



**Multifunctional Energy- and Space-Saving Reactor for the Treatment
of Landfill Leachate. Year II. Incorporation of Electrocoagulation**

November 30, 2016

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Report #

FINAL REPORT

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PROJECT TITLE: Multifunctional Energy- and Space-Saving Reactor for the Treatment of Landfill Leachate. Year II. Incorporation of Electrocoagulation

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ABSTRACT (1 page only)

In our prior research, we designed a multifunctional energy- and space-saving reactor and tested the designed reactor for the treatment of landfill leachate with high ammonium, chloride and heavy metal contents. It has been demonstrated that this unique design provides an efficient and energy- and space-saving means of onsite management of landfill leachate. To further reduce the chemical costs and simplify the operation, electrocoagulation was incorporated into the multifunctional reactor in this research for enhanced arsenic and phosphorus removal. In addition, two stages of fiber filtration/biofiltration were included after electrocoagulation to ensure the removal of micro-sized coagulated particles and decomposition of residual organic compounds. This technology makes the onsite leachate treatment possible, which may reduce the current high costs of off-site leachate disposal 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 |
|------------------------------|-------------------------|-------------------------------------|------------------|--------------------------|
| Houzheng Wei | Postdoctoral Researcher | Civil and Environmental Engineering | Gang Chen | Florida State University |
| Runwei Li | Ph.D. | Civil and Environmental Engineering | Gang Chen | Florida State University |
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2. List undergraduate researchers working on this Hinkley Center project

| Last name, first name | Department | Professor | Institution |
|------------------------------|-------------------------------------|------------------|--------------------------|
| Quinn Zacharias | Civil and Environmental Engineering | Gang Chen | Florida State University |

3. List research publications resulting from this Hinkley Center project

Chen, G., P. Grasel, G. Millington, J. Hallas, H. Ahmad and K. Tawfiq, 2016, Chloride removal from landfill leachate by the ultra-high lime with aluminum process. Journal of Urban and Environmental Engineering, under review.

Xue, H., W. Xie, H. Ahmad, K. Tawfiq and G. Chen, 2016, Arsenic adsorption and reduction in iron-rich soils nearby landfills in northwest Florida, Journal of Urban and Environmental Engineering, 10, 98-105.

4. List research presentations resulting from this Hinkley Center project

Li, R., Wang, B. and Chen, G. "Arsenic and Phosphorous Removal from Landfill Leachate by Biofiltration". 2016 Florida Branch Meeting, American Society for Microbiology Florida Branch, Miami, FL. Oct. 14-16, 2016.

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

Current research has just been published. No citation is available.

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 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 Owete Owete, Peter Grasel and Joe Dertien, who are in charge of landfill management and groundwater monitoring. In addition, we discussed the results with Talquin Electric Cooperative, Inc., which operates seven wastewater treatment plants.

EXECUTIVE SUMMARY

December 1, 2015 to November 30, 2016

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PROJECT TAG MEMBERS: Peter Grasel, Joe Dertien, Owete Owete, John Hallas, Lin Chen, Hafiz Ahmad, Youneng Tang and Matthew Hendrix

COMPLETION DATE: November 30, 2016

Objective:

To further improve the performance of the multifunctional energy- and space-saving reactor, electrocoagulation and fiber filtration/biofiltration were incorporated. The electrocoagulation further promoted onsite treatment of landfill leachate by enhanced *in situ* coagulation and the fiber filtration/biofiltration removed the micro-sized particles and decomposed residual organic contaminants. The overall objective of this project was to demonstrate that the incorporation of electrocoagulation and fiber filtration/biofiltration into the multifunctional reactor could achieve landfill leachate treatment goals with reduced operation costs. Besides the benefits of onsite leachate treatment that reduced the current high costs of off-site leachate disposal means such as transporting landfill leachate via tanker trucks to local wastewater treatment plants, this treatment system also performed efficiently. Specific objectives of this research included:

1. Incorporation of Electrocoagulation and Fiber Filtration/Biofiltration into the Multifunctional Reactor. Multi-anodic electrodes were arranged in the multifunctional reactor and two stages of fiber filtration and biofiltration were included after electrocoagulation.

2. Operation of the Multifunction Reactor with the Incorporated Electrocoagulation and Fiber Filtration/Biofiltration. Operational factors of electrocoagulation including electrocoagulation time and current density were examined for COD, arsenic, iron and phosphorus removal. The impact of pH on arsenic and phosphorus was further investigated.

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

Methodology:

Multiple anodic electrodes were coupled with coagulation, flocculation and filtration in this research. Since the anodic electrodes were arranged in parallel, the electric current was divided between all the electrodes. The electrocoagulation process was operated on the basis of the principle that the cations were produced electrolytically from the anodes which were responsible for the coagulation of contaminants from the aqueous media. During the electrocoagulation operation, the consumable iron or aluminum anodes continuously produced polyvalent iron or aluminum cations in the region of the anodes and these polyvalent iron or aluminum cations released from the oxidation of the sacrificial anodes neutralized the negative charges of the particles moving towards the anodes. At the same time, electrolysis gases (i.e., hydrogen) evolved at the cathodes.

Results:

The multifunctional reactor with the incorporated electrocoagulation achieved 94% COD, 87% arsenic, 96% iron, and 86% phosphorus removal. Different operating conditions were required for each contaminant to be removed efficiently by the multi-functional reactor when combined with electrocoagulation for the treatment of landfill leachate. Significant reduction in the residual concentrations of the odor- and color-causing contaminants, and suspended solids was also achieved. Results of this study suggested that the multifunctional reactor could be an effective and economic treatment method for the onsite treatment of landfill leachate when combined with electrocoagulation. Because of the low external power requirements for the electrocoagulation, this treatment was also cost-effective. In addition, removal of each contaminant by this treatment system was robust against the landfill leachate characteristics as well as system operation conditions, including the electrode type, pH, and electrocoagulation time, etc. During electrocoagulation, the micro-particles that could not be settled by gravity was removed by the first stage of fiber filtration. Owing to the significant surface areas of the fiber, these micro-sized particles could be removed efficiently. Organic contaminants in the leachate was removed by biodegradation in the second stage of fiber biofiltration after the electrocoagulation. Oxidation by radicals and oxidants formed during electrocoagulation also contributed the destruction and oxidation of organics besides organic degradation during the fiber biofiltration.

In Northwest Florida, besides high organic contents, iron and arsenic are also of great concerns. Especially, high concentrations of iron are commonly detected in landfill leachate owing to changes in pH and redox conditions resulted from organic decomposition. Arsenic release has been proven to be from unlined construction and demolition debris (C&D) landfills. Currently, elevated concentrations of arsenic have also been detected in the leachate from lined landfills. In this research, iron and arsenic were removed by electrocoagulation, which was achieved by coagulation, adsorption, and precipitation. The integration of electrocoagulation into the multifunctional reactor also offers the possibility to tailor the treatment performance based on the specific treatment requirement. This multifunctional reactor treatment system makes the onsite leachate treatment possible, reducing the current high costs of off-site leachate disposal means such as transporting landfill leachate via tanker trucks to local wastewater treatment plants.

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1. Introduction

1.1 Concerns of Contaminants in 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 owing to its complex composition and high concentrations of contaminants (Masoner et al., 2014). Landfill leachate refers to the liquid generated from the moisture associated with the solid waste deposited in the landfill cell and is mainly 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 (Bendz et al., 1997). 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. (Matejka et al., 1994; Emenike et al., 2012; De et al., 2016). The potential long-term environmental impact of landfill management depends on the leachate characteristics. Specifically, contaminant concentrations of the landfill leachate are expected to evolve over time, increasing from initial values to a peak and then subsequently decreasing with the potential biodegradation or precipitation of the contaminants (Aziz et al., 2010). Owing to the high contaminant concentration, landfill leachate is required to be treated before being allowed to be discharged to the sewer water treatment process (Frasconi et al., 2004). Subsequently, there is an urgent need for the development of inventive, effective, and low-cost onsite techniques for the treatment of landfill leachate.

In Northwest Florida, besides high organic contents, other major concerns of landfill leachate include ammonium released from hydrolysis of proteins of the solid waste, chloride from ashes of waste-to-energy processes, iron from reduction of iron-rich soil with organic decomposition, and arsenic from decomposition of chromated copper arsenate (CCA)-treated wood (Dohms et al., 1993). Many investigations report that concentrations of ammonium-nitrogen are in the range of 500 to 2000 mg/L with a decreasing trend with time (at neutral pH, NH_4^+ dominates over NH_3 ; at pH 7 and 20°C, NH_4^+ accounts for 99.61% and NH_3 accounts for 0.39%). Except for air stripping, the

only mechanism by which the ammonium concentration can decrease during refuse decomposition is through conversion to nitrate, which occurs under aerobic conditions (Gotvajin et al., 2012; Spagni et al., 2014; Chen et al., 2016b). For this reason, several researchers have identified ammonium as the most significant contaminant of leachate in the long term (Heinemann, 1989; Wahrendorf et al., 1989). It has been demonstrated that the ammonium concentration can remain high even in the leachate from old landfills that is otherwise low in organic content (Wahrendorf et al., 1989). Nevertheless, ammonium in landfill leachate can be effectively removed by means of magnesium ammonium phosphate ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ or struvite) precipitation, which is a potential valuable commodity that can be recovered and used as a fertilizer (Di Iaconi et al., 2010). Recently, high concentrations of chloride have also been observed in several landfills, especially with waste-to-energy applications. Chloride tends to percolate and cause surface salt formation and soil alkalinity increase, thereby resulting in loss of soil (Clarke et al., 2009). A variety of techniques have been investigated for the removal of chloride, which include ion exchange, reverse osmosis, and norecure, etc. (Shaban, 1981; Gartner and Witkamp, 2005). These techniques, though effective, are not feasible from the cost perspective. As an innovative technology, the ultra-high lime with aluminum process can remove chloride efficiently. For this technology, chloride is removed as calcium chloroaluminate [$\text{Ca}_4\text{Al}_2\text{Cl}_2(\text{OH})_{12}$] through precipitation in the presence of calcium and aluminum at high pH (Abdel-Wahab and Batchelor, 2002, 2006). In Northwest Florida, high concentrations of iron are commonly detected in the 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 leads to reducing conditions, favoring iron reduction and release. In our prior research, we have investigated the geomicrobial iron reduction processes and have quantified the 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. For struvite, calcium chloroaluminate and iron

hydroxide precipitation, micro-scale particles cannot settle down efficiently, which is the typical case when the concentrations of the concerned contaminants are not very high. To improve the removal efficiency of these micro-scale particles, filtration process is required. Another option is through the application of the coagulation.

Arsenic release has been proven to be from unlined construction and demolition debris (C&D) landfills. Currently, elevated concentrations of arsenic have also been detected in the leachate from lined landfills. When coming out of circulation as construction debris, wood treated with chromated copper arsenate (CCA) for protection from fungus, water damage and termites is primarily disposed within the landfills. In the leachate, As(V) and As(III) are the most commonly found arsenic species (Fang et al., 2009). Thermodynamic calculations and experimental results indicate that at high redox levels ($pe + pH > 10$), As(V) is the predominant arsenic species; while under moderately reduced conditions ($pe + pH < 8$), As(III) is the most abundant form of arsenic (Fang et al., 2009). As(V) adsorbs strongly to Al(III) and Fe(III) oxides (Laird et al., 2010). Studies show that 90% of arsenic can be associated with the iron fraction in the form of As(V). As(V) readily undergoes reduction in anaerobic environments to As(III), which is predominantly driven by microbial mediated biogeochemical interactions. After reduction, As(III) mainly exists in the form of H_3AsO_3 , which is very mobile because of its neutral nature. So far, a handful of microorganisms capable of respiring As(V) have been isolated, which include *Sulfurospirillum*, *Clostridium*, *Caloramator*, *Clostridium*, and *Bacillus*, etc. (Gaskin et al., 2008; Rutigliano et al., 2014). In addition, iron reducing bacteria such as *Shewanella* species are also able to reduce As(V) to As (III). As a dissimilatory process, arsenic reduction must be coupled to the oxidation of an energy source, most commonly organic carbon, i.e., the organic content of landfill leachate (Kamegawa et al., 1979; Engstrom et al., 2009).

1.2 Multifunctional Reactor

In our first year's study, we have designed and tested a multifunctional energy- and space-saving reactor for the removal of ammonium, chloride and iron from landfill leachate. This multifunctional reactor integrates physicochemical reactions and

separation operations in one apparatus. The integration of reaction and separation processes offers the possibility to tailor the concentration profiles inside the reactor to achieve a better process performance (e.g. higher selectivity and higher yield). Especially, the *in situ* separation results in continuous removal of the product, which not only overcomes the limitation of chemical equilibrium but also suppresses the side reactions (Murray, 1998). Therefore, the integration gives rise to synergetic effects and enhances the performance of the whole system. The advantages of the integration are realized by using reactions to improve separation, e.g., reacting away contaminants. 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. Experimental work has been carried out to ensure optimal and safe operations of the integrated process. In our prior work, the integrated process has been successfully practiced. Specifically, ammonium was removed by means of magnesium ammonium phosphate ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ or struvite) precipitation, which was also a potential valuable commodity that can be recovered (Di Iaconi et al., 2010); chloride was removed as calcium chloroaluminate [$\text{Ca}_4\text{Al}_2\text{Cl}_2(\text{OH})_{12}$] through precipitation in the presence of calcium and aluminum at high pH; and iron was removed as iron hydroxide in the multifunctional reactor. This technology also makes the onsite leachate treatment possible, reducing the current high costs of off-site leachate disposal means such as transporting landfill leachate via tanker trucks to local wastewater treatment plants. However, the wide applications of this technology may be limited by the chemical costs. Another weakness of the multifunctional energy- and space-saving reactor is that organic removal processes are not included in the design.

Electrocoagulation and biofiltration may be the solution for above concerns, which can be easily incorporated into the multifunctional reactor (Yu et al., 2005; Oumar et al., 2016). Electrocoagulation offers an alternative to the use of metal salts or polymers. In terms of sustainability, as an electrochemical method, electrocoagulation is promising because of its high effectiveness, low maintenance cost and need for labor, and rapid

achievement of results. Similarly, biofiltration is selected for organic removal due to its inexpensive costs and simple applications. Overall, the characteristics of electrocoagulation and biofiltration, i.e., simple equipment and easy operation, shortened reactive retention period, negligible apparatus for chemical addition, and decreased sludge production will bring new perspectives to the multifunctional reactor.

1.3 Electrocoagulation

Removal mechanisms of the electrocoagulation process include coagulation, adsorption, precipitation, and flotation (Darcovich et al., 2009; Sanchez and Bourhrara, 2011). In comparison with treatment by conventional coagulation, electrocoagulation has greater ability for the removal of COD and suspended solids from the solution. The effect of electric fields on COD removal during the electrocoagulation process has been investigated and optimum operation conditions have been determined (Sanchez and Bourhrara, 2011). 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% (Ferrier, 1981). Electrochemical technology can also be used to remove iron, silicate, humus, dissolved oxygen, and color (Yamane et al., 1969; Funaki, 1979). In practice, electrocoagulation has been applied successfully to treat potable water, food and protein wastewater, yeast wastewater, urban wastewater, restaurant wastewater, tar sand, oil shale wastewater, nitrate containing wastewater, heavy metals, textile dyes, fluorine, polymeric waste, organic matter from landfill leachate, suspended particles, chemical and mechanical polishing waste, aqueous suspension of ultrafine particles, and phenolic waste (Rose et al., 2007). Presently, electrocoagulation technologies are more efficient and more compact.

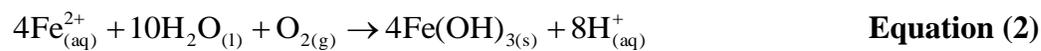
During electrocoagulation, coagulation is achieved *in situ* by electrolytic oxidation of an appropriate anode material. Subsequently, the electrocoagulation setup includes an electrolytic cell with one anode and one cathode. When connected to an external power source, the anode material electrochemically corrodes due to oxidation, while the cathode is subjected to passivation. Electrocoagulation has four main processes: 1. electrolytic

oxidation of the sacrificial electrode, 2. coagulant formation in the aqueous phase, 3. destabilization of the contaminants and subsequent adsorption of colloidal pollutants on coagulants, and 4. aggregation of the destabilized colloidal contaminants to form flocks and removal by sedimentation or floatation (Garg and Prasad, 2016). When electrocoagulation is used for landfill leachate treatment, ionization, electrolysis, hydrolysis, and free-radical formation also exist, which can alter the physical and chemical properties of the landfill leachate as landfill leachate moves through the applied electric field. As a result, the reactive and excited state causes contaminants to be more easily removed from the leachate (Hassani et al., 2016; Oumar et al., 2016). Usually, electrode materials for electrocoagulation are aluminum and iron, which, after corrosion and hydrolysis, can function as coagulants. During electrocoagulation, these electrodes (i.e., Fe or Al) release aluminum and iron cations that form highly charged polymeric metal hydroxides to the aqueous media to neutralize suspended solids and facilitate coagulation and separation from the aqueous phase. This treatment technology also prompts the precipitation of certain metals and salts.

For iron electrode, two mechanisms have been proposed for the reactions of the electrochemical treatment process (Setlow, 2002):

Mechanism 1:

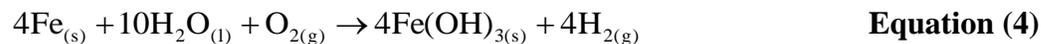
Anode:



Cathode:



Overall:



With the formation of Fe(OH)_3 , polymeric hydroxyl complexes such as $\text{Fe(H}_2\text{O)}_6^{3+}$, $\text{Fe(H}_2\text{O)}_5^{2+}$, $\text{Fe(H}_2\text{O)}_4(\text{OH})_2^{+}$, $\text{Fe(H}_2\text{O)}_8(\text{OH})_2^{4+}$ and $\text{Fe}_2(\text{H}_2\text{O)}_6(\text{OH})_4^{4+}$ form accordingly depending upon the pH of the aqueous media.

Mechanism 2:

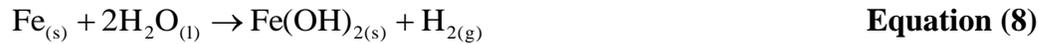
Anode:



Cathode:



Overall:



Due to the increased OH⁻ concentration near the cathode, the pH of the media begins to rise. With iron melting in the presence of hydroxyl alkalinity, Fe(OH)₂ forms in the aqueous media. After oxidation, formation of Fe(OH)₃ flocks develops. For both mechanisms, oxidants such as O₂ or H₂O₂ in the electrolysis cell are needed to promote the formation of Fe(OH)₃ flocks.

In the case of aluminum electrode, reactions are as follows (Setlow, 2002):

Anode:



Cathod:



After release, Al³⁺_(aq) ions immediately undergo further spontaneous reactions and hydrolysis to generate corresponding hydroxides and polyhydroxides such as Al(H₂O)₆³⁺, Al(H₂O)₅(OH)₂⁺, Al(H₂O)(OH)₂⁺, Al₂(OH)₂⁴⁺, Al(OH)₄⁺, Al₆(OH)₁₅³⁺, Al₇(OH)₁₇⁴⁺, Al₈(OH)₂₀⁴⁺, Al₁₃O₄(OH)₂₄⁷⁺, and Al₁₃(OH)₃₄⁵⁺, etc.

Electrocoagulation has several unique benefits unavailable for conventional iron-based approaches (e.g., iron oxide-coated sand filters, Fe(II) or Fe(III) salt addition, and passive Fe(0) corrosion, etc.). The most important one is that electrocoagulation using Fe(0) electrode has the potential to be used to remediate arsenic-contaminated wastewater, which is efficient and cost-effective. It is believed that this iron-based technique relies on the oxidation of As(III) to As(V) and subsequent adsorption onto the generated metal

hydroxides during electrocoagulation (Figure 1). In the Fe(II)/O₂ system at neutral pH, Fe(IV) is generated from Fe(II) oxidation (Rybanska et al., 2010):



Fe(IV) goes on to be consumed in oxidation reactions with either Fe(II) or As(III):

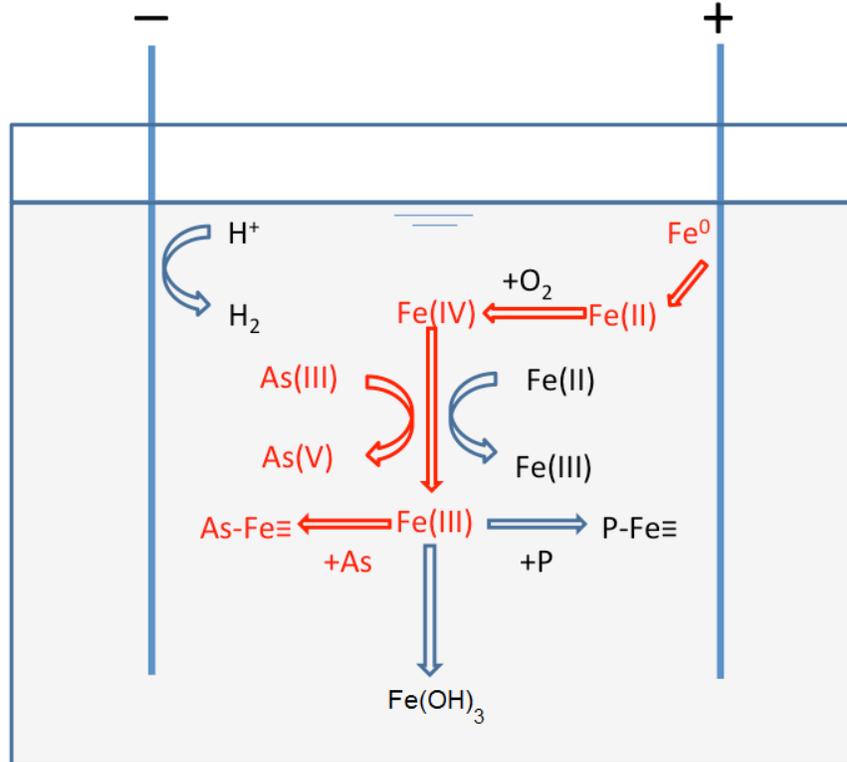


Figure 1. Electrocoagulation with Arsenic Removal

1.4 Suspended Fiber Biofiltration

In our prior research, we have tested the usage of suspended fiber (polypropylene) filters and biofilters for the treatment of landfill leachate (Figure 2). Inside the suspended biofilter, organic compounds and iron were removed through contact oxidation, which depended on the microorganisms to degrade organic compounds and fix iron. These consortia strategically positioned themselves on the suspended fiber to form a biofilm. Bacteria in the biofilm produced a matrix of materials so that they stuck to the fiber. Degradation of complex molecules was known to be carried out better by bacterial

cultures in consortia than in monocultures. The performance of consortia for degradation of complex molecules required a stability of association, which can be best achieved by growing compatible cultures in a mixture. Using cultures in consortia for efficient degradation of proteins, carbohydrates and lipids had been demonstrated. This was an importance discovery since proteins were major organic components in landfill leachate (Pichler and Kogel-Knabner, 2000).



Figure 2. Polypropylene Fibers Used in Biofilter

Both gram negative bacteria (57%) and gram positive bacteria (43%) were present in almost equal frequencies in the consortia. *Bacillus* dominated the generic composition by 25%, which was followed by *Vibrio* (17%). Dominance of *Bacillus* was in agreement with the findings by Krishnan and Saramma (Krishnan and Saramma, 2005). The other genera resembled the *Enterobacteriaceae* group, *Arthrobacter*, *Brevibacterium*, *Aeromonas*, and *Pseudomonas*, etc. Recently, some iron fixation bacteria that can derive energy they need to live and multiply by oxidizing dissolved ferrous iron (or the less frequently available manganese) have also been identified. They were known to grow and proliferate in waters containing as low as 0.1 mg/L of iron. However, at least 0.3 ppm of dissolved oxygen was needed to carry out the oxidation (Nazaruk et al., 1980). Suspended fiber biofiltration can efficiently remove organics from landfill leachate

(Oumar et al., 2016). In addition, the low construction and operation costs and easiness of operation and maintenance also make fiber biofiltration a promising treatment means in degrading organic contaminants. Depending on the specific requirements, fiber biofiltration can be operated either aerobically or anaerobically. Inside the fiber biofilter, inoculated microorganisms can decompose organic compounds, which would consume alkalinity:



Fiber biofiltration can promote the microbial mediated organic degradation and metal precipitation. It is also expected that aeration or other oxidation means needs to be included to help precipitate heavy metals. For the metal precipitation, pH plays an important role since pH affects the solubility of metals and the kinetics of the oxidation and hydrolysis processes. In addition, the relationship between pH and metal removal processes varies among metals and also between biotic and abiotic processes. Fiber biofiltration also makes the chlorine removal possible by means of the ultra high lime with aluminum process in terms of calcium chloroaluminate ($\text{Ca}_4\text{Al}_2\text{Cl}_2(\text{OH})_{12}$) precipitation. For this process, the addition of aluminum and calcium is required in addition to elevated pH.

1.5 Objectives

To further improve the performance of the multifunctional energy- and space-saving reactor, electrocoagulation and fiber filtration/biofiltration were further incorporated. The electrocoagulation promoted onsite treatment of landfill leachate by the multifunctional reactor in terms of iron, arsenic and phosphorus removal and the fiber filtration/biofiltration removed micro-sized particles and decomposed residual organic contaminants. The overall objective of this project was to demonstrate that the incorporation of electrocoagulation and fiber filtration/biofiltration into the multifunctional reactor could achieve landfill leachate treatment goals with reduced operation costs. Besides the benefits of onsite leachate treatment that reduced the current high costs of off-site leachate disposal means such as transporting landfill leachate via

tanker trucks to local wastewater treatment plants, this proposed treatment system was also assumed to perform efficiently. From this research, the efficient, low-maintenance and cost-saving multifunctional reactor with the incorporated electrocoagulation and fiber filtration/biofiltration 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 of this research included:

- Incorporation of Electrocoagulation and Fiber Filtration/Biofiltration into the Multifunctional Reactor. Multi-anodic electrodes were arranged in the multifunctional reactor and two stages of fiber filtration and biofiltration were included after electrocoagulation.
- Operation of the Multifunction Reactor with the Incorporated Electrocoagulation and Fiber Filtration/Biofiltration. Operational factors for electrocoagulation including electrocoagulation time and current density were examined for COD, arsenic, iron and phosphorus removal. The impact of pH on arsenic and phosphorus was further investigated.
- System Optimization and Cost Analysis. The newly renovated 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

2.1 Electrocoagulation for Landfill Leachate Treatment

Traditional treatment technologies such as hydrolysis, biological treatment processes, chemical precipitation, chemical oxidation, activated carbon adsorption, resin adsorption, and steam or air stripping, etc. have been proposed and practiced for the treatment of various types of wastewater. Innovative technologies, such as photocatalytic oxidation, photo-assisted Fenton reaction, ultrasonic radiation, have also been proposed. However, many of these technologies suffer the limitation of either being too expensive or not being able to treat concentrated wastewater such as landfill leachate (Ying et al., 2012).

The composition of landfill leachate is complicated, which may vary dramatically with the aging of the landfill. Typically, the pollutants in municipal solid waste landfill leachate can be divided into dissolved organic matter, dissolved salts, heavy metals and xenobiotic organic compounds (Kulikowska and Klimiuk, 2008). Dissolved organic matter is often quantified as chemical oxygen demand (COD) or Total Organic Carbon (TOC), which includes volatile fatty acids and more refractory compounds such as fulvic-like and humic-like compounds. Inorganic salts include calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), potassium (K^+), ammonium (NH_4^+), iron (Fe^{2+}), manganese (Mn^{2+}), chloride (Cl^-), sulfate (SO_4^{2-}) and hydrogen carbonate (HCO_3^-), etc. Heavy metals include cadmium (Cd^{2+}), chromium (Cr^{3+}), copper (Cu^{2+}), lead (Pb^{2+}), nickel (Ni^{2+}) and zinc (Zn^{2+}). For onsite treatment of landfill leachate, an ideal treatment scheme is to pretreat the leachate by physiochemical processes to remove most of the organic contaminants and toxicity before biological treatment (Novelo et al., 2009; Weng et al., 2011). The pretreatment processes should not only be low cost, but also robust in performance while requiring relatively little maintenance. Chemical coagulation by the use of inorganic coagulants such as alum, magnesium carbonate, ferrous salt, and clays has been successfully applied in pretreatment of wastewater (Samadi et al., 2010; An and Xu, 2013). A recent study showed that both alum and FeCl_3 were effective in pretreatment of wastewater by coagulation, and 55% of COD and 95 to 100% of suspended solids could be removed with coagulant dosage of 90–100 mg/L (Liu and

Lien, 2001). Compared to processes such as chemical oxidation, coagulation has been shown to be simpler and more cost-effective. Recently, electrochemical methods have also attracted significant attention for treating recalcitrant toxic waste. When the anode is made of iron or aluminum, corrosion of the anode during electrolysis releases active coagulant precursors (Fe^{2+} or Al^{3+}) into of the contaminated solution (Contreras et al., 2009; Li et al., 2011). The *in situ* production of coagulating ions involves three successive stages: (i) formation of coagulants by electrolytic oxidation of the sacrificial electrode; (ii) destabilization of the contaminants, particulate suspension, and breaking of emulsions; and (iii) aggregation of the destabilized phases to form flocs. Studies have shown that organic contaminants in the wastewater could be effectively removed by such electrocoagulation treatment, with processes such as adsorption and co-precipitation also contributed to the overall contaminant removal (Labanowski et al., 2010). Under acidic conditions, both Fe^{2+} and Fe^{3+} are difficult to precipitate, while $\text{Fe}(\text{OH})_6^{3-}$ may form under alkaline pH, which interferes with coagulation (Li et al., 2011). A pH range of 6 – 8 has been found to be optimal for Fe^{3+} precipitation in chemical coagulation and electrocoagulation. Aeration can potentially accelerate oxidation of organic contaminants by supplying more oxygen to the treatment system. Meanwhile, this also accelerates the oxidation of Fe^{2+} to Fe^{3+} , which is less soluble and a better coagulant.

2.2 Electrocoagulation Theory

For electrocoagulation, the anode is connected to a positive terminal of a DC power supply with the negative terminal being attached to the cathode (Chen et al., 2016a). Current flows in from the power supply and the cathode is the terminal where current flows back to the power supply (Figure 3). Cathode polarity with respect to the anode can be positive or negative depending on the device and the way it operates. Positively charged cations always move towards the cathode and negatively charged anions move away from it. The electrolyte is the substance that produces an electrically conducting solution when dissolved in a polar solvent, such as water. The dissolved electrolyte separates into cations and anions, which disperse uniformly through the solvent. The cations of the solution would be drawn to the electrode that has an abundance of electrons, while the anions would be drawn to the electrode that has a deficit of electrons.

The movement of anions and cations in opposite directions within the solution amounts to a current.

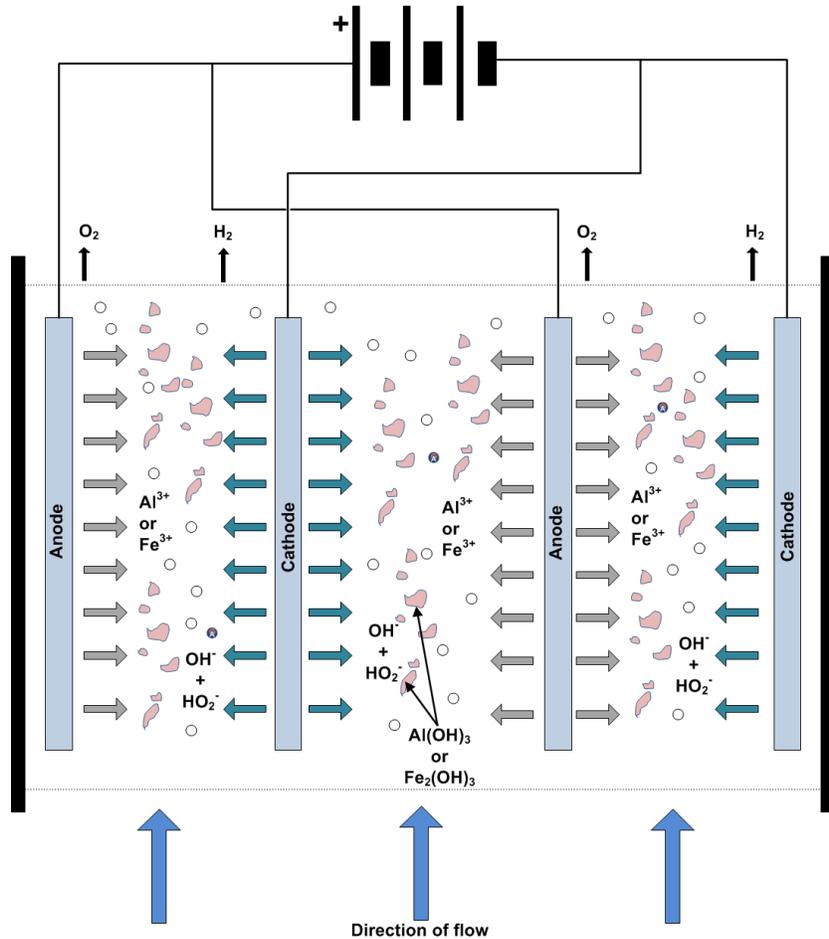


Figure 3. Illustration of Electrocoagulation Theory

Faraday's laws provide the theoretical basis of electrode potential and current density (Moreno et al., 2009). However, in a real application, many factors influence the electrocoagulation. Faraday's laws state that the amount of chemical charge at an electrode is exactly proportional to the total quantity of the electricity. However, side reactions may consume the product if taking place simultaneously at the electrode. Therefore, inefficiencies may arise from the side reactions other than the intended reaction that takes place at the electrode. In electrocoagulation, sufficient voltage should be provided by the power source. The voltage-current relationship follows the Ohm's

law, i.e., the current is driven by a potential difference, or voltage through the conducting medium, either electrolytic or metallic. The local current density is a very important variable in electrocoagulation operations and affects the final coagulation. The local current density on an electrode, defined as the current in amperes per unit area of the electrode, is a function of the position on the electrode surface and the current passing through the electrode that accomplishes the desired electrocoagulation. It is often expressed in terms of current efficiency. The current distribution over an electrode surface is complicated and tends to concentrate at edges and points, and unless the resistance of the solution is very low, the current will flow to the opposite electrode more readily than to the more distant electrode (Maximova and Dahl, 2006). It is desired to operate processes with uniform current distribution, i.e., the current density is the same at all points on the electrode surface.

When the electrodes are immersed into a solution, equilibrium is reached between the tendency of the metal to enter solution as ions and the opposing tendency of other ions to accept the electrons and deposit on the cathode (or H₂ gas formation on the cathode). The equilibrium is dynamic with the metal being ionized and discharged as well as being deposited and reduced (Picard et al., 2000; Al-Shannag et al., 2015). These two effects cancel each other and there is no net change in the system. For the realization of gas formation at the cathode and metal dissolution at the anode, the equilibrium is broken by an external potential, which makes the electrode reactions take place at a practical rate. The extra energy needed to force the electrode reactions to proceed at a required rate (or its equivalent current density) is quantified in terms of over-potential or electrode polarization, which is the difference of the electrode equilibrium potential and its operating potential when a current is flowing. The operating potential of an anode is always more positive than its equilibrium potential, while the operating potential of a cathode is always more negative than its equilibrium potential. The value of the over-potential depends on the inherent speed of the electrode reactions, which increase with increasing current density. A slow reaction (with small exchange current density) will require a larger over-potential for a given current density than a fast reaction (with large exchange current density). The term over-potential is sometimes called overvoltage,

which refers to the difference between the cell voltage (with a current flowing) and the open-circuit voltage (Esmailirad et al., 2015).

The pulse current has been vastly used in electrocoagulation processes, in which the potential or current is alternated at different levels (Eyvaz, 2016). This leads to a series voltage or current pulses of nearly equal amplitude, duration and polarity, segregated by reference current (usually zero). The key parameters related to voltage-current curve includes applied voltage range, the current density range and the factors related to electrolytes, including the component ratio of the species, temperature, convection of the electrolyte, and duration of the whole electrocoagulation time (Mao et al., 2008). As many factors are involved and have to be optimized in an electrocoagulation process, there is no one-fit-all parameter set for all electrocoagulation. First, the electrode selection should be specified. The choice of electrodes is highly dependent on the anodic metal type. Second, the parameters related the electrocoagulation processes are normally optimized against available current-voltage relationship, which has normally been documented in literature for specific electrode systems. Many studies on the electrocoagulation mechanisms have revealed that the electrocoagulation is a diffusion-dominated process, which occurs at a certain limiting current (Feng et al., 2004). Hence, the electrocoagulation can be treated similar to the mass transfer in a cathodic deposition process, in which mass transfer theory has been well established. Many works have been performed in studying the forced convection mass transfer during electrocoagulation (Korbahti, 2014). Natural convection conditions have also been studied. The convection flow is believed to be driven by the electrolyte density difference between the bulk and anodic surface.

Prior to electrocoagulation, the electrodes should be pre-treated, including surface cleaning. The purpose of surface pretreatment is to remove contaminants, such as dust and films from the substrate surface. The surface contamination can be extrinsic, composed of organic debris and mineral dust from the environment or preceding processes. It can also be intrinsic, such as a native oxide layer. Contaminants and films interfere with metal dissolution, which can cause poor electrocoagulation (Fekete et al.,

2016). Therefore, surface pretreatment is important to ensure good electrocoagulation results. Cleaning methods should be able to remove the contaminants, dust, film, and or debris. Cleaning processes are usually based chemical approach including solvent degreasing, alkaline cleaning, soak cleaning, and acid cleaning, etc. For instance, if the metal surface contains contaminants of oils, grease, waxes, and miscellaneous organic materials, they can be removed by appropriate organic solvents, either by dipping the electrode in the solvent or by vapor decreasing. Table 1 summaries the treatment results by electrocoagulation (Cheng et al., 2007).

Table 1. Wastewater Treatment by Electrocoagulation

| Indicator | Before Pretreatment | Coagulation ^a | Electrolysis ^b | Electrocoagulation ^c |
|------------------|---------------------|--------------------------|---------------------------|---------------------------------|
| Suspended Solids | Visible | Invisible | Invisible | Invisible |
| Odor | Strongly Pungent | Weakly Pungent | Weakly Pungent | Weakly Pungent |
| Color | Dark Red | Light Brown | Light Brown | Light Brown |
| COD (mg/L) | 97,850 | 81,000 | 65,400 | 38,630 |
| COD Removal (%) | | 17.2 | 33.2 | 60.5 |

a. Measured after pretreatment with 0.5 g/L PAC, mixed at 340 rpm for 1 min, then at 150 rpm for 10 min, followed by 85 min settling.

b. Measured after being electrolyzed at 2 A for 180 min.

c. Measured after for 132 hr at iron/GAC/wastewater volumetric ratio of 3:2:490 and air sparge ratio of 2:490 min⁻¹.

2.3 Arsenic Removal

2.3.1 Redox Reactions of Arsenate and Arsenite

Arsenic is a redox-sensitive element, and its important oxidation states are -3, 0, +3, and +5 (Masscheleyn et al., 1991). Arsine (AsH₃) is a highly poisonous and flammable gas and rarely occurs in nature, while arsenate [As(V)] and arsenite [As(III)] are the most commonly found arsenic species in the groundwater. The Eh-pH diagram for arsenic species at a total concentration of 10⁻⁶ mol/L is illustrated in Figure 4. Arsenate generally predominates under oxidizing conditions, while arsenite predominates when conditions become sufficiently reducing. Thermodynamic calculations and experimental results indicate that at high redox levels (pe + pH > 10), arsenate is the predominant arsenic species while under moderately reduced and reduced conditions (pe + pH < 8), arsenite is the most abundant form of arsenic (Villa-Lojo et al., 1997). Redox reactions can control

aqueous arsenic concentrations by their effects on arsenic speciation, and hence, arsenic adsorption and desorption. Through the interconversion between arsenate and arsenite, redox reactions involving either aqueous or adsorbed arsenic can affect arsenic mobility (Couture and Van Cappellen, 2011).

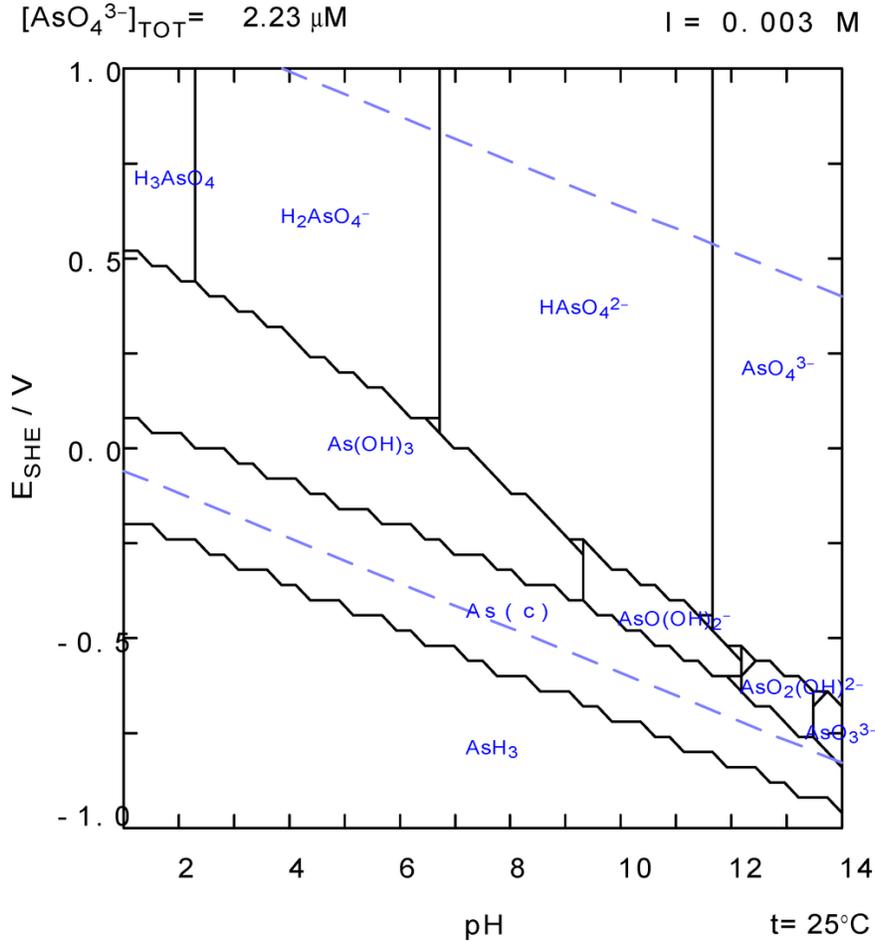


Figure 4. Eh-pH Diagram of Arsenic Speciation

Notes:

- Fe^{2+} , Mn^{2+} , Co^{2+} , Fe^{3+} , Co^{3+} , Mn^{3+} concentrations are assumed to be constant at 10^{-6} mol/L at the entire pH range without any speciation;
- Redox couples $\text{Mn}^{3+}/\text{Mn}^{2+}$ and $\text{Co}^{3+}/\text{Co}^{2+}$ are not shown because they are outside of the stability field of water in the entire pH range of interest;
- For accurate description of the pe of As(V)/As(III) redox couple with respect to pH change, speciation of both As(V) and As(III) with solution pH are considered in pe calculation (based on total As concentration of 10^{-6} mol/L);
- The upper and lower boundaries for water stability are based on the partial pressure of O_2 and H_2 at 1 atm.

Overall, redox conditions can determine the speciation of dissolved arsenic in the aqueous phase. Arsenate is the predominant species when the solution is well oxygenated. On the other hand, if the solution is rich in reduced species (e.g., S^{2-}), arsenic mainly exists in form of arsenite species instead of arsenate (Masscheleyn et al., 1991). The acidity (pH) is also an important factor controlling arsenic speciation. Figure 5 shows the distribution of different arsenate and arsenite species as function of solution pH. At the low pH range, H_3AsO_4 and $H_2AsO_4^-$ are the major species for arsenate, while arsenite primarily exists in form of H_3AsO_3 . Under the typical pH conditions (4 to 9) of most surface water and groundwater, arsenate is present as the negatively charged oxyanions $H_2AsO_4^-$ or $HAsO_4^{2-}$, whereas arsenite is present as a neutral species H_3AsO_3 (Figure 5).

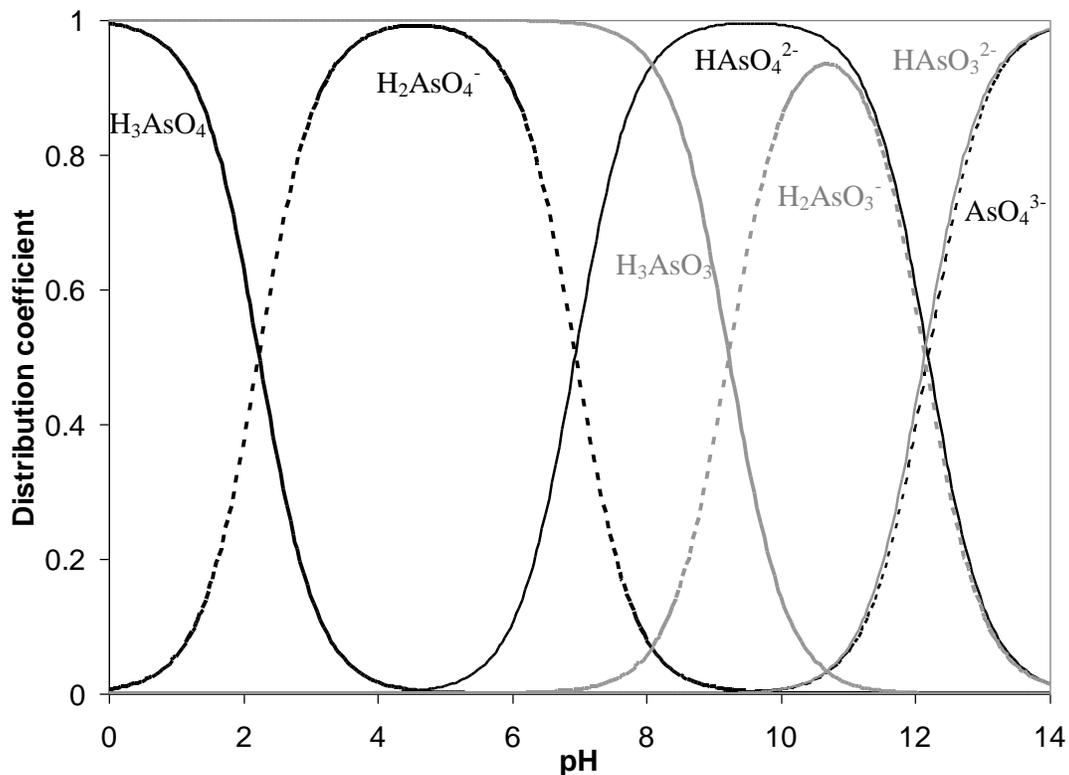


Figure 5. Arsenate and Arsenite Speciation as a Function of Solution pH

2.3.2 Arsenate Removal by Adsorption

Arsenic species can adsorb on many soil colloids, including (hydr)oxides of iron, aluminum, and manganese, clay, calcium carbonate and organic matter (Devitre et al., 1991). In general, iron (hydr)oxides are the most commonly involved natural minerals in the adsorption of arsenic in both acidic and alkaline soils, while aluminum (hydr)oxides, clay, manganese oxides, and organic matter may play some roles only in acidic soils (Babaeiveli and Khodadoust, 2016). For adsorption of inorganic arsenic species on mineral surfaces, electrostatic interactions are the major motivating forces, which depend on the charges of both the solid surfaces and the arsenic species, both of which are pH dependent. In the near neutral pH range, iron and aluminum (hydr)oxides and calcite are positively charged while the clay minerals are negatively charged, which suggests that the former ones are important sorption “sinks” for negatively charged species under such conditions. Charges of dissolved arsenic species originate from the association and dissociation of H^+ as a function of solution pH. Arsenate mainly exists in the form of negatively charged $H_2AsO_4^-$ or $HAsO_4^{2-}$ complex within the pH range for natural water (i.e., 4 to 9), while arsenite primarily exists as neutral H_3AsO_3 . Therefore, arsenate is sorbed very effectively by iron, manganese, and aluminum (hydr)oxides, and even clay minerals, while arsenite is not strongly sorbed under typical soil and groundwater aquifer conditions (Goldberg and Brown, 2000).

Alum and iron precipitation is also a common method used in water treatment for arsenic removal (Scott et al., 1995; Francisca and Carro Perez, 2014; Song and Gallegos-Garcia, 2014). The solubility product constants of the corresponding arsenate salts suggest that they can limit aqueous arsenate concentration to very low levels, but metal arsenate precipitation is not generally believed to be the major arsenate removal mechanism. The poorly formed crystalline ferric arsenate precipitate produced during arsenic removal is similar to “arsenical ferrihydrite”, which is ferrihydrite containing strongly adsorbed arsenate anions, and it appears to be stable for many years under slightly acidic pH and oxidizing conditions (Lacasa et al., 2013). It is believed that the solubility of arsenic is controlled by the equilibrium of $Fe_3(AsO_4)_2 \cdot 8H_2O(c)$ / $Fe_4Fe_2(OH)_{12} \cdot SO_4(c)$ (McNeill and Edwards, 1997; Lacasa et al., 2013).

During wastewater treatment, including landfill leachate treatment, arsenic may co-precipitate with hydrous oxides and hydroxides of iron, aluminum, and manganese. Co-precipitation is the simultaneous precipitation of a normally soluble component with a macro-component from the same solution through the formation of mixed crystals, by adsorption, occlusion or mechanical entrapment. Arsenic may be sequestered from the solution during the precipitation of soluble iron, resulting in the formation of a poorly crystalline hydrous ferric oxide containing co-precipitated arsenic. Adsorption and co-precipitation of arsenate with iron and aluminum flocs are believed to be the primary arsenic removal mechanisms in water treatment plants. At high Fe/As weight ratio (>5:1) and elevated pH, surface complexation and electrostatic attraction lead to co-precipitation of arsenate. It has been found that Fe(III) is more efficient than Fe(II) in removing arsenite from groundwater through co-precipitation, possibly due to the low oxidation rate of Fe(II). It is also suggested that adsorption may be the primary mechanism controlling arsenite removal when the Fe/As weight ratio is greater than 10. Fe/As weight ratios of greater than 40 are required to reduce arsenic concentration to less than 50 µg/L due to the presence of elevated phosphate and silicate concentrations. It has also been observed that the proportion of arsenic associated with amorphous iron oxyhydroxides is much greater than that associated with crystalline iron oxyhydroxides and oxide minerals. Arsenate co-precipitated with hydrous ferric oxide is stabilized against dissolution during transformation of hydrous ferric oxide to the more crystalline hematite and goethite.

2.3.3 Microbial-Mediated Arsenic Transformation

Although these two oxidation states of arsenic dominate in most terrestrial environments, the biogeochemical cycle of arsenic is rather more complicated. Microbial-mediated arsenic transformation plays the key role in arsenic speciation (Figure 6). Arsenite adsorbed less strongly to some mineral phases and the relative strength of sorption depends upon a range of factors, including microbial mediated arsenic transformation. Microbial mediated reduction of the sorbed arsenate could potentially result in the mobilization of the more mobile arsenite, which is also more toxic than arsenate. However, this is clearly an oversimplification of the natural biogeochemical processes

that control the solubility of arsenic. For example, the mineral phases hosting arsenate can change during As^{5+} reduction because Fe^{3+} oxyhydroxides may also be reduced by anaerobic bacteria under conditions similar to those required for As^{5+} reduction, potentially altering arsenic mobility.

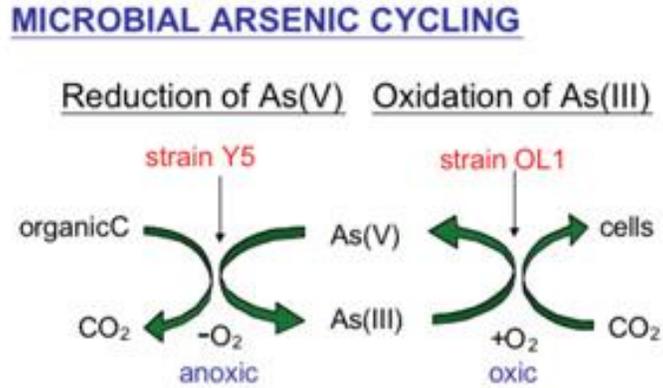


Figure 6. Microbial Mediated Arsenic Transformation

2.4 Biofiltration

Among the attached-growth biomass systems, biofiltration has the most promising potential for landfill leachate treatment. Biofiltration refers to the biological transformation or treatment of contaminants on a solid surface. The fact that soluble contaminants can be biodegraded by active bacteria in biofilters has been known for quite some time. Main advantages of this method compared to conventional suspended-growth processes include higher biomass concentrations, no sludge settling requirement, low sensitivity to toxic compounds, and combined organic and ammonia removal in a single process. Considering the advantage of anaerobic leachate treatment, anaerobic biofiltration has also been practiced in landfill leachate treatment. The types of support media used in biofilters are mainly synthetic media, such as ceramic, plastic, etc., with active bacteria immobilized on the surface in the form of biofilms. Currently, the design of support media has been modified differently as compared to other applications to enhance the growth of biomass. When the biofilters are used for wastewater treatment such as landfill leachate, the wastewater flows as a liquid film on the biofilm surface, and sufficient distance between the support media is designed to accommodate biomass

growth and the air, which provides oxygen for the biodegradation reactions. The contaminants, present in the wastewater, diffuse into the biofilm as the water flows over the biofilms, and are biodegraded. Inside the biofilters, the contaminants diffuse perpendicular to the direction of flow. Since the process is diffusion controlled, designing a large distance between the supported biofilms reduces the overall degradation rate in the filter.

For heavy metal removal, several low-cost filter materials have been investigated, which could be included in the system based on filter-bed techniques. For ammonium removal, experiments have been conducted with zeolites to assess their sorption of ammonium nitrogen. For both heavy metal and nitrogen removal from landfill leachate, three filter media, sand, blast-furnace slag (BFS) and polonite have been investigated, which is based on the determination of the saturation potential of heavy metals and nitrogen in a long-term column study. This method can provide a good indicator of capacity of the filter material to retain the elements, and can serve as a parameter for estimating the lifetime of full-scale systems. The results demonstrated that these filter media could achieve the treatment goals to different extents. Pressurized biofilters can further enhance contaminant removal from landfill leachate, which have been practiced for organic and inorganic chemical removal, radiological removal, iron and manganese control, water softening, and pH adjustment, etc. Typically, pressurized biofilters are commonly used for the removal of iron and manganese. Greensand filters can also be configured as pressurized filters for the removal of arsenic.

Since compost contains a higher concentration of microorganisms, compost is also an option of media choice for biofilters. Major problems encountered when compost is used as the filter media are the settling of the compost, which results in increased gas-phase pressure drop. In addition, availability of nutrients, such as nitrogen and phosphorus may contribute to organic and nutrient load for the treatment. Alternatively, wood chips, which provide mechanical support to minimize settling can be used as the filter media. Besides as supporting material for the microorganisms, they encourage aeration to promote aerated degradation of organic contaminants. For both the compost beds and

wood chip beds, it is necessary to have shallow beds (height < 1.5 m or 4.5 feet) to prevent compaction of the material and drying of the bed from the top surface. This requires the beds to have large cross-sectional areas, and in many cases are simply left completely open from the top. In some cases, powdered activated carbon is added to buffer the concentration changes since activated carbon is known to adsorb contaminants. Currently, there are several companies that offer compost biofilters for treatment of various wastewater.

Because of its wide range of application, many studies have been done on biofiltration systems in last few decades. However, theoretically it is still difficult to explain the behavior of a biofilter. The growth of different types of microorganisms in different working conditions makes it impossible to generalize the microbial activities in a biofilter. The biofilters operated under different filtration rate and influent characteristic conditions can have diverse efficiency for different target pollutants. Besides, due to some of the operational drawbacks of the biofilters such as performance fluctuation, maintenance of biomass, and disinfection adequacy of the biofilter effluent, research on biofiltration processes has become imperative. Biofiltration is an economically viable treatment process, which can effectively capture pollutants from the wastewater. Although biofiltration has been successfully practiced for the treatment of contaminated wastewater such as landfill leachate, the development of consortia that are responsible for the degradation of various contaminants present in the landfill leachate is still under investigation.

Initially, biofiltration involves the use of naturally bioactive media, such as soil, peat, compost, etc. Presently, synthetic supporting media such as ceramic and plastic have been popularly used. In both naturally bioactive media and synthetic media, microorganisms have been known to biodegrade contaminants, which have been successfully employed in biodegradation of contaminated wastewater including landfill leachate. It is only in the last 10 years, fiber biofiltration has begun to emerge as an economically viable treatment process. To enhance biodegradation, significantly increased surface area is required to house the microorganisms. This leads to the

development of fiber biofilters, in which the fiber packed in the filter bed provides dramatically increased surface areas for enhanced contact of the attached microorganisms with the contaminants. As more research has been conducted on this simple process, it becomes clear that the biodegradation rates are more dependent upon the consortia in the filter.

3. Materials and Methods

3.1 Leachate Collection

Based on our prior research results, it is highly recommended that landfill leachate be treated by aerated re-circulation before further treatment because aerated recirculation appears to be one of the least expensive methods for partial treatment of landfill leachate at landfill sites. Through aerated leachate recirculation, organic contents can be significantly reduced. The leachate recirculation not only improves the leachate quality, but also shortens the time required for landfill stabilization. After this process, leachate can be further treated by multi-stage electrocoagulation, flocculation, inclined-plate sedimentation, and fiber filtration/biofiltration. For this research, landfill leachate was collected from the Leon County Landfill, Springhill Landfill (Jackson County) and Perdido Landfill (Escambia County). Our prior research has demonstrated that above 70% of organic components can be removed through multiple steps of leachate recirculation and 90% of chloride, 80% of ammonia, and 95% of iron can be removed by the multifunctional reactor treatment. For this research, the leachate was diluted to simulate effluent of leachate recirculation, after which the leachate was treated in the multifunctional reactors with the incorporated electrocoagulation followed by two stages of fiber filtration and biofiltration. The incorporation of electrocoagulation into the multifunctional reactor dramatically reduced of the costs of chemical addition for the leachate treatment.

3.2 Incorporation of Electrocoagulation into the Multifunctional Reactor

The multifunctional reactor consisted of a series of continuous-mixing reactors. Both single anodic electrode and multiple anodic electrodes (arranged both in parallel and in series) were tested in this research (Figure 7). In parallel arrangement, the electric current was divided between all the electrodes in relation to the resistance of the individual cells, and each electrode had a different polarity. On the other hand, in series cell arrangement, a higher potential difference was required for a given current to flow because the cells connected in series had higher resistance. The same current would, however, flow through all the electrodes. The selection of electrode materials was also very important

because electrode consumption contributed significantly to the dissolution of the electrodes to generate coagulant metal cations in the electrocoagulation besides electrochemical and chemical reactions. Both iron and aluminum anodic electrodes were examined in this research. A digital multimeter (Agilent, 34410A) was used to measure the operating current supplied by a DC power supply (HP, E3631A). The surfaces of the iron and aluminum anodes were mechanically cleaned prior to experiments to remove any passive film that might have formed. Iron and aluminum electrodes were cheap, readily, available and effective. When iron and aluminum electrodes were used, the generated Fe^{3+} or Al^{3+} ions immediately underwent further spontaneous reactions to produce corresponding hydroxides and/or polyhydroxides. These insoluble iron and aluminum hydroxides reacted with the concerned contaminants and precipitated. Besides coagulation, adsorption also helped contaminant removal together with precipitation. Metal anode dissolution was accompanied by hydrogen gas evolution at cathodes with the bubbles capturing and floating the suspended solids, thus removing contaminants.

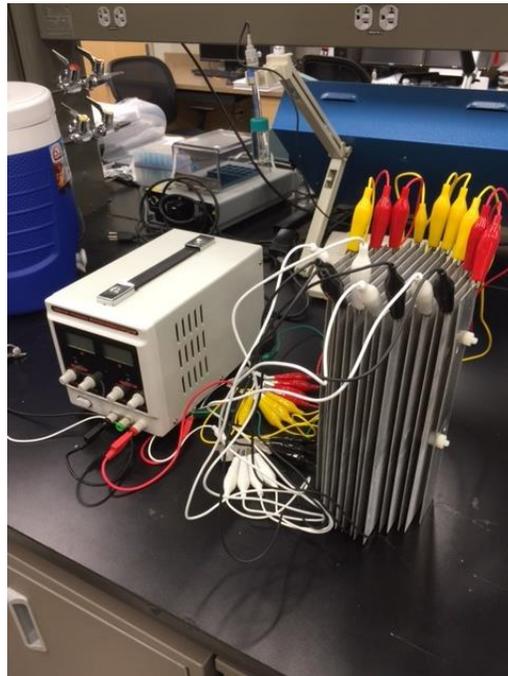


Figure 7. Electrocoagulation Experimental Setup

The experimental setup of this research is illustrated in Figure 8. In this setup, multiple anodic electrodes (arranged in parallel) were coupled with coagulation, flocculation and filtration in this research. Since aluminum or iron anodic electrodes were arranged in parallel, the electric current was divided between all the electrodes. The surfaces of aluminum or iron anodes were first mechanically cleaned prior to experiments to remove any passive film that may have formed. The electrocoagulation process was operated on the basis of the principle that the cations were produced electrolytically from aluminum or iron anodes, which were responsible for the coagulation of contaminants from the aqueous media. During the electrocoagulation operation, the consumable metal anodes continuously produced polyvalent metal cations in the region of the anode and these polyvalent cations released from the oxidation of the sacrificial anodes neutralized the negative charges of the particles moving towards the anodes. At the same time, electrolysis gases (i.e., hydrogen) evolved at the cathode. We used combined experimentation with modeling methods to conduct this research to accomplish the three objectives systemically, and to promote the implementation of the research discovery eventually.

The treatment performance of the system was evaluated via optimization of the electrical current and electrode types, which were the two most important parameters for electrocoagulation. Electrocoagulation time was another significant parameter that was influential on the electrocoagulation performance since the formation and concentration of metal hydroxides, which played the key role on pollutant removal, depended on the electrocoagulation time (Sahu et al., 2014). The effect of electrical current was usually evaluated in terms of current density (Butler et al., 2011). High current density led to increased decomposition of the electrode material and enhanced coagulation. Eventually, the quantity of electricity passed through was actually responsible for dissolution of metal ions at the electrodes. In this research, the relationship of the current density (A/cm^2) and the quantity of the metals dissolved (g/cm^2) was described by the Faraday's law:

$$W = \frac{i \times t \times M}{n \times F} \qquad \text{Equation (15)}$$

where W is the amount of dissolved electrode (g/cm^2); i is the current density (A/cm^2); t is the electrocoagulation time (sec); M is the relative molar mass of the electrode (g); n is the number of electrons involved in the oxidation/reduction reaction (-); and F is the Faraday's constant ($96,500 \text{ C}/\text{mol}$).

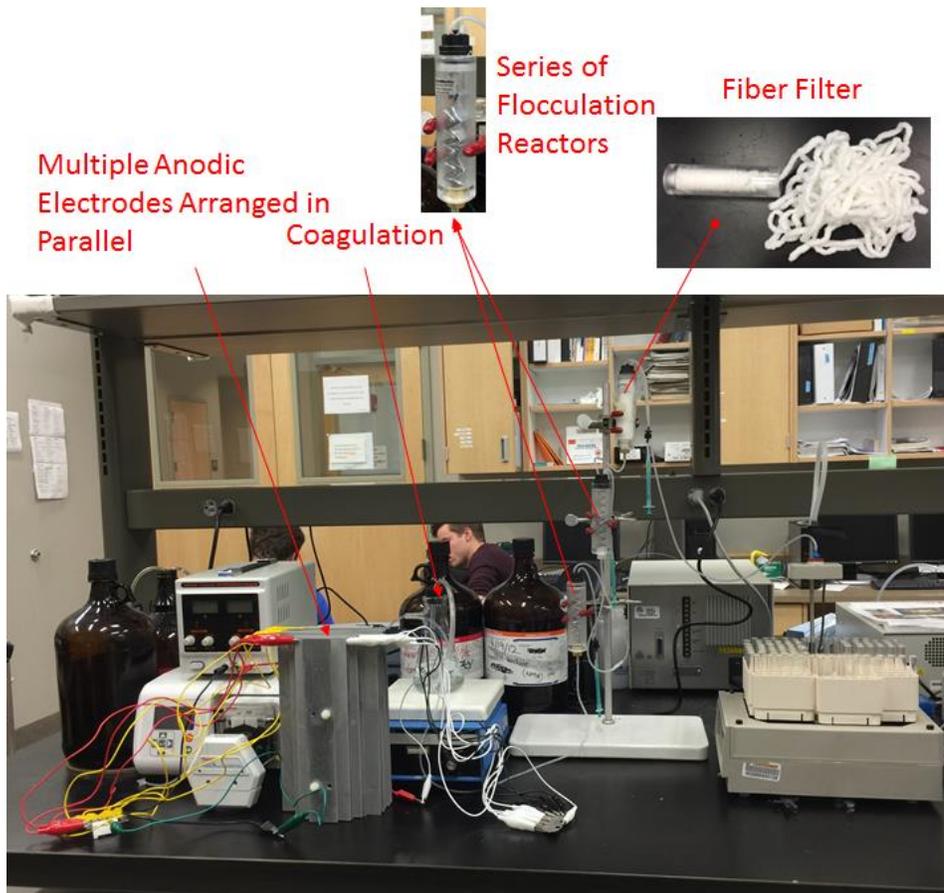


Figure 8. Multifunctional Reactor with Incorporated Electrocoagulation

In this research, energy consumption was calculated in terms of per unit COD removal and landfill leachate was diluted to provide variable COD loading. It was obvious that the energy consumed increased with the increase of the electrical power and the electrocoagulation time, and the electrical power and electrocoagulation time displayed an inverse relationship. Energy consumption of 0.5 to $5 \text{ kW}\cdot\text{h}/\text{m}^3$ with an incremental increase of $0.5 \text{ kW}\cdot\text{h}/\text{m}^3$ was tested by varying the electrical power and electrocoagulation time in the range from 5 to 20 minutes with an incremental increase of

5 min. Optimum energy costs were determined based on the acceptable treatment results and reasonable energy consumption. It was suspected that the electrocoagulation time was the predominant factor in the electrocoagulation process for the treatment of landfill leachate. It has also been demonstrated that pH is an important factor influencing the treatment performance. Therefore, pH in the range of 5 to 10 was tested, which was adjusted to the desired value using sulfuric acid or sodium hydroxide. Inorganic carbon (such as HCO_3^- at near-neutral pH) was a concern in electrocoagulation systems because it was commonly found at high concentrations and was able to influence the kinetics of both Fe(II) and As(III) oxidation. To investigate the influence of $\text{HCO}_3^-/\text{CO}_3^{2-}$ on Fe(II) and As(III) oxidation in the electrocoagulation system, electrocoagulation was also conducted for a range of HCO_3^- concentrations from 5 to 100 mM, which covered a significant fraction of $\text{HCO}_3^-/\text{CO}_3^{2-}$ concentrations in landfill leachate.

3.3 ζ -potential Measurements

ζ -potential was quantified based on electrophoretic mobility by 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 it. The scattered light was then detected by a photo-multiplier after passing the electrophoresis cell. ζ -potential was related to the electrophoretic mobility by the following equation:

$$U_E = \frac{\epsilon_r \epsilon_0 \zeta}{\eta} \quad \text{Equation (16)}$$

where U_E is the electrophoretic mobility [$\text{m}/(\text{V}\cdot\text{sec})$]; ϵ_r and ϵ_0 are the relative dielectric permittivities of the dispersion medium and the permittivity of vacuum [$\text{C}/(\text{V}\cdot\text{m})$] respectively; and η is the viscosity. Each test was repeated 6 times and the average value was reported.

3.4 Suspended Fiber Filtration and Biofiltration

After aluminum or iron release from the electrodes, aluminum or iron coagulants formed in the aqueous phase, which destabilized the contaminants in the landfill leachate. In the flocculation reactors, aggregation of the destabilized colloidal contaminants formed

flocks. After treatment in the multifunctional reactor, the treated landfill leachate was introduced to a series of fiber filters. Both the fiber filter and fiber biofilter had a dimension of 2.5 cm ID \times 10 cm length. The first stage fiber filter was used to retain the flocs formed during electrocoagulation and the second stage biofilter was used for the removal of organics by biodegrading. Continuous cultivation and enrichment of organic degrading consortia was carried out in the second stage biofilter using organic-enriched landfill leachate as the inocula. The final effluent was collected and measured for organic, iron, arsenic, and phosphorus contents. Impact of pH was investigated separately for arsenic and phosphorus removal, which was adjusted to 5, 6, 7, 8, 9 and 10 with sulfuric acid or sodium hydroxide.

4. Results

4.1 Electrocoagulation Performance

Since the quantity of electricity passed through was actually responsible for dissolution of metal ions at the electrodes, the relationship between current density and the quantity of the metal dissolved followed the Faraday's law. The aluminum and iron release was thus calculated. Aluminum release linearly increased with the increase of reaction time (Figure 9). However, iron release exponentially increased with the increase of reaction time (Figure 10).

4.2 Leachate Behavior

The UV-vis spectrum variation of the Springhill Landfill leachate after electrocoagulation with aluminum electrode is illustrated in Figure 11. With the increase of electrocoagulation, the absorbance decreased accordingly. This indicated that bigger particles formed with the increase of electrocoagulation time.

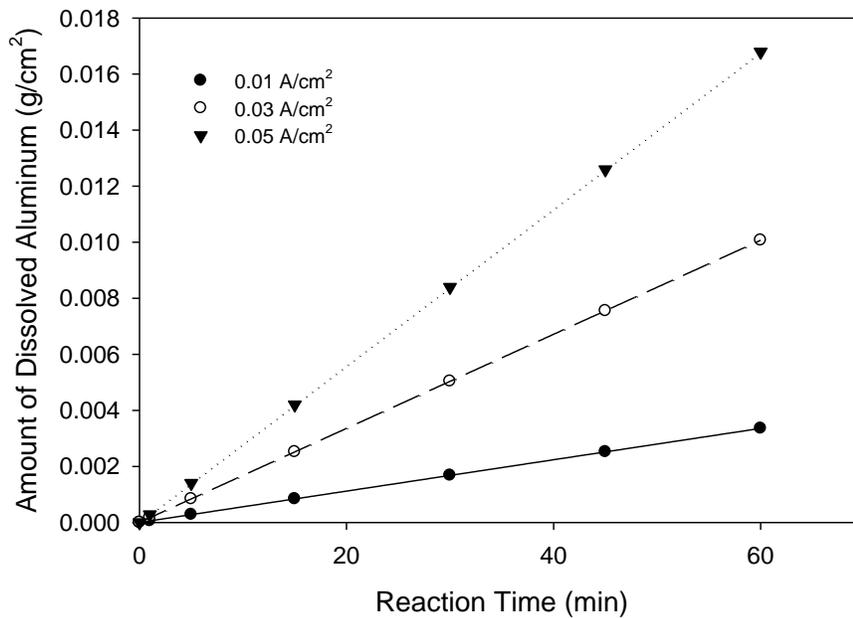


Figure 9. Current Intensity and Time on Aluminum Dissolution

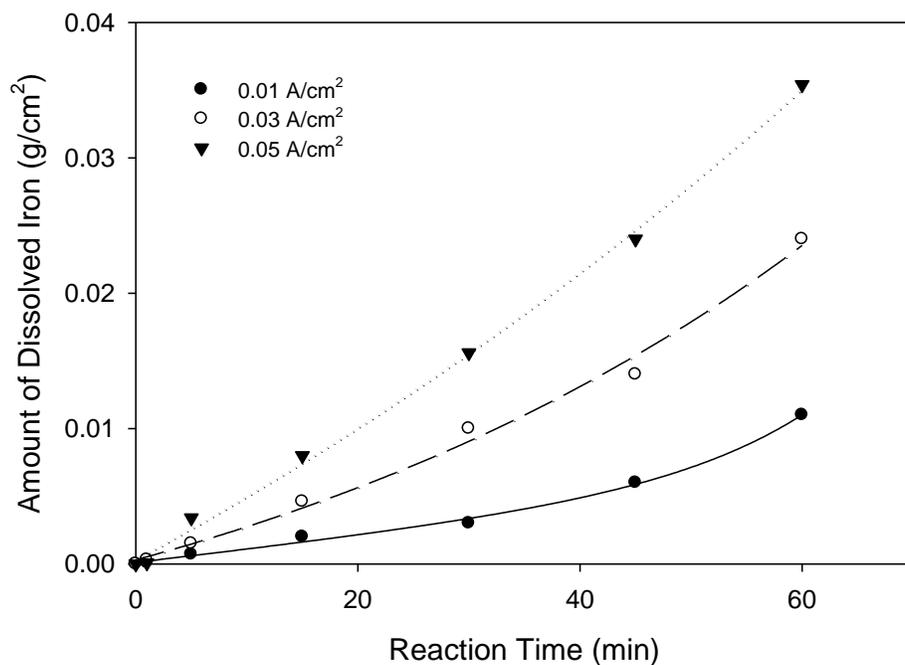


Figure 10. Current Intensity and Time on Iron Dissolution

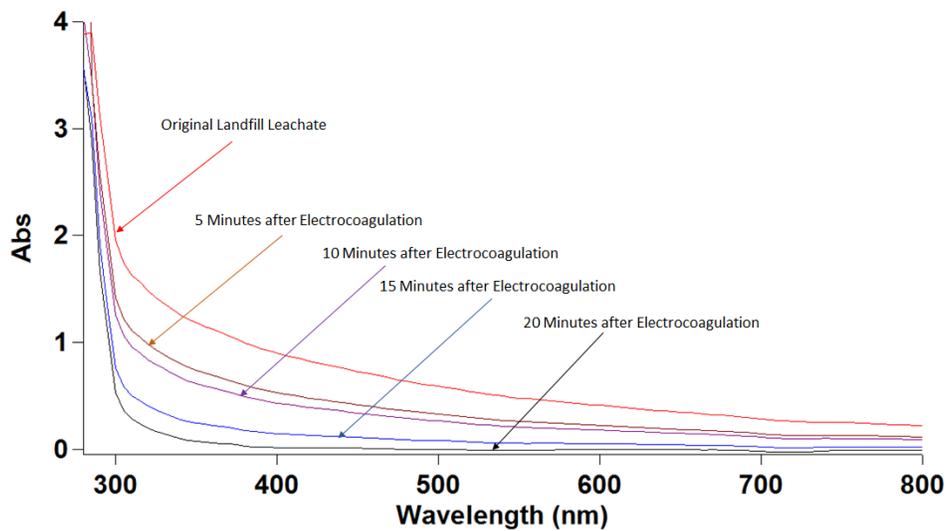


Figure 11. Leachate UV-Vis Spectrum after Electrocoagulation

4.3 COD Removal by Electrocoagulation

After evaluation of metal release as a function of electrical current (i.e., current density) and reaction time, the treatment performance of the system was examined in terms of COD removal using landfill leachate collected from Springhill Landfill. High current density led to increased decomposition of the electrode material and enhanced coagulation and COD removal (Figure 12 and Figure 13). Similarly, enhanced coagulation and COD removal were also observed for prolonged reaction time, i.e., COD removal increased with the increase of reaction time until 30 minutes, after which the increase became moderate.

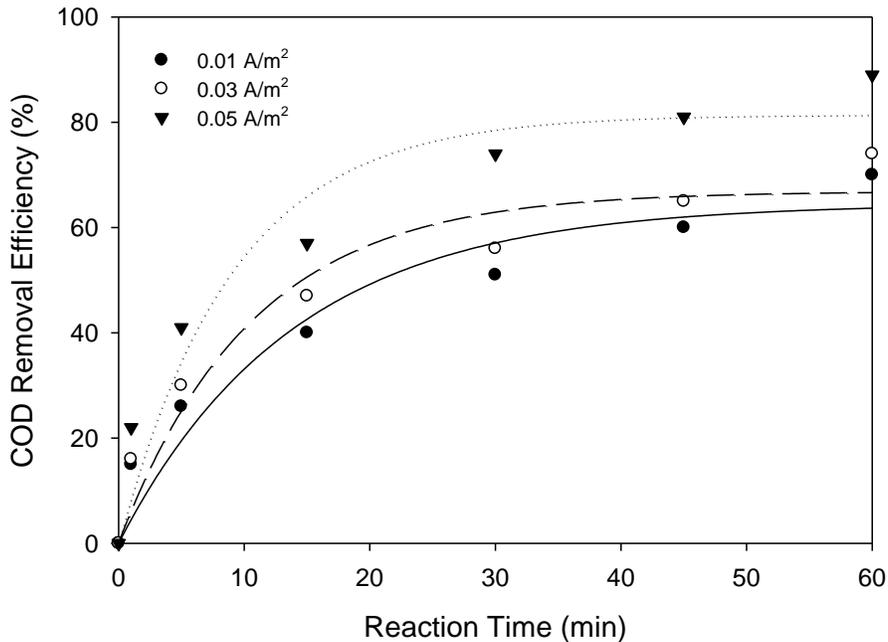


Figure 12. Current Intensity and Time on COD Removal with Aluminum Electrode

Figure 12 shows the COD removal by electrocoagulation with aluminum electrode and Figure 13 shows the COD removal by electrocoagulation with iron electrode. For both cases, the removal became flat after 30 minutes. A clearer solution was observed after coagulation and subsequent sedimentation. Organic contaminants in the leachate were probably removed through an array of processes such as adsorption, electrostatic

interactions, co-precipitation, and enmeshment in the flocs. These processes were affected by many factors, such as the stability and size of the flocs formed. Despite the lack of a clear trend, the result indicated that higher coagulant dosage and longer settling times did improve COD removal. Compared to iron electrode, electrocoagulation with aluminum electrode had better COD removal observation.

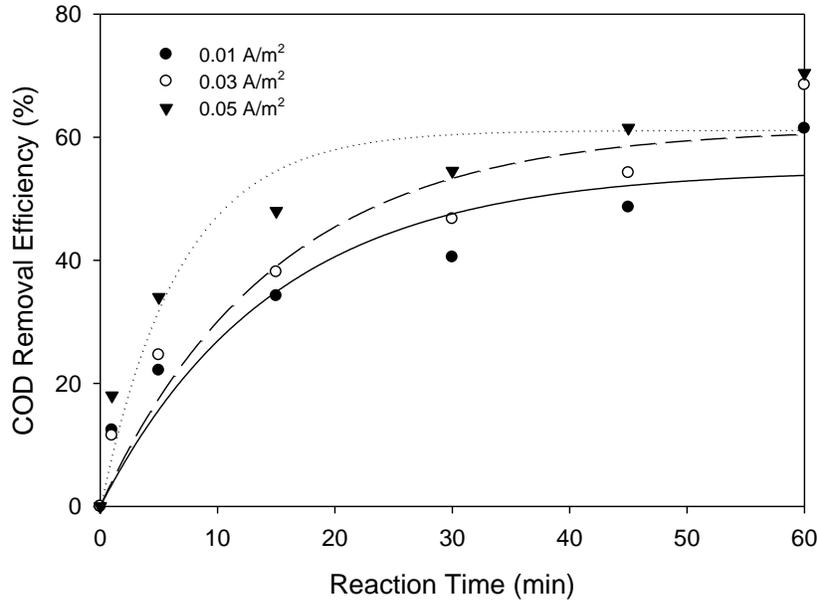


Figure 13. Current Intensity and Time on COD Removal with Iron Electrode

For electrocoagulation with aluminum electrode, there was not much difference of COD removal for the current density of 0.01 A/m² and 0.03 A/m². However, when the current density increased to 0.05 A/m², COD removal increased from 60% to 80%. For electrocoagulation with iron electrode, increase of current density to 0.03 A/m² from 0.01 A/m² led COD removal increase from 45% to 60%. Further increase of current density to 0.05 A/m² did not further increase COD removal. In addition, when iron electrode was used, the treated leachate turned greenish during treatment with the accumulation of greenish precipitate (Fe(OH)₂), which gradually darkened and turned to brown color (Fe(OH)₃). After complete settling of the precipitate, the leachate became a clear solution, similar to that of aluminum electrode. These results indicated that coagulation by ferrous and ferric hydroxides played the key role in the observed COD removal. COD

removal by electrocoagulation was also plotted against the released aluminum and iron. There was a trend that COD removal increased with the increase of released aluminum and iron (Figure 14 and Figure 15).

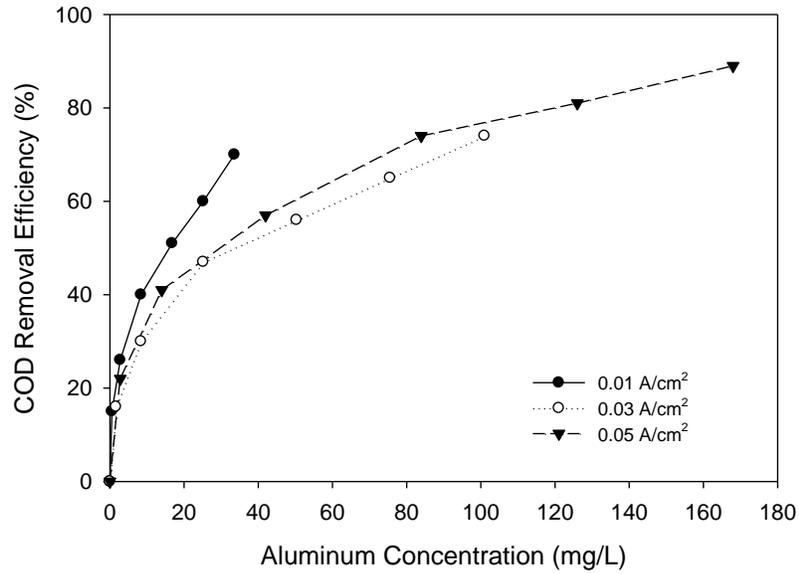


Figure 14. COD Removal as a Function of Released Aluminum

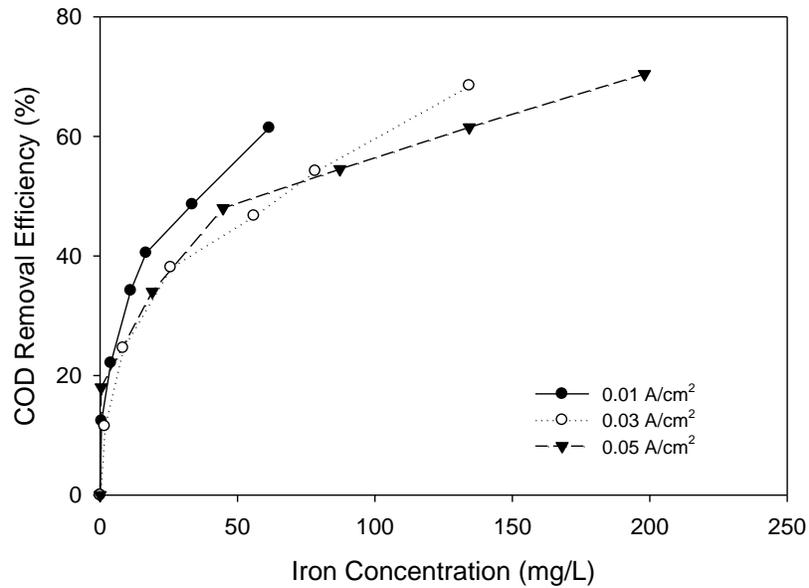


Figure 15. COD Removal as a Function of Released Iron

Because of the high salt concentrations in the landfill leachate, violent reactions occurred during electrocoagulation. The thus formed radicals ($\text{OH}\cdot$ and $\text{O}\cdot$) and oxidants (O_2 , O_3 , and H_2O_2) could also be responsible for COD reduction. Overall, COD removal during electrocoagulation was postulated to be achieved through a combination of electrocoagulation and anodic oxidation of the organic contaminants in the leachate.

Although the COD removal efficiency was not comparable with that of aluminum, electrocoagulation with iron electrode had obvious advantages in that organic contaminants with carboxyl functional groups (e.g., benzoic acid) were expected to bind strongly to ferrous and ferric hydroxides. Over longer reaction time, formation of ferrous and ferric hydroxide or aluminum hydroxide coatings on the electrode surfaces started to block electron transfer and caused deactivation of the electrodes during electrocoagulation for both aluminum and iron electrodes. This gradually reduced the occurrence of electrochemical reactions and the production of salt coagulants.

4.4 Arsenic Removal by Electrocoagulation

In our prior research, we studied Fe(III) and As(V) reduction nearby the landfills. With the decomposition of organic compounds in the leachate, Fe(II) and As(III) release was observed, which increased with the proceeding of the experiments, with Fe(II) release more pronounced. Since Fe(III) reduction was thermodynamically more favorable as compared to As(V) reduction, Fe(III) reduction preceded As(V) reduction. Owing to the strong adsorption of As(V) to Fe(III), it was proposed that iron reduction and associated dissolution eventually led to As(III) release and elution. Fe(III) oxide dissolution-induced arsenic release was more pronounced after 15 to 20 hours (Figure 16). Our experimental results demonstrated that arsenic dissolution was driven by Fe(III) oxide reduction, a microbial dominated reduction process. Arsenic mobilization was only possible after As(V) was reduced to As(III) as facilitated by reductive dissolution of Fe(III) oxides in the iron-rich soil since the released As(V) would still be severely constrained by re-adsorption and cannot be mobilized until it was reduced.

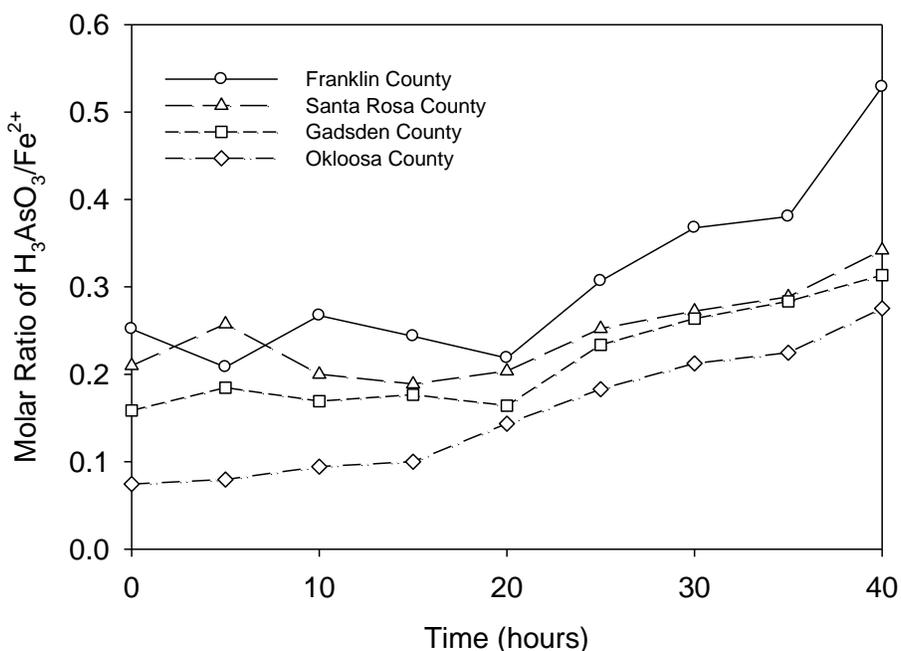


Figure 16. Iron and Arsenic Release for Different Landfill Soils

Currently, elevated concentrations of arsenic were detected in the leachate from lined landfills. In the leachate, As(V) and As(III) were the most commonly found arsenic species. Thermodynamic calculations and experimental results indicated that at high redox levels ($pe + pH > 10$), As(V) was the predominant arsenic species; while under moderately reduced conditions ($pe + pH < 8$), As(III) was the most abundant form of arsenic. As(V) adsorbed strongly to Al(III) and Fe(III) oxides. Studies show that 90% of arsenic can be associated with the iron fraction in the form of As(V).

In this research, arsenic removal was found to be strongly influenced by electrocoagulation and pH played a very important role for arsenic removal (Figure 17). In the leachate, inorganic arsenic occurred primarily as H₃AsO₄ at pH below 2, and both H₂AsO₄⁻ and HAsO₄²⁻ species existed in the pH range of 2 to 11. Based on the redox condition of our leachate sample, at pH higher than 9, As(V) started to dominate. With electrocoagulation, the released iron was subjected to hydrolysis. The subsequently formed iron hydroxide had strong adsorption for arsenate. Therefore, arsenic removal

showed a sharp increase after pH was higher than 9. At low pH, however, As(III) was the dominating species. As(III) did not adsorb strongly to iron hydroxide. Subsequently, As(III) removal was not sensitive to pH at this pH range (Figure 17).

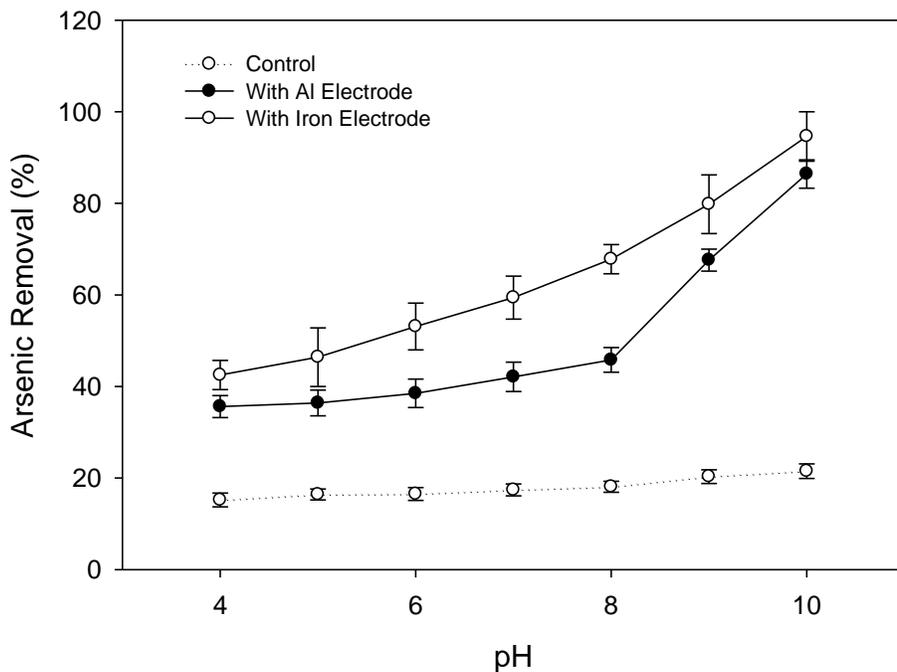


Figure 17. Arsenic Removal by Electrocoagulation as a Function of pH

Arsenic removal by electrocoagulation with both aluminum and iron electrodes was tested. Arsenic removal was found to be influenced by electrical current (i.e., current density) and reaction time during electrocoagulation (Figure 18 and Figure 19). As(III) (if existing) should be oxidized and subsequently As(V) should be able to be removed by co-precipitation. With iron electrode, arsenic removal also attributed to adsorption to the formed iron hydroxide. Under this condition, the released iron was subjected to hydrolysis and arsenic removal was achieved by its strong adsorption with precipitated ferric iron hydroxide. Therefore, desired hydrolysis time is required for arsenic removal. From this research, it was discovered that reaction time of 30 minutes was required for proper arsenic removal by electrocoagulation. High current density led to increased decomposition of the electrode material and enhanced arsenic removal.

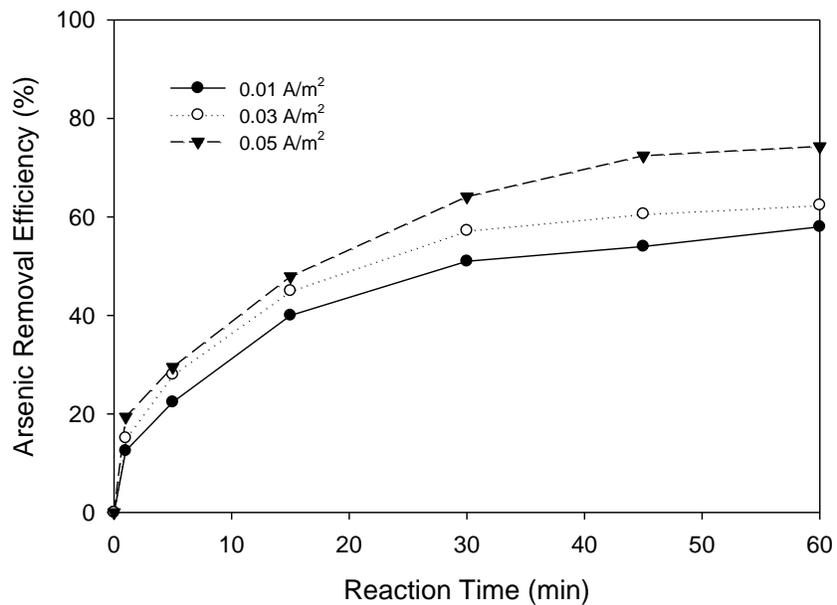


Figure 18. Current Intensity and Time on Arsenic Removal with Aluminum Electrode

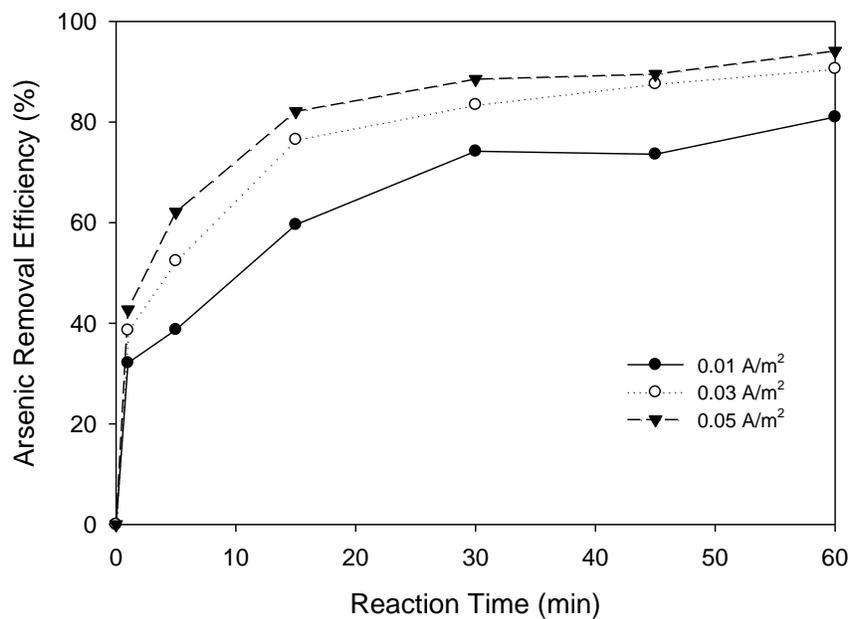


Figure 19. Current Intensity and Time on Arsenic Removal with Iron Electrode

Arsenic removal by electrocoagulation was also plotted against the released aluminum and iron. There was a trend that arsenic removal increased with the increase of released aluminum and iron (Figure 20 and Figure 21).

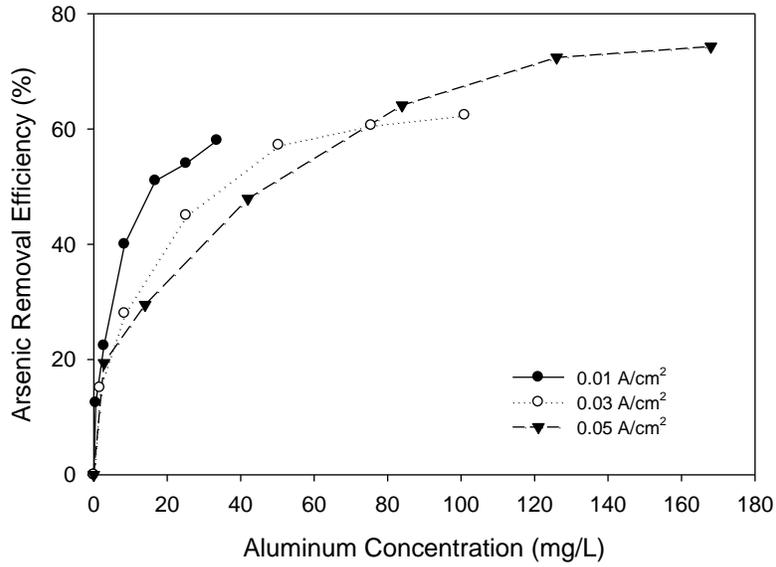


Figure 20. Arsenic Removal as a Function of Released Aluminum

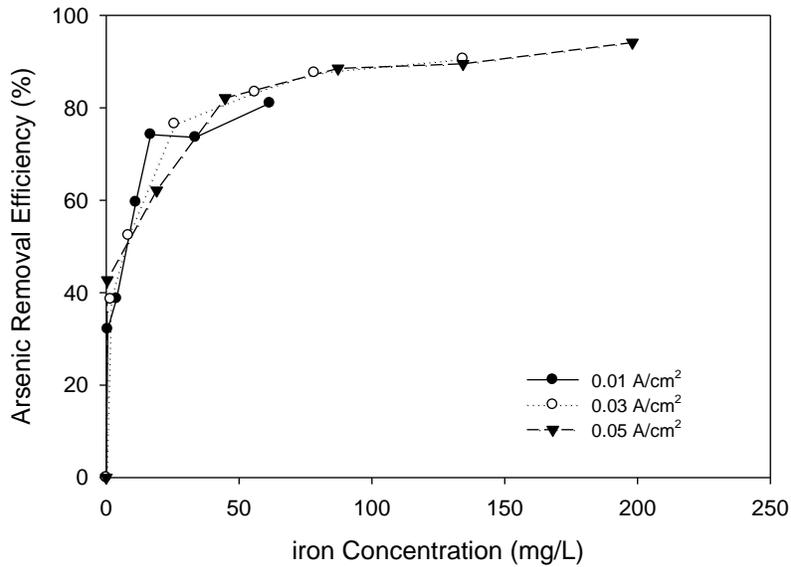


Figure 21. Arsenic Removal as a Function of Released Iron

4.5 Phosphorous Removal

For phosphorus removal by coagulation, aluminum and iron salts were usually used and pH, temperature, and ionic strength were the major impact factors. Aluminum and iron salts had advantages over other metal salts since they were not sensitive to pH. In addition, they produced much less sludge. pH also played the key role for phosphorus removal and the optimum pH for phosphorus removal was 4.5. With the addition of coagulants, solution pH decreased accordingly (Figure 22). 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., $\text{Al}(\text{H}_2\text{O})_6^{3+}$ and $\text{Fe}(\text{H}_2\text{O})_6^{3+}$. Hydrolysis of $\text{Al}(\text{H}_2\text{O})_6^{3+}$ and $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ was a sequential replacement of the water molecules with hydroxyl ions, the progressive of which involved in many competing reactions. Compared to Al^{3+} , Fe^{3+} reacted slowly with the natural alkalinity, and consequently, iron salt coagulants encountered less pH decrease.

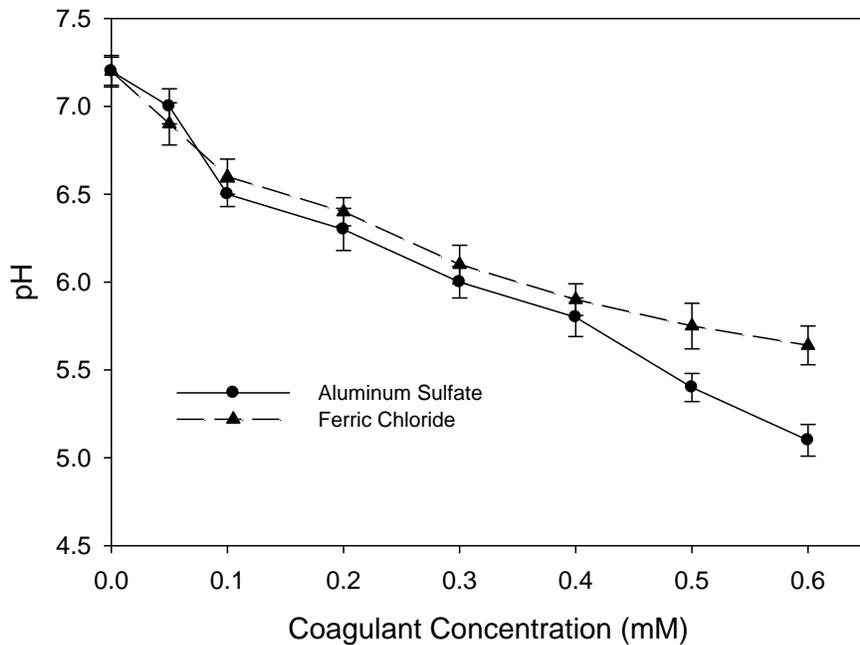


Figure 22. Arsenic Removal by Coagulation as a Function of pH

The amorphous $\text{Fe}(\text{OH})_3$ and $\text{Al}(\text{OH})_3$ were the species that were responsible for phosphorus precipitation. $\text{Fe}(\text{OH})^+$, AlOH^{2+} , and $\text{Al}(\text{OH})_2^+$ were the species for the adsorption of phosphorus to occur. For phosphorus to adsorb to $\text{Fe}(\text{OH})^+$, AlOH^{2+} , and $\text{Al}(\text{OH})_2^+$, phosphorus replaced singly coordinated OH^- groups and then reorganized into a very stable binuclear bridge between the cations. This chemisorption process was coupled with the release of OH^- , thus this process was favored by low pH values. Since these species co-existed, adsorption and precipitation of phosphorus were functioned at the same time. Owing to the fact that AlOH^{2+} and $\text{Al}(\text{OH})_2^+$ was the dominating species at the pH range of this research and aluminum salt coagulants had a better removal phosphorus removal result, it could thus be predicted that adsorption should play an more important role in phosphorus removal, which was consistent with prior research (Peak et al., 2002). Impact of pH on phosphorus removal during electrocoagulation is illustrated in Figure 24.

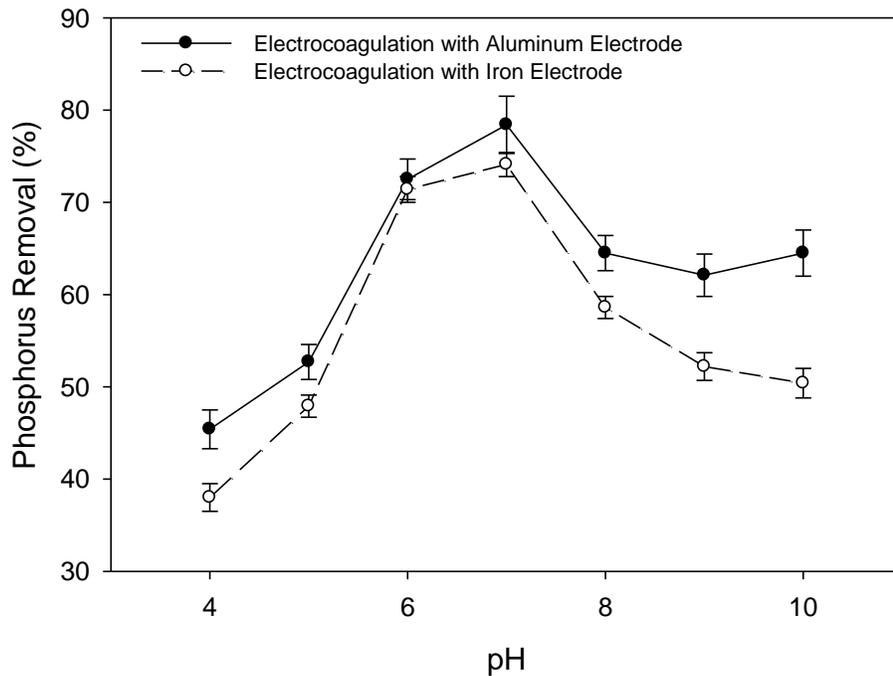


Figure 24. Phosphorus Removal by Electrocoagulation as a Function of pH

With electrocoagulation, the released iron or aluminum formed ferric iron or aluminum hydroxide through hydrolysis, which had strong adsorption and co-precipitated phosphorus. In this research, we discovered that neutral pH was preferred for phosphorous removal. As discussed above, phosphorus adsorption was favored by low pH values. However, low pH prevented ferric iron hydrolysis. Neutral pH seemed to be the suitable range for phosphorous removal by electrocoagulation.

4.6 Reactor Performance

The multifunctional reactor with incorporated electrocoagulation and two stages of fiber filtration and biofiltration was evaluated for the treatment of landfill leachate. The treatment process was composed of electrocoagulation, static mixing, stage I fiber filtration and stage II fiber biofiltration (Figure 25). The stage I fiber filtration was for the removal the flocs formed by electrocoagulation and stage II fiber biofiltration was for the degradation of organics in the leachate.

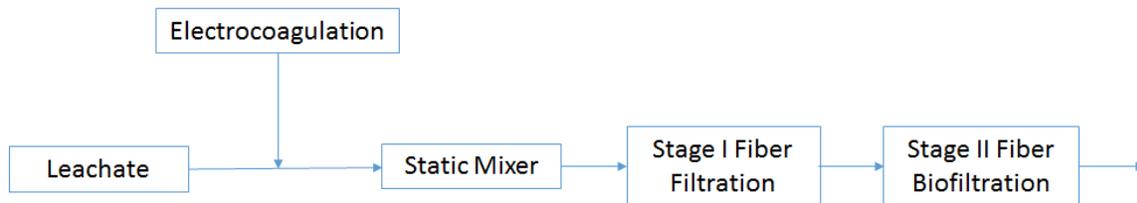


Figure 25. Flowchart of the Treatment Process

For different electrode and current density, we had different COD removal observations (Figures 26 – Figure 31). For electrocoagulation using aluminum or iron electrode followed by corresponding stage I fiber filtration and stage II fiber biofiltration, aluminum electrode had better treatment results than that of iron electrode, i.e., COD was reduced from 752 mg/L to 4.8 mg/L with a current density of 0.05 A/m² (Figure 32). Iron electrode with a current density of 0.01 A/m² could reduce the COD to 67 mg/L.

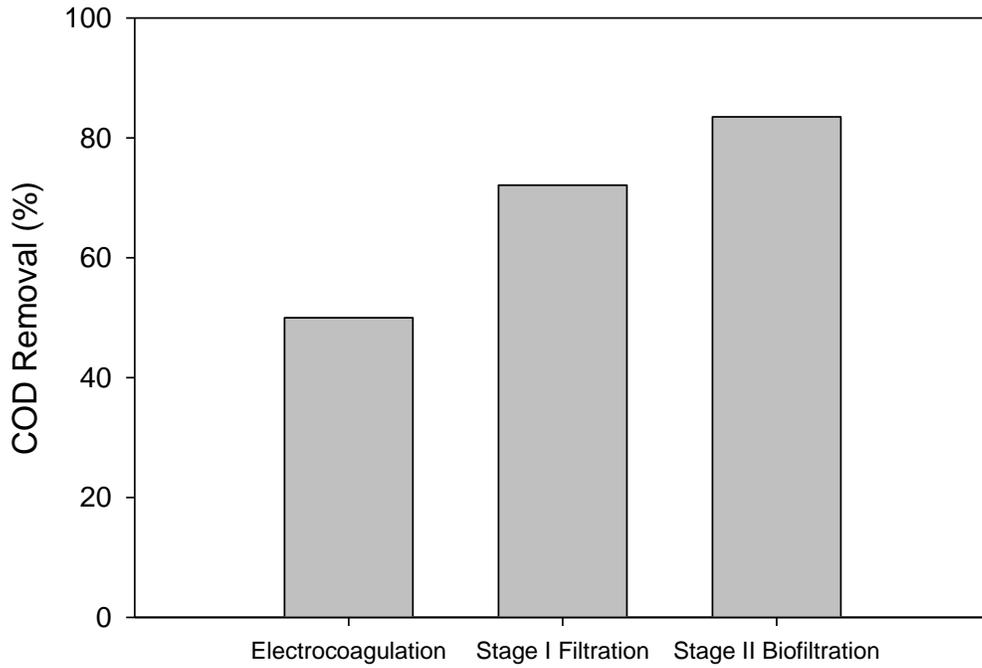


Figure 26. COD Removal with Aluminum Electrode at 0.01 A/m²

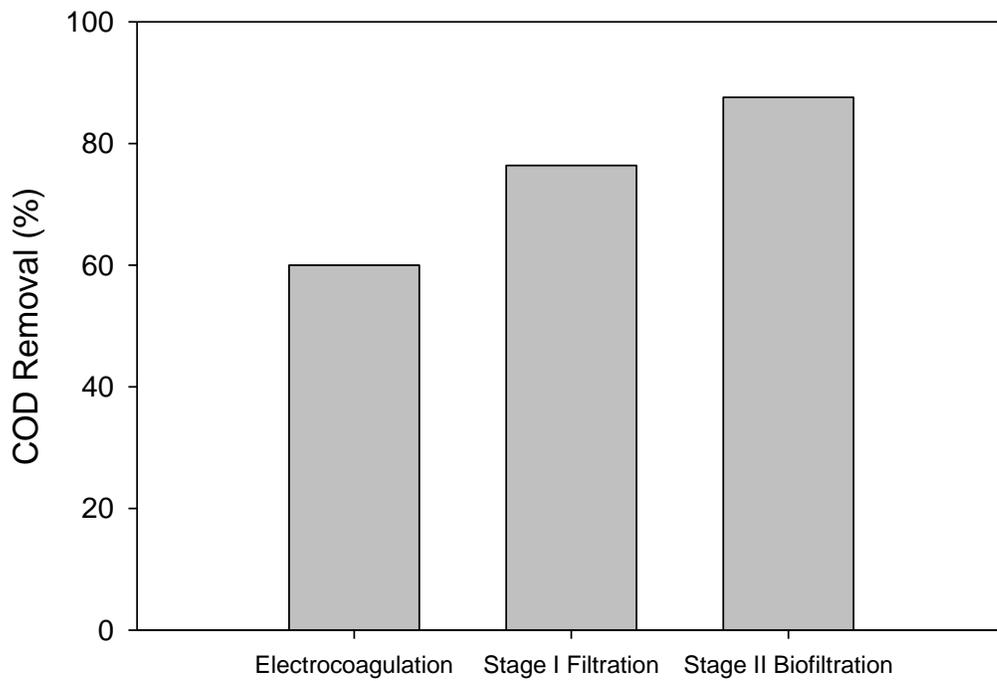


Figure 27. COD Removal with Aluminum Electrode at 0.03 A/m²

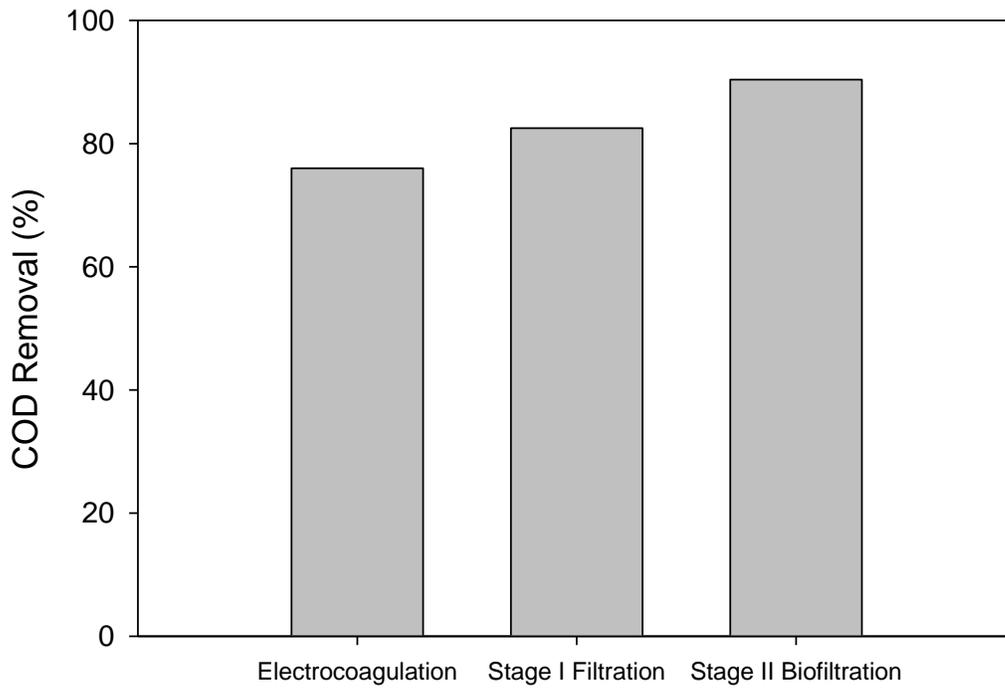


Figure 28. COD Removal with Aluminum Electrode at 0.05 A/m²

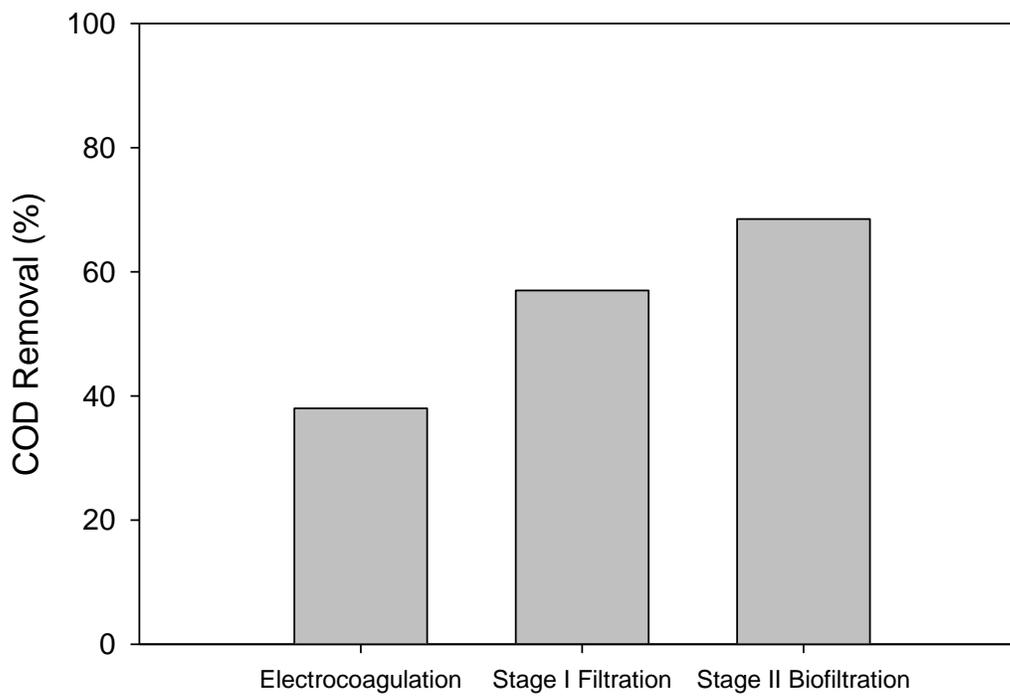


Figure 29. COD Removal with Iron Electrode at 0.01 A/m²

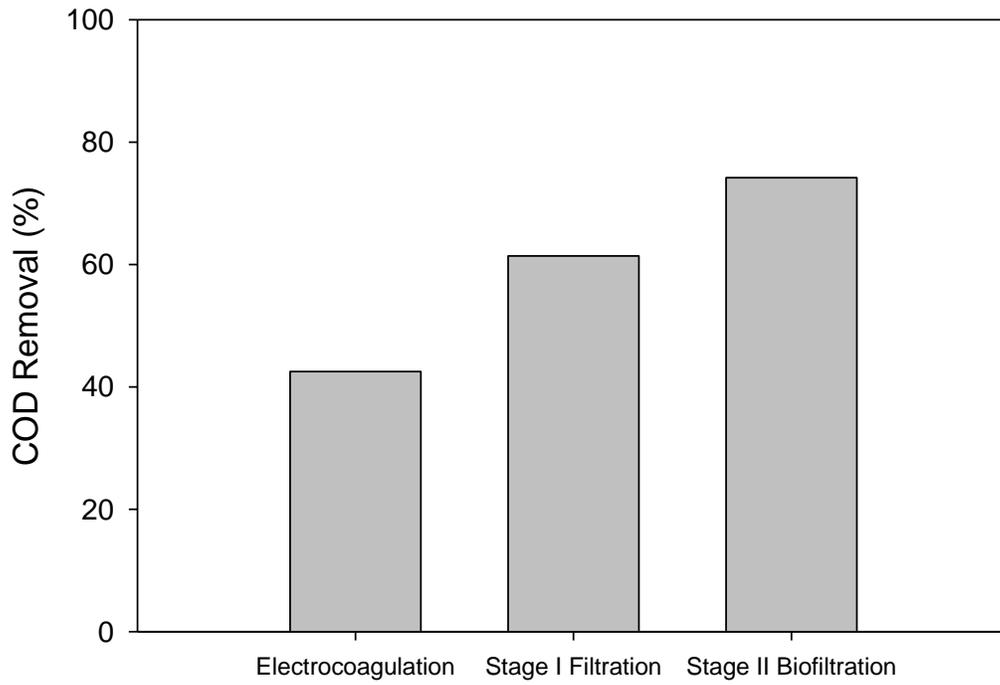


Figure 30. COD Removal with Iron Electrode at 0.03 A/m²

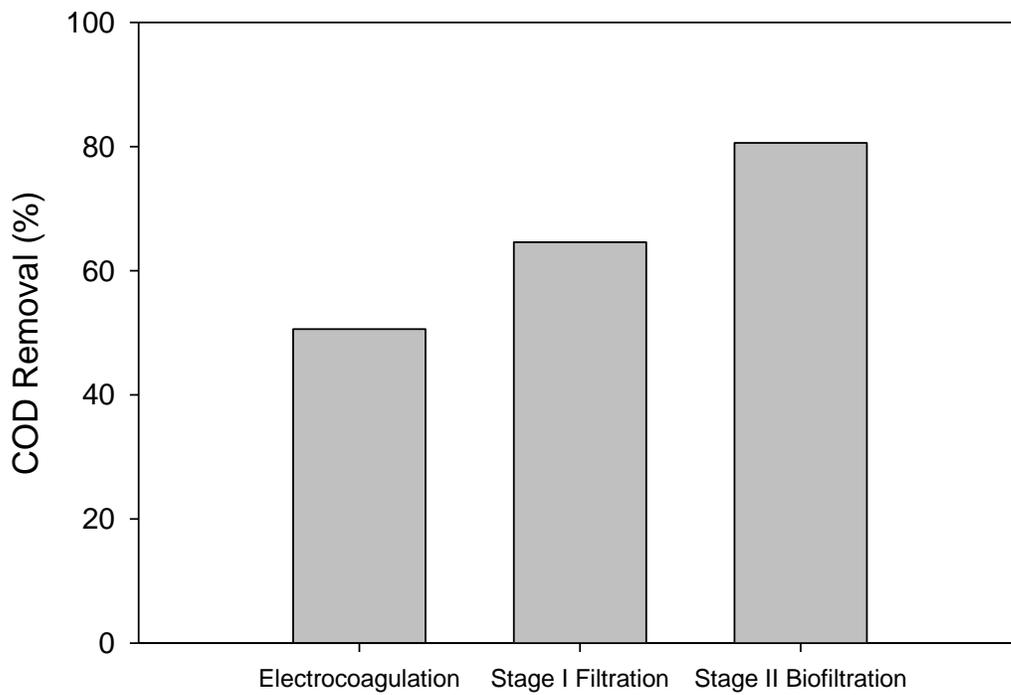


Figure 31. COD Removal with Iron Electrode at 0.05 A/m²

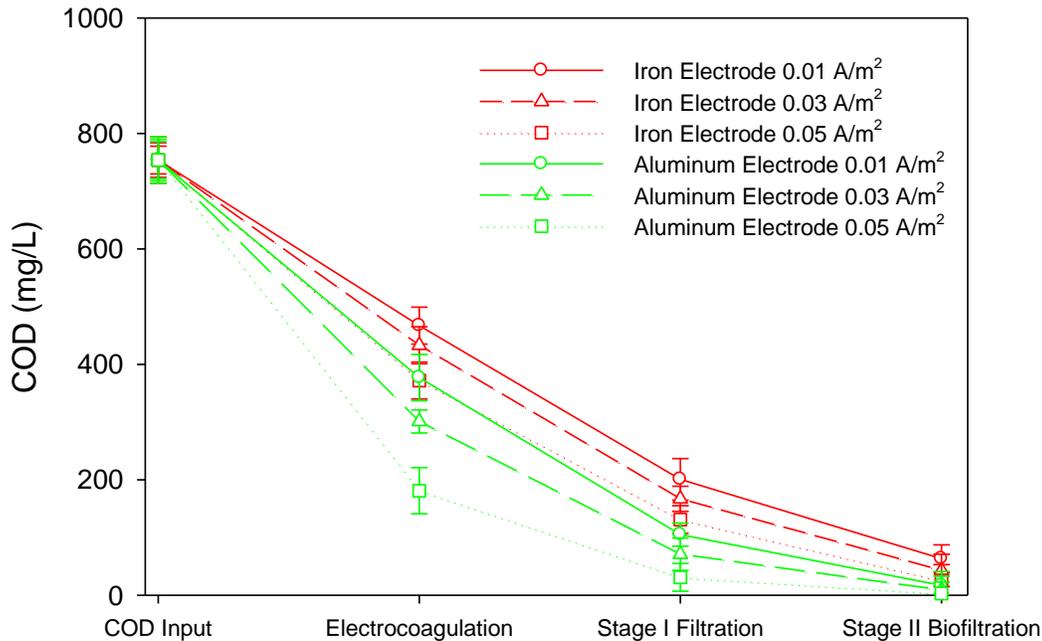


Figure 32. Comparison of COD Removal by Aluminum and Iron Electrodes

Iron removal was 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}) was reduced to ferrous iron (Fe^{+2}) and released to the leachate. Ferrous iron was removed during the coagulation treatment by oxidation and precipitation. Ferric hydroxide ($\text{Fe}(\text{OH})_3$) was the direct result of ferrous iron oxidation and precipitation. During landfill leachate treatment, there was also an opportunity for ferrous iron to be oxidized to ferric iron hydroxide by iron-oxidizing microbes. In this research, iron removal was evaluated for electrocoagulation with aluminum electrode. This was based on the consideration that iron electrode might further introduce iron oxide particles that were uneasy to settle in the solution. Majority iron was removed by electrocoagulation, after which iron was further removed by the following two stages of fiber filtration and biofiltration (Figure 33). With the current density of 0.05 A/m^2 , the effluent iron concentration was 1.5 mg/L as compared to 5.7 mg/L for that of 0.01 A/m^2 . It should be noted that the coagulation reaction was fixed to 30 minutes, which was proved to be the most optimal economically and technically.

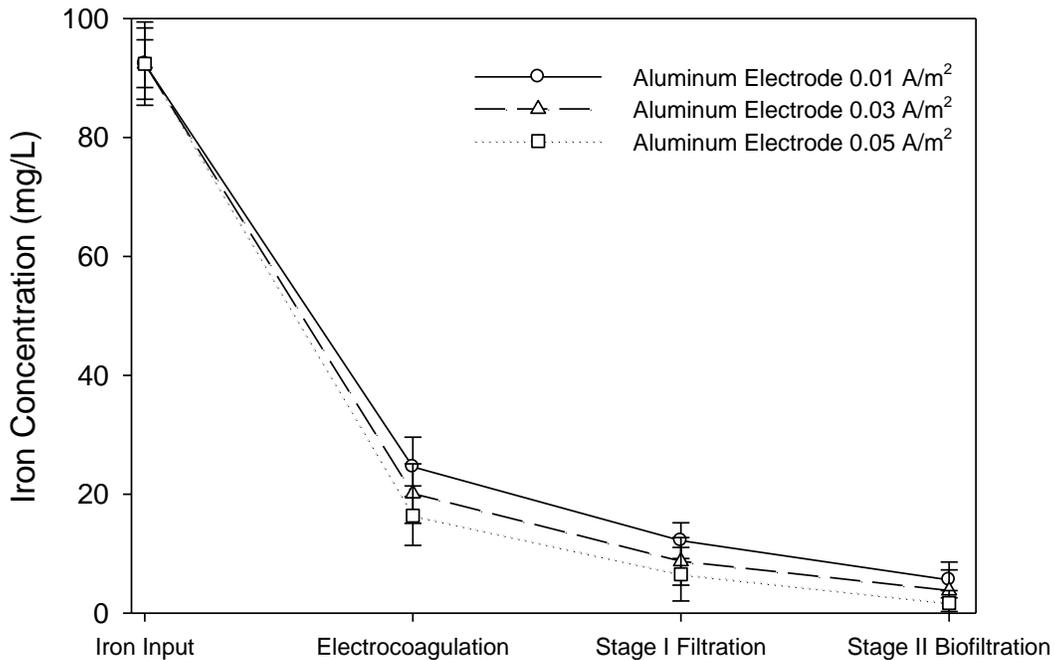


Figure 33. Iron Removal by Aluminum Electrode at Different Current Density

For phosphorous removal, besides co-precipitation with iron hydroxide during electrocoagulation, iron oxide coated on the fiber surfaces may also play the key roles, on which phosphorus was adsorbed. For phosphorus to adsorb to iron oxide-coated surfaces, 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^- , thus this process was favored by low pH values. The experimental results indicated that phosphorus co-precipitation with iron hydroxide during electrocoagulation and adsorption on iron oxide coated fiber surfaces played similar roles since the removal rates were similar (i.e., similar slope of the phosphorus depletion curves of Figure 34). In addition, both of the two stages of fiber filtration and biofiltration contributed to the phosphorus removal at a similar level.

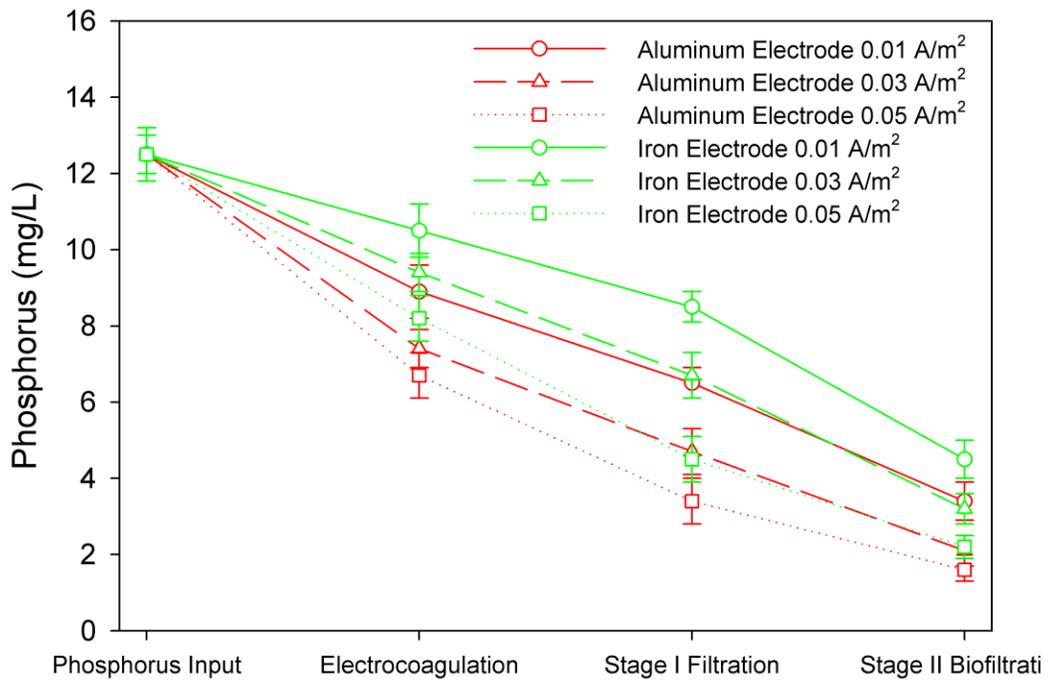


Figure 34. Comparison of Phosphorus Removal by Aluminum and Iron Electrodes

5. Discussion

5.1 Arsenic Removal by Co-Precipitation and Adsorption

Arsenic removal was attributed to co-precipitation with iron hydroxide during electrocoagulation (Figure 35). However, during filtration, arsenic might also be removed by adsorption to iron oxide that coated the fiber. To further investigate arsenic adsorption, arsenic solution was introduced to a column filled with goethite-coated polypropylene fiber. Goethite, a frequent and abundant form of iron oxide in the soil and sediments, is an important component influencing arsenic adsorption.

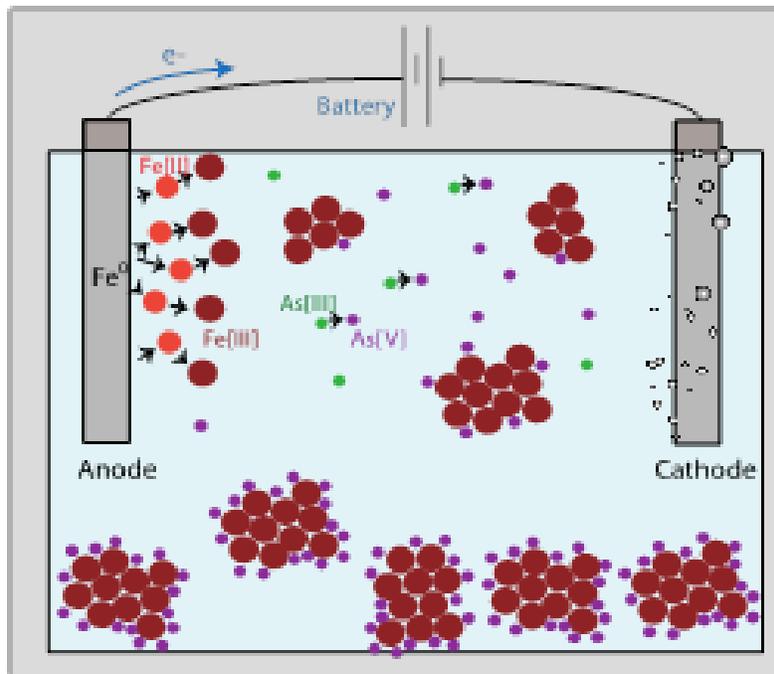


Figure 35. Arsenic Removal by Co-Precipitation

Goethite was prepared as described by Schwertmann et al. (Schwertmann and Cornell, 1991). Briefly, 1.0 M ferric nitrate was mixed with 1.0M KOH (1:9, v/v) and aged for 21 days at 25°C. This suspension was then washed extensively with de-ionized water via centrifugation. The rinsed solid was re-suspended in 0.4M HCl. After washed and dialyzed against de-ionized water, it was freeze dried to obtain crystalline goethite. Thus

obtained goethite was then coated on polypropylene fiber following the following method. Goethite was mixed with the fiber in 0.01M NaNO₃ solution (pH 7.5) for 48 hours. Coated fiber was then washed with 0.1M NaNO₃ (pH 7.0). After rinsed with de-ionized water, coated fiber was oven-dried at 110°C. Goethite coating was determined by dissolving coated fiber in HNO₃ (95%) and HF (40%) (2:1, v/v).

Column experiments were conducted using an acrylic column with a dimension of 2.5 cm ID × 10 cm length to investigate arsenic adsorption on the goethite-coated polypropylene fiber. The column was oriented vertically and sealed at the bottom with a custom frit to permit the flow of water and retain the media. Prior to starting each experiment, approximately 100 pore volumes of nano-pure de-ionized water was eluted through the column by a peristaltic pump to stabilize the column. Before the introduction of arsenate solution into the column, a conservative tracer of chloride was introduced to the column to estimate the porous media properties. After the tracer study, two pore volume of arsenate solution was pumped into the column at a flow rate of 0.56 mL/min. The column was then flushed with nano-pure de-ionized water alone for up to 50 pore volumes until no arsenate could be detected in the elution. Elution was collected by a fraction collector and was measured for arsenate by an atomic absorption spectrophotometer. A breakthrough curve was generated and mass balance analysis was performed. For the column experiment, three runs were performed, and the inconsistency of breakthrough curves was within 5% (95% CI). As a control experiment, transport of arsenate in uncoated fiber was also conducted.

Under saturated conditions, arsenate transport in goethite-coated fiber was controlled by both equilibrium adsorption and kinetic deposition, which can be described by:

$$\left(1 + \frac{\rho_b(1-\theta)}{\theta} K_d\right) \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} - \mu C \quad \text{Equation (17)}$$

where C is the arsenate concentration in the solution (g/m³); t is the elapsed time (sec); ρ_b is the fiber bulk density (g/m³); K_d is the partitioning coefficient of arsenate between the aqueous phase and fiber (m³/g); θ is the porosity of the fiber (m³/m³); D is the longitudinal dispersion coefficient (m²/sec); x is the coordinate parallel to the flow (m); v

is the pore velocity (m/sec); and μ is the first order arsenate deposition coefficient on goethite-coated fiber (sec^{-1}). $1 + \frac{\rho_b(1-\theta)}{\theta} K_d$ is defined as the retardation factor, R , which is an indicator of the “lag” of arsenate transport due to reversible adsorption.

Transport parameters in Equation (17) were obtained by fitting the experimentally obtained arsenate breakthrough data using an implicit, finite-difference scheme. All the parameters were optimized by minimizing the sum of squared differences between observed and fitted concentrations using the nonlinear least-square method (Toride, 1995). Tracer (Cl^-) transport was studied before arsenate transport experiments in both uncoated fiber and goethite-coated fiber. For both cases, nearly all the input tracer was eluted from the column. The tracer breakthrough curve was also simulated with Equation (17). During the model simulation, the retardation factor was set to 1.0, i.e., $K_d = 0$. This was based on the consideration that the tracer should not be retarded in the media as the tracer was assumed not to adsorb in the media. In addition, the deposition coefficient μ was set to zero, i.e., no retention of the tracer in the media. This was true since nearly all the inputted tracer was eluted from the column at the end of the transport experiments. During the simulation, the velocity was fixed at 0.18 cm/min and the initial D was set as $8.00 \text{ cm}^2/\text{min}$ for both uncoated and goethite-coated fiber. After the simulation, D was determined to be $14.2 \text{ cm}^2/\text{min}$ for uncoated fiber and $16.1 \text{ cm}^2/\text{min}$ for goethite-coated fiber. These D values were then used for the simulations of arsenate transport in the corresponding media. From the tracer study, the porous media porosity was found to be 0.43 for uncoated fiber and 0.48 for goethite-coated fiber.

The arsenate breakthrough curve was characterized by a breakthrough front and an elution tail (Figure 36). The lasting tail of the arsenate breakthrough curve indicated kinetic-controlled arsenate deposition in the column. The arsenate breakthrough curves were fitted well with Equation (17) and the accuracy of transport modeling was expressed by the sum of the squared differences between observed and fitted concentrations. The mean square for error of arsenate transport was 0.982. There was a small retardation and minimal deposition when arsenate was transported in uncoated fiber ($R = 1.08$ and $\mu = 1$

$\times 10^{-4} \text{ min}^{-1}$) (Figure 36). When transported in goethite-coated fiber, however, more arsenate was retarded as evidenced by the delayed breakthrough front ($R = 2.45$). There was also arsenate retention in the column as the peak value of the breakthrough curve was much lower than that of the uncoated fiber.

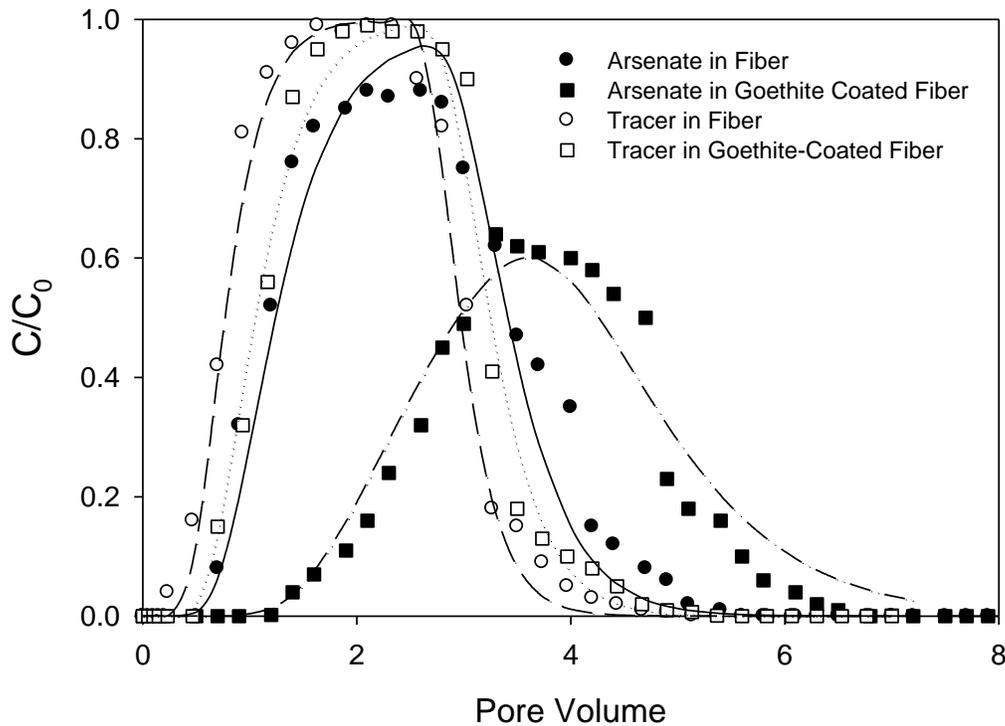


Figure 36. Arsenic Breakthrough Curves in Goethite-Coated Fiber Filter

As discussed previously, arsenate co-precipitation by electrocoagulation was thought to play similar roles of arsenate removal from landfill leachate as that of adsorption on iron oxide-coated fiber. Above investigation verified this assumption and indicated that adsorption of iron oxide coated fiber played an important role in arsenate removal. As demonstrated by the column experiments (i.e., integration of the breakthrough curve), around 57% of arsenate could be retained through adsorption by goethite-coated fiber. The retention of arsenate on goethite-coated fiber was attributed to the adsorption since there was no precipitation during the transport experiments.

Compared to adsorption, coagulation with iron coagulants such as electrocoagulation was more economical. It should be noted that pH and the ferric dose induced by current density were the most important variables controlling arsenic removal by electrocoagulation. It was also evidenced that Fe(OH)₃(s) was not as effective as ferric hydroxide formed-in-place (hydrolyzed *in situ*) by electrocoagulation or direct adding FeCl₃ to water since arsenate anions were easily adsorbed by surface complexation onto the short-chain polymers (oligomers) of Fe_x(OH)_y^{z+} when forming into Fe(OH)₃(s) floc particles. On the contrary, Fe(OH)₃ did not have the available surface area in comparison to the oligomers and polymers of Fe(OH)₃(s) formed during Fe³⁺ hydrolysis.

5.2 Iron and Phosphorous 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 Fe²⁺ or Fe(OH)⁺) or complex form like the ferric iron (trivalent iron of Fe³⁺ 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.

Ferrous iron is soluble as a cation, while ferric iron is not. 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:



Once ferrous iron is oxidized, hydrolysis proceeds:



This research demonstrated that electrocoagulation with aluminum electrode allowed the removal of a significant proportion of iron. It was observed that iron removal attributed to the co-precipitation of iron hydroxide particles with eight products of aluminum hydrolysis including Al^{3+} , $\text{Al}(\text{OH})^{2+}$, $\text{Al}(\text{OH})_2^+$, $\text{Al}(\text{OH})_3$, $\text{Al}(\text{OH})_4^-$, $\text{Al}_2(\text{OH})_2^{4+}$, $\text{Al}_3(\text{OH})_4^{5+}$, and $\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})^{7+}_{12}$.

Phosphorus removal was through adsorption to iron or aluminum oxide during electrocoagulation with either iron or aluminum electrode. This was especially the case of fiber filtration during which the polypropylene fiber was coated with iron hydroxide. It was believed that phosphorous adsorption on iron hydroxide was generally dominated by ligand exchange in which two singly coordinated hydroxyl groups or water molecules were replaced by a single phosphate anion (Mars et al., 2004). Since H_2O was a more mobile ligand than OH^- , adsorption was therefore favored at lower pH. It was believed that four key characteristics impacted phosphorus adsorption on the iron hydroxide-coated surfaces, i.e., the easiness of hydroxyl release, the specificity toward binding sites, hysteresis, and the surface charges (Michel et al., 2004; Oberleithner, 2004; Chen et al., 2006; Banu et al., 2008).

To further investigate the mechanism, ζ -potential of the solution was monitored. Compared to electrocoagulation with iron electrode, the decrease of ζ -potential for electrocoagulation with aluminum electrode was more obvious. The results of our experiment indicated that phosphorus adsorption was a chemical sorption process and covalent bonds were formed between phosphorus and the adsorbent surfaces such as $(\text{Al}(\text{OH})_3)_n$, $(\text{Fe}(\text{OH})_3)_m$ or $(\text{Fe}(\text{OH})_2)_p$.

5.3 Electro-Oxidation Effects

Besides electrocoagulation, electro-oxidation can also be used for wastewater treatment. In fact, these two processes cannot be totally separated from each other and co-exist in the treatment processes. Electro-oxidation occurs either by direct oxidation by hydroxyl radicals produced on the anode's surface or by an indirect process where oxidants like

chlorine, hypochlorous acid, hypochlorite, or hydrogen peroxide/ozone are formed at electrodes by following reactions:



Several electrodes have been used for water and wastewater treatment by electro-oxidation. Traditionally anodes used for water and wastewater treatment include lead and lead dioxide electrode, dimensionally stable anode (DSA) electrode, graphite and boron-doped diamond (BDD) electrode. Lead and lead dioxide electrode has the advantages such as high stability, low cost, and high oxygen evolution potential which delays O₂ evolution and favors Cl₂ evolution. During electrocoagulation, although metal electrodes are used, above mentioned direct and indirect oxidation can occur spontaneously. Wastewater is therefore oxidized by both direct anodic oxidation (by means of radicals such as OH• and O•) and indirect electro-oxidation via mediators (i.e., hydrogen peroxide). The production of oxidants such as hydroxyl radicals, peroxy radicals and ozone from the electrodes increases with increased current densities.

Chloride ion oxidation and subsequent hydrolysis of the produced chlorine yields hypochlorous acid or the hypochlorite ion. This process is dependent on the solution pH. The chlorine and hypochlorite oxidize the pollutants and are thus reduced to chloride ion. It has been reported that both organic pollutants and NH₄⁺ can be destroyed electrochemically if the landfill leachate contains chloride concentration larger than 3000 mg/L. The formed oxidant oxidizes ammonium nitrogen to N₂:



Hydroxyl radicals or other reactive species also participate in the electrochemical oxidation of organics. It should be noted that direct oxidation of organic compounds at the anode is also possible.

5.4 Ammonia Stripping

Ammonia removal from leachate is usually achieved with several physicochemical processes including air stripping, precipitation as magnesium ammonium phosphate (or struvite) precipitate, photochemical and electrochemical processes, ion-exchange, membrane processes, and chemical oxidation and adsorption. While many of these are still applied research, stripping have been successfully implemented. Especially, air stripping process has been successfully implemented to remove ammonia from different ammonia-rich streams including landfill leachate. During electrocoagulation, due to the hydrogen production in the cathode, ammonia stripping is possible in this region. Temperature, air flow rate and pH are the major impact factors on the removal of ammonia from the leachate. Ammonia stripping can remove up to 95% of ammonium and 90% of total nitrogen. High pH has the most significant effect on stripping, leading to changes in ammonia/ammonium ratios, favorably for ammonia stripping. For ammonia stripping by electrocoagulation in the cathode, pH adjustment may be required in order to enhance the ammonia stripping performance.

5.5 Cost Analysis

The results of this research indicated the multi-functional reactor can be combined with electrocoagulation for the treatment of landfill leachate. Different operating conditions were required for each contaminant to be removed, and the performances varied depending on the operation conditions. By electrocoagulation with aluminum electrode, the multifunctional with the corresponding fiber filter and biofilter could remove 94% COD, 96% iron and 86% phosphorus. With iron electrode, 84% COD, 87% arsenic and 88% phosphorus can be removed.

Significant reduction in the residual concentrations of the odor- and color-causing contaminants, and suspended solids was also achieved in all these treatment processes.

Results of this study suggested that electrocoagulation was effective and economic when incorporated into the multi-functional reactor for decontaminating highly concentrated landfill leachate. It should be noted that COD and other contaminant removal was relatively sensitive to electrocoagulation time. Therefore, the major costs of the electrocoagulation were the electricity costs. Compared to conventional coagulation, chemical costs can be saved. In addition, compared to traditional biological system, this treatment produced less sludge and sludge handling costs can thus be saved. The combined different stages of fiber filtration can also be configured depending on the treatment requirements by adding or deleting series of suspended fiber filters or biofilters. The infrastructure costs could therefore be adjusted. The cost analysis is summarized in Table 2. Although the electricity costs and infrastructure costs are associated with the proposed treatment system proposed by this research, i.e., the multifunctional reactor with combined electrocoagulation for the treatment of landfill leachate, this treatment system has obvious advantages, including on-site treatment availability and low sludge production.

Table 2. Treatment Cost Comparison with Traditional Biological Leachate Treatment

| | Multifunctional Reactor with Electrocoagulation | Biological Treatment | Treatment Cost Saving |
|--------------------|---|----------------------|---------------------------------|
| Sludge Production | Low | High | Around 50% for Sludge Treatment |
| Electricity Costs | Medium | High (Aeration) | Decreased Electricity Costs |
| Space Requirements | Low | High | Reduced Infrastructure Costs |

6. Conclusions

In Northwest Florida, besides high organic contents, iron and arsenic are also of great concerns. Especially, high concentrations of iron are commonly detected in landfill leachate owing to changes in pH and redox conditions resulted from organic decomposition. Arsenic release has been proven to be from unlined construction and demolition debris (C&D) landfills. Currently, elevated concentrations of arsenic have also been detected in the leachate from lined landfills. In our first year's study, we have designed and tested the multifunctional energy- and space-saving reactor for the removal of ammonium, chloride and iron from landfill leachate. This multifunctional reactor integrates physicochemical reactions and separation operations in one apparatus. In this year, we integrated electrocoagulation into the reactor for arsenic removal. Removal mechanisms of the electrocoagulation process include coagulation, adsorption, precipitation, and flotation. Comparing with treatment of conventional coagulation, electrocoagulation treatment also demonstrates the capacity of COD and suspended solid removal. When electrocoagulation is used for landfill leachate treatment, ionization, electrolysis, hydrolysis, and free-radical formation also exist, which can alter the physical and chemical properties of the landfill leachate as landfill leachate moves through the applied electric field. As a result, the reactive and excited state causes contaminants to be more easily removed from the leachate. The integration of reaction and separation within the multifunctional reactor offers the possibility to tailor the concentration profiles inside the reactor to achieve a better process performance.

In this research, the multifunctional reactor with the incorporated electrocoagulation achieved 94% of COD, 96% of iron, and 86% of phosphorus removal using aluminum electrode and 84% of COD, 87% of arsenic, and 88% of phosphorus removal using iron electrode. Different operating conditions were required for each contaminant to be removed efficiently by the multi-functional reactor when combined with electrocoagulation for the treatment of landfill leachate. Significant reduction in the residual concentrations of the odor- and color-causing contaminants, and suspended solids was also achieved. Results of this study suggested that the multifunctional reactor

could be an effective and economic treatment method for the onsite treatment of landfill leachate when combined with electrocoagulation. Because of the low external power requirements for the electrocoagulation, this treatment was low-cost and effective. In addition, removal of each contaminant by this treatment system was robust against the landfill leachate characteristics as well as system operation conditions, including the electrode type, pH, and electrocoagulation time, etc. During electrocoagulation, the micro-particles that could not be settled by gravity was removed by the first stage of fiber filtration. Owing to the significant surface areas of the fiber, these micro-sized particles could be easily removed. Organic contaminants in the leachate was removed through biodegradation by the second stage of fiber biofiltration after the electrocoagulation. Oxidation by radicals and oxidants formed during electrocoagulation also contributed to the destruction and oxidation of organics besides organic degradation in the fiber biofiltration. This multifunctional reactor treatment system makes the onsite leachate treatment possible, reducing the current high costs of off-site leachate disposal means such as transporting landfill leachate via tanker trucks to local wastewater treatment plants.

7. Recommendation

For the treatment of landfill leachate using the multifunctional reactor with integrated electrocoagulation, different strategies are recommended for different contaminant removal. Based on the experimental observations, the following recommendations are made:

Organic Removal:

Electrode: Aluminum

Current Density: 0.03 – 0.05 A/m²

Stage I Fiber Filtration + Stage II Fiber Biofiltration

Hydraulic Loading < 1.0 m³/m²/hr

Arsenic Removal:

Electrode: Iron

Current Density: 0.03 – 0.05 A/m²

Hydraulic Loading < 1.0 m³/m²/hr

Iron Removal:

Electrode: Aluminum

Current Density: 0.05 A/m²

Stage I Fiber Filtration + Stage II Fiber Biofiltration

Hydraulic Loading < 1.0 m³/m²/hr

Phosphorous Removal:

Electrode: Aluminum

Current Density: 0.05 A/m²

pH ~ 7

Stage I Fiber Filtration + Stage II Fiber Biofiltration

Hydraulic Loading < 1.0 m³/m²/hr

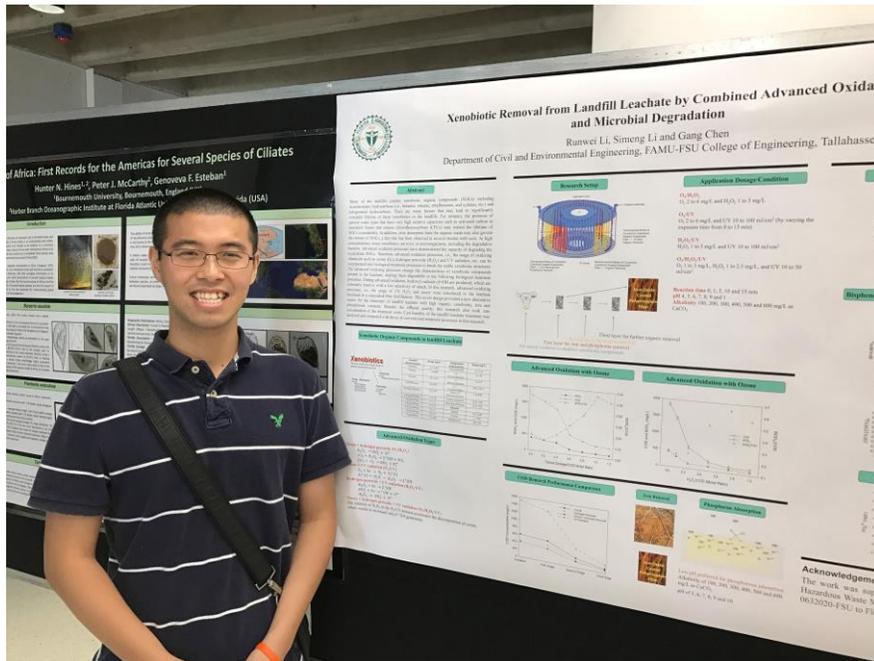
8. Future Work

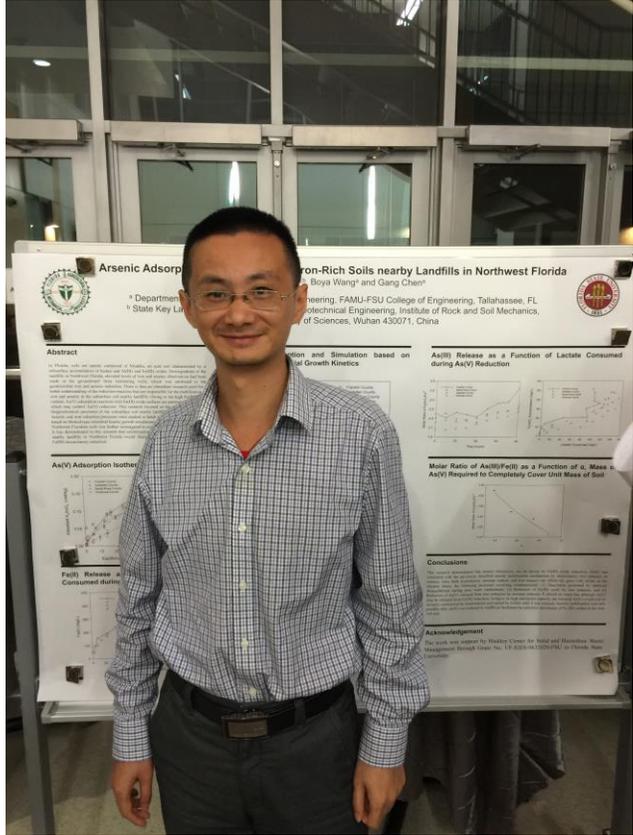
Organic contamination is the major concern of landfill leachate. For most cases, volatile organic compounds (VOCs) can be easily degraded. However, nonvolatile organic compounds including aromatic compounds are recalcitrant to be decomposed. Besides organic compounds, heavy metals and nutrients are also attracting more and more attention. Onsite leachate treatment is currently being investigated 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. The adsorption process can be used as a stage of integrated chemical-physical-biological process for landfill leachate treatment, or simultaneously with a biological process. The most frequently used adsorbent is granular or powdered activated carbon. It has been demonstrated that carbon adsorption permits 50–70% removal of both COD and ammonia nitrogen. We are interested in the usage of activated carbon to (i) remove toxic heavy metals and/or organics i.e., AOXs, PCB by adsorption, and (ii) support microorganisms as porous media. We will also test other materials, including zeolite, vermiculite, illite, kaolinite, activated alumina, and municipal waste incinerator bottom ash as sorbents or supporting media for leachate treatment.

Electrochemical treatment such as membrane electro-dialysis has also contributed to the electro-degradation of stabilized landfill leachate. Prior research has demonstrated that 73% and 49% COD and NH₃-N with initial concentrations of 1855 and 1060 mg/L can be removed. The results suggest that electro-degradation is an alternative means to breakdown recalcitrant organic compounds in the landfill leachate. We thus also have interest in examining landfill leachate treatment by membrane electro-dialysis.

9. Student Training

Two graduate students, Runwei Li and Boya Wang were trained in this project. Both of them are currently pursuing their Ph.D. in our laboratory. They were very active and productive in their research. So far, they have published several 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 at national conferences. A postdoctoral research associate, Houzhen Wei was also trained in this project. He joined our research group in August 2015 and was involved in this research ever since. The following images were taken when Runwei Li and Houzhen Wei presented their work at Florida Branch ASM 2016 Annual Meeting in Miami, FL in October 2016 and 101th Annual American Society of Microbiology Southeastern Branch Conference in Kennesaw, GA in November 2015.





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10.1 Peer-Reviewed Journal Paper Publication:

1. Chen, G., P. Grasel, G. Millington, J. Hallas, H. Ahmad and K. Tawfiq, 2016, Chloride removal from landfill leachate by the ultra-high lime with aluminum process. *Journal of Urban and Environmental Engineering*, under review.
2. Xue, H., W. Xie, H. Ahmad, K. Tawfiq and G. Chen, 2016, Arsenic adsorption and reduction in iron-rich soils nearby landfills in northwest Florida, *Journal of Urban and Environmental Engineering*, 10, 98-105.

10.2 Conference Presentation:

1. Li, R., Wang, B. and Chen, G. "Arsenic and Phosphorous Removal from Landfill Leachate by Biofiltration". 2016 Florida Branch Meeting, American Society for Microbiology Florida Branch, Miami, FL. Oct. 14-16, 2016.

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