatment Cost Saving
Aeration	Low	High	Around 80% Electric Power
Sludge Production	Medium	High	Around 50% for Sludge Treatment
Chemical Costs	High	Low	Increased Chemical Costs
Space Requirements	Low	High	Reduced Infrastructure Costs

The chemical costs associated with the multifunctional reactor are analyzed based on the chemical unit cost illustrated in Table 7. Besides coagulant costs, such as aluminum sulfate or ferric chloride, acids and bases are required for pH adjustment. The chemical costs for the landfill leachate treatment range from $0.75 to $3.00 per gallon depending on the treatment requirements. The more contaminants that need to be removed, the higher the associated costs will be. These contaminants include organics, ammonium, chloride, iron, and phosphorous. There are also costs associated with sludge dewatering. It should be noted that different landfill operators can choose to remove only the contaminants of concern at their site as well as to tailor the treatment for the level that their municipal wastewater treatment plants can accept.

Table 7. Unit Chemical Costs

	Unit	Value ($)
Aluminum Sulfate	ton	150-250
Ferric Chloride	ton	550
$NaHCO_3$	ton	200-225
Sulfuric Acid	ton	250-500
Lime	ton	18-22

To reduce the chemical costs, alum sludge suspension and the supernatant of alum sludge were tested in this research. The supernatant of alum sludge can achieve chloride removal to the level close to that of alum. This will have two beneficial effects: 1) the beneficial use of a waste material by the use of alum sludge and 2) significant savings of chemical costs. The major contributor of the supernatant of alum sludge is aluminate (AlO_4^-), which enhances chloride removal by the ultra-high lime process at high pH. It is therefore recommended that supernatant of alum sludge be used for chloride removal, which not only reduces the chemical costs, but also provides an alternative means for alum sludge disposal.

6. Conclusions

From this research, it is demonstrated that landfill leachate can be treated in the multifunctional reactor for struvite recovery, chloride removal, iron removal and phosphorous removal after aerated recirculation. Aerated recirculation can remove organics and solid components from the landfill leachate. Through aerated recirculation, the organic removal reached an average of 84% for Leon County Landfill leachate and 87% for Springhill Landfill leachate when organic removal became stable at dissolved oxygen of 2 mg/L. Chloride removal in the multifunctional reactor was a function of both pH and alum concentration. With the increase of pH, obviously more chloride was removed. Chloride removal increased with the increase of alum addition until 20 mg/L, after which additional chloride removal became less effective. It is therefore recommended that alum of 20 mg/L be used for chloride removal during leachate treatment. For struvite recovery, the stoichiometry of $NH_4^+/Mg^{2+}/PO_4^{3-}$ molar ratio should be maintained at 1:0.75:0.75. For Leon County Landfill leachate with ammonium content of 384 mg/L, 98% of ammonium can be recovered with 20 mg/L of alum addition at pH 10. With dissolved oxygen of 2 mg/L, around 97% of iron existed in the form ferric iron after 10 minutes of oxidation at pH 8.0. It was demonstrated that a pH of 8.0 and above was required for efficient iron oxidation. Around 95% of iron was removed in the presence of 20 mg/L alum at pH 10.0. For pH 7 and 8, around 91% and 87% were removed. For phosphorous removal, alum had obvious better removal efficiency than that of ferric chloride. At 20 mg/L of alum, 85% phosphorous can be removed efficiently.

The chemical costs are the major disadvantages of this treatment process. To save on operational costs, both powdered alum sludge and the supernatant of alum sludge suspension were tested for their efficiencies in removing chloride. Compared to the powdered alum sludge, the supernatant of alum sludge suspension had better chloride removal observation, which was very close to that of alum. It is highly recommended that supernatant of alum sludge be used instead of alum for chloride removal.

7. Recommendation

From this research, it was discovered that the factors that influence the leachate treatment followed the following order (from most influence to lest influence): leahcate quality > pH > reaction time > settling time > alum dosage > alum or powdered alum sludge. The greatest influential factors were leachate quality and pH. Based on the experimental observations, the following recommendations are made:

Aerated Recirculation:

Aeration: Dissolved oxygen of 2.0 mg/L is recommended.

Recirculation Cycle: A recirculation cycle of 4 or 5 is recommended.

Recirculation Ratio: 50% recirculation ratio is recommended.

Chloride Removal:

Alum of 20 mg/L is required.

It is highly recommended that supernatant of alum sludge be used instead of alum for chloride removal.

Struvite Recovery:

The stoichiometry of $NH_4^+/Mg^{2+}/PO_4^{3-}$ molar ratio should be maintained at 1:0.75:0.75.

Alum of 20 mg/L is required.

pH should be maintained at 10 ± 0.2.

Iron Removal:

Alum of 20 mg/L is required.

pH should be maintained at 10.

Phosphorous Removal:

Alum of 20 mg/L is required.

pH should be maintained at 6.

8. Future Work

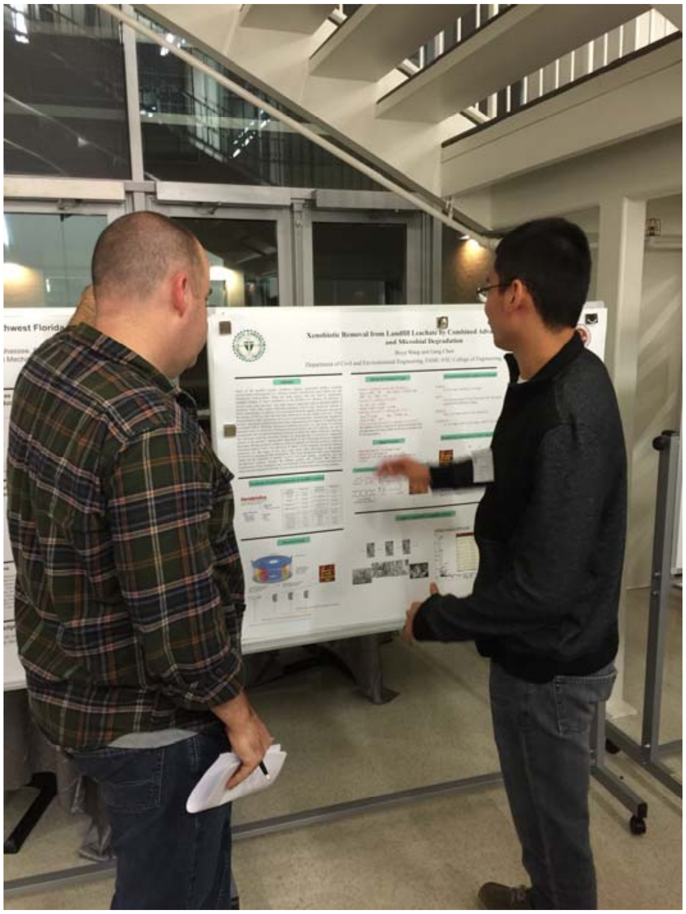
To further improve the performance of the multifunctional energy- and space-saving reactor, electrocoagulation and limestone biofiltration will be incorporated. The electrocoagulation will further promote on-site treatment of landfill leachate by the multifunctional reactor in terms of ammonium, chloride, iron and arsenic removal and the limestone biofiltration will decompose residual organic contaminants.

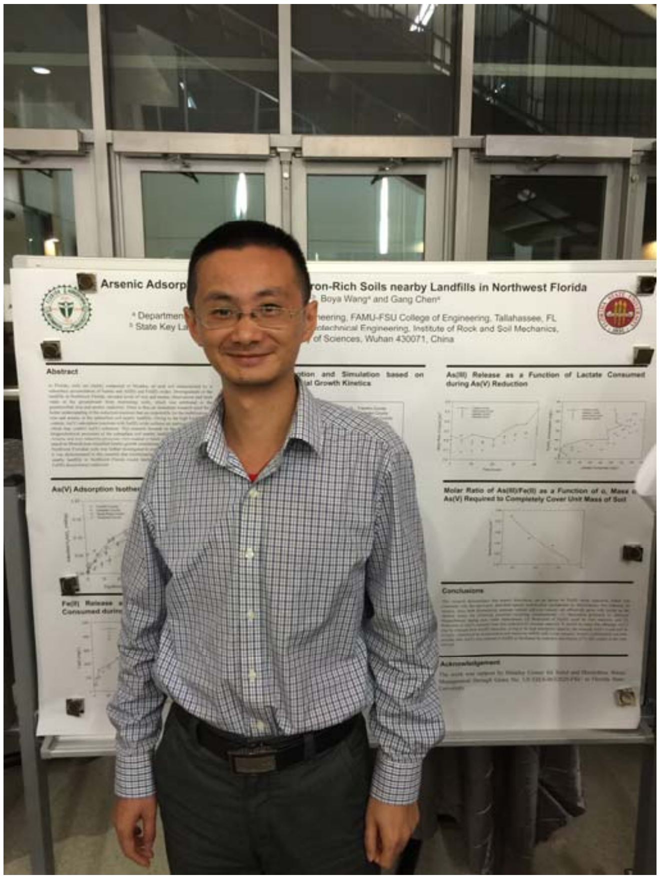
Removal mechanisms of the electrocoagulation process include coagulation, adsorption, precipitation, and flotation. In comparison with treatment by conventional coagulation, electrocoagulation treatment has greater ability for the removal of COD and suspended solid from effluents. In addition, removal of nitrogen compounds has also been successfully realized using a rotating electrobiological contactor, in which over 83% efficiency of the denitrification was observed at a nitrification efficiency of 68.9%. The most important application of electrocoagulation is the usage of Fe(0) electrodes, which has the potential to be used to remediate arsenic-containing leachate.

Limestone biofiltration can efficiently remove organics from landfill leachate. In addition, the low construction and operation costs and ease of operation and maintenance also make limestone biofiltration a promising treatment method for degrading organic contaminants. Depending on the specific requirements, limestone biofilteration can be operated either aerobically or anaerobically. Owing to the high calcite content, limestone promotes the microbial mediated organic degradation and metal precipitation by raising the water alkalinity and pH.

9. Student Training

Two graduate students, Kien Vu and Boya Wang were involved in this project. Kein Vu is currently pursuing his Ph.D. in our laboratory. Boya Wang joined our group in August 2014 as a new master student. Both of these two 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 multiple times in national conferences. In addition, a postdoctoral research associate, Houzhen Wei joined our research group in August 2015 and became involved in this research. The following images were taken when Boyang Wang and Houzhen Wei presented their work at 101th Annual American Society of Microbiology Southeastern Branch Conference, Kennesaw, GA in November 2015.

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Boya Wang and Gang Chen
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Abstract
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10. Acknowledgements

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10.1 Peer-Reviewed Journal Paper Publication:

1. Wang, B., Grasel, P., Millington, G., Hallas, J., Ahmad, H. and Chen, G. "Chloride removal from landfill leachate by the ultra-high lime with aluminum process", J. Urban Environ. Engr. Under review (2015).
2. Wang, B., Grasel, P., Millington, G., Hallas, J., Ahmad, H. and Chen, G. "Landfill Leachate Treatment by Aerated Recirculation and Pressurized Suspended Fiber Biofiltration", Frontier in Environmental Engineering, 2015, 4 (1) 7-18.

10.2 Conference Presentation:

1. Wang, B. and Chen, G. "Multifunctional Energy- and Space-Saving Reactor for the Treatment of Landfill Leachate". 101th Annual American Society of Microbiology Southeastern Branch Conference, Kennesaw, GA. Nov 13-15, 2015.
2. Chen, G., Wang, B. and Tawfiq, K. "Design and Testing of a Multifunctional Energy- and Space-Saving Reactor for the Treatment of Landfill Leachate", South Carolina Environmental Conference, Myrtle Beach, SC, March 14 to March 17, 2015.
3. Chen, G. "On-Site Leachate Treatment —— Challenges and New Development", the 2015 Hinkley Center Colloquium, Florida State University, Tallahassee, Sept 24, 2015.

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