

STABILIZED LANDFILL LEACHATE TREATMENT USING PHYSICO-CHEMICAL
TREATMENT PROCESSES: COAGULATION, ANION EXCHANGE, OZONATION,
MEMBRANE FILTRATION, AND ADSORPTION

By

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To my parents
who sacrificed their present for my future

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Leachate is generated by the percolation of rainwater through the layers of wastes in a landfill. A combination of several physical, chemical, and microbial processes in the landfill results in contaminants being transferred from the waste to the leachate. Several wastewater treatment processes have been studied to effectively treat contaminants in leachate. Reliability, simplicity, and cost efficiency make biological treatment the most commonly used leachate treatment method. However, these methods are not very effective in treating leachate containing less biodegradable organics drawn out from stabilized landfills. Physico-chemical treatment methods have been found more effective in treating such leachate; however, studies on leachate treatment by physico-chemical treatment methods suggest that use of a single treatment or a combination of more than one treatment process often does not produce effluent water that meets water quality standards for direct discharge to groundwater or surface water.

Among the physico-chemical processes, membrane filtration technologies, especially reverse osmosis (RO), has been found effective in removing the contaminants from leachate to meet effluent discharge regulations; however, increased

fouling of these membranes due to the presence of high concentrations of organic matter and salts reduces the cost effectiveness of these systems. Reducing the concentration of leachate organic matter prior to membrane treatment was hypothesized to reduce the fouling frequency of membranes. The objective of this doctoral research was to evaluate the effectiveness of coagulation, anion exchange and ozonation as a pretreatment option for treating stabilized leachate using high pressure nano-filtration (NF) and reverse osmosis (RO) membranes. Additionally, adsorption of organic matter using activated carbon (AC) has been traditionally used in water and wastewater treatment; however, the selectivity of AC based on their pore sizes (micro-porous and meso-porous) for leachate treatment has never been investigated. Part of this study therefore focused the organic matter adsorption profile of three different ACs for stabilized leachate treatment.

A maximum of 70%, 34%, and 23% reduction in DOC was observed after Fe (III), MIEX, and ozone treatment, respectively. Coagulation (Fe (III)), magnetic ion exchange resin (MIEX), and ozonation effectively removed humic and fulvic-like organic matter from stabilized leachate; more than 60% removal was observed for these types of organic matter. However, these pretreatments did not improve in the permeate flux of NF and RO membranes as compared to raw leachate treatments. In the coagulation and MIEX pretreated leachate, the pH of the feed leachate increased throughout the experiment. This was suspected to have caused excessive precipitation of carbonate minerals as compared to the raw leachate treatment on the membrane surface, causing a greater decline in permeate flux. During the membrane treatment of ozone pretreated leachate, the divalent ions present in the ozonated leachate are hypothesized to have

coagulated with the by-products formed during ozonation, with these coagulated solids then precipitating on the membrane surface, leading to a greater permeate flux decline as compared to the raw leachate treatment. The adsorption study showed that the micro and meso-porous AC had similar organic matter adsorption capacity (0.2 g TOC/g AC) during stabilized leachate treatment with faster organic matter diffusion in meso-porous AC. A maximum of 80% TOC was removed from both types of AC.

CHAPTER 1 INTRODUCTION

1.1 Background and Problem Statement

Economic advantages of landfills still make them the most accepted method for ultimate disposal of municipal and industrial solid waste (Renou et al., 2008). However, landfills face a major challenge of managing leachate generated by the percolation of rainwater through the layers of waste. A combination of several physical, chemical, and microbial processes in the waste results in contaminants from the waste being transferred to the leachate. Improper management of leachate can potentially contaminate the surface and groundwater bodies (Christensen et al., 2001; Cossu et al., 2003; Eggen et al., 2010). Hence, leachate treatment is an essential part of effective landfill management process.

The characteristics of leachate are very heterogeneous and typically contain high concentrations of organic matter, salts, ammonia, and toxic trace components. A variety of parameters such as age, landfill operation method, moisture availability, waste composition, and climate, control the concentration of contaminants in the leachate. In particular, the composition of leachate varies greatly depending upon the age of a landfill and can be characterized as young, intermediate, and stabilized leachate (Kjeldsen et al., 2002). Generally, young leachate contains higher concentrations of organic and inorganic contaminants, which gradually decreases in the subsequent years (Statum et al., 2004). As the landfill grows old, the concentration of biodegradable organic matter (Biochemical Oxygen Demand (BOD₅)) may approach zero with leachate containing mostly refractory organic matter (Chemical Oxygen

Demand (COD)); leachate with $BOD_5/COD < 0.1$, is traditionally termed as 'stabilized leachate' (Reinhart and Grosh, 1998).

Traditional landfill leachate treatment methods can be classified into three major categories: (a) leachate transfer, which includes leachate recirculation into the landfill, or hauling the leachate to domestic wastewater treatment plant, (b) biological treatment using aerobic and anaerobic processes, and (c) physico-chemical treatment methods such as chemical oxidation, coagulation-flocculation, adsorption, chemical precipitation, air stripping, and membrane filtration. Each leachate treatment method has its own advantages and disadvantages.

The controlled leachate recirculation has been largely used in the past decade and has shown advantages in terms of faster waste stabilization and decrease in COD of leachate, however, a very limited data are available about the quality of long-term recirculated leachate (Rodriguez et al., 2004). Additionally, leachate recirculation cannot be continued throughout the life of a landfill; leachate needs to be removed from the landfill and treated, to dry the waste in the landfill. Leachate mixing with domestic wastewater has also been used, but the presence of organic inhibitory compounds with low biodegradability and heavy metals reduces the treatment efficiency of the wastewater treatment plant (Cecen and Aktas, 2004).

Reliability, simplicity, and cost efficiency make biological treatment the most commonly used leachate treatment method (Li et al., 2007). Biological treatment methods effectively remove the high biodegradable organic concentration of the leachate generated from young landfills when the BOD_5/COD ratio has a high value

(>0.5) (Renou et al., 2008). However, the major presence of refractory organic matter in the stabilized leachate tends to limit the effectiveness of these processes.

Leachate generated from stabilized landfills is typically characterized by COD in the range of 500 to 5000 mg/L, pH ranging from 7.5 to 8.5, a low biodegradability, and a significant amount of high molecular weight organic compounds (Rivas et al., 2004). Physico-chemical treatment methods have been found useful for treating leachate-containing refractory soluble organics (humic and fulvic-like compounds) or as a polishing step for biologically treated leachate (Alvarez-Vazquez et al., 2004; Kurniawan et al., 2006). These physico-chemical methods have been used individually or in combination with other methods at various landfill sites (Chianese et al., 1999; Trebouet et al., 2001; Tatsi et al., 2003; Monze-Ramirez and Velasquez, 2004; Kurniawan et al., 2006; Maranon et al., 2009).

Studies on leachate treatment by physico-chemical treatment methods suggest that use of a single treatment methodology does not produce effluent water that meets water quality standards for direct discharge to groundwater or surface water (Renou et al., 2008). Treatment of stabilized leachate with a combination of biological and physico-chemical methods may provide efficient removal of contaminants but often does not meet the stringent regulations required to discharge the treated water (Rivas et al., 2003, 2004; Monje-Ramirez and Velasquez, 2004; Ntampou et al., 2006; Kurniawan et al., 2006). For an instance, Rivas et al. (2003, 2004) obtained COD removal in the range of 80 to 96% for an initial COD value of 11,000 mg/L from stabilized leachate by using various combinations of pH shift, ozonation, coagulation-flocculation, oxidation, and adsorption by activated carbon, but none of the tested processes reduced the COD

levels enough that the effluent could be directly discharged. However, membrane filtration technologies such as nano-filtration (NF) and reverse osmosis (RO) have been studied individually and in combination with other treatment methods by various researchers and have been found effective in removing the contaminants from the leachate to meet effluent discharge regulations (Baumgarten and Seyfried, 1996; Peters, 1998; Bohdziewicz et al., 2001; Tabet et al., 2002; Palma et al., 2002; Thorneby et al., 2003).

Although use of membrane filtration systems such as NF and RO has been found effective for treating landfill leachate, these systems may not provide a cost-effective treatment (Trebouet et al., 2001; Kurniawan et al., 2006). Heavy loading of particulate matter as well as the organic and inorganic compounds typically found in leachate, tend to accumulate on the membrane surface and clog the pores of membranes, a process known as *fouling* (Pearce, 2007). Most of the natural organic matter (NOM) components have been considered as a major membrane fouling agents. In particular, the compounds of low diffusion coefficients such as humic and fulvic-like organic matter, which are hydrophobic in nature, have high fouling potential (Hong and Elimelech, 1997; Tang et al. 2007, Bruggen et al., 2008; Huang et al., 2009; Wang et al., 2011). At high divalent ion concentrations, the electrostatic repulsion between negatively charged humic and fulvic-like organic matter and the membrane surfaces reduces. The decreased repulsion of these compounds with the membrane surfaces lead to increased deposition of these compounds on the membrane surface. This causes increased fouling of the membrane (Yuan and Zydney, 2000; Tang et al. 2007). Additionally, other NOM such as organic macro molecules polysaccharides, proteins,

and their colloids may alter the pore structures through the pore blocking, pore narrowing, and cake layer formation, resulting in decrease in membrane permeability (Hermia et al., 1982; Huang et al., 2008). Feed water containing higher concentrations of polysaccharide and protein- like organic matter as compared to humic and fulvic-like organic matter may thus exhibit more pronounced fouling (Kwon et al. 2006; Lee and Lee, 2007; Amy, 2008).

Fouling severely limits the filtration efficiency of membranes and causes flux decline, a decrease in permeate quality, gradual membrane degradation, and increased operational costs of the treatment system. However, pretreatment of leachate that can reduce the concentrations of humic and fulvic-like organic matter can be helpful in reducing the concentration of foulant on the membrane surfaces and thereby in preventing frequent fouling and flux decline, which in turn may increase the life of the membranes (Shon et al., 2004; Xu et al., 2006; Agenson and Urase, 2007; Herzberg and Elimelech, 2007).

Several studies have been conducted for the leachate treatment using membrane systems; however, the studies were generally focused on improving the rejection of contaminants from the leachate by changing the membrane configuration, membrane surface properties and membrane cleaning regime (Peters, 1998; Palma et al., 2002; Ushikoshi et al., 2002; Thorneby et al., 2003). The studies conducted with the pretreatment methods were also generally focused on improving the treatment performance in terms of contaminants rejection (Linde et al., 1995; Bohdziewicz et al., 2001; Ahn et al., 2002; Li et al., 2007). Very few studies were conducted on evaluating pretreatment methods for reducing the fouling of commonly used membranes while

treating landfill leachate (Baumgarten and Seyfried, 1996; Trebouet et al., 2001; Meier et al., 2002; Liu et al., 2008). Among the pre-treatment methods studied, biological pre-treatment methods were often found ineffective with the membranes; hence, this research was conducted to evaluate the performance of cost effective commonly used physico-chemical methods (coagulation, anion exchange, and ozonation) as pretreatment options to treat stabilized leachate using RO and NF membranes.

Traditionally, these processes have been found effective in removing or transforming the humic and fulvic-like organic matter from the aqueous matrix. Coagulants remove organic matter by charge stabilization process (Fettig et al., 1996; Amokrane et al., 1997; Tatsi et al., 2003; Ntampou et al., 2006). When coagulant is added to the aqueous matrix, the negatively charged organic molecules bind or adsorb on the positively charged hydroxides and precipitate as shown in Figure 1-1 (a). Anion exchange resins replace their anions by preferential binding with negatively charged organic molecule as shown in Figure 1-1 (b) (Fearing et al., 2004; Allpike et al., 2005; Boyer and Singer, 2005; Humbert et al., 2005; Boyer and Singer, 2006). Ozone breaks the unsaturated and aromatic structures present as part of this organic matter into smaller aliphatic organic matter as shown in Figure 1-1 (c) and reduces the concentration of humic and fulvic-like organic matter (Rivas et al., 2003;; Bila et al., 2005; Tizaoui et al, 2007). Reduced concentrations of these organic matter reduces the fouling potential of membranes (Amokrane et al., 1997; Bila et al., 2005; Humbert et al., 2005; Ntampou et al., 2006; Tizaoui et al, 2007). Figures 1-1(a, b, and c) are also presented individually in more detail in later chapters.

Additionally, the literature suggests that activated carbon (AC) is an effective method to remove high molecular weight organic matter from the aqueous solution, but very few studies can be found on the use of AC for landfill leachate treatment. In the leachate treatments, AC has been generally studied in combination with other treatment methods, but a detailed study that determined the adsorption profile of organic matter removal using AC from the stabilized leachate, which helps in designing an AC treatment system has not been reported (Fettig et al., 1996; Kurniawan et al., 2006). These studies have always used micro-porous AC (pore size < 2nm), whereas stabilized leachate contain high molecular weight and size organic matter, which may reduce the adsorption efficiency of AC due to pore blockage. A detailed study on the use of different types of AC based on their pore sizes for stabilized leachate treatment has not been found.

1.2 Research Objectives

Stabilized landfill leachate contains higher amounts of biologically refractory organic matter and the literature suggests that the use of physico-chemical treatment methods such as coagulation, anion exchange, ozonation, and adsorption by activated carbon can reduce the concentration of heavier organics in leachate, thereby should reduce the frequency of fouling of membranes. The objectives of this doctoral research were to explore the effectiveness of coagulation, anion exchange, and ozonation for reducing the fouling of NF and RO membranes while treating stabilized landfill leachate and to study the selectivity of AC based on their pore sizes for treating stabilized landfill leachate.

More specifically, an objective of the first study was to evaluate the efficiency of Fe (III) salt (coagulant) and MIEX (anion exchange) as a pretreatment option for treating

stabilized landfill leachate using NF and RO membranes. In the coagulation process, the hydrolysis products of the positively charged coagulant react with the negatively charged high molecular weight organic matter and precipitates. Iron salt has been found better for performing coagulation for leachate treatment, however, there is no perfect correlation obtained between the coagulant dose and the treatment efficiency. Additionally, the anion exchange resin in particular, magnetic ion exchange (MIEX) has shown greater potential as an alternative to coagulation process for the removal of high molecular weight organic matter and removes a wider range of organics than coagulation (Boyer and Singer, 2006). This study is an important contribution to evaluate the efficiency of Fe(III) coagulant and MIEX for treating stabilized leachate using membranes.

The objective of the second study was to investigate the effectiveness of ozone (oxidation process) as a pretreatment for stabilized landfill leachate treatment using NF and RO membranes. Ozone has a high oxidation potential and high reactivity with the humic and fulvic-like organic matter. It transforms these recalcitrant organic matters into more biodegradable form, or even oxidizes them to carbon dioxide (Monze-Ramirez and Velasquez, 2004). Additionally, ozone has been shown to reduce the fouling of micro-filtration and ultra-filtration membranes (Lee et al., 2005; Kim et al., 2008). However, very little or no information is available on using ozone as a pretreatment option while treating stabilized landfill leachate using NF and RO membranes.

Adsorption on to AC has been reported as an effective method for the removal of high molecular weight refractory organic matter from aqueous solution. AC has been seldom used for landfill leachate treatment, either as a single treatment step or in

combination with other treatment options. In addition to the availability of very few studies on the use of AC for leachate treatment, more rigorous studies in terms of adsorption isotherm determination and diffusion of organic matter onto AC, which are the primary factors to design and optimize a full-scale or pilot-scale AC treatment system has been rarely found. The specific objective of the third study was to determine the effectiveness of organic matter adsorption on to three ACs selected based on their pore sizes for treating stabilized landfill leachate.

1.3 Research Approach

Laboratory scale experiments were conducted to achieve the objectives described in section 1.2.

Objective 1. To evaluate the efficiency of Fe (III) (coagulant) and MIEX (anion exchange) as a pretreatment option for treating stabilized landfill leachate using NF and RO membrane systems.

Approach. Leachate samples were collected from three different landfills. Leachate characteristics were determined based on their dissolved organic carbon (DOC), ultra violet-254 (UV-254) absorbance, and florescence excitation emission matrix (EEM). Batch experiments of coagulation and anion exchange process were conducted and the treatment efficiency was evaluated for various doses. The optimum coagulant and MIEX doses were determined to run fouling experiments using one NF and one RO membranes each in unadjusted pH conditions. Permeate flux and permeate quality were also analyzed.

Objective 2. To investigate the effectiveness of ozonation as a pretreatment for treating stabilized landfill leachate using RO and NF membranes.

Approach. Leachate from three different landfills was collected. The characteristics of leachate were determined and laboratory-scale experiments were conducted in two-phases. At first, leachate was treated with a fixed dose of ozone for variable durations and optimum ozonation duration was determined in terms of removal of DOC, UV-254 absorbance, and different types of organic matter derived from EEM. In the second-phase, the ozonated leachate was tested for the time-dependent permeate flux and the permeate quality. The permeate flux data was used to determine the type of fouling occurred during membrane treatment using Hermia's constant pressure, cross flow filtration model (Hermia, 1982).

Objective 3. To determine the equilibrium adsorption and intra-particle diffusion of organic matter into micro and meso-porous AC while treating stabilized landfill leachate.

Approach. Three commercial AC; one micro-porous and two-meso porous were selected for treating leachate collected from a stabilized landfill. Isotherm and diffusivity experiments were performed to determine the isotherm profile, the adsorption capacity, the rate limiting adsorption process, and the rate of organic matter diffusion onto AC. Rapid small scale column tests (RSSCT) were conducted to determine the amount and the type of organic matter removed using these three AC for leachate treatment.

1.4 Outline of Dissertation

This dissertation is divided into five Chapters. Chapter 1 introduces the research, the problem statement, the research objectives, and the approach followed to achieve specific objectives. Chapters 2 to 4 are classified into three stand alone manuscripts. Chapter 2 describes the efficiency of Fe (III) (coagulant) and MIEX (anion exchange) as a pretreatment option for treating stabilized landfill leachate using NF and RO

membrane systems. Chapter 3 evaluates the use of ozone as a pretreatment option for treating stabilized landfill leachate using NF and RO membrane systems. Chapter 4 describes the effectiveness of AC for treating stabilized landfill leachate. Chapter 5 provides summary, conclusions, and recommendations for future work. The references cited are listed at the end of dissertation.

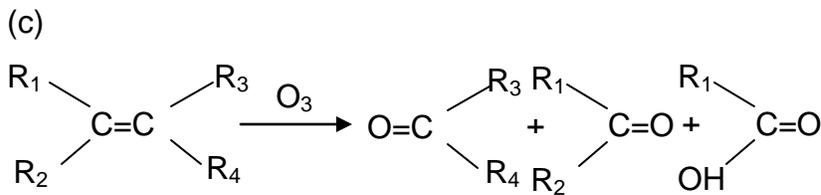
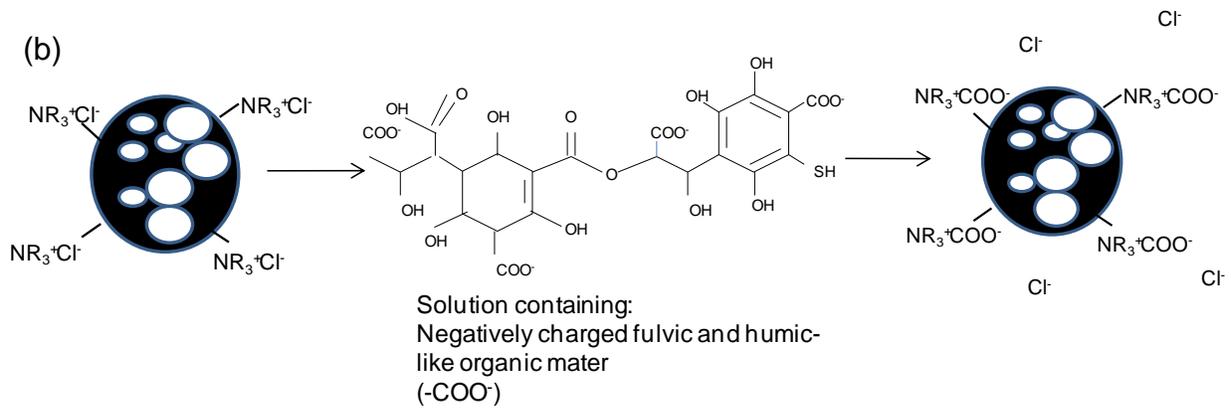
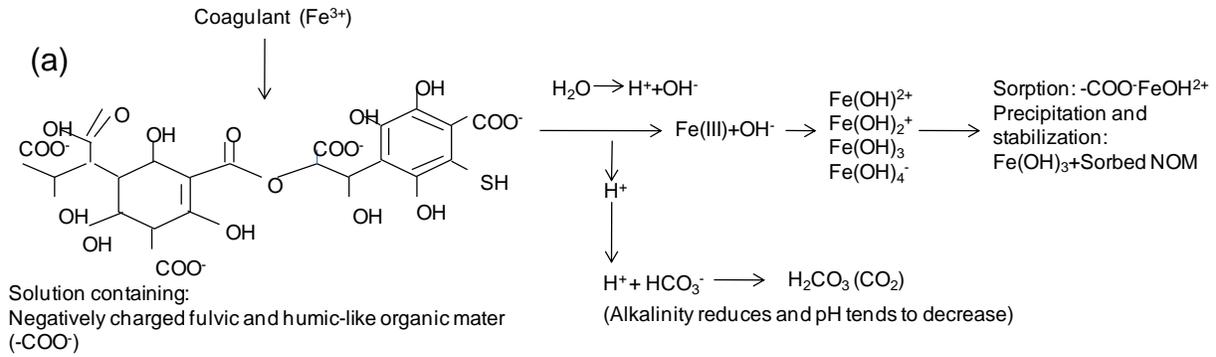


Figure 1-1. (a) Reaction that hydrolysis products of coagulants follow when coagulant is added to water containing natural organic matter. (b) MIEX resin anion exchange process. (c) Model reaction of ozonation of unsaturated organic compound

CHAPTER 2
EVALUATION OF COAGULATION AND ANION EXCHANGE AS A PRETREATMENT
FOR STABILIZED LANDFILL LEACHATE TREATMENT USING HIGH PRESSURE
MEMBRANES

2.1 Introduction

The percolation of rainwater through the layers of degraded waste in the landfill generates high strength contaminated wastewater referred as leachate. A combination of several physical, chemical, and microbial processes in the waste results in contaminants from the waste being transferred to the leachate, which makes leachate potential contaminant source to the surface and groundwater bodies (Christensen et al., 2001). Despite the fact that the modern landfill designs minimize leachate generation by reducing the influx of moisture; landfills still face a major challenge of efficient management or treatment of leachate.

The heterogeneous nature of leachate composition that varies with age, landfill operation method, moisture availability, waste composition, and climate, makes the selection of leachate treatment process even more difficult. In particular, composition of leachate varies greatly on the age of the landfill and can be characterized as young, intermediate, and stabilized leachate (Kjeldsen et al., 2002). Young leachate generally contains high concentrations of inorganic and biodegradable organic contaminants and biological methods have been found effective for its treatment. However, as the landfill grows old, the concentration of BOD₅ reduces and leachate contains mostly refractory organic matter making biological treatment methods less effective. When the leachate has BOD₅/COD<0.1, it is termed as stabilized leachate; the physico-chemical treatment methods such as coagulation flocculation, chemical oxidation, adsorption, and

membrane systems are more effective than biological treatment for such leachate (Renou et al., 2008).

Treatment of stabilized leachate with one or combination of more than one biological or physico-chemical treatment methods often does not meet the stringent regulations required to discharge the treated water (Monje-Ramirez and Velasquez, 2004; Kurniawan et al., 2006; Ntampou et al., 2006). However, the membrane filtrations technologies especially reverse osmosis (RO) has been found effective in removing the contaminants from the leachate to meet effluent discharge regulations (Peters, 1998; Palma et al., 2002; Tabet et al., 2002).

A common issue with the membrane systems when treating landfill leachate is the fouling by organic matter and salts present in leachate, which limit the filtration efficiency and cause flux decline. Fouling of membranes is generally influenced by the composition of feed water, concentration of constituents (hydrophilic and hydrophobic organic matter), water chemistry (pH and divalent ion concentration), hydrodynamic conditions (permeate flux and cross-flow velocity), and membrane surface properties (hydrophobicity, surface morphology, and charge) (Li and Elimelech, 2004; Xu, 2006). Several researchers have shown that the high molecular weight humic and fulvic-like organics (natural organic matter (NOM)) present in the feed water may adsorb on the hydrophobic membrane surfaces and increase the fouling (Jucker and Clark, 1994; Nilson and DiGiano, 1996). Stabilized leachate contains higher concentrations of these types of organic matter; hence their reduction from stabilized leachate prior to membrane treatment can provide a substantial increase in membrane performance (Huang et al., 2009).

Coagulation with inorganic salts (Fe (III) and Al (III)) has been used to remove dissolved organic matter (DOM) from leachate and has shown 50 to 75% COD removal from stabilized leachate (Amokrane et al., 1997; Tatsi et al., 2003). When the inorganic coagulants are dissolved in water they form a series of intermediate hydrolysis products and the negatively charged organic molecules present in solution may bind or adsorb with the precipitating hydrolysis products as shown in Figure 2-1 (Letterman et al., 1999). The coagulation process is highly dependent on the pH of the solution and a typical profile of coagulation dose on the pH and organic matter removal efficiency is explained in Appendix-A, using the results of present study.

A considerable amount of studies have been conducted on leachate treatment using coagulant as shown in Table 2-1. Generally, iron and aluminum salts have been used as coagulant for leachate treatment and iron salt has been found a better performing coagulant. These studies were mainly focused on the effect of different operating variables such as coagulant dose and pH on the treatment efficiency achieved in terms of COD; however, there is no perfect correlation obtained between coagulant dose and treatment efficiency (Amokrane et al., 1997; Yoon et al., 1998; Wang et al., 2002; Tatsi et al., 2003). For instance, Amokrane et al. (1998) obtained a maximum of 55% COD removal at a dose of 2 g/L Fe (III), whereas Wang et al. (2002) obtained 80% COD removal efficiency at a dose of 1.5 g/L Fe (III) salt for leachate containing slightly higher COD than the leachate used by Amokrane et al. (1998). Comstock et al. (2010) studied the use of sulfate salt of Fe (III) for treatment of stabilized leachate collected from different landfills and observed a considerably wide range of DOC removal due to the specific characteristics of each leachate. They also

concluded that the coagulation process for leachate treatment should be selected based on the specific UV absorbance of leachate, instead of ratio of BOD₅ and COD (Comstock et al., 2010).

Few studies have been conducted using coagulant as a pretreatment option for leachate treatment using membranes; such as, Amokrane et al. (1997) used a Fe (III) coagulant along with lime and hydrogen peroxide oxidant and found that treated leachate had lower fouling potential than raw leachate for reverse osmosis (RO) membranes. Yoon et al. (1998) have reported a 59 to 73% removal of larger organic matter (MW>500) that are mostly responsible for organic fouling of membranes; hence, coagulation can be used as a pretreatment option for reducing the fouling frequency of membranes. However, a comprehensive study on the effectiveness of coagulation as a pretreatment option for treating stabilized leachate using high pressure membranes NF and RO have not been reported.

Magnetic ion exchange resin (MIEX) has also been found to have a greater potential to remove DOC and UV absorbing compounds and remove wider range of molecular weight and aromaticity of organic matter than coagulants, such that MIEX can effectively remove organic matter of molecular weight > 1000 Da and water with low SUVA values (<2) (Fearing et al., 2004; Allpike et al., 2005). However, coagulants selectively remove high molecular weight (>5000 Da) and aromatic rich organic matter (SUVA>2) (Edzwald and Tobiason, 1999; Fearing et al., 2004; Allpike et al., 2005; Humbert et al., 2005; Boyer and Singer, 2005; Boyer and Singer, 2006). MIEX has macro-porous structure, strong base functional group, polyacrylic matrix in chloride form and is used in completely mixed reactor in contrast to traditional ion exchange resin. It

has also been tested as a pretreatment option to reduce fouling of low pressure membranes for low DOC water (Fabris et al., 2007). However, its application for the landfill leachate treatment has been very limited. The stabilized leachate contains higher portion of negatively charged humic and fulvic-like organic material (Baker and Curry, 2004) and MIEX resin shows preferential removal of UV-absorbing compounds, which are represented by the humic and fulvic-like organic matter as shown in Figure 2-2; hence, it was hypothesized that MIEX can be used as a pretreatment option to reduce organic fouling of membranes and improve the treatment performance. No studies were found on evaluation of treatment of MIEX treated leachate with high pressure NF and RO membrane systems.

The objective of this research was to evaluate the effectiveness of coagulation and anion exchange process for stabilized landfill leachate treatment and their use as a pretreatment option for treating stabilized landfill leachate using NF and RO membrane systems. Leachate samples were collected from three different landfills and were characterized based on their dissolved organic carbon (DOC), ultra-violet-254 (UV-254) absorbance, specific ultra-violet absorbance (SUVA), and fluorescence excitation emission matrix (EEM). These DOM properties were studied as an indicator parameter for providing the insight of selecting and determining efficiency of coagulation and anion exchange for stabilized leachate treatment with membranes.

2.2 Experimental Materials Methods and Analysis

2.2.1 Materials

Experiments were conducted on leachate generated from three municipal solid waste (MSW) lined landfills located in Florida, USA. Leachate samples were collected from the leachate lift stations or the leachate manholes in Nalgene containers and kept

at 4⁰C in the dark. All three landfills have been fully or partially operated as a bioreactor landfill where leachate has been injected into the waste to accelerate the rate of waste degradation. The Alachua County Southwest Landfill (ACL) has a closed lined MSW cell that has been operated as a bioreactor since 1990. Leachate samples were collected multiple times for conducting experiments in the duration from November 2009 to February 2010. The North Central Landfill (NCL) located in Polk County, Florida has two landfill cells; the first cell was closed in April 2000 after accepting waste for 11 years and the second cell was closed in 2007 after seven years accepting waste. The second cell was operated as a bioreactor landfill. The leachate samples were collected from the leachate storage tank, where leachate from both the cells is mixed. The New River Regional Landfill (NRL) located at Union county, Florida, has three cells of waste ranging in age from 5 to 15 years. The leachate samples were collected from a common manhole where leachate from all the landfill cells is drained.

Technical grade ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) purchased from Fisher Scientific was used as a coagulant for the experiments. The magnetically enhanced polyacrylic resin (MIEX) was obtained from the Orica Watercare of Watkins, CO, USA in the slurry form. Dow filmtec (Minneapolis, MN) provided flat-sheet NF-90 and BW-30 membranes for conducting membrane performance studies. Membrane filtration experiments were conducted using high-pressure-cross-flow system Osmonics SEPA CF Membrane Cell as shown in the schematic diagram (Figure 2-3).

2.2.2 Coagulation Experiment

Preliminary jar-test coagulation experiments were performed to determine the optimum coagulant dose. A bench-scale jar-testing apparatus (Phipps and Bird, Richmond, VA) equipped with six 2000 mL beakers was used to conduct the

experiments. Before starting the experiments, leachate was brought to room temperature (approximately 23⁰C). Leachate samples were thoroughly shaken for re-suspension of settled solids and 1000 mL of leachate was transferred to each jar-test beaker. All experiments were conducted in duplicate. Dry crystals of coagulant were weighed using an analytical balance (Mettler Toledo) and were added to leachate. Coagulant doses in the range of 1 to 10 g/L of ferric salt (FeCl₃.6H₂O) were used in the experiment, corresponding to 3.7 to 37.0 mmol/L of Fe(III) salt, respectively. Immediately after adding the coagulant, samples were rapidly mixed at 100 rpm for 5 minutes followed by gentle mixing for 25 minutes at 35 rpm. Finally, the flocs were allowed to settle for another 30 minutes (Trebouet et al., 2001; Tatsi et al., 2003), after which the samples were collected from the sampling port located approximately 2 cm above the bottom of beaker at the 500 mL mark. A control experiment was conducted without adding any coagulant. No pH adjustment was made during the experiment.

Previous studies have used COD, color, and turbidity as a parameter for selecting and determining the efficiency of coagulation as a leachate treatment option (Comstock, et al., 2010); however, in order to use coagulation as a pretreatment option with membranes, characterization of DOM present in leachate is important because the characteristics of DOM present in leachate directly influences the membrane treatment efficiency (Bellona et al., 2004). Each sample was analyzed for pH and DOC. To determine the chemical complexity of DOM, SUVA, and fluorescence EEM were also analyzed.

2.2.3 MIEX Experiment

Preliminary MIEX experiments were performed using a jar-test procedure to determine optimal MIEX dose and mixing time. Unless otherwise indicated, the same apparatus and procedures as used for the coagulation experiment were used.

The experiments were conducted at MIEX doses ranging from 2 to 10 mL/L. To prepare the MIEX doses, MIEX slurry was vigorously shaken and transferred to a 10 mL graduated cylinder and allowed to settle for 30 minutes. After settling, specific doses were prepared by adding or removing the resin with a glass pipette. These MIEX doses were added to the 1000 mL leachate samples using de-ionized organic free water. Immediately after adding the MIEX doses, the leachate samples were rapidly mixed at 100 rpm for 60 minutes followed by 30 minutes of settling. During the mixing period, aliquots were periodically collected (5, 10, 20, 30, 60, and 90 minutes) using a glass pipette. The samples were analyzed for pH and UV-254 absorbing organic matter. After 60 minutes of mixing followed by 30 minutes of settling, samples were analyzed for DOC, SUVA, and EEM. To determine the optimum mixing time and the MIEX dose, the results of UV-254 analysis were plotted with respect to the mixing time for all different MIEX doses.

2.2.4 Membrane Experiment

Experiments were conducted to evaluate the performance of raw and treated ACL leachate using NF and RO membranes. The ACL leachate was found hardest to treat in terms of DOC and SUVA removal by Fe (III) salt and was the most stabilized in terms of lowest BOD₅/COD; hence the membrane performance was evaluated following a conservative approach and using only ACL leachate. Membrane performance was evaluated by measuring permeate flux and rejection of DOM and salt. To conduct the

membrane experiments, approximately 8 to 10 L of ACL leachate was pretreated separately using the optimum dose of coagulant FeCl_3 and MIEX as determined by the batch experiments.

The flat-sheet membranes were cut into 14.6 cm x 9.5 cm coupons and stored as dry in the dark. These coupons were soaked in MilliQ water in the dark for 24 hours before use. The coupons were placed into the membrane cell sandwiched between a low-foulant feed spacer of thickness 0.86 mm (34 mil) and a permeate carrier of thickness 0.2 mm (7.8 mil). Feed solution was pumped using a variable speed Hydra-Cell Industrial pump from a Nalgene feed tank. The temperature of the feed tank was maintained constant ($23 \pm 1^\circ\text{C}$) using the recirculation water bath (RTE-5B, Neslab Instruments Inc.). The membrane cell was pressurized using a hydraulic hand pump (Enerpac, P142) and the pressure was maintained constant (20.7 bar) throughout each experiment. The cross-flow and the operational pressures were adjusted using the concentrate return valve and the bypass valve and were monitored by a flow meter and a pressure gauge. The flow meter and pressure gauge were connected in the concentrate line. The permeate flux was determined volumetrically by measuring the time taken to a predetermined volume of permeate generated. Concentrate and permeate were recycled to the feed tank except for the intermittently collected permeate samples for DOC and UV-254 absorbance measurement.

The physical and the operational characteristics of NF and RO membranes are presented in Table 2-2. Both the membranes are aromatic polyamides thin-film composite with zeta potential of -26.5 mV, and -5.2 mV, respectively. Pure water flux

(flux after pre-compaction) of NF and RO membranes was obtained as 1.2 ± 0.3 and 2.6 ± 0.4 m/day, respectively.

Membrane runs were conducted in two steps. First, the membranes were pre-compacted by filtering de-ionized water for 48 hours at a constant pressure of 13.8 bar (200 psi) and a cross-flow velocity of 20 cm/sec, until constant permeate flux (pure water flux) was achieved. After the pre-compaction run, the membrane system was stopped and the de-ionized water was drained out from the feed tank. Approximately 8 to 10 L of feed leachate was filtered using 0.7 μm glass-fiber filter (whatman) and added to the tank. The membrane system was restarted and operated at similar pressure and cross-flow velocity as in pre-compaction run for 24 hours. Feed pressure and cross-flow velocity were maintained constant throughout the experiment and permeate flux was measured intermittently. Feed and permeate samples were collected intermittently.

2.2.5 Analytical Methods

Water quality parameters pH, conductivity, and temperature was measured using a multi-function Orion Research instrument. Solution pH was measured with an accuracy of ± 0.02 . Temperature was measured in degrees celsius with a scale accuracy of $\pm 0.15^{\circ}\text{C}$. Conductivity was measured in mS/cm or $\mu\text{S/cm}$ depending upon the concentration of sample. Salt rejection in the membrane experiments were measured by measuring conductivity of feed and permeate.

Samples were filtered through pre-rinsed 0.45 μm nitrocellulose filter (Millipore) to measure DOC, UV-254 absorbance, and EEM. The filtered samples were stored in capped 40-mL glass vials at 4°C in the dark; samples were brought to room

temperature before analysis. DOC was measured using Tekmer TOC analyzer. UV-254 absorbance was measured using HACH DR 4000 spectrophotometer.

EEM was measured using a 1-cm quartz cell on a Hitachi F-2500 fluorescence spectrophotometer. The EEM was obtained by scanning the samples at 5 nm increments over an excitation (E_x) wavelength in the range of 200 nm to 500 nm. For each E_x wavelength, the emission (E_m) wavelengths were detected at 5 nm increments in the range of 290 nm to 550 nm. To limit the second order Rayleigh scattering, a limit of 290 nm cutoff was used for all the samples (Chen et al., 2003). The data were processed in MATLAB following the procedures by Chen et al., 2003 and Cory and Mcknight, 2005. Each time the instrument was used; the EEM of de-ionized water was analyzed and was subtracted from the EEM response of samples containing DOC to reduce the effect of scattering (Chen et al., 2003). The area under the Raman water peak (at E_x 350 nm) was calculated for de-ionized water and the intensities of the EEM response for the samples were normalized by the Raman water area; the EEM response of the samples was then normalized by the DOC concentration; and EEMs were plotted in MATLAB using the contour function. The amount of various types of DOM was quantified using Fluorescence Regional Integration (FRI) technique (Chen et al., 2003). The FRI was used to integrate the area under the EEM spectra as shown in equation 2-1.

$$V_i = \int_{E_x} \int_{E_m} I(\lambda_{Ex} \lambda_{Em}) d\lambda_{Ex} d\lambda_{Em} \quad (2-1)$$

where, V_i represents the volume under region 'i', $I(\lambda_{Ex} \lambda_{Em})$ is the fluorescence intensity at a particular Ex-Em wavelength pair, $d\lambda_{Ex}$ is the increment of Ex wavelength (5 nm) and $d\lambda_{Em}$ is the increment of Em wavelength (5 nm).

EEM were divided into five E_x - E_m regions and concentration of DOM in each region was quantified by integrated volume in each region. The E_x - E_m regions were divided based on the EEM peaks associated with specific type of organic compounds as shown in Figure 2-4. These regions were selected using the literature (Chen et al., 2003; Chen et al., 2003; Baker, 2004; Hudson, 2007). Shorter E_x (<250 nm) and shorter E_m wavelengths (<380nm) are associated with simple aromatic protein-like compounds such as tyrosine (Regions-I and Region-II). The peaks at E_x wavelengths in the range of 250 to 280 nm and E_m wavelengths <380 nm are associated with soluble microbial byproducts type compounds and are kept in Region IV. The fulvic-like compounds (Region-III) show peaks at shorter E_x wavelengths (<250 nm) and longer E_m wavelengths (>350 nm). Peaks at longer E_x wavelengths and longer E_m wavelengths are associated with humic-like compounds and shown in Region-V. More specifically the fulvic-like compounds show peak intensities at E_x - E_m wavelength band of 220-250/400-450 nm and humic-like compounds at 320-360/400-470 nm.

2.3 Results and Discussion

2.3.1 Leachate Characteristics

Relevant physico-chemical characteristics of ACL, NCL, and NRL leachate samples collected during the research period are summarized in Table 2-3. Multiple samples were collected and composition of leachate was relatively constant over the research period. All three leachates were characterized by slightly alkaline pH, dark brown color, a low concentration of biodegradable content as represented by BOD_5 , and high concentration of refractory organics represented by COD. Leachate from all three landfills had BOD_5/COD in the range of 0.02 to 0.14. These properties are consistent with typical stabilized or intermediate stabilized leachate (Reinhart and Grosh, 1998;

Statom et al., 2004). These types of leachate are found difficult to treat using conventional biological treatment methods and in most cases require more intensive physico-chemical treatment. All three leachates had DOC in the range of 425 to 670 mg/L with UV-254 absorbance of 8.3 to 14.7 cm⁻¹. The SUVA for three leachate were in the range of 1.6 to 2.22 m⁻¹/(mg/L DOC).

The Fluorescence EEM of leachate from all three landfills is shown in Figure 2-5. Leachate from all three landfills showed an overlapping peak in Region-III and V, representing the presence of fulvic and humic-like organics in leachate. ACL and NCL leachate also showed overlapping peak in the region-IV and V and peaks in Region-I and II representing the presence of microbial derived organic and protein-like organic matter. The distribution of DOM in each region was derived using FRI analysis as shown in Table 2-4. Among all three leachates, NRL leachate had the highest total volume (V_t) representing maximum concentrations of DOM in NRL leachate. Additionally, Region-V showed maximum volume among all five regions in all three leachates representing leachates contained maximum concentrations of humic-like organic matter.

2.3.2 Leachate Treatment Using Coagulant

Coagulation dose efficiency was assessed by measuring the change in leachate pH, DOC, SUVA, and fluorescence EEM. A decreasing pH was observed with an increase in coagulant dose in all three leachates (Figure 2-6 (a)). The results are shown as average of the duplicate experiments with error bars as standard deviation. The pH of leachate dropped in the range of 3 to 5.2 at different coagulant doses. Amokrane et al. (1995) also observed a decrease in supernatant pH with an increase in coagulant dose due to the increased release of H⁺ in solution after hydrolysis. NRL

leachate had a lower alkalinity (3000 mg/L as CaCO_3) as compared to ACL (6600 mg/L as CaCO_3) and NCL (5400 mg/L as CaCO_3) leachate, which caused a faster decrease in pH of NRL leachate than ACL and NCL leachate. Contrary to ACL leachate, the NCL and NRL leachate showed an increase in pH at higher coagulant doses, due to formation of hydrolysis product $\text{Fe}(\text{OH})_4^-$ that starts accepting available hydrogen ions and reducing free H^+ in the solution (Letterman et al., 1999; O'Melia et al., 1999).

As the pH of supernatant in the coagulation process reduces, the charge densities of the DOM also decreases (Ritchie and Perdue, 2003). Lower charge densities of DOM require lower coagulant doses to initiate charge neutralization and precipitation (Shin et al. 2003). Hence, as the coagulant dose was increased, higher DOC and SUVA removal was observed as shown in Figure 2-6 (b and c). A maximum of 68%, 71%, and 45% DOC (Figure 2-6 (b)), and 48%, 60% and 90% SUVA removal was observed in ACL, NCL, and NRL leachate, respectively (Figure 2-6(c)). However, these maximum removals were observed at different coagulant doses. The ACL leachate showed maximum removal at a coagulant dose of 37 mmol Fe(III)/L, whereas NCL, and NRL leachate showed at 29.6 and 18.5 mmol Fe(III)/L, respectively. Yoon et al. (1998) also observed 59 to 73% TOC reduction while treating landfill leachate using Fe (III) salt. Comstock et al. (2010) studied the use of sulfate salt of Fe (III) for treating leachate collected from ACL, NCL, and NRL landfills and observed 20%, 30%, and 70% DOC reduction, respectively for a fix dose of 17.9 mmol Fe (III)/L. In the present study, at a coagulant dose of 17.9 mmol Fe(III)/L of chloride salt, slightly lower DOC removal was observed in all three leachates. Maximum removal of DOC and SUVA was observed at lower coagulant doses in NCL and NRL leachate as compared to ACL

leachate because the coagulation efficiency was dominated by the solution pH. The pH of coagulated leachate corresponding to the maximum reduction of DOC and SUVA in all three leachates was in the range of 4.2 to 5.2, which is the pH range for highest coagulation efficiency for Fe(III) salt (Babcock and Singer, 1979). Amokrane et al. (1995) also observed optimum pH of 5.5 for maximum COD removal from stabilized leachate.

Effects of coagulant doses on removal of different types of organics in all three leachates as derived by FRI analysis are shown in Figure 2-7. DOM present in Region-V showed the highest removal among DOM of all regions and the order of removal of in all three leachates was found similar as Region-V>Region-III>Region-IV>Region-II>Region-I. The highest removal of DOM from Region-V and Region-III was expected because they belong to humic and fulvic-like organics that are favorable to coagulation process (Letterman et al., 1999). The DOM present in Region-I did not show any particular pattern with increase in coagulant dose due to low concentrations of DOM in this region. Low DOM concentration may show some noise during EEM measurement leading error in FRI analysis.

A coagulant dose of 22 mmol Fe (III)/L was used for leachate pretreatment to conduct the membrane experiments. At this coagulant dose, NRL leachate showed the maximum DOC removal whereas ACL leachate showed the least removal. Membrane experiments were performed using the leachate that showed lowest DOC removal among all three leachate. Approximately 40% of the DOC and 40 to 60% of the humic and fulvic-like organic matter as determined by FRI analysis was removed from all three leachate at this coagulant dose.

2.3.3 MIEX Experiment

Leachate treatment using MIEX showed an increased removal of UV-254 absorbing organic compounds with the increase in MIEX dose in all three leachates (Figure 2-8). UV-254 absorbance reduced at high rate at the start of mixing for each MIEX dose, while it plateaued after some time. The UV-254 absorbance was observed constant after approximately 30 minutes of mixing. It was also observed that majority of UV-254 absorbing materials were removed in initial 20 minutes of mixing in all three leachates for each MIEX dose, which is consistent with the results observed by Boyer and Singer (2005) for drinking water treatment.

Increased DOC and SUVA removal was observed with the increase of MIEX doses (Figure 2-9 (a and b)). Highest reduction in DOC was observed in NRL leachate followed by ACL and NCL leachate, respectively. Higher concentrations of TDS might have caused lowest rejection of DOC and UV-254 absorbance in NCL leachate because inorganic ions present in solution may occupy some spaces of MIEX resin causing reduction in DOC removal capacity (Boyer and Singer, 2006). A maximum of 30%, 20%, and 34% DOC removal was observed from ACL, NCL, and NRL leachate, respectively at a MIEX dose of 10 mL/L. A recent study on the use of MIEX for treating leachate collected from similar landfills also showed an average of 35% DOC removal for slightly higher MIEX doses (Boyer et al., 2010). The results suggest that for all three leachates most of the DOC was removed using low MIEX doses and with the increase of MIEX doses, rate of DOC removal decreases. A maximum of 18%, 19% and 21% of SUVA removal was observed from ACL, NCL, and NRL leachate, respectively. It was also observed that the pH of all three leachates were slightly increased for each MIEX doses and remain approximately same as shown in Figure 2-8 (c).

The FRI analysis results of the DOM removed from each region of the MIEX treated leachate are shown in Figure 2-10. The pattern for DOM rejection in each region was found similar in all three leachates with respect to rate of removal of organics from each region. Protein-like DOM present in Region-I and II had the maximum rate of removal followed by fulvic and humic-like DOM present in Region-III and V, respectively. On comparing the amount of DOM removed from each region, the results show that the DOM present in Region-III and V were removed to maximum in all three leachates. The FRI analysis results also showed that the rate of DOM removal decreased with the increase of MIEX dose. The DOM removal profile gets almost plateau after a MIEX dose of 4 mL/L in all three leachates, which is in agreement with the results obtained for the removal of DOC and SUVA.

A dose of 5 mL/L MIEX was selected for membrane experiment because most of the DOC was removed at an applied MIEX dose of 4 to 6 mL/L in all three leachates. Also, a mixing time of 30 minutes was selected for MIEX treatment, because in all three leachates most of the UV-254 absorbing organic material was removed in initial 20-30 minutes of mixing.

2.3.4 Comparison of Coagulation to MIEX Treatment

Both the coagulation and anion exchange process effectively removes humic and fulvic-like organics from leachate as represented by removal of DOC, SUVA, and results obtained from FRI analysis; however, coagulation process was found more effective than MIEX treatment. Leachate treatment using MIEX removed DOC in the range of 20 to 34% for the applied doses, which is approximately 40% lower reduction than coagulation process. A high removal (>50%) of SUVA were observed in all three leachates using the coagulant whereas MIEX removed an average of 20% SUVA from

all three leachates. The coagulant showed better performance than MIEX in terms of removing high molecular weight organics (humic and fulvic-like organic matter) and a maximum of 80% these organics were removed by coagulant in all three leachates. MIEX removed a maximum of 40% humic and fulvic-like organic matter and showed removal of wider range of organics in terms of molecular weight as observed by maximum removal of protein-like organic matter in all three leachates. However, the amount of low molecular weight organic matter (protein-like) removed by coagulation process was still higher than MIEX treatment. Microbial derived organics (region-IV) were least removed after MIEX treatment, whereas coagulant showed least removal for protein-like organic matter. Fearing et al., (2004) and Allpike et al., (2005) have also found similar results in terms of removing organic matter of different range of molecular weight using coagulant and MIEX for treatment of low DOM containing water.

2.3.5 Leachate Treatment Using Membranes

As expected both membranes showed high rejection for DOM and salts present in the feed leachates. More than 99% of DOM and 93% salts were rejected from all three leachates from both the membranes with slightly greater salt rejection from RO membrane than NF membrane.

The effect on permeate flux for treatment of raw and pretreated leachate using NF and RO membranes is shown in Figure 2-11. An average initial flux of 0.85 m/day (8.2 mL/min) and 0.55 m/day (5.3 mL/min) was observed with the NF and RO membranes, respectively. At the start of membrane treatment, a sharp decrease in permeate flux was observed in all three feed leachates, however, in long-term operation of raw and coagulated leachate the rate of permeate flux reduction slowed down, whereas MIEX treated leachate showed continuous sharp reduction in permeate flux with both

membranes. The rate of permeate flux decline was observed to be faster for the coagulant and MIEX treated leachate than that of raw leachate with both the membranes. The maximum flux decline was observed in MIEX treated leachate. Although, the rate of permeate flux decline for the raw and coagulated leachate in RO membrane was comparable, the NF membranes showed a distinctly higher rate of flux decline for pretreated leachate as compared to raw leachate.

The plausible reason of increased flux decline with pretreated leachate lies within the complex chemistry of feed leachate and the membrane surfaces that might have changed during the experimental run because the feed pH of all three feed solutions in NF as well as RO operation increased during the run as shown in Figure 2.12. The increase in feed pH may have been caused by the permeation of CO_2 of the solution through the membranes. NF and RO membranes are well known to be highly permeable to gases such as CO_2 (Mitsoyannis and Saravacos, 1977). In the aqueous phase, CO_2 gas is dissolved as carbonic acid (H_2CO_3) ($\text{CO}_2 \text{ gas} + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3$). The permeation of CO_2 gas through the membrane will tend to decrease H_2CO_3 in the solution. As the H_2CO_3 decreases, bicarbonate anions (HCO_3^-) will transform to H_2CO_3 to maintain the equilibrium ($\text{HCO}_3^- + \text{H}^+ \leftrightarrow \text{H}_2\text{CO}_3$). This leads to an increase in solution pH.

The change in feed pH might have affected the flux decline in two ways. First, an increase in pH may increase the potential for scaling on the membrane surface due to precipitation of CaCO_3 (Mitsoyannis and Saravacos, 1977 and Linde and Jonsson, 1995). Amokrane et al. (1998) studied the use of Fe (III) salt for reducing the fouling potential of RO membranes and observed that alkaline pH conditions increased the

fouling potential of membranes due to alkalinity precipitation; however, they did not operate the membrane system with treated leachate.

Second, as the solution pH increases, the surfaces of these membranes tend to get more negatively charged due to deprotonation of carboxyl groups ($\equiv\text{COOH} \rightarrow \equiv\text{COO}^-$) of membranes. However, the rate of deprotonation of membrane surface molecules may not be the same as the H^+ consumed by bicarbonate and an increase in pH of feed water may still be observed. The increase in negative charge of the membrane surface molecule may experience increased repulsion causing membrane pores to shrink. Childress and Elimelech (2000) have found increased negative charge and reduction in pore sizes of NF membrane surfaces at high pH conditions. This reduction in pore size reduces the permeate flux generation. However, the effect of feed pH on permeate flux is contradictory. A few researchers have found no effect on water flux with the change in feed pH for the RO membranes, though the membrane surfaces became more negatively charged with the increase in pH (Wagner et al., 2009; Hoang et al., 2010).

Another possible reason for increased fouling after Fe (III) salt coagulation might be the complex formation between iron and remaining NOM that may also precipitate on the membrane surface and causes fouling (Hong and Elimelech, 1997). Trebouet et al., (2001) also observed that leachate without any pre-treatment is the best way to use with NF membranes.

MIEX treated leachate had the highest pH of 8.1 among all three leachates at the start of experiments and at this pH, most of the alkalinity is generally in the form of carbonate, which does not easily pass through the membrane due to increased

repulsion between carbonates and negatively charged membrane surfaces. The precipitation of carbonate alkalinity might have caused even greater permeate flux reduction in MIEX treated leachate than other two feed leachate (Mitsoyannis and Saravacos, 1977; Qin et al., 2004). Cornelissen et al. (2010) used an anion exchange resin (Fluidized Ion Exchange (FIX)) to reduce fouling of NF membranes but did not observe reduced fouling and concluded that after anion exchange treatment the fouling of membranes was more pronounced by other organic matter such as polysaccharides than humic-like organic matter. These compounds are harder to remove by the MIEX as shown in Figure 2-10 and may cause pronounced fouling due to their charge neutrality (Kwon et al. 2006; Lee and Lee, 2007; Amy, 2008). Humbert et al. (2007) also observed increased fouling of ultrafiltration membranes while using MIEX as a pretreatment option for surface water treatment and concluded that the microbial derived organics present in MIEX pretreated water contributed to a larger extent in the fouling as compared to the raw water treatment. A complete understanding of increased flux decline was beyond the scope of this study.

2.4 Conclusions

This research was conducted to investigate the treatment of stabilized bioreactor landfill leachate using coagulation, anion exchange, and membrane treatment processes. Coagulation and anion exchange were also studied as a pretreatment step for leachate treatment using membranes.

FRI analysis of fluorescence EEM of coagulated leachate showed that the coagulant has highest affinity to remove humic and fulvic-like organic matter. Approximately 80% of humic and fulvic-like organics were removed by coagulation. A maximum of 68%, 71%, and 45% reduction in DOC was obtained from coagulation of

ACL, NCL, and NRL leachate, respectively. All three leachates had low SUVA values representing smaller fraction of humic and fulvic-like organics that lead to smaller DOC removal from coagulation. A coagulant dose of 22 mmol Fe(III)/L was selected for the membrane experiment because this dose generated optimum pH condition for coagulation in all three leachates.

Use of anion exchange resin MIEX showed lesser DOC removal from all three leachates as compared to coagulation treatment. A maximum of 30%, 20%, and 34% DOC removal was observed from ACL, NCL, and NRL leachate. However, most of the DOC was removed at lower MIEX doses. MIEX removed 30 to 60% of negatively charged humic and fulvic-like organics present in leachate. A MIEX dose of 5 mL/L was selected for membrane experiments for membrane experiments.

The research showed that a pretreatment (coagulant (Fe III) and anion exchange resin (MIEX)) that only reduces humic and fulvic-like organic matter from stabilized leachate did not improve the permeate flux of NF and RO membranes. An increased permeate flux decline was observed for pretreated leachate as compared to raw leachate in both membrane treatments, possibly due to a continuous high increase in pH of the pretreated leachates that might have caused increased precipitation of CaCO_3 on the membrane surface. The MIEX pretreated leachate showed even higher permeate flux decline as compared to leachate pretreated with coagulant, possibly due to pronounced fouling caused by microbial derived organics.

As future work, further analysis is required to study the cause of increased flux decline of pretreated leachate as compared to raw leachate. Additional membrane fouling experiments need to be conducted at fixed pH conditions to determine the effect

of pH on permeate flux. Additionally, the effect of pretreated leachate at variable coagulant and MIEX dose should be studied. A different coagulant (e.g. alum) can also be studied as a pretreatment option to avoid potential iron fouling.

Table 2-1. Previous studies on leachate treatment using coagulation process.

Reference	Initial concentrations in leachate			Coagulant	Dose (g/L)	Experimental pH condition	Maximum COD/TOC* Removal (%)
	COD or TOC* (mg/L)	BOD ₅ /COD	pH				
Amokarane et al. (1998)	4,100	0.05	8.2	FeCl ₃	2	4.9	55
				Al ₂ (SO ₄) ₃	0.9	5.5	42
Yoon et al. (1998)	282-417*	-	-	FeCl ₃	1.0	-	48*
Wang et al. (2002)	5,800	0.07	7.6	FeCl ₃ ·6H ₂ O	1.0	3	24
Tatsi et al. (2003)	5,350	0.20	7.9	FeCl ₃	1.5	10	80
				Al ₂ (SO ₄) ₃	1.5	6.2	30
	70,900	0.38	6.2	FeCl ₃	5.5	10	38
				Al ₂ (SO ₄) ₃	3.0	6.2	40
Ntampou et al. (2006)	1,010	0.17	-	FeCl ₃	1.1	3.5	72
Wang et al. (2009)	600-700	0.01	-	Fe ₂ (SO ₄) ₃	0.6	-	66.7
				Polymeric aluminum	1.0	-	33
Pi et al. (2009)	18,725	0.05	6.3	FeCl ₃	0.7	5	38
				Poly FeCl ₃	0.6	5	43.6
Li et al. (2010)	2,817	0.05	8.6	FeCl ₃	1.7	5.5	68
				Al ₂ (SO ₄) ₃	3.9	6.0	53
Comstock et al. (2010)	2,076	0.03	8.01	Fe ₂ (SO ₄) ₃	0.06	-	28

Table 2-2. Properties of NF-90 and BW-30 membranes used in the study

Parameter	NF 90	BW 30
Membrane type ¹	Fully aromatic membrane	Fully aromatic membrane
Operating pH range ¹	3-10	2-11
Maximum operating temperature (°C) ¹	45	45
Maximum operating pressure (bar (psi)) ¹	41.4 (600)	41.4 (600)
Pure water flux (m/day) ²	2.6±0.4	1.2±0.3
Salt rejection (%) ²	96.0±0.86	96.7±1.0
Virgin membrane zeta potential (pH 4.5/7) (mV) ³	17.5/-26.5	3.8/-5.2

¹ From Dow FilmTec; ² Pure water flux was considered as permeate flux at the end of 48-h compaction period. Salt rejection was determined for the feed solution containing 10 mM NaCl at pH 7; ³ Tang et al. 2007.

Table 2-3. Physico-chemical characteristics of ACL, NCL, and NRL leachate during the study period

Parameter	ACL		NCL		NRL	
	Average	Std dev	Average	Std dev	Average	Std dev
pH (S.U.)	7.71	0.09	7.61	0.06	7.50	0.05
Conductivity (mS/cm)	13.14	1.4	14.44		7.97	
TDS (mg/L)	6,280	65	7,163	19	4,418	22
BOD ₅ (mg/L)	46		146.5		410	
COD (mg/L)	2,300	46.8	2,225	35.3	2,915	190
BOD ₅ /COD	0.02		0.06		0.14	
DOC (mg/L)	527	56.6	425	35.9	663	
NH ₃ -N (mg/L)	1060	63	740	42	400	28.3
Alkalinity (mg/L as CaCO ₃)	6,600		5,400		3,000	
UV-254	8.3	0.4	8.58	1.5	14.7	
SUVA (m ⁻¹ /mg/L DOC)	1.6	0.1	2.01		2.22	

Table 2-4. Percentage distribution and total volume (V_t) of DOM in Region-I to Region-V of ACL, NCL, and NRL leachate derived from FRI analysis

Region	ACL leachate	NCL leachate	NRL leachate
Region 1	1	1	1
Region 2	6	4	2
Region 3	13	13	12
Region 4	18	15	9
Region 5	61	66	75
V _t (AU-nm ² -[mg-C/L] ⁻¹)	6,205	5,317	6,926
Fluorescence Index	2.23	2.15	1.61

Table 2-5. Percentage rejection¹ of salts² and DOM³ in permeate in RO and NF experiment*

Type of feed water	Initial concentration	RO treatment (BW-30)	NF treatment (NF-90)
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	Conductivity (mS/cm)	UV-254 absorbance (cm ⁻¹)	Salt rejection (%)	DOM rejection (%)	Salt rejection (%)	DOM rejection (%)
Raw leachate	13.1±1.4	8.3±0.4	93.5±0.3	99.4±0.1	93.0±0.3	99.8±0.1
FeCl ₃ treatment	14.4±1.1	3.8±0.8	93.5±0.5	98.8±0.3	93.1±0.4	99.6±0.1
MIEX treatment	11.2±0.3	5.1±0.4	93.8±0.3	99.3±0.1	92.3±0.3	99.5±0.1

¹ Percentage rejection of salt and DOM was calculated using average concentrations of permeate samples collected during each experiment and the initial concentration; ² Salt concentrations was measured using conductivity; ³ DOM was measured as UV-254 absorbance.

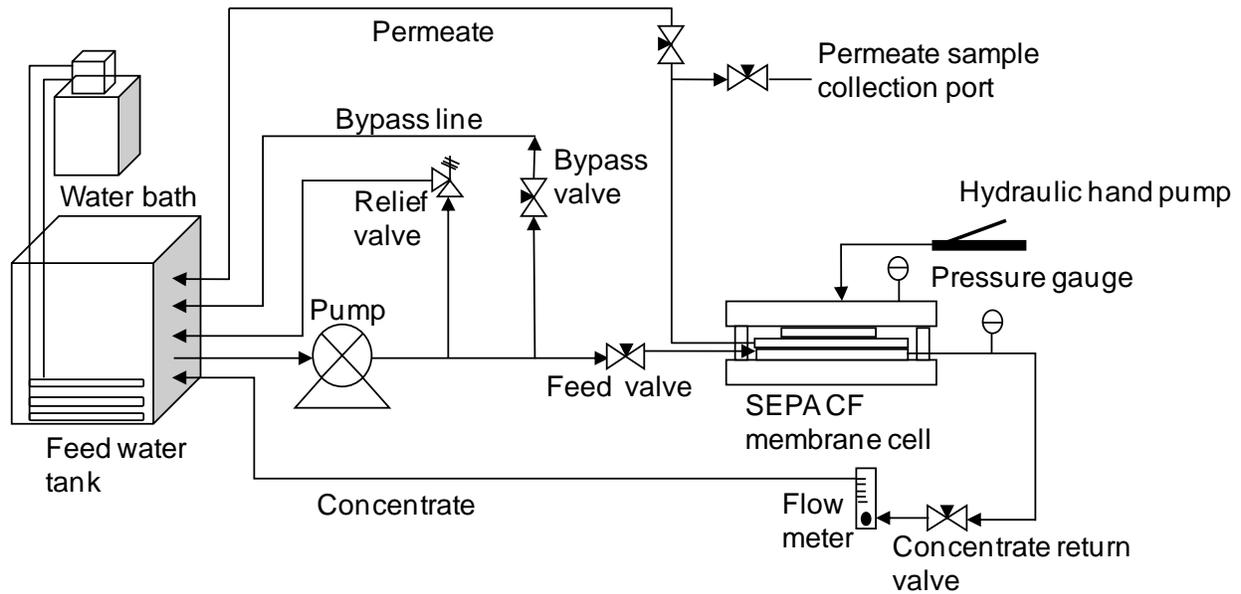


Figure 2-3. Laboratory-scale Osmonics SEPA CF membrane experimental setup

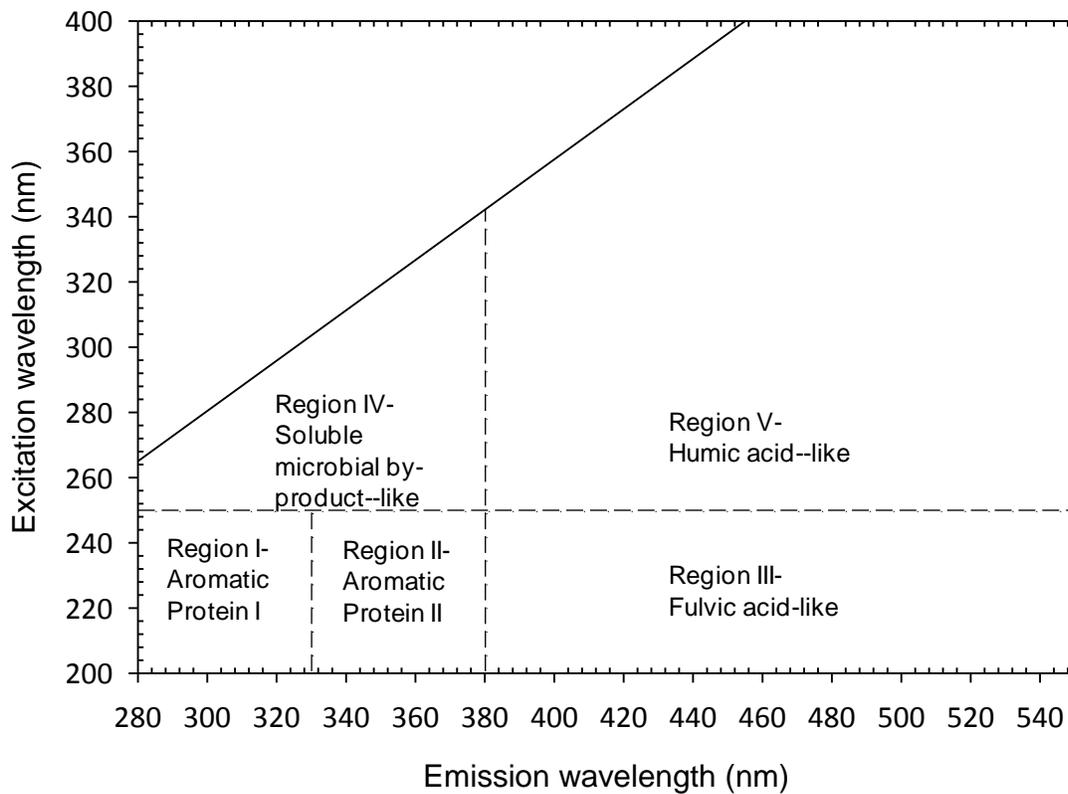


Figure 2-4. Operationally defined excitation and emission wavelength boundaries for five EEM regions (Chen et al., 2003).

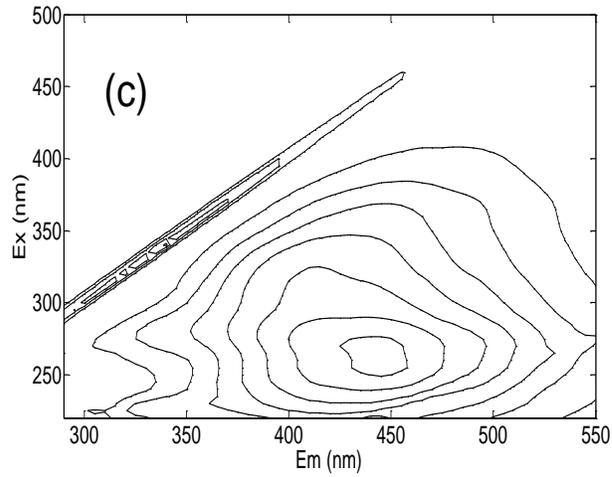
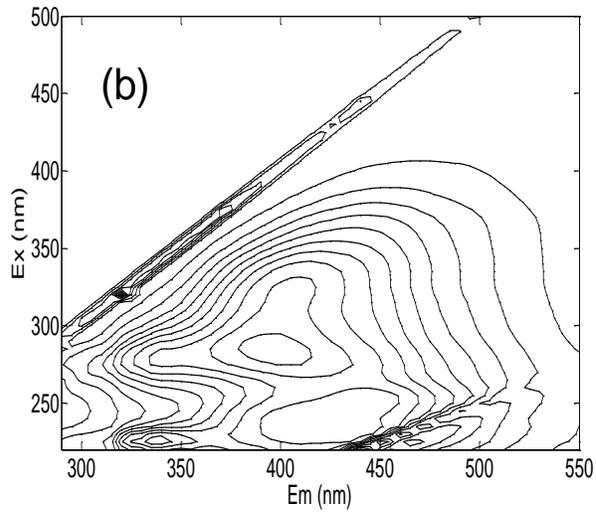
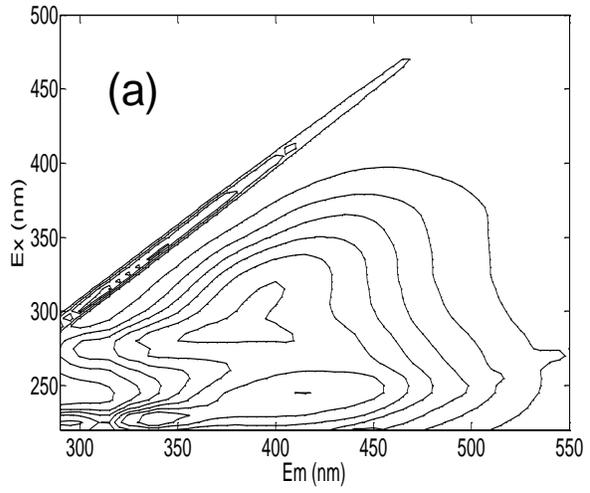


Figure 2-5. Fluorescence EEMs for leachate samples (a) ACL leachate (b) NCL leachate (c) NRL leachate

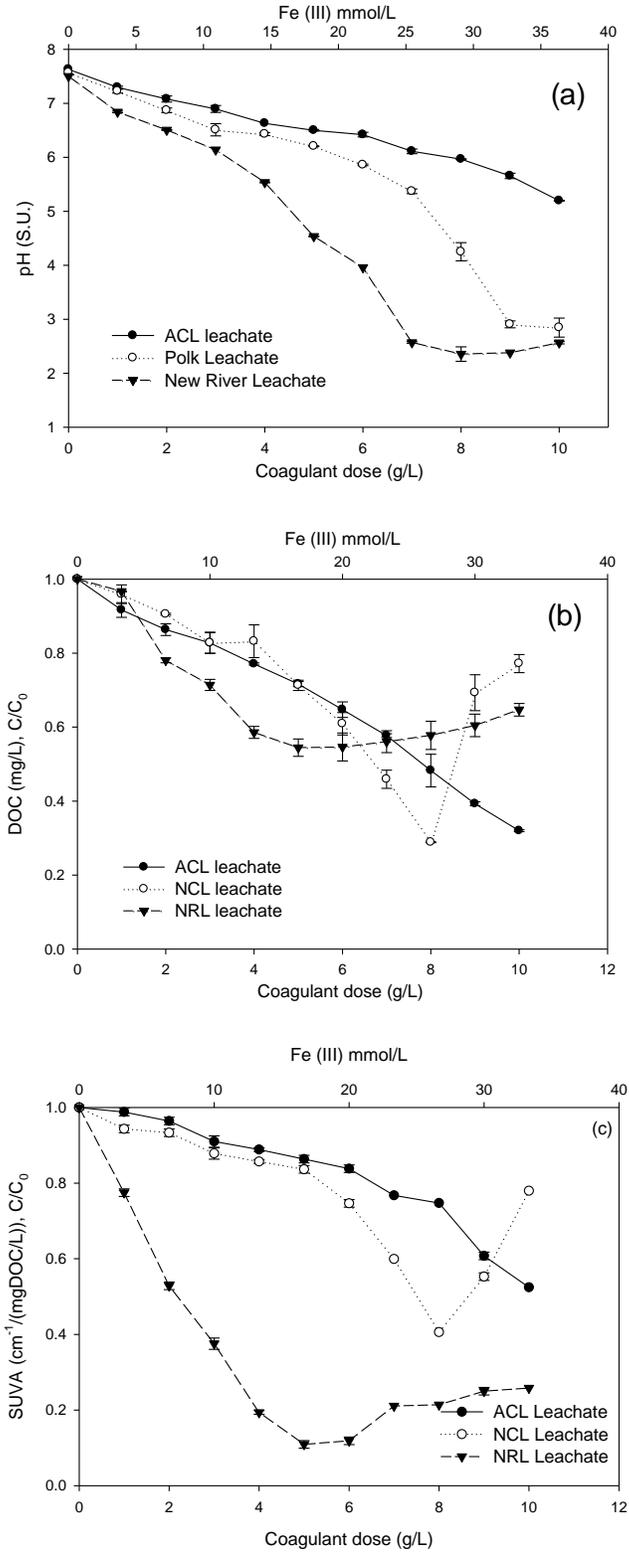


Figure 2-6. Effect of coagulant dose on (a) pH, (b) DOC and (c) SUVA of ACL, NCL, and NRL leachate. The data points and error bars represent average and standard deviation of duplicate experiments, respectively.

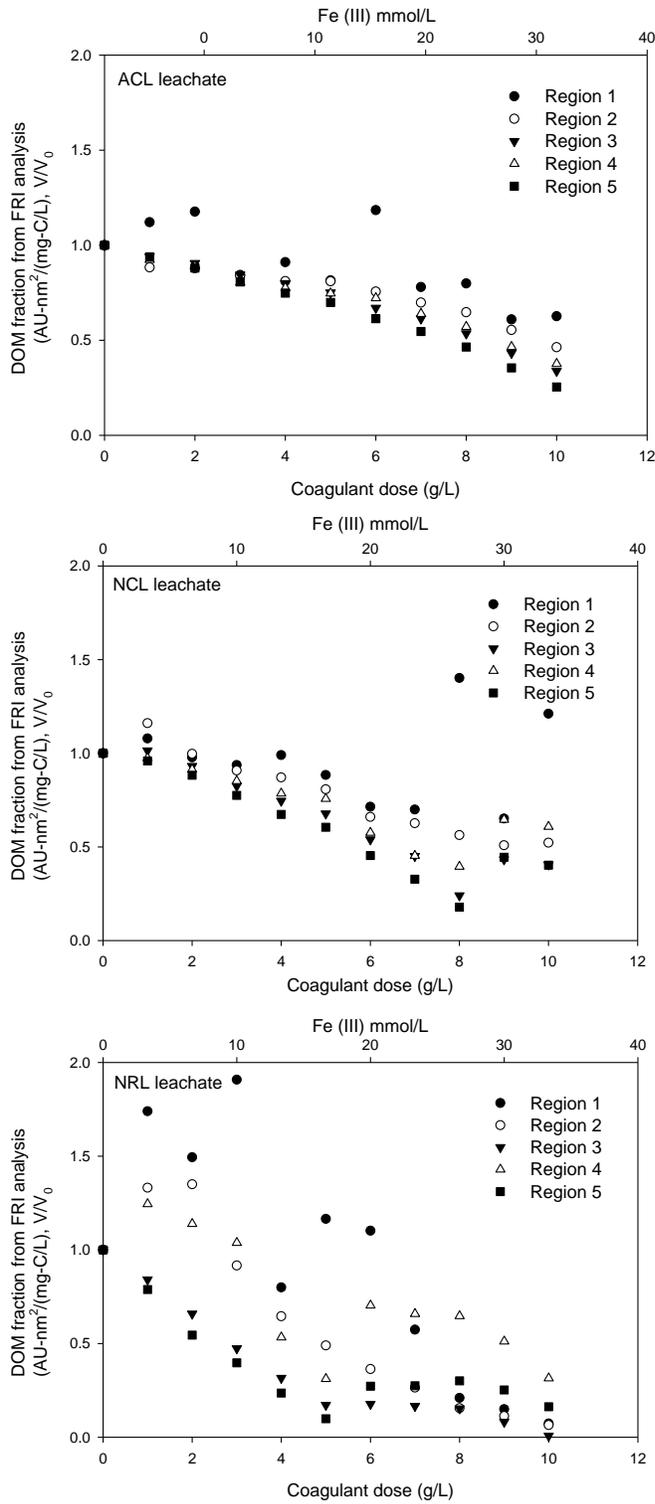


Figure 2-7. Effect of coagulation on removal of DOM in each region derived from FRI analysis of ACL, NCL, and NRL leachate

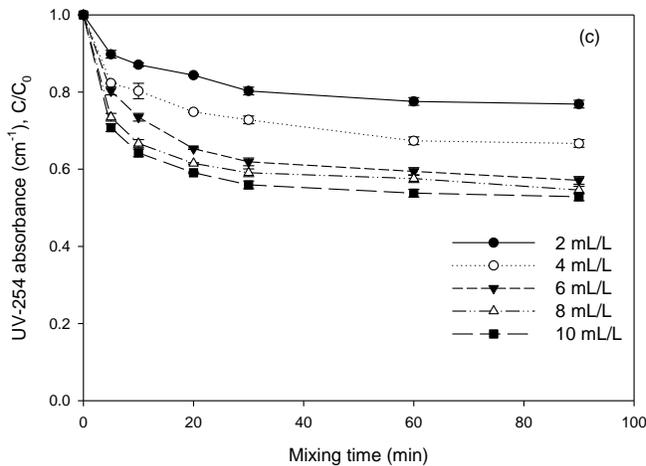
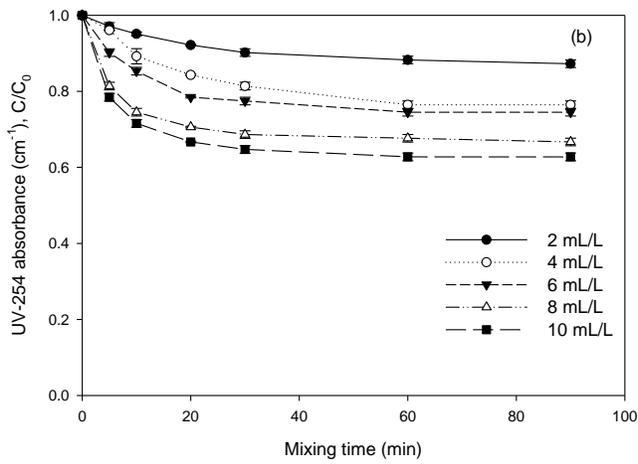
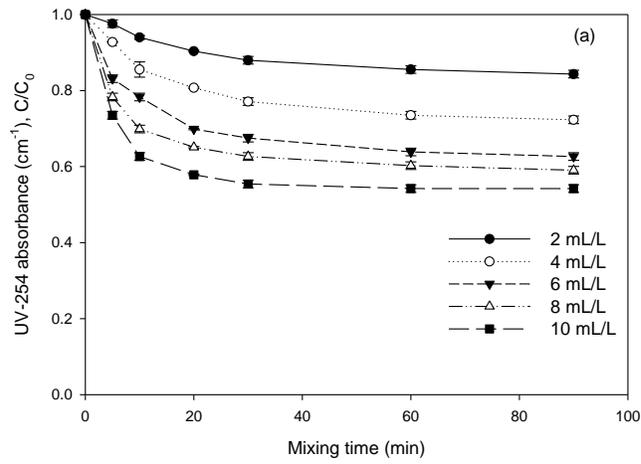


Figure 2-8. Effect of MIEX dose and mixing time on UV-254 absorbance of (a) ACL, (b) NCL, and (c) NRL leachate. Data points and error bars represent average and standard deviation of duplicate experiments, respectively.

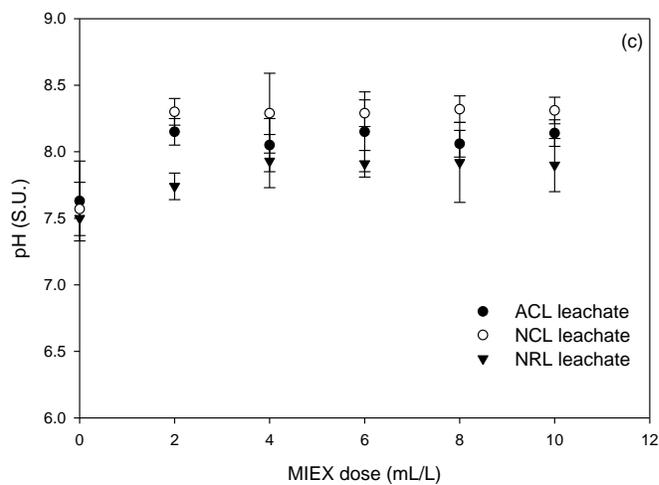
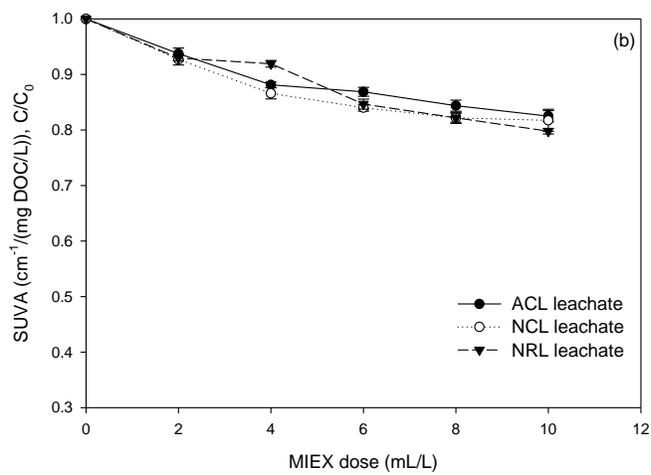
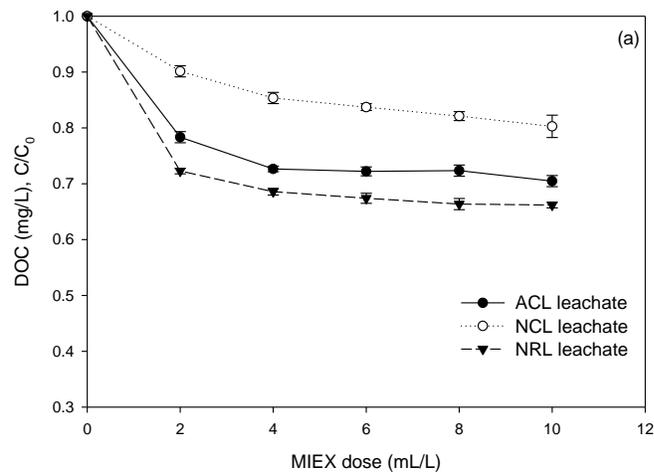


Figure 2-9. Effect of MIEX treatment on (a) DOC, (b) SUVA, and (c) pH of ACL, NCL, and NRL leachate. Data points and error bars represent average and standard deviation of duplicate experiments, respectively.

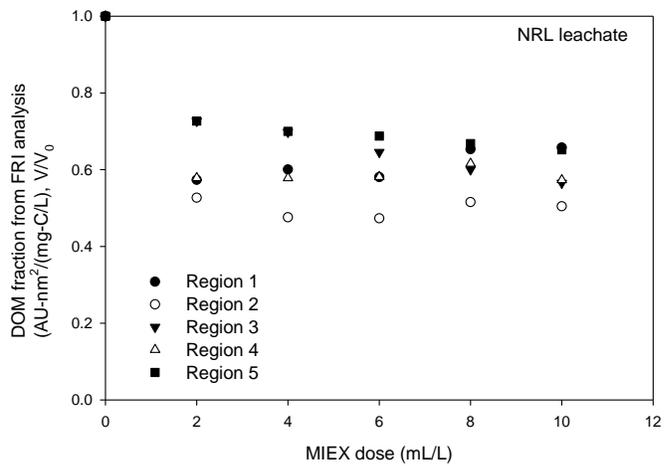
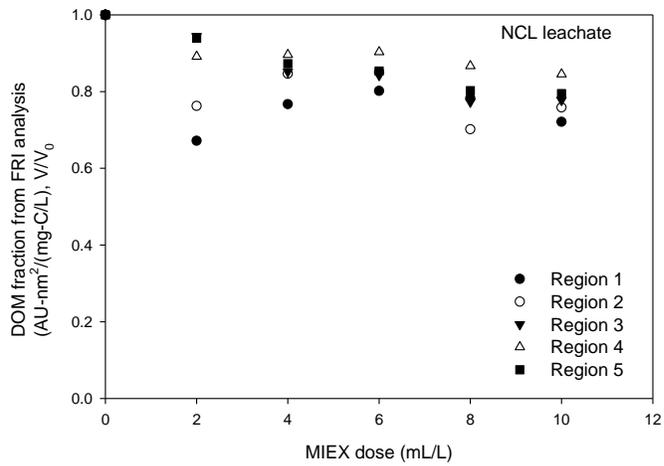
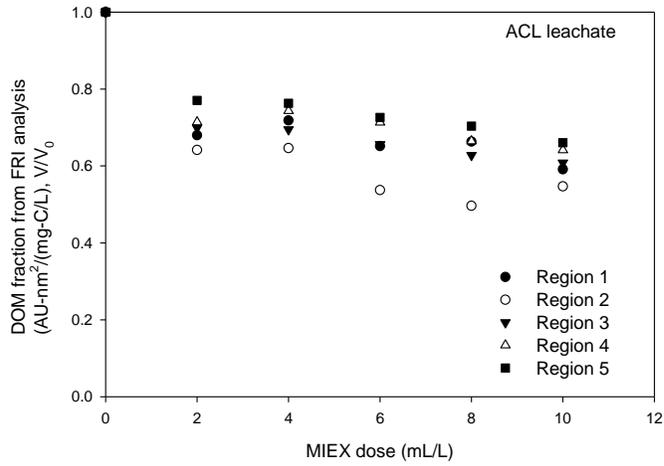


Figure 2-10. Effect of MIEX on removal of DOM of each region derived from FRI analysis of ACL, NCL, and NRL leachate.

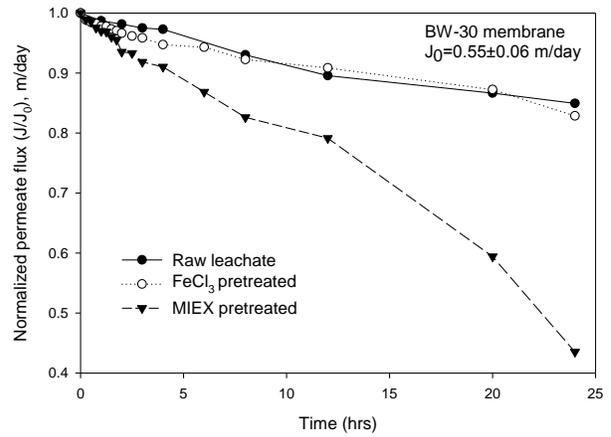
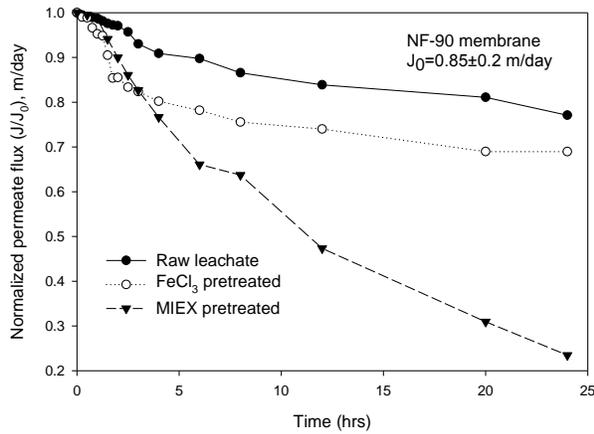


Figure 2-11. Effect on normalized permeate flux as a function of filtration time for pretreated (FeCl₃ and MIEX) and raw ACL leachate using NF-90 and BW-30 membrane

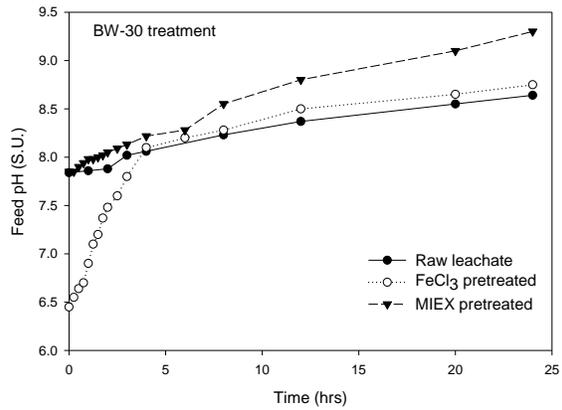
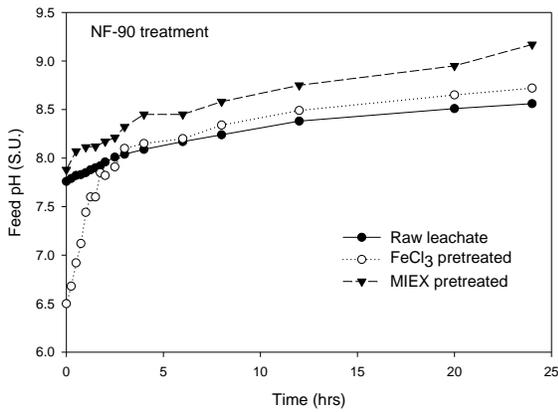


Figure 2-12. Effect on feed pH as a function of time for pretreated (FeCl₃ and MIEX) and raw ACL leachate using NF-90 and BW-30 membrane operation

CHAPTER 3
EFFECT OF OZONATION AS A PRETREATMENT FOR STABILIZED LANDFILL
LEACHATE TREATMENT USING HIGH PRESSURE MEMBRANES

3.1 Introduction

Though the modern landfill designs minimize the generation of leachate by reducing the influx of moisture, landfills still face a major challenge of managing leachate generated by the percolation of rainwater through the layers of waste. In the process, waste transfers its contaminants into leachate, which if improperly managed may pollute surrounding surface and groundwater bodies (Christensen et al., 2001).

The characteristics of leachate are complex and influenced by the factors such as age of landfill, type of waste disposed, cover material used in landfill, and management of liquid and gas production at the landfill. Traditionally, leachate is characterized based on the age of landfill as young, intermediate, and stabilized leachate. Young leachate contains high amount of biodegradable organic matter and effectively treated by biological treatment methods. As the landfills grow old, biodegradable content of leachate reduces and leachate mostly contains biologically refractory organic matter. The stabilized leachate typically contains a ratio of BOD and COD less than 0.1, making physico-chemical treatment methods such as coagulation, chemical oxidation, adsorption, and membrane systems more effective (Wiszniewski et al., 2006; Renou et al., 2008).

Several studies have been conducted to treat stabilized leachate using individual or combination of more than one treatment methods but often treated leachate do not meet the stringent regulations required to discharge the treated water (Monje-Ramirez and Velasquez, 2004; Kurniawan et al., 2006; Ntampou et al., 2006). High pressure membrane filtrations such as nano-filtration (NF) and reverse osmosis (RO) have been

effectively used to treat stabilized leachate that can meet the effluent discharge standards (Peters, 1998; Palma et al., 2002; Tabet et al., 2002).

However, high concentrations of organic matter and salts present in stabilized leachate tend to adsorb on the membrane surface and block the pores, also termed as fouling reduces the filtration and economic efficiency of the membrane systems. Fouling of membranes is also influenced by the presence of specific type of compounds such as hydrophobic humic and fulvic-like organic matter and divalent calcium, pH, and the membrane surface properties (Hong and Elimelech, 1997; Li and Elimelech, 2004; Xu, 2006). Hence, a pretreatment that reduces humic and fulvic-like organic matter from leachate can provide an effective increase in the life of membranes.

Ozone has high oxidation potential ($E_0=2.07V$) and high reactivity and selectivity toward organic pollutants such as aromatic compounds. Ozone ruptures the C=C bonds or aromatic ring and produces aliphatic acids and aldehydes (Anderson et al., 1985; Westerhoff et al., 1998, Jing et al., 2008). At high pH conditions ($pH>8$), ozone produces hydroxyl radicals ($O_3+H_2O\rightarrow O_2+2\cdot OH$) that have even higher oxidation potential ($E_0=2.8V$) than ozone molecule, and accelerate the removal of recalcitrant organic matter from complex wastewater matrix (Wang et al., 2003). A typical ozone reaction mechanism with the organics is presented in Appendix-B.

Ozone transforms recalcitrant organic matter into more biodegradable form; hence, ozone has been normally used as a pretreatment step for treating mature landfill leachate (Monze-Ramirez and Velasquez, 2004; Wu et al., 2004; Bila et al., 2005; Ntampou et al., 2006). A summary of pertinent literature on leachate treatment using ozonation process is presented in Table 3-1. These studies were generally focused on

improving the biodegradability of leachate or the use of ozone in combination with other treatment methods such as advance oxidation, coagulation, and adsorption (Fettig et al., 1996; Rivas et al., 2003; Bila et al., 2005; Ntampou et al., 2006; Tizaoui et al., 2007). Rivas et al. (2003) studied the effect of ozonation on stabilized leachate treatment and observed a maximum of 30% COD reduction for an initial COD of 5,000 mg/L. Bila et al. (2005) studied the effect of ozonation on the biodegradability of mature landfill leachate and observed an increase in BOD₅/COD ratio from 0.05 to 0.3 that can be further treated by biological processes. Ntampou et al. (2006) used a combination of ozonation and coagulation processes for removing the COD from the leachate and observed 65% COD removal after 60 minutes of ozonation using 2 g/h ozone and an overall COD removal of 80% using the combined process.

Though ozone can oxidize all the organic matter into its highest oxidation state, the complexity of leachate composition requires high ozone doses and the respective reaction may take longer time, causing this process to be economically unfavorable (Monze-Ramirez and Velasquez, 2004). However, ozone has high reactivity with potential membrane fouling humic and fulvic-like organic matter; hence pre ozonation of leachate may reduce the membrane fouling during leachate treatment. Ozone has been shown to reduce the fouling of membranes during surface and ground water treatment (Karnik et al., 2005; Lee et al., 2005; Brown et al., 2008; Kim et al., 2008). Karnik et al. (2005) showed a significant decrease in ceramic membrane fouling by application of ozone gas prior to filtration for lake water containing a maximum TOC of 11.6 mg/L. Brown et al. (2008) applied variable doses of ozone to surface water for studying their effect on fouling characteristics of RO membranes and observed

increased permeate flux at lower ozonation dose of 0.3 mg ozone/L. However, no information could be found on using ozone as a pretreatment option while treating stabilized leachate using nanofiltration (NF) and reverse osmosis (RO) membranes.

The objective of this research was to investigate the effectiveness of ozonation as a pretreatment option for treating stabilized landfill leachate using RO and NF membranes. The experiments were conducted in two phases, wherein at first, an optimum ozone dose was determined for leachate treatment. In the second phase, the ozonated leachate was tested for the time dependent permeate flux and the permeate quality. The permeate flux data was used to determine the type of fouling occurred during membrane treatment using Hermia's constant pressure, cross flow filtration model (Hermia, 1982).

3.2 Experimental Material Methods and Analysis

3.2.1 Materials

Leachate samples were collected from three municipal solid waste landfills; the Alachua County Southwest Landfill (ACL), the North Central Landfill (NCL), and the New River Regional Landfill (NRL), all located in different counties in Florida, USA. All three landfills have been fully or partially operated as a bioreactor landfill where leachate has been added into the waste to accelerate the rate of waste degradation. The ACL has a lined MSW cell that accepted waste for 10 years before closing in 1998 and has been operated as a bioreactor since 1990. Leachate samples were collected from the leachate lift station where all the leachate is collected. The NCL has two landfill cells; the first cell was closed in 2000 after accepting waste for 11 years and the second cell was closed in 2007 after eight years of accepting waste. The second cell was operated as a bioreactor landfill. The leachate samples were collected from the

leachate storage tank, where leachate from both the cells is mixed. NRL has three cells having waste ranging in age from 5-15 years. The leachate samples were collected from a common aeration tank where leachate from all the landfill cells is drained and aerated. The leachate samples were collected multiple times in the duration from February 2010 to July 2010 in Nalgene containers and kept at 4⁰C in the dark until used in experiments.

Landfill leachate ozonation experiments were carried out in laboratory-scale semi-batch bubble reactor consisting of a Plexiglas column with height of 45.7 cm and internal diameter of 10 cm, having a total volume of 2000 mL, as shown in schematic diagram (Figure 3-1). Ozone was produced using high purity oxygen as a feed gas to the laboratory-scale ozone generator (Pacific lab series ozone generator, Model: L20) and supplied to the ozonation column through a ceramic porous diffuser of porosity 10 to 15 μm , at the bottom of the reactor. The concentration of ozone in the inlet and the outlet gas stream of the column was measured using gas phase digital ozone analyzer (T-API Model 452). The residual gas stream was passed through an ozone destruction unit.

Dow filmtec (Minneapolis, MN) provided RO (BW-30) and NF (NF-90) membranes as flat-sheet for conducting membrane performance studies. The physical and the operational characteristics of these membranes are presented in Table 3-2. The flat-sheet membranes were cut into 14.6 cm x 9.5 cm coupons and stored as dry in the dark. These coupons were soaked in MilliQ water in the dark for 24 hours before use.

Membrane filtration experiments were conducted using high-pressure-cross-flow Osmonics SEPA CF Membrane Cell as shown in the schematic diagram (Figure 3-2).

The membrane coupons were placed into the membrane cell sandwiched between a low-foulant feed spacer of thickness 0.86 mm (34 mil) and a permeate carrier of thickness 0.2 mm (7.8 mil). Feed solution was pumped using a variable speed Hydra-Cell Industrial pump from a 15 L Nalgene feed tank. A recirculation water bath (RTE-5B, Neslab Instruments Inc.) was used to control the feed water temperature. A hydraulic hand pump (Enerpac, P142) was used to pressurize membrane cells and the pressure was maintained constant (300 psi) throughout the experiment. The cross-flow velocity and the operation pressure were controlled by valves connected in the concentrate return line and the bypass line and monitored by a flow meter (0.13 to 3.15 lpm) and a pressure gauge (0 to 68.9 bar).

3.2.2 Landfill Leachate Ozonation

The ozone generator was turned on approximately 20 minutes prior to the start of each experiment to stabilize the rate of ozone generation by the instrument. The concentration of ozone in the ozone/oxygen gas mixture was controlled by adjusting the ozone production rate from the ozone generator by changing the feed gas (oxygen) pressure into the generator and the voltage applied.

Before starting the experiments, leachate was brought to room temperature of approximately 23⁰C. Leachate samples were thoroughly shaken for re-suspension of settled solids and 1000 mL of leachate was transferred to the column. To determine the optimum ozonation time for the selected ozone dose, leachate samples were ozonated for 5, 10, 15, and 30 min at an ozone dose of 13.8×10^{-4} mol/L (66.7±0.3 mg/L) and feed gas flow rate of 3.5 L/min. At the end of each experiment, samples were withdrawn from the column and analyzed. The experiments were conducted without any adjustment of pH and at the end of experiments; samples were analyzed for pH,

dissolved organic carbon (DOC), ultra violet-254 (UV-254) absorbance, and fluorescence excitation emission matrix (EEM). All experiments were conducted in duplicate. The amount of ozone consumed in ozonation of leachate was calculated by subtracting the ozone concentration of outlet gas stream to the feed gas.

3.2.3 Landfill Leachate Treatment Using Membrane

Experiments were conducted to evaluate the performance of raw and ozone treated leachate using RO and NF membranes. The performance was evaluated by measuring permeate flux and rejection of dissolved organic matter (DOM) and salt. To conduct the membrane experiments, approximately 8 to 10 L of all three leachates was pretreated separately using optimum ozone dose and time as determined by the batch experiments.

Membrane experiments were conducted in two steps; wherein membranes were first pre-compacted by filtering de-ionized water for 24 to 48 hours at constant pressure of 13.8 bar (200 psi), constant cross-flow velocity of 20 cm/sec, and at constant temperature of $23 \pm 1^{\circ}\text{C}$, until constant permeate flux (pure water flux) was achieved. After pre-compaction run, the membrane system was stopped and the de-ionized water was drained out from the feed tank. Approximately 8 to 10 L of pre-filtered feed leachate was added to the tank. The leachate was pre-filtered using 0.7 μm glass-fiber filter (whatman). The membrane system was then restarted and operated at similar operating conditions as in pre-compaction run for 24 hours. Feed pressure, cross-flow velocity, and temperature were maintained constant throughout the experiment. The permeate flux was measured intermittently by measuring the time taken to a predetermined volume of permeate generated. Concentrate and permeate were

recycled to the feed tank except for the intermittently collected samples for pH, conductivity, DOC and UV-254 absorbance measurement.

3.2.4 Analytical Methods

A multi-function Orion Research instrument was used to analyze water quality parameters pH, conductivity, and temperature. Solution pH was measured to an accuracy of ± 0.02 . Temperature was measured in degrees celsius with a scale accuracy of $\pm 0.15^{\circ}\text{C}$. Conductivity was measured in mS/cm or $\mu\text{S/cm}$ depending upon the concentration of sample. Salt rejection in the membrane experiments were measured by measuring conductivity of feed and permeate.

All samples were filtered through pre-rinsed 0.45 μm nitrocellulose filter (Millipore) to analyze DOC, UV-254 absorbance, and EEM. The filtered samples were stored in capped 40-mL glass vials at a 4°C in the dark; samples were brought to room temperature before analysis. DOC was measured using Tekmer TOC analyzer. UV-254 absorbance was measured using HACH DR 4000 spectrophotometer. Organic free de-ionized water was used to calibrate the spectrophotometer for UV-254 absorbance measurement.

EEM was measured using a 1-cm quartz cell on a Hitachi F-2500 fluorescence spectrophotometer. The EEM was obtained by scanning the samples at 5 nm increments over an excitation wavelength (E_x) in the range of 200 nm to 500 nm. For each E_x the emission wavelengths (E_m) were detected at 5 nm increments in the range of 290 nm to 550 nm. To limit the second order Rayleigh scattering, a limit of 290 nm cutoff was used for all the samples (Chen et al., 2003). The data were processed in MATLAB following the procedures Chen et al., 2003 and Cory and Mcknight, 2005.

Each time the instrument was used, the EEM of de-ionized water was analyzed and was subtracted from the EEM response of samples containing DOC to reduce the effect of scattering (Chen et al., 2003). The area under the Raman water peak (at E_x 350 nm) was calculated for de-ionized water and the intensities of the EEM response for the samples were normalized by the Raman water area; the EEM response of the samples was then normalized by the DOC concentration; and EEM were plotted in MATLAB using the contour function. The amount of various types of DOM removed by each treatment was quantified using Fluorescence Regional Integration technique (FRI) (Chen et al., 2003). The FRI was used to integrate the area under the EEM spectra as shown in equation 3-1.

$$V_i = \int_{ex} \int_{em} I(\lambda_{ex} \lambda_{em}) d\lambda_{ex} d\lambda_{em} \quad (3-1)$$

where, V_i represents the volume under region “i”, $I(\lambda_{ex} \lambda_{em})$ is the fluorescence intensity at a particular E_x - E_m wavelength pair, $d\lambda_{ex}$ is the increment of E_x (5 nm) and $d\lambda_{em}$ is the increment of E_m (5 nm).

EEM were divided into five E_x - E_m regions and concentration of DOM in each region was quantified by integrated volume in each region. The E_x - E_m regions were divided based on the EEM peaks associated with specific types of organic compounds (Figure 3-3). These regions were selected using the literature (Chen et al., 2003; Chen et al., 2003; Baker, 2004; Hudson, 2007). Shorter E_x (<250 nm) and shorter E_m (<350nm) are associated with simple aromatic protein-like compounds such as tyrosine (Regions-I and Region-II). The peaks at E_x in the range of 250 to 280 nm and E_m <380 nm are associated with soluble microbial byproducts type compounds and kept in Region-IV. The fulvic-like compounds (Region-III) show peaks at shorter E_x (<250 nm)

and longer E_m (>350 nm). Peaks at longer E_x and longer E_m are associated with humic-like compounds and shown in Region-V.

3.2.5 Characterization of Fouling Mechanism Using Hermia's Filtration Model

The fouling occurred during raw and ozone treated leachate treatment using RO and NF membranes were characterized by Hermia's filtration model (Hermia, 1982; Koltuniewicz et al., 1995). Hermia's filtration model is a classic filtration model that uses flux decline data to determine the type and cause of fouling occurred during the filtration process (Reis and Zydney, 2007). The model equations have been previously used by several researchers for various types of feed water with different types of membranes, however, no study was found that analyzes fouling mechanism due to stabilized leachate treatment using NF and RO membranes (Koltuniewicz et al., 1995; Keskinler et al., 2004; Brown et al, 2008; Lohwacharin and Takizawa, 2009).

The model assumes a single pore size of the membrane and the operations are performed at constant pressure in cross-flow filtration system. The filtration model describes four fouling mechanisms during membrane filtration as standard pore blocking, cake filtration, intermediate pore blocking, and complete blocking of pores.

For standard pore blocking of membranes, it is assumed that the particle diameter is less than the pore diameter and pore diameter is decreased by deposition of particles on the pore walls can be expressed as equation (3-2);

$$\frac{1}{J_t^{1/2}} = \frac{1}{J_0^{1/2}} + K_s' t; \text{ where } K_s' = \frac{1}{2} \cdot K_s \cdot A \cdot J_0^{1/2} \quad (3-2)$$

where, J_t is flux rate (L/m^2h) at time t ; J_0 is initial flux rate (L/m^2h); K_s is standard blocking constant (L^{-1}); A is area of membrane (m^2); t is time of filtration; (h).

The cake filtration model (equation 3-3) assumes that particles do not enter into the pores due to their large sizes and form a cake layer over the membrane surface.

$$\frac{1}{J_t^2} = \frac{1}{J_0^2} + K_c' t; \text{ where } K_c' = 2K_c' A^2 \quad (3-3)$$

where, K_c is cake filtration constant (h/L^2).

Intermediate pore blocking is defined as the pore blockage due to the deposition of particles on the pores as well as on the pore surface and can be expressed as equation 3-4.

$$\frac{1}{J_t} = \frac{1}{J_0} + K_i' t; \text{ where } K_i' = K_i \cdot A \quad (3-4)$$

where, K_i is intermediate pore blocking constant (L^{-1}).

When the particles seal the membrane pores but do not accumulate on each other, the blocking is assumed as complete blocking and is modeled as equation 3-5.

$$\ln\left(\frac{1}{J_t}\right) = \ln\left(\frac{1}{J_0}\right) + k_b t \quad (3-5)$$

where, K_b is complete blocking constant (h^{-1}).

The flux data obtained from the membrane experiments were fitted in the Hermia model equations (equations 3-2 to 3-5) for each leachate to determine the type of pore blocking mechanism and to calculate the correlation coefficient (r^2) of each model.

3.3 Results and Discussion

3.3.1 Leachate Characterization

Relevant physicochemical characteristics of ACL, NCL, and NRL leachate samples collected during the research period are summarized in Table 3-3. The

composition of leachate was relatively constant over the research period. All leachate were characterized by slightly alkaline pH, dark in color, a low concentration of biodegradable content as represented by BOD₅, and high concentration of refractory organic matter represented by COD. Leachate from all three landfills has BOD₅/COD in the range of 0.02 to 0.11 and pH above 7. These properties are consistent with typical stabilized or intermediate stabilized leachate (Reinhart and Grosh, 1998; Statom et al., 2004). All three leachates contained high DOC and UV-254 absorbing organic compounds. These types of leachate are characterized as refractory to conventional biological treatment processes and require physicochemical treatment processes for treatment.

The fluorescence EEM of all three leachates is shown in Figure 3-4. All three leachates showed distinct peak in the region-III representing the presence of fulvic-like organics. ACL and NCL landfills are older than NRL, and showed more contour lines in region-V, representing higher presence of humic-like organic compounds in ACL and NCL leachate than NRL leachate. The distribution of DOM in each region was derived from FRI analysis as shown in Table 3-4. Among all three leachates ACL leachate had the highest total volume (V_t) representing maximum concentrations of DOM in ACL leachate. Additionally, Region-V showed maximum volume among all five regions in all three leachates representing leachates contained maximum concentrations of humic-like organic matter. The ACL leachate also showed the maximum DOM in region-V among all three leachates.

3.3.2 Ozonation

Experiments were conducted to determine the efficiency of ozone for treatment of stabilized landfill leachate. An ozone dose of 70 mg/L was passed through the bubble

column for variable durations. The off-gas ozone concentration from the column was measured with the ozonation time as shown in Figure 3-5. The data points for all three leachates of different batch experiments were found overlapping, representing the reproducibility of results and the validity of experimental procedure. The off-gas ozone concentration was observed to increase slowly at the start of experiment in all three leachates, representing faster kinetics of ozone reaction at the start of experiment. After this period, the off-gas ozone concentration was observed to increase more or less exponentially due to the decreased availability of organic compounds that can react with ozone. The ACL and NCL leachate showed a slower increase in off-gas ozone concentration than NRL leachate, right from the start of experiment, showing a relatively faster kinetics of ozonation in ACL and NCL leachate. Higher concentrations of humic and fulvic-like organic compounds lead to faster ozonation in ACL and NCL leachate. In the initial alkaline pH conditions of all three leachates (7 to 8), ozone (O_3) molecules directly react with the susceptible organic compounds present in the leachate. Additionally, formation of high oxidation potential hydroxyl radicals ($\cdot OH$) contribute in the oxidation reaction (Kurniawan et al., 2006). The off-gas ozone concentration almost plateaued after an ozonation of 8 to 10 minutes in ACL and NCL leachate and 15 minutes in NRL leachate at lower concentration than input ozone dose, representing a constant rate of ozonation after initial faster kinetics of ozonation and less availability of compounds that easily reacts with ozone. It also indicates that ozone reactions are still taking place with possibly the products of initial reactions. If the experiments were carried out for much longer time, the off-gas ozone concentration would level off with approximately input ozone concentrations.

The pH of ozonated samples were measured as a function of ozonation time as presented in Figure 3-6 (a) and it was found that in the NRL leachate, pH of ozonated leachate decreased from 7.7 to 7.0 because oxidation of organic matter forms secondary by-products of acidic nature causing a decrease in pH of solution. However, application of ozone may also strip carbon dioxide from the leachate and the decrease in carbon dioxide may lead to decrease in bicarbonate concentrations in the solution (Wu et al., 2004). This drop in bicarbonate may consume H^+ ions, causing an increase in pH. The ACL and the NCL leachate contained high alkalinity, and CO_2 stripping due to ozonation might have caused a slight increase in pH. A 15 to 20% decrease in alkalinity was also observed in all three leachates with a trend of higher decrease in alkalinity with the ozonation time and showed a maximum alkalinity drop after 30 minutes of ozonation.

The UV-254 absorbing compounds can be attributed to the presence of unsaturated and aromatic organic compounds with $C=C$ and $C=O$ structures such as phenolic, poly-aromatic hydrocarbons (PAHs), aromatic ketones, and aromatic aldehydes. A significant reduction in UV-254 absorbance was observed with the increase in ozonation time as shown in Figure 3-6 (b). After 30 minutes of ozonation, more than 65% of UV-254 absorbing compounds from the ACL leachate and 78% from NCL and NRL leachate were either removed or transformed into other forms. Few other researchers also observed approximately similar reduction in UV-254 absorbance during ozonation of similar type of leachate (Ntampou et al., 2006; Rivas et al., 2003). Ntampou et al. (2006) observed a 70% reduction in UV-254 absorbance and a 50% reduction in COD after 30 minutes of ozonation for an initial UV 254 absorbance and

COD of 6.76 cm^{-1} and 1010 mg/L , respectively. Rivas et al. (2003) observed a 60% reduction in UV-254 absorbance after 30 minutes of ozonation at initial UV 254 absorbance of 1.5 cm^{-1} .

The rate of reduction of UV-254 absorbance was almost similar in all three leachates, independent of their initial value; however, UV-254 absorbance reduction was found faster at the start of ozonation, which slowed down with the increase in ozonation time. The possible reason behind this type of ozone kinetics is the mechanism of ozone reaction, where molecular ozone quickly oxidizes the unsaturated bonds of aromatic rings and form by-products such as aliphatic acids and aldehydes. These by-products slow down the oxidation reaction (Westerhoff et al., 1999; Tizaoui et al., 2007).

A maximum of 13 to 17% reduction in DOC was observed in all three leachates; after 30 minutes of ozonation (Figure 3-6 (c)), which is comparable to the results of previous studies. Cortez et al. (2010) observed approximately 11% TOC (initial TOC 284 mg/L) reduction in landfill leachate for almost similar ozone dose. With the increase in ozonation time, the reduction of DOC increased; however, the rate of DOC reduction was not always constant in all three leachates. All three leachates showed a faster DOC removal at the start of ozonation which slowed down as the ozonation progressed. Ntampou et al. (2006) observed a similar trend for COD removal with the ozonation time. A slightly higher DOC removal rate was observed in the NRL leachate as compared to ACL and NCL leachate because mineralization of humic and fulvic-like organic matter is harder than smaller organic matter and ACL and NCL leachate had higher concentrations of humic and fulvic-like organics than NRL leachate. These

results are consistent with the off-gas ozone concentrations also, such that lower the off-gas ozone concentration, higher the DOC removal and with the increase in ozonation time, the rate of DOC removal became almost constant. ACL leachate showed highest amount of DOC removal among all three leachates at the 30 minute ozonation time due to its slightly increased pH. Increased pH conditions increase the formation of $\cdot\text{OH}$ radicals that has higher oxidation potential than ozone, leading to faster oxidation of organic matter (Kurniawan et al., 2006). The rate of DOC removal was observed lower than that of UV-254 absorbance removal, representing faster ozone reaction with the unsaturated and aromatic compounds and smaller rate of complete mineralization of DOC.

Effect of ozonation on the removal of different types of organics with the increase in ozonation time was derived from the FRI analysis. The normalized concentrations of DOM in each region are presented in Figure 3-7. All three leachates showed almost similar pattern of DOM removal, such that, DOM present in region-V and region-III had a maximum reduction at each ozonation time. Ozone preferentially reacts with humic and fulvic-like organic compounds that contain aromatic and unsaturated organic compounds. These humic and fulvic-like compounds break into smaller aliphatic organic compounds; confirming the slightly smaller rate of DOM removal of organics present in region-I and region-II. The rate of DOM removal became almost constant after 10 minutes of ozonation in all three leachates.

The kinetics of UV-254 absorbance, DOC, and DOM in region-III and region-V removal was observed to be decreased after 10 minutes of ozonation; hence, an optimum ozonation time of 10 minutes was selected for the membrane experiments. An

ozonation of 10 minutes corresponds to an average of 55% UV-254 absorbance and 8% of DOC removal in all three leachates. The pH after 10 minutes of ozonation was in the range of 7 to 8 for all three leachates, which is also within the pH range of raw leachate.

3.3.3 Leachate Treatment Using Membranes

As expected, RO and NF membrane treatment for raw and ozone treated leachate showed a high rejection efficiency of salts and DOM (Table 3-5). RO membrane rejected approximately 93 to 96% salts from RO membranes and 91 to 95% from the NF membrane for all three leachates treatment. The DOM as measured by the UV-254 absorbance was rejected to more than 99% by RO and NF membrane treatment of all three leachates.

The effect on permeate flux for treatment of raw and ozone treated leachate using RO and NF membrane is shown in Figure 3-8. A slight fluctuation in the data was observed that can be explained by the smaller variations in feed temperature, pressure, and random sampling during the experiment. At the start of experiment (for approximately 2 hours), the permeate flux decreased rapidly in all conditions, which slowed down for remainder of the experiment. The pattern of flux decline in all conditions were fitted in the power law model equation ($y=ax^b$) with a value of $r^2>0.87$ as shown in Table 3-6. Hyuang et al. (2000) evaluated ozonation as a pretreatment on flux parameters of ultra-filtration membranes for water treatment and observed similar pattern in the permeate flux decline. The derived power law equations can be used to predict the performance of these RO and NF membranes for treating raw and ozone treated leachate in the applied conditions.

A 10 to 14% decrease in permeate flux was observed for raw leachate treatment using RO membrane, whereas the NF membranes showed a flux decline of approximately 18 to 19% after 24 hours of experiment. Though, leachate pretreated with ozone had approximately 4%, 12%, and 10% less DOC and 54%, 64% and 59% less UV-254 absorbance with respect to raw ACL, NCL, and NRL leachate, respectively; leachate pretreatment with ozone did not reduce fouling of membranes and a faster permeate flux decline was observed, for the applied experimental conditions. The RO treatment of these leachate showed a permeate flux reduction of 17 to 23% at the end of experiment. The NF treatment showed even greater flux decline of 23% in ACL leachate and 32% in NCL and NRL leachate. Clearly, the reduction in DOC and UV-254 absorbance after ozonation did not reduce the fouling of membranes.

The increased fouling can be caused by the factors such as constituents of feed water, membrane properties, and the hydrodynamic conditions (Bellona et al., 2004; Tang et al., 2007). During the experiments, the hydrodynamic conditions were kept constants; hence, the fouling was mainly caused by different characteristics of raw and ozone treated leachate and different membrane surface properties of RO and NF membranes. The pH of each solution was in the range of 7 to 8 for all three leachates and during the membrane experiments the pH of each solution were not significantly changed. Hence, the changes in pH of feed solution during membrane experiments should not have a significant effect on permeate flux.

Among all three leachates, ACL leachate contained slightly higher concentrations of humic and fulvic-like organic compounds (Table 3-4) that are hydrophobic in nature

and have tendency to adsorb on the hydrophobic membrane surfaces at high pressure operations, which might be a possible reason of slightly higher flux decline in ACL leachate as compared to NCL and NRL leachate (Bellona et al., 2004; Tang et al., 2007). Additionally, the membrane surface roughness plays an important role in fouling such that higher the roughness, higher the fouling potential in presence of humic and fulvic-like organic matter (Hobbs et al., 2000). NF membranes have higher surface roughness than RO membranes (Table 3-2), which explains higher flux decline of NF membranes than RO membranes.

In order to determine the possible reasons of increased flux decline of ozone treated leachate than raw leachate, the Herima's filtration model was used. The model uses flux decline data and determines the type and cause of fouling. As presented in Table 3-7 and Table 3-8, each membrane showed closely related correlation coefficients (r^2) that vary to a small percentage (0 to 10%) for standard, cake, intermediate, and complete fouling mechanisms. This implies that the membranes have faced all four types of fouling by each feed waters throughout the experiment duration; however the rate of occurrence of each fouling was not the same. Among all four types of fouling constants, K_p was highest in all leachate treatment experiments, which shows the complete pore blocking mechanism was the most dominant fouling processes and the particles of the feed water block the pores by accumulating on the membrane surface but not over each other. Comparing the results between raw and ozonated leachate treatment showed that the ozonated leachate had higher fouling constant values than the raw leachate in all experiments, showing a faster flux decline in ozone treated leachate. Ozonation may increase the particle sizes due to ozone induced

particle destabilization (Lee et al., 2005). The destabilization reduces the net negative charge and thus increases the possibilities of particle collision and coagulation. Ozonation increases the concentration of carboxylic acids in the solution that may cause increased association with calcium present in the leachate, resulting in precipitation of complexes of calcium on the membrane surfaces and reduced permeate flux. Chandrakanth and Amy (1996) found that calcium in feed water act as a coagulant aid for the by-products formed during ozonation of NOM along with the formation of increased Ca-NOM complexes. The increased formation of Ca-NOM complexes and coagulated NOM over calcium may precipitate on the membrane surface and increases flux decline. Karnik et al. (2005) observed that increasing the ozone concentration beyond a threshold value had no beneficial effect on permeate flux recovery. Brown et al. (2008) also observed a decrease in permeate flux of RO membranes due to increase in particle sizes at high ozone doses caused by coagulation of calcium and NOM.,

3.4 Summary and Conclusions

Application of high pressure membrane system such as NF and RO can provide a efficient landfill leachate treatment option, however, the frequent fouling of these membranes due to the presence of higher concentrations of humic and fulvic-like organics limits its operation. The literature suggest that the use of ozone can decrease the concentrations of DOM and COD from the landfill leachate but there is no literature available on the effectiveness of ozone as a pretreatment method for treating landfill leachate using high pressure membranes. The first objective of this research was to determine the effectiveness of ozone for treating stabilized landfill leachate and to determine optimum ozone dose for membrane treatment operations. A fixed ozone dose of 70 mg/L was used at a feed gas flow rate of 3.5 L/min for 5 to 30 minutes to

treat leachate from three different landfills. A maximum of 78% drop in UV-254 absorbance and 23% drop in DOC was observed. Faster ozone kinetics was observed at the start of experiments, which plateaued after 8 to 10 minutes of ozonation in all three leachates. The characterization of organic matter using fluorescence EEM and FRI analysis also showed that the ozone removed most of the humic and fulvic like organics at the start of ozonation.

The second objective was to evaluate the performance of membrane operations for treatment of raw and ozone treated leachate. An optimum ozonation time of 10 minutes was used to run the membrane experiment. RO and NF membranes rejected greater than 99% of DOM and 91% salts from all three leachates in the experiment duration. The flux decline with the operation time was measured, which followed a power law equation; such that a faster flux decline at start of membrane operation was observed. The developed power law equations can be used to predict the performance of these RO and NF membranes for treatment of these types of leachate. A faster flux decline was observed for the ozonated leachate treatment than raw leachate in all conditions and NF membranes showed a faster flux decline as compared to the RO membranes. These flux declines were explained by Hermia's cross-flow, constant pressure filtration model and the results suggest that the fouling was primarily caused by the blocking of the membrane pores by the particles that accumulate on the membrane surface but not over each other thereby not allowing the filtrate to pass through. The rates of fouling constants were found higher in NF membranes than RO membranes confirming a higher flux decline in NF membranes.

This research showed that the use of ozonation as a pretreatment option for treating stabilized leachate using high pressure membranes did not help increase the permeate flux. In the applied experimental conditions, the ozonation of leachate before membrane treatment did not reduce the fouling potential of membranes. The ozonation provided a significant reduction or transformation of humic and fulvic-like organic matter from leachate; however, the selected ozone dose for membrane treatment might have caused additional complexation of calcium and the by-products of ozonation reaction, which might have reduced the permeate flux of membrane. Hence, a careful selection of ozone dose is required to consider ozonation as a pretreatment option for stabilized leachate treatment using membranes.

Furthermore, membrane fouling experiments should be conducted for the pretreated leachate using variable ozone doses. Possibly, a lower ozone dose can be used as compared to the dose used in the present study to pre-treat leachate. Lower doses may cause lesser coagulation caused by the calcium ions present in leachate. Anti-scalant can also be used as an additional pretreatment to reduce the possible coagulation caused by divalent ions.

Table 3-1. Previous studies on application of ozonation for landfill leachate treatment.

Initial concentrations in leachate			Maximum COD or DOC* Removal by ozonation (%)	Ozone dose	Additional treatment with ozone	Reference
COD/DOC* (mg/L)	BOD ₅ /COD	pH				
640/205**	-	8.24	-	-	Adsorption+O ₃	Fettig et al. (1996)
518	-	8.3	66	1.7 g O ₃ /g COD	Biological treatment +O ₃	Baig and Liechti (2001)
5,000	0.17	8-9	30	1.3-3.5 g O ₃ /hr	Adsorption+O ₃	Rivas et al. (2003)
3,460	0.04	8.2	48/-10 TOC	0.5-3 g O ₃ /L	Coagulation+O ₃ and NH ₃ stripping	Silva et al. (2004)
6,500/4,000 TOC	0.08	8.1	15 TOC	1.2 g O ₃ /L	Coagulation+O ₃ , O ₃ /H ₂ O ₂ , and O ₃ /UV	Wu et al. (2004)
1,090	0.04	8.3	75	1.2-12.5 g O ₃ /L	O ₃ and O ₃ /H ₂ O ₂	Wang et al. (2004)
4,000	0.05	8-8.5	70/48*	0.5-9.0 g O ₃ /L	Coagulation+O ₃	Bila et al. (2005)
1,010	0.17	8	80	1.5-2.0 g O ₃ /hr	Coagulation+O ₃	Ntampou et al. (2006)
5,230	0.09	8.7	27	1.1 g O ₃ /L	O ₃ and O ₃ /H ₂ O ₂	Tizaoui et al. (2007)
743/284 TOC	0.01	3.5	10/7 TOC	8 g O ₃ /hr	O ₃ and O ₃ /H ₂ O ₂	Cortez et al. (2010)

Table 3-2. Properties of reverse osmosis (BW-30) and nano filtration (NF-90) membranes used in the study

Parameter	BW 30	NF 90
Membrane type ¹	Fully aromatic membrane	Fully aromatic membrane
Operating pH range ¹	2-11	3-10
Maximum operating temperature (°C) ¹	45	45
Maximum operating pressure (bar (psi)) ¹	41.4 (600)	41.4 (600)
Pure water flux (m/day) ²	1.1±0.4	2.4±0.3
Salt rejection (%) ²	96.7±1.0	96.0±0.86
Virgin membrane zeta potential (pH 4.5/7) (mV) ³	3.8/-5.2	17.5/-26.5
Surface roughness (nm) ³	68.3 (±12.5)	129.5 (±23.4)

¹ From Dow FilmTec; ² Pure water flux was considered as permeate flux at the end of 48-h compaction period. Salt rejection were determined for the feed solution containing 10 mM NaCl at pH 7; ³ Tang et al., 2007.

Table 3-3. Leachate characteristics of ACL, NCL, and NRL leachate during the study period

Parameter	ACL		NCL		NRL	
	Average	Std dev	Average	Std dev	Average	Std dev
pH (S.U.)	7.71	0.01	7.47	0.02	7.74	0.05
Conductivity (mS/cm)	13.79	1.4	8.36		7.90	
TDS (mg/L)	6,546	30	4,221	11	4,034	24
BOD ₅ (mg/L)	57		135		260	
COD (mg/L)	2,286	46	2166	33	2,025	190
BOD ₅ /COD	0.02		0.06		0.12	
DOC (mg/L)	523	10.7	413	9.9	276	2.4
Alkalinity (mg/L as CaCO ₃)	6,800		3,200		800	
UV-254 (cm ⁻¹)	9.0		11.9		7.1	
SUVA (m ⁻¹ /mg/L DOC)	1.7		2.9		2.6	

Table 3-4. Percentage distribution and total volume (V_t) of DOM in Region-I to Region-V of ACL, NCL, and NRL leachate derived from FRI analysis

Region	ACL leachate	NCL leachate	NRL leachate
Region-I	1	1	0
Region-II	5	4	2
Region-III	13	13	12
Region-IV	17	14	10
Region-V	64	68	76
V _t (AU-nm ² -[mg-C/L] ⁻¹)	4,946	4,185	3,846
Fluorescence Index	2.21	2.04	1.89

Table 3-5. Percentage rejection¹ of salts² and DOM³ from raw and ozonated ACL, NCL, and NRL leachate treatment using RO and NF membranes

Leachate	Feed	Initial concentration	RO treatment	NF treatment
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from	leachate	Conductivity (mS/cm)	UV-254 (cm ⁻¹)	Salt rejection (%)	DOM rejection (%)	Salt rejection (%)	DOM rejection (%)
ACL	Raw	13.2±0.2	8.0±0.4	93.5±0.5	99.3±0.1	91.5±0.4	99.7±0.01
	Ozonated	12.9±0.2	4.0±0.1	92.6±0.6	98.8±0.1	91.4±0.3	98.8±0.04
NCL	Raw	12.9±0.2	12.1±0.3	93.1±0.9	99.4±0.1	93.1±0.4	99.8±0.02
	Ozonated	12.8±0.1	4.2±0.1	93.6±0.4	98.6±0.2	94.0±0.2	99.3±0.04
NRL	Raw	6.8±0.1	6.4±0.1	96.1±0.2	99.7±0.1	95.9±0.1	99.7±0.02
	Ozonated	6.7±0.1	2.4±0.1	96.4±0.3	99.3±0.1	95.6±0.2	99.5±0.05

¹ Percentage rejection of salt and DOM was calculated using average concentrations of permeate samples collected during each experiment and the initial concentration; ² Salt concentrations was measured using conductivity; ³ DOM was measured as UV-254 absorbance.

Table 3-6. Power law equation and the value of r² of flux decline with ozonation time for raw and ozonated leachate treatment using RO and NF membranes

Leachate from	Type of Feed leachate	RO		NF	
		Equation	r ²	Equation	r ²
ACL	Raw	y=1.0163x ^{-0.051}	0.90	y=0.9779x ^{-0.058}	0.87
	Ozonated	y=0.9448x ^{-0.041}	0.96	y=0.9576x ^{-0.063}	0.92
NCL	Raw	y=0.9784x ^{-0.028}	0.93	y=0.9422x ^{-0.047}	0.96
	Ozonated	y=0.9595x ^{-0.068}	0.92	y=0.9282x ^{-0.094}	0.96
NRL	Raw	y=0.9722x ^{-0.022}	0.92	y=0.9465x ^{-0.04}	0.89
	Ozonated	y=0.9680x ^{-0.051}	0.91	y=0.8943x ^{-0.084}	0.91

y=Permeate flux (m/day); x= Ozonation time (hrs)

Table 3-7. The correlation coefficient (r²) and the filtration constants of the Hermia's filtration model for raw and ozonated ACL, NCL, and NRL leachate treatment using RO membranes

Leachate from	Type of Feed leachate	Standard		Cake		Intermediate		Complete	
		r ²	K _s (L ⁻¹)	r ²	K _c (hr.L ⁻²)	r ²	K _i (L ⁻¹)	r ²	K _b (h ⁻¹)
ACL	Raw	0.98	1.97E-03	0.98	1.04E-03	0.98	2.88E-03	0.98	6.90E-03
	Ozonated	0.86	2.85E-03	0.89	1.30E-03	0.87	3.60E-03	0.85	9.50E-03
NCL	Raw	0.85	1.93E-03	0.86	7.80E-04	0.86	2.16E-03	0.85	6.00E-03
	Ozonated	0.78	4.56E-03	0.98	1.82E-03	0.88	5.05E-03	0.87	1.51E-02
NRL	Raw	0.89	7.44E-04	0.80	1.82E-04	0.89	7.21E-04	0.88	4.30E-03
	Ozonated	0.88	2.28E-03	0.89	5.20E-04	0.88	2.16E-03	0.87	9.60E-03

Table 3-8. The correlation coefficient (r²) and the filtration constants of the Hermia's filtration model for raw and ozonated ACL, NCL, and NRL leachate treatment using NF membranes

Leachate from	Type of Feed leachate	Standard		Cake		Intermediate		Complete	
		r ²	K _s (L ⁻¹)	r ²	K _c (hr.L ⁻²)	r ²	K _i (L ⁻¹)	r ²	K _b (h ⁻¹)
ACL	Raw	0.91	4.39E-03	0.93	1.30E-03	0.92	4.33E-03	0.90	1.43E-02
	Ozonated	0.90	4.29E-03	0.93	1.30E-03	0.91	4.33E-03	0.89	1.50E-02
NCL	Raw	0.87	2.42E-03	0.89	7.80E-04	0.95	4.33E-03	0.86	1.01E-02

	Ozonated	0.85	4.55E-03	0.90	1.30E-03	0.87	5.05E-03	0.83	2.13E-02
NRL	Raw	0.84	2.17E-03	0.86	2.60E-04	0.84	1.44E-03	0.83	1.22E-02
	Ozonated	0.93	3.16E-03	0.96	7.80E-04	0.94	3.60E-03	0.91	2.04E-02

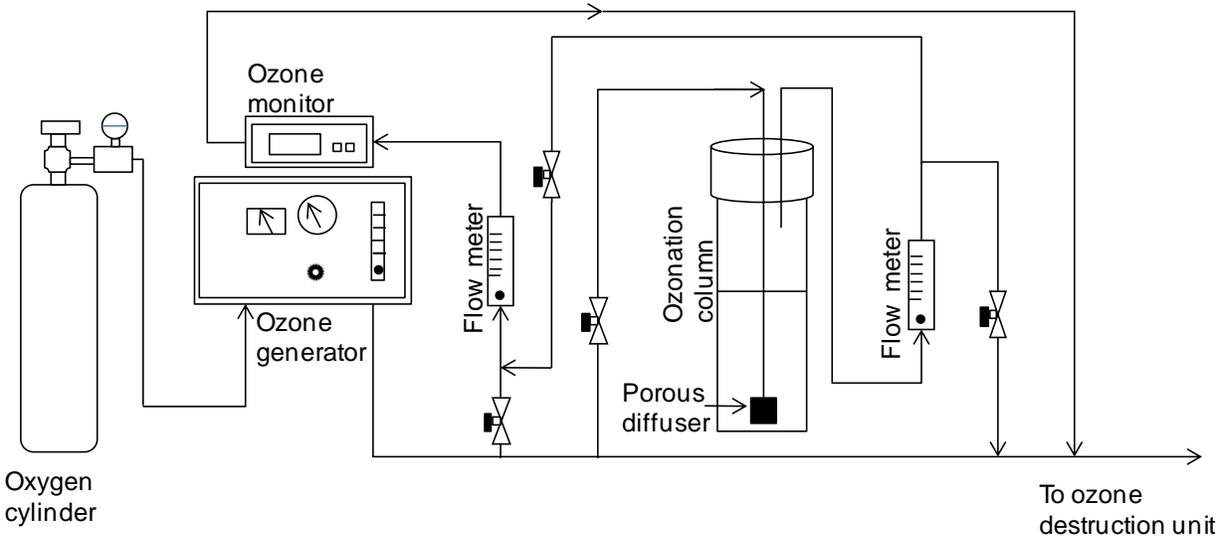


Figure 3-1. Schematic diagram of laboratory-scale ozonation setup

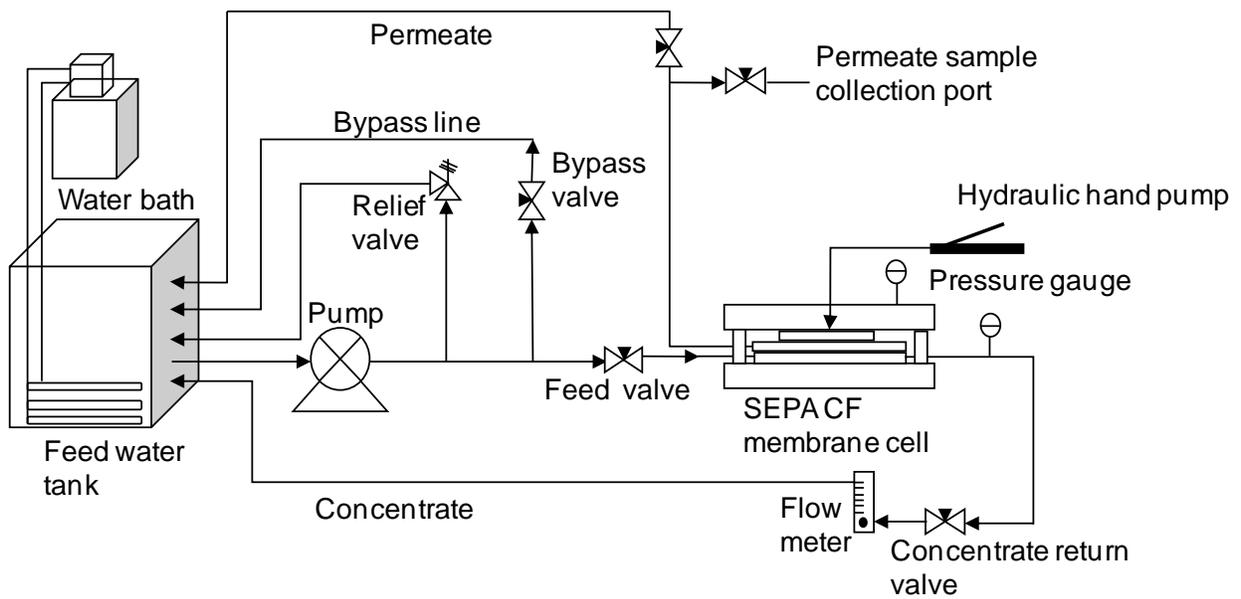


Figure 3-2. Experimental setup of laboratory-scale Osmonics SEPA CF membrane

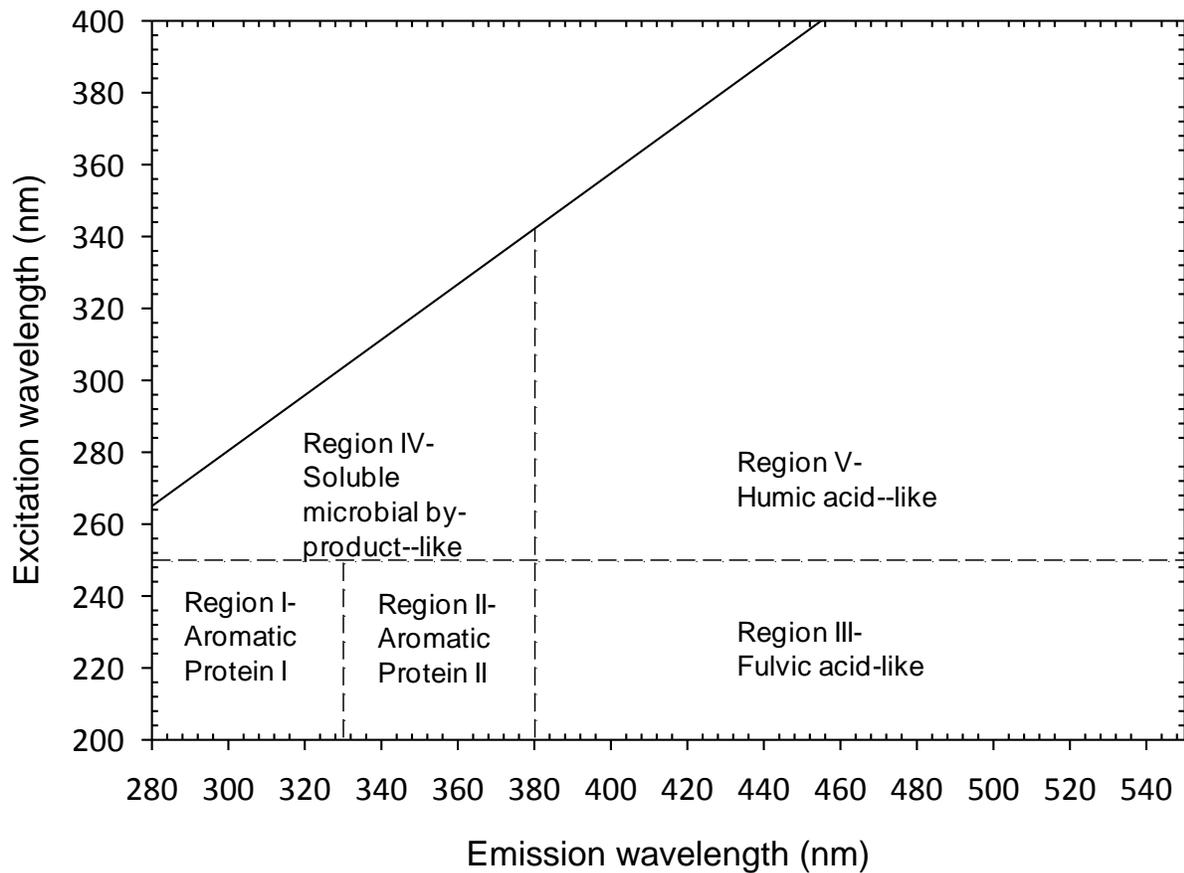


Figure 3-3. Operationally defined excitation and emission wavelength boundaries for five regions of excitation emission matrix (Chen et al., 2003).

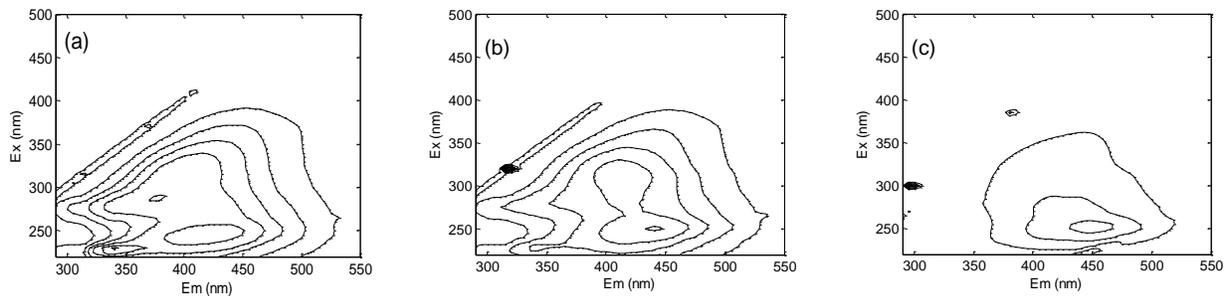


Figure 3-4. Fluorescence EEM of (a) ACL, (b) NCL, and (c) NRL leachate

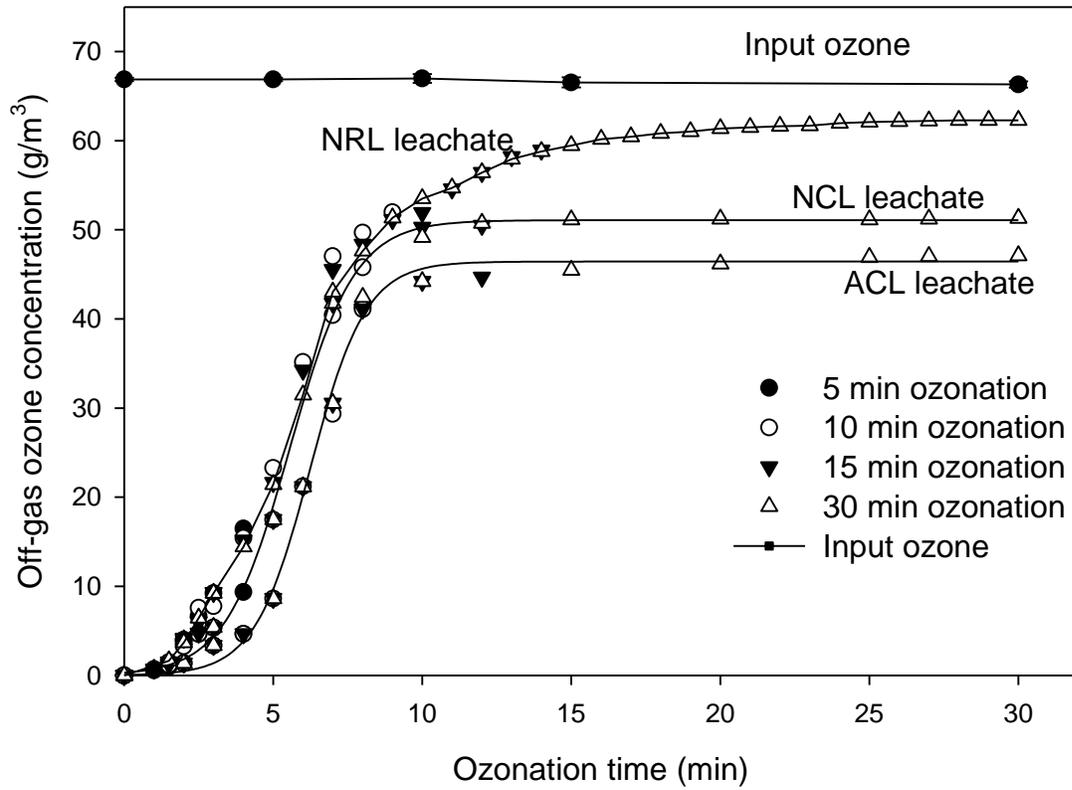


Figure 3-5. Evolution of the off-gas ozone concentration as a function of ozonation time for ACL, NCL, and NRL leachate

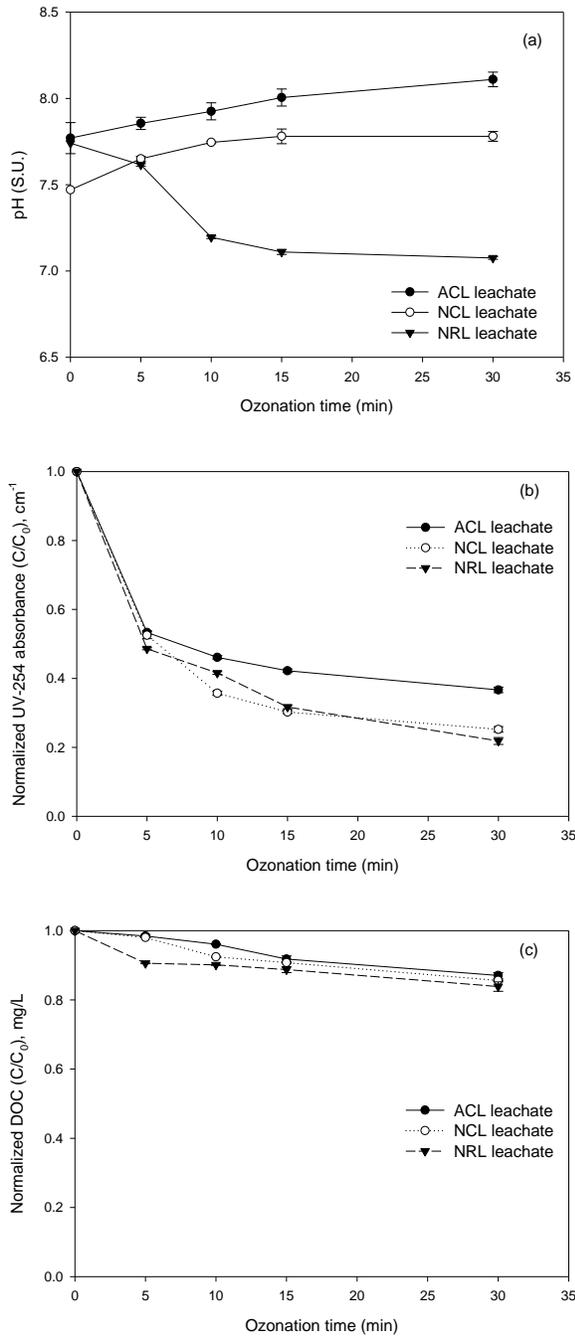


Figure 3-6. Effect of ozonation on (a) pH, (b) UV-254 absorbance, and (c) DOC of ACL, NCL, and NRL leachate. The data points and error bars represent average and standard deviation of duplicate experiments, respectively.

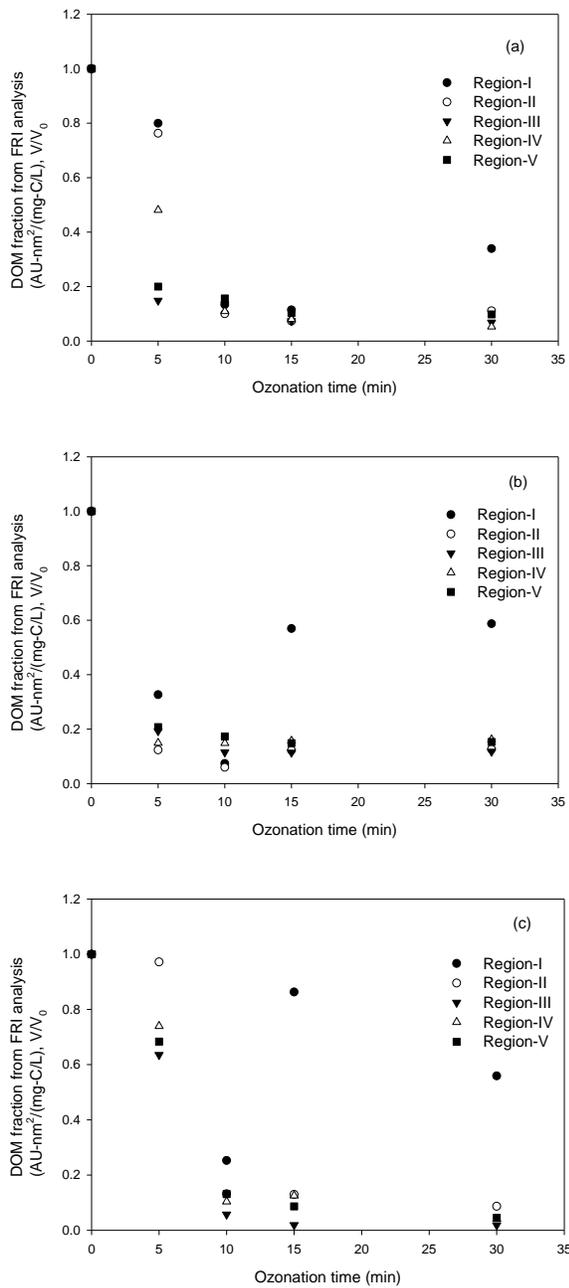


Figure 3-7. Effect of ozonation on removal of DOM for each EEM region derived from FRI analysis of (a) ACL, (b) NCL, and (c) NRL leachate

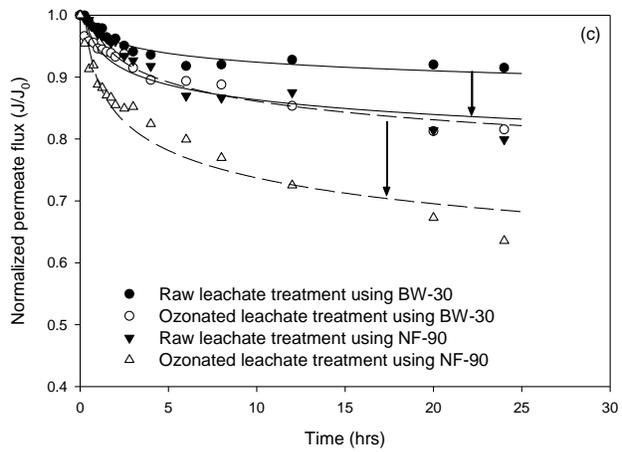
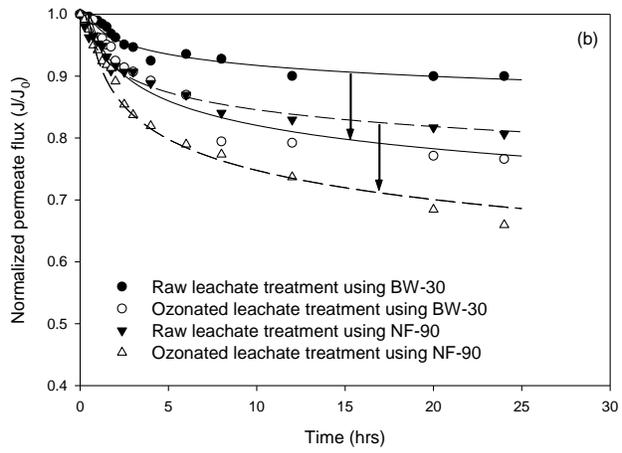
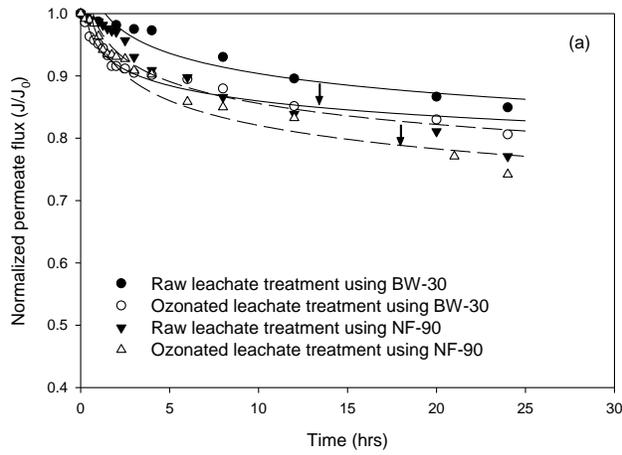


Figure 3-8. Effect on normalized permeate flux for treatment of raw and ozonated (a) ACL, (b) NCL, and (c) NRL leachate using BW-30 and NF-90 membrane

CHAPTER 4 EQUILIBRIUM AND INTRA-PARTICLE DIFFUSION OF STABILIZED LANDFILL LEACHATE ONTO MICRO AND MESO-POROUS ACTIVATED CARBON

4.1 Introduction

Leachate is generated when rainwater percolates through the layers of waste in the landfill. In the process, waste transfer pollutants to the percolating water, which might cause serious problems to the surrounding surface and groundwater bodies, if not properly managed (Christensen et al., 2001). Hence, leachate treatment is an essential part of effective landfill management.

Several treatment methods have been reported in the literatures that help reduce the hazardous nature of leachate; however, selection of treatment method depend upon leachate characteristics that change with age, landfill operation method, moisture availability, waste composition, and climate. In particular, composition of leachate varies greatly on the age of the landfill and can be characterized as young, intermediate, and stabilized leachate (Kjeldsen et al., 2002). Biological methods have been found effective to reduce the contaminants from the leachate generated from young landfills, as it contains high concentrations of biodegradable organic matter (Timur et al., 2000; Borghi et al., 2003). However, as the landfill grows old, leachate contains mostly refractory organic matter, making biological treatment methods less effective. When the leachate contains $BOD_5/COD < 0.1$, it is termed as stabilized leachate and physicochemical treatment methods have been found more effective for treating such old leachate. Several different treatment methods such as coagulation and flocculation (Tatsi et al., 2003), chemical oxidation (Monze-Ramirez and Velasquez, 2004), membrane based technologies (Chianese et al., 1999; Trebouet et al., 2001), and activated carbon adsorption (Kurniawan et al., 2006; Maranon et al., 2009) have

been investigated, however, high concentrations of refractory organic matter present in stabilized leachate always limit their treatment efficiency.

Adsorption on to activated carbon (AC) has been reported as an effective method for the removal of high molecular weight refractory organic matter from aqueous solution (Halim et al., 2010). Foo and Hameed (2009) have recently reviewed the studies on the landfill leachate treatment using AC and have found it a potentially viable leachate treatment method. Very few studies can be found on the use of AC for landfill leachate treatment, either as a single treatment step or in combination with other treatment options as presented in Table 4-1. Generally, the AC adsorption process has been used in combination with other treatment methods such as biological treatment methods, ozonation, and coagulation processes and has shown a wide range of treatment efficiencies for organic matter. Powdered AC (PAC) has been often found to be used with biological treatment methods. Kargi and Pamukoglu (2003) used a PAC with biological treatment system and achieved 49% COD removal efficiency for an initial COD of 7,000 mg/L. Granular AC (GAC) has been often used with physico-chemical treatment processes in leachate treatment; however, Morawe et al. (1995) used GAC as a polishing step after biological treatment of landfill leachate and observed a 70% COD removal efficiency for an initial COD of 940 mg/L. Kurniawan et al. (2006) investigated the treatment of landfill leachate using ozone and GAC together and achieved an 86% reduction in COD from an initial COD of 7,811 mg/L. Maranon et al. (2009) used AC adsorption as a tertiary treatment option for biologically pretreated landfill leachate and achieved a maximum of 63% reduction in COD from an initial COD of 785 mg/L. The

COD adsorption capacities were in the range of 0.06 to 0.56 g/g AC, depending upon the type of leachate and the additional treatment used with AC.

Several other studies have also been reported in the literature, however, all these studies have used micro-porous AC (pore size < 2 nm) due to their higher adsorption capacity (Morawe et al., 1995; Gotvajn et al., 2009). However, use of meso-porous AC (pore size 2 to 50 nm) can be an ideal option for stabilized leachate treatment, which has not been reported in the literature. Stabilized leachate contains high molecular size organic matter that might not be able to enter into commonly used micro-porous structure of AC and may block the pore openings at the surface of granule, consequently, reducing the adsorption capacity (Pignatello et al., 2006). However, the meso-porous AC have bigger pore opening and should allow the large organic molecules to diffuse within the pore and not affecting the adsorption capacity.

In addition to the availability of very few studies on the use of AC for leachate treatment, the studies in terms of adsorption isotherm determination and diffusion of organic matter onto AC, which are the primary factors to design and optimize a full-scale or pilot-scale AC treatment system has been rarely found in the literature. Hence, in the present research, the adsorption of organic matter present in stabilized leachate was studied onto three different ACs, which were selected based upon their pore sizes. One micro-porous and two meso-porous ACs were selected to compare their adsorption isotherm profile, the rate limiting adsorption processes, and the rate of organic matter diffusion. Rapid small scale column tests (RSSCT) were conducted to determine the amount and the type of organic matter removed using these three ACs for leachate treatment.

4.2 Experimental Material and Methods

4.2.1 Landfill Leachate and Activated Carbons

Experiments were conducted using leachate generated from a lined and capped waste disposal unit of the Alachua County Southwest Landfill (ACL) located in Florida, USA. Landfill accepted municipal solid waste in the duration of May 1988 to December 1998 and has been operated as a bioreactor landfill since 1990 through various leachate recirculation activities. Leachate was collected from the leachate lift-station, where all the leachate from the landfill is drained. Leachate samples were collected multiple times in the duration from August 2009 to December 2009 in Nalgene containers and kept at 4⁰C in the dark until used in experiments. Relevant physico-chemical characteristics of leachate are presented in Table 4-2. The composition of leachate was relatively constant over the research period and was characterized by slightly alkaline pH, dark in color, with a low concentration of biodegradable content as represented by BOD₅, and high concentration of refractory organic matter as represented by COD. These properties are consistent with typical stabilized leachate (Statom et al., 2004).

Three AC used in the study were Calgon Filtrasorb F-300 (Calgon Carbon Corporation, Pittsburgh PA), Norit HD-4000 (The Netherlands), and Darco 12x40 (Norit Americas Inc. Texas). General characteristics of AC are detailed in Table 4-3. ACs were selected with varying pore sizes. The Calgon F-300 showed an average pore size diameter of 18 Å with predominantly micro-porous AC structure. The Norit HD-4000 and the Darco 12x40 were predominantly meso-porous ACs with pore size diameters of 32 Å and 42 Å, respectively.

4.2.2 Batch Experiments

Batch experiments were conducted for developing the adsorption isotherms and to determine the intra-particle diffusivity of organic matter onto selected AC. Leachate was filtered using a glass-fiber filter prior to each experiment. All experiments were conducted in duplicate for quality control purposes and at constant temperature of 23⁰C.

Isotherm experiment

Isotherm experiments were conducted using predetermined adsorbent doses of 0 to 100 g /L. Activated carbon from 0 to 10 g was added in separate cleaned, pre-dried amber bottles and 100 mL of filtered leachate was added in each amber bottle. Amber bottles were kept on a rotary shaker, which was operated at 150 rpm. Amber bottles were wrapped with aluminum foil to avoid their exposure to light. Samples were shaken for approximately 240 hours until the equilibrium was achieved. Rivas et al. (2006) also achieved the equilibrium within 200 hours while studying the kinetics of adsorption of landfill leachate onto AC. After equilibration time, samples were filtered using glass-fiber filter to avoid AC particles entering into the samples to be analyzed. Samples were analyzed for total organic carbon (TOC).

Diffusivity experiment

The intra-particle diffusivity of organic matter was determined by short-term kinetic experiment using AC particles of different sizes. Activated carbon were crushed and sieved through the sieve numbers 20, 35, 50, and 200. Particles retained at the top of the sieves were used in the experiment. All fractions were cleaned with deionized water and were dried at 105 ⁰C for 24 hours.

Each type and particle size of AC were weighed to 1 g and taken into clean dried 40 mL glass vials. Glass vials were filled with 30 mL leachate and kept on the rotary

shaker, which was operated at 150 rpm. After every hour, one sample containing each size AC was removed from the shaker and samples were collected for TOC analysis by filtering leachate-AC solution using glass-fiber filters.

4.2.3 Rapid Small Scale Column Tests

Crittenden et al. (1986, 1991) presented the methodology for predicting full-scale AC column performance using RSSCTs that can generate breakthrough profile in a very short period of time as compared to full-scale or pilot-scale studies. RSSCTs also require lesser volumes of water for testing performance of AC to that water (Crittenden et al., 1986; 1991).

The small-scale columns used in the study were designed depending upon the design parameters of a full-scale column (Table 4-4) and the scaling equations (equations 4-1 and 4-2) developed by Crittenden et al. (1991).

$$\frac{EBCT_{SC}}{EBCT_{LC}} = \left(\frac{R_{SC}}{R_{LC}}\right)^{2-x} = \frac{t_{SC}}{t_{LC}} \quad (4-1)$$

$$\frac{V_{SC}}{V_{LC}} = \frac{R_{SC}}{R_{LC}} \times \frac{R_{eSC}}{R_{eLC}} \quad (4-2)$$

where, EBCT is empty bed contact time (min), R is AC particle radius (cm), t is time (min) to complete the test, V is hydraulic loading rate (m/min), and R_e is Reynolds number. The subscripts SC and LC represent the small and long column.

The calculated design parameters of RSSCT columns for each AC are presented in Table 4-4. RSSCT columns (0.5 cm diameter x 12 cm length) were made-up of quartz glass with PTFE inserts to prevent the sorption of organic matter. Syringe pump (Harvard apparatus model 33) was used to supply the constant flow rate to the columns. The flow rate of leachate to the column was monitored by the flow meter installed in the syringe pump. Experiments were conducted at 6.6, 10, 15, 30, and 60 minutes empty

bed contact time (EBCT) of long-column; corresponding EBCT for small-scale columns as calculated by equation 4-1 and 4-2 for each AC are listed in Table 4-5. Samples were collected after 15 minutes of small-scale column run and were analyzed for TOC to determine the amount of organic matter removed at each EBCT. Type of organic matter adsorption onto AC with respect to EBCT was analyzed by characterizing the organic matter present in the samples using fluorescence spectroscopy. The samples were filtered using 0.45 μm filter before analyzing the fluorescence spectrum.

4.2.4 Analysis

A multi-function Orion Research instrument was used to analyze water quality parameters pH and temperature. TOC was measured using TOC-V CPH/CPN analyzer and the fluorescence excitation-emission spectrum was measured using the Hitachi F-2500 Fluorescence spectrophotometer.

Excitation emission matrix (EEM) was generated for the excitation wavelength (E_x) of 200 nm to 500 nm at 5 nm increments and for each E_x , the emission wavelength (E_m) was detected at 5 nm increments in the range of 290 to 550 nm. Data were processed in MATLAB following the procedures developed by Chen et al. (2003) and Cory and Mcknight (2005). First, the effect of scattering was reduced by subtracting EEM response of de-ionized water to EEM response of DOM containing samples followed by calculating the area under the Raman water peak (at E_x 350 nm) for de-ionized water. Then, the intensities of the EEM response for the DOM containing samples were normalized by the Raman water area. Afterwards; the calculated EEM response of the sample was normalized by the DOC concentration; and EEM were plotted in MATLAB using the contour function.

The contour plot of EEM response was divided into five E_x - E_m regions based on the EEM peaks associated with specific types of organic compounds. These regions were decided using the literature Chen et al. (2003); Chen et al. (2003); Baker (2004); Hudson (2007). The amount of DOM present in each region was quantified using Fluorescence Regional Integration (FRI) technique (Chen et al., 2003). The volume of each region under the EEM spectra was calculated using equation 4-3.

$$V_i = \int_{ex} \int_{em} I(\lambda_{ex} \lambda_{em}) d\lambda_{ex} d\lambda_{em} \quad (4-3)$$

where, V_i represents the volume under region “i”; $I(\lambda_{ex} \lambda_{em})$ is the fluorescence intensity at a particular E_x - E_m pair; $d\lambda_{ex}$ is the increment of E_x (5 nm), and $d\lambda_{em}$ is the increment of E_m (5 nm).

4.3 Results and Discussion

4.3.1 Adsorption Equilibrium Study

To effectively design an adsorption system, it is essential to develop most appropriate mathematical description of adsorption isotherms. Several isotherm equations (e.g. equations 4-4, 4-5, and 4-6) have been developed for the AC and organic matter adsorption process and the parameters of these equations express the surface properties and the affinity of adsorbent at a fixed temperature and pH. Each model varies with respect to their assumption of thermodynamic adsorption process and has their own set of advantages and disadvantages. The Freundlich isotherm (equation 4-4) has been widely used and can be applied for heterogeneous surfaces along with multi-layer adsorption processes and the amount of adsorbate adsorbed onto adsorbent increases infinitely with increase in concentration; however, it does not fit data very well for the low concentration systems (Freundlich, 1906). The Langmuir adsorption

isotherm (equation 4-5) assumes the monolayer sorption process, which limits its applicability at high concentration systems (Langmuir, 1916). Freundlich and Langmuir isotherms are two parameter isotherm equations with their own limitations; Redlich and Peterson (1959) developed a three parameter isotherm equation (equation 4-6) to incorporate the features of both Freundlich and Langmuir isotherms. At low concentrations, the Redlich-Peterson isotherm follows monolayer sorption and at high concentrations its behavior approaches to Freundlich isotherm.

Freundlich isotherm:

$$Q_e = K_F C_e^{\frac{1}{n}} \quad (4-4)$$

Langmuir isotherm:

$$Q_e = \frac{Q_m b C_e}{1 + b C_e} \quad (4-5)$$

Redlich-Peterson isotherm:

$$Q_e = \frac{K_R C_e}{1 + a_R C_e^{b_R}} \quad (4-6)$$

where, Q_e is the amount of solute adsorbed at equilibrium (mg/g); C_e is the concentration of adsorbate in solution at equilibrium (mg/L); K_F and n are adjustable parameter in Freundlich equation; Q_m and b are adjustable parameter in Langmuir equation; K_R , a_R , and b_R are adjustable parameter in Redlich-Peterson equation.

The most common approach to assess the adsorption capacity using above mentioned isotherm equations is to use the linear regression analysis of the experimental data and the isotherm with R^2 closest to one was assumed to be the best fit isotherm equation. However, transforming non-linear equation to linear form may generate an error in analysis; hence, a non-linear analysis approach as developed by Ho et al. (2001) was followed for each isotherm. Non-linear regression error functions

(equations 4-7 to 4-11) were used to assess most suitable isotherm models that fit to the experimental data.

Sum of absolute errors:

$$SAE = \sum_{i=1}^{i=N} |Q_e - \bar{Q}_e|_i \quad (4-7)$$

Sum of error square:

$$Err^2 = \sum_{i=1}^{i=N} (Q_e - \bar{Q}_e)_i^2 \quad (4-8)$$

Composite fractional error method

$$CFEF = \sum_{i=1}^{i=N} \left[\frac{(Q_e - \bar{Q}_e)_i^2}{Q_e} \right]_i \quad (4-9)$$

Derivative Marquardt's percent standard deviation

$$DMPSD = \sum_{i=1}^{i=N} \left[\frac{Q_e - \bar{Q}_e}{Q_e} \right]_i^2 \quad (4-10)$$

Average relative error

$$ARE = \sum_{i=1}^{i=N} \left| \frac{Q_e - \bar{Q}_e}{Q_e} \right|_i \quad (4-11)$$

where, Q_e is measured equilibrium concentration of adsorbate in the solid phase, and \bar{Q}_e is the calculated concentration of adsorbate in the solid phase.

Each error function generated different sets of isotherm parameters; hence, a procedure that normalizes the parameters and combines the errors was adopted. First, one isotherm and one error function was selected and isotherm parameter values that minimize the error function were determined using solver add-in function of Microsoft Excel. Using these isotherm parameter values, values for other error functions were determined and at the end five values were obtained. A similar procedure of minimizing the error function was applied to each error function and a different isotherm parameter set and error function values was obtained. Then, the five values of each error function

were normalized using the maximum of these values and the normalized values were summed up. The parameter set that provided smallest sum of normalized error was considered as the best parameter set values.

The non-linear isotherm plots for three different AC are presented in Figure 4-1. Among each of the three isotherms, Freundlich and Redlich-Peterson isotherms gave a better fit to the experimental data, with the best fit in Redlich-Peterson isotherm. Langmuir isotherm did not show a good fit to the experimental data, further strengthening the fact that it does not fit for high concentration solutions. The model equation for Langmuir isotherm also showed a sharp increase in Q_e for higher C_e values. Rivas et al. (2006) also observed a sharp increase in Q_e for COD adsorption Langmuir isotherm at high C_e values. The parameters of the three isotherm equations for the three ACs are shown in Table 4-6. The Freundlich and Redlich-Peterson isotherms predicted almost similar adsorption capacity to the organic matter for each of the three AC. The Freundlich isotherm constant (K_F) for each of the three ACs were in the range of 0.04 to 0.05. The values of 'n' also showed a stronger adsorption bond between organic matter and AC in each of the three AC.

Freundlich isotherm predicted a rate of 0.3 g TOC adsorption/g AC for 50% TOC removal from the leachate by Norit HD-4000 AC. A slightly higher adsorption of 0.47 g TOC adsorption/g AC was observed with Calgon F-300. The Redlich-Peterson Model predicted lower values than Freundlich model as 0.22, 0.18, and 0.19 g TOC adsorption/g AC with Calgon F-300, Norit HD-4000, and Darco 12x40 AC, respectively. Though, the micro-porous AC has larger surface area and should have higher adsorption capacity than meso-porous AC, the presence of high molecular weight and

size organic matter (humic and fulvic-like) may block the pores of micro-porous AC at the surface due to steric effect and reduce the adsorption capacity during stabilized leachate treatment (Karanfil et al., 2006; Pignatello et al., 2006). The meso-porous AC have pore opening in the range of 2 to 50 nm, which are in the molecular size range of humic-like organic molecule (<2.5 nm to 40 nm) (Osterberg et al., 1992). These bigger organic molecule should not block the pores of meso-porous AC particle and AC should use their effective adsorption capacity. This might be the possible reason of almost similar adsorption capacities observed in micro-porous and meso-porous AC (Pignatello et al., 2006). Although, there is little data available on landfill leachate adsorption onto AC, Xing et al. (2008) reported 0.2 g TOC adsorption/g of coal based AC, a similar adsorption capacity as predicted by Redlich-Peterson model for the set of ACs and leachate used in this study.

4.3.2 Intra-particle Diffusivity

The sorption of organic matter onto AC is a complex phenomenon, where properties of both adsorbate and adsorbent play an important role. The adsorption process can be controlled by following sequential steps: (1) the bulk solution transport, where the adsorbate diffuses from solution to the boundary layer of solution surrounding the AC particles, (2) film diffusion, where adsorbate diffuses through the liquid film surrounding the AC particles, and (3) pore diffusion and adsorption, where adsorbent is transported to the pores of AC to available adsorption sites. One or more than one process can be involved in the adsorption process and the slowest process controls the rate of adsorption process.

Weber and Moris (1963) (equation 4-12) developed a widely accepted kinetic based model that represents the time dependent intra-particle diffusion of components

and showed that the sorption process is diffusion controlled if its rate is dependent upon the rate at which adsorbate and adsorbent diffuse towards one another.

$$q_t = k_{id}t^{1/2} + C \quad (4-12)$$

where, q_t (mg/g) is the adsorbate loading on the solid phase at time t , k_{id} (mg/g min^{1/2}) is the intra-particle diffusion rate constant, and C (mg/g) is the constant that is proportional to the thickness of boundary layer; larger the value of C greater the boundary layer thickness (Mckay et al., 1980). The straight line plot of q_t and $t^{1/2}$ represents the sorption process as diffusion controlled, however, if the data shows multiple linear plots, the sorption process is controlled by more than one processes. At first, the sharper portion of the plot represents external resistance to mass transfer followed by gradual adsorption where intra-particle diffusion is the controlling factor.

Figure 4-2 shows the relation of mass of TOC adsorbed per unit mass of different particle sizes of three different AC to the $t^{1/2}$. Each of the three AC showed two straight lines for the particle sizes greater than 0.3 mm. The first portion of straight line represents the diffusion process controlled by external surfaces and the second portion of straight line showed the intra-particle diffusion. Extrapolation of the linear portion of the plots to the y-axis shows intercepts that provide the boundary layer thicknesses. An increased boundary layer thickness was observed with the decrease in AC particle sizes (Table 4-7) representing slower intra-particle diffusion for smaller AC particle. The deviation of straight lines from the origin represents the difference in diffusion rate in initial and final stages of adsorption. The diffusion rate constants (k_{id}) were observed to be decreasing with the decreasing AC particle sizes (Table 4-7) and k_{id} varied to approximate square root of the AC particle sizes similar to as observed by McKay et al.

(1980; 1987). The dependence of k_{id} on particle diameter shows that the intra-particle diffusion is the predominant rate controlling step during part of adsorption process

McKay et al. (1980).

The AC particle sizes less than 0.3 mm did not show similar intra-particle diffusion pattern in micro and meso-porous AC, wherein, the micro-porous Calgon F-300 AC showed two straight lines but the meso-porous AC Norit HD-4000 and Darco 12x40 showed only one straight line representing only micro-porous diffusion as the main diffusion process in meso-porous AC for these sizes of AC particles. A higher boundary layer thickness in the meso-porous AC as shown in Table 4-7 also supports the observed results.

The Weber-Morris model (equation 4-12) predicted that the intra-particle diffusion was the main rate limiting factor for organic matter adsorption onto each of the three AC. Additionally Boyd et al. (1947) generated a homogeneous particle diffusion model (HPDM) (equation 4-13) for adsorbent phase controlled diffusion (such as intra-particle diffusion) of adsorbate onto spherical particles to determine the rate of diffusion process.

$$F(t) = 1 - \frac{6}{\pi^2} \sum_{z=1}^{\infty} \frac{1}{z^2} \exp \left[\frac{-z^2 \pi^2 D_e t}{r^2} \right] \quad (4-13)$$

where, $F(t)$ is the fractional attainment of equilibrium at time t , D_e the effective diffusion coefficient of adsorbate onto adsorbent (m^2/sec), r the radius of adsorbent particle assumed to be spherical (m), and z in an integer.

$F(t)$ values can be calculated as $F(t) = \frac{q_t}{q_e}$, where q_t and q_e are adsorbate loading on the adsorbent at time t and when equilibrium is achieved respectively.

Vermeulen's approximation of HPDM model fit the whole range $0 < F(t) < 1$, for adsorption on spherical particles as shown in equations 4-14 and 4-15 (Vermeulen, 1953);

$$F(t) = \left[1 - \exp\left(\frac{-\pi^2 D_e t}{r^2}\right) \right]^{1/2} \quad (4-14)$$

$$-\ln(1 - F^2(t)) = kt, \quad (4-15)$$

where, $k = \frac{\pi^2 D_e}{r^2}$.

The slope of plot $-\ln[1-F^2(t)]$ and t as shown in Figure 4-3 gives the value of effective diffusion coefficient (D_e). From the plots, it is evident that the data satisfactorily fit in the entire range of diffusion for each size AC particles. The r^2 values of each plot are presented in Table 4-8. The D_e values as presented in Table 4-8 shows that the meso-porous Norit HD-4000 has the highest rate of diffusion among all three AC in an order of Norit HD-4000 > Darco 12x40 > Calgon F-300. There is no data available to compare the results of TOC adsorption onto these AC.

The type of intra-particle diffusivity of TOC onto AC was determined as shown in Figure 4-4. Generally, the intra-particle diffusivity can be termed as 'constant' if the kinetic adsorption profile does not vary with the change in size of AC particles, however, if the adsorption profile varies with the size of AC particles, the diffusivity is termed as 'proportional' (Crittenden et al., 1991). The micro-porous Calgon F-300 AC showed that as the size of AC particles was changed the kinetic adsorption profile also changed, representing the proportional diffusivity of organic matter into AC. However, the meso-porous Norit HD-4000 and Draco 12x40 AC showed constant intra-particle diffusivity of organic matter onto AC. The possible reason of such behavior in meso-porous AC was bigger pore diameters of AC particles that allow bigger organic molecules (humic and

fulvic-like) to enter into the pores and least effect of the particle sizes, whereas in the micro-porous AC, the pore diameters are small, which does not allow these organic molecules to enter into the pore as easily as in meso-porous AC.

4.3.3 Column Experiment

RSSCT experiments were conducted to determine the efficiency of AC columns for removal of organic matter at different EBCT. As shown in Figure 4-5, an increased TOC removal was observed with the increase in EBCT. However, EBCT greater than 30 minutes did not show any significant increase in TOC removal in each of the three AC, representing at least 30 minutes of EBCT was required for maximum TOC removal. Additionally, each of the three AC showed almost similar TOC removal efficiency, with slightly better TOC removal performance in Calgon F-300 AC. More than 85% of TOC was removed from leachate using any of the three AC at 60 min of EBCT. Rivas et al. (2003) obtained a 90% COD removal using micro-porous AC which is comparable to the results of current study.

The fluorescence EEM analysis of leachate and samples generated at different EBCT was conducted. The EEM shows the presence of organic matter at specific E_x and E_m wavelengths by peaks. Shorter E_x (<250 nm) and shorter E_m (<350nm) are generally associated with the simple aromatic protein-like compounds such as tyrosine (Regions-I and Region-II). The peaks at E_x in the range of 250 to 280 nm and E_m <380 nm are associated with soluble microbial byproducts type compounds and are shown in Region-IV. The fulvic-like compounds (Region-III) show peaks at shorter E_x (<250 nm) and longer E_m (>350 nm). Peaks at longer E_x and longer E_m are associated with humic-like compounds and shown in Region-V. The EEM of leachate as shown in Figure 4-6 showed peaks in the Region-II, Region-III, and Region-V, representing the presence of

protein, fulvic, and humic-like organic matter in the leachate. The FRI analysis was conducted using equation 4-1 and showed the maximum concentration of organic matter in the Region-V (Table 4-9). The fractional removal of organic matter of each region with respect to the EBCT for each of the three AC is shown in Figure 4-7. Each type of organic matter was removed and the amount of organic matter removed was found increasing with the increase in EBCT. However, among all type of organic matter, highest removal was observed for the fulvic-like organic matter from each AC. Smaller organic matter of Region-I showed increased adsorption for smaller EBCT, however, they desorbed at higher EBCT due to preferential adsorption of humic and fulvic-like organic matter on to AC.

4.4 Summary and Conclusions

Adsorption of leachate onto three different AC micro-porous Calgon F-300, meso-porous Norit HD-4000 and Darco 12x40 AC was studied to assess their effectiveness for organic matter removal. The adsorption capacity, the rate of organic matter diffusion, and the type of organic matter removed were studied using isotherms, diffusivity, and RSSCT experiments, respectively.

Each of the three AC showed almost similar organic matter adsorption capacity, with slightly better adsorption capacity in micro-porous Calgon F-300 AC. Among the adsorption isotherm model tested, three parameter model Redlich-Peterson gave the best fit to the experimental data, which contains the feature of Freundlich and Langmuir isotherm. The Langmuir isotherm did not give a good fit for the experimental data.

The Weber-Moris model equation of diffusivity showed that the overall diffusion of organic matter was controlled by the intra-particle diffusion process, which is a two-step process. The diffusion process was initially controlled by macro-pore diffusion followed

by relatively slow micro-pore diffusion. The effect of AC particle sizes on the diffusion process showed that as the AC particle sizes were reduced, the overall diffusion rate constant also decreased and the boundary layer thickness across the adsorbent particles increased. Among all three AC studied, meso-porous Norit HD-4000 AC showed maximum rate of diffusion of organic matter onto AC. Micro-porous Calgon AC showed a proportional diffusivity of organic matter, whereas meso-porous Norit HD-4000 and Darco 12x40 AC showed constant diffusivity onto AC particles.

The RSSCT results showed a slightly almost similar performance in terms of TOC removal with slightly better TOC removal by micro-porous AC at smaller EBCT. The FRI analysis of fluorescence EEM showed greatest removal for fulvic-like organic compounds by each of the three AC. The protein-like organic matter tends to adsorb at smaller EBCT and then desorbs at higher EBCT.

Hence, this study demonstrates that micro as well as meso-porous AC provide almost similar organic matter adsorption capacity while treating stabilized leachate, however, meso porous AC provide slightly faster organic removal than micro-porous AC. Even though the AC showed very encouraging results in terms of TOC removal, the process will be best suited when combined with other pretreatments. The high concentrations of organic matter present in leachate may exhaust the AC quickly and making the treatment process economically unfavorable.

Furthermore, it will be valuable to determine the effectiveness of meso-porous AC for stabilized leachate treatments using field-scale design parameters, because, generally all the studies been conducted for leachate treatment have used micro-porous AC. The performance of RSSCTs should also be validated with the filed-scale study.

Table 4-1. Previous studies on landfill leachate treatment using activated carbon adsorption process

Initial concentrations		AC	Micro-	COD	Maximum	Additional	Reference
COD	BOD ₅	type/precursor/GAC/ PAC	porous/Meso- porous AC	Removal (%)	Adsorption capacity (g/g AC)	treatment with AC	
/DOC* (mg/L)	/COD						
879-940	0.004	Calgon F400 (GAC)	Micro-Porous	70	0.56	Biological treatment+AC	Morawe et al. (1995)
205*	-	Norit NRS EA (PAC)	-	-	0.06/0.08	AC/Ozone+AC	Fettig et al. (1996)
10,750	0.6	Norit SA 4 (PAC)	-	38	-	ASP+AC	Aktas and Cecen (2001)
7,000	-	Commercial PAC	-	49	-	Biological treatment+AC	Kargi and Pamukoglu (2003)
5,000	0.17	Norit 0.8	Micro-porous	90	0.2	Ozone+AC	Rivas et al. (2003)
3,600	0.11	Norit 0.8 (GAC)	Micro-porous	75	0.9-1.4	AC	Rivas et al. (2004)
		Chemviron AQ 40 (GAC)	Micro-porous	55			
		Picacarb 1240 (GAC)	Micro-porous	55			
7,811	0.08	GAC (type PHO 8/35 LBD)	Micro-Porous	60/86	0.16	AC/ Ozone+AC	Kurniawan et al. (2006)
110 TOC	-	Coal based PAC	Micro-Porous	54	-	Coagulation+ AC	Xing et al. (2008)
		Coal based GAC		50			
		Wood based GAC		33			
		Wood based PAC		14			
2,461	0.24	Darco 20x40 (GAC)	-	40	-	AC	Gotvajn et al. (2009)
785	-	Organosorb 10MB	Micro-Porous	55	0.150-0.157	AC	Maranon et al. (2009)
		Filtracarb CC65/1240	Micro-Porous	51	0.145-0.175		

Table 4-2. Physico-chemical characteristics of ACL leachate during the study period

Parameter	Average	Std dev
pH (S.U.)	7.71	0.01
Conductivity (mS/cm)	13.79	1.4
TDS (mg/L)	6546	30
BOD ₅ (mg/L)	57	
COD (mg/L)	2300	46
BOD ₅ /COD	0.02	
DOC (mg/L)	523	10.7
NH ₃ -N (mg/L)	1060	63
Alkalinity (mg/L as CaCO ₃)	6800	
UV-254 (cm ⁻¹)	9.0	
SUVA (m ⁻¹ /mg/L DOC)	1.7	

Table 4-3. Characteristics of Calgon F-300, Norit HD-4000, and Darco 12x40 AC

Parameter	Calgon F-300	Norit HD-4000	Darco 12x40
Iodine number (mg/g)	900 ^a	500 ^b	625 ^b
Surface area (m ² /g)	816	546	588
Pore size (Å)	18	32	42
Mesh size	8x30 ^a	10x30 ^b	12x40 ^b
Effective particle size (mm)	0.8-1.0 ^a	0.6-0.8	0.65 ^b

^a Values obtained from Calgon group; ^b Values obtained from Norit group

Table 4-4. Design parameters of full-scale and RSSCT

Parameter	Full-scale	Calgon F-300	Norit HD-4000	Darco 12x40
Grain size-US mesh	8x30	35x50	35x50	35x50
EBCT (min)	5-60	1.3-12	0.9-8.4	0.6-5.2
Hydraulic loading rate (mm/min)	17-205	4.6	4.6	4.6
Time to process (hours)	28.8	4	4	4

Table 4-5. Comparative empty bed contact time (EBCT) of full-scale and RSSCT columns for Calgon F-300, Norit HD-4000, and Darco 12x40 AC

EBCT full-scale column (min)	EBCT for RSSCT (min)		
	Calgon F-300	Norit HD-4000	Darco 12x40
6.6	1.3	0.9	0.6
10	2	1.4	0.9
15	3	2.1	1.3
30	6	4.2	2.6
60	12	8.4	5.2

Table 4-6. Isotherm parameters obtained using non-linear method for organic matter absorption onto Calgon F-300, Norit HD-4000, and Darco 12x40 AC

Isotherm	Constant	Calgon F-300	Norit HD-4000	Darco 12x40
Freundlich	K_F	0.04	0.05	0.04
	$1/n$	1.63	1.52	1.59
Langmuir	Q_M	-16.98	-5.69	-7.09
	b	-0.001	-0.01	-0.01
Redlich-Peterson	K_R	0.71	0.56	0.63
	a_R	578.81	917.82	647.16
	b_R	-1.89	-2.03	-1.88

Table 4-7. Boundary layer thickness (C) of different particle sizes of Calgon F-300, Norit HD-4000, and Darco 12x40 AC

Mean AC particle size (mm)	Diffusion rate constant (k_{id}), (mg/g min ^{1/2})			Boundary layer thickness (C), (mg/g)		
	Calgon F-300	Norit HD-4000	Darco 12x40	Calgon F-300	Norit HD-4000	Darco 12x40
0.84	3.27	2.26	4.01	14.6	14.8	16.8
0.68	2.96	1.36	3.29	16.1	15.1	16.9
0.40	2.89	1.53	2.97	16.5	15.1	17.3
0.19	2.73	0.10	0.04	16.6	15.2	17.5

Table 4-8. Effective diffusion coefficient (D_e) of organic matter onto different particle sizes of Calgon F-300, Norit HD-4000, and Darco 12x40 AC

AC Particle size range (mean sizes)mm	Calgon F-300		Norit HD-4000		Darco 12x40	
	Diffusion coefficients (m ² /s)	F(t) vs. (t) R ²	Diffusion coefficient s (m ² /s)	F(t) vs. (t) R ²	Diffusion coefficients (m ² /s)	F(t) vs. (t) R ²
>0.84 (0.84)	145×10^{-10}	0.95	369×10^{-10}	0.93	253×10^{-10}	0.99
0.50-0.85 (0.68)	109×10^{-10}	0.97	182×10^{-10}	0.93	124×10^{-10}	0.96
0.30-0.50 (0.40)	533×10^{-11}	0.97	643×10^{-11}	0.97	728×10^{-11}	0.95
0.075-0.30 (0.19)	151×10^{-11}	0.99	105×10^{-11}	0.70	809×10^{-12}	0.86

Table 4-9. Volume distribution of DOM in region-I to region-V of leachate derived from FRI analysis

Region	Volume (AU-nm ² /mg-C/L)
Region-I	137.56
Region-II	302.58
Region-III	706.35
Region-IV	996.18
Region-V	3,267.10

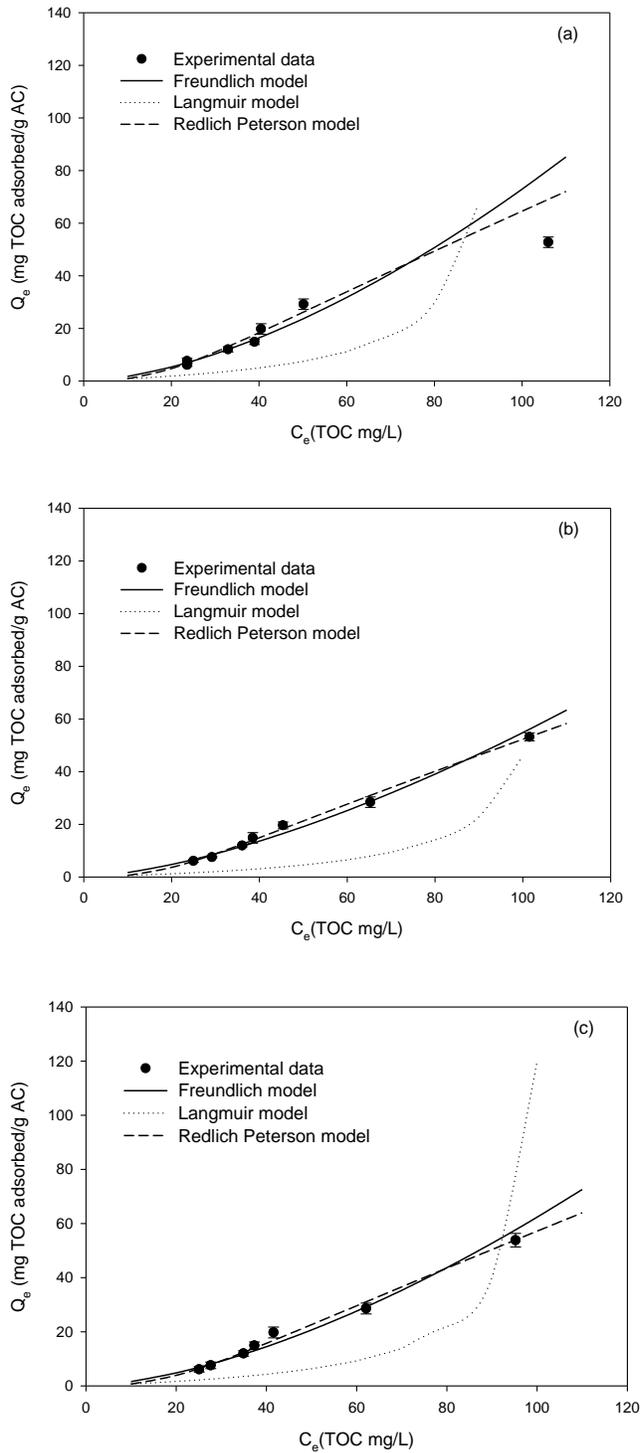


Figure 4-1. Adsorption of leachate onto (a) Calgon F-300, (b) Norit HD-4000, and (c) Darco 12x40 AC. Data points and error bars are average and standard deviation of the duplicate experiments, respectively.

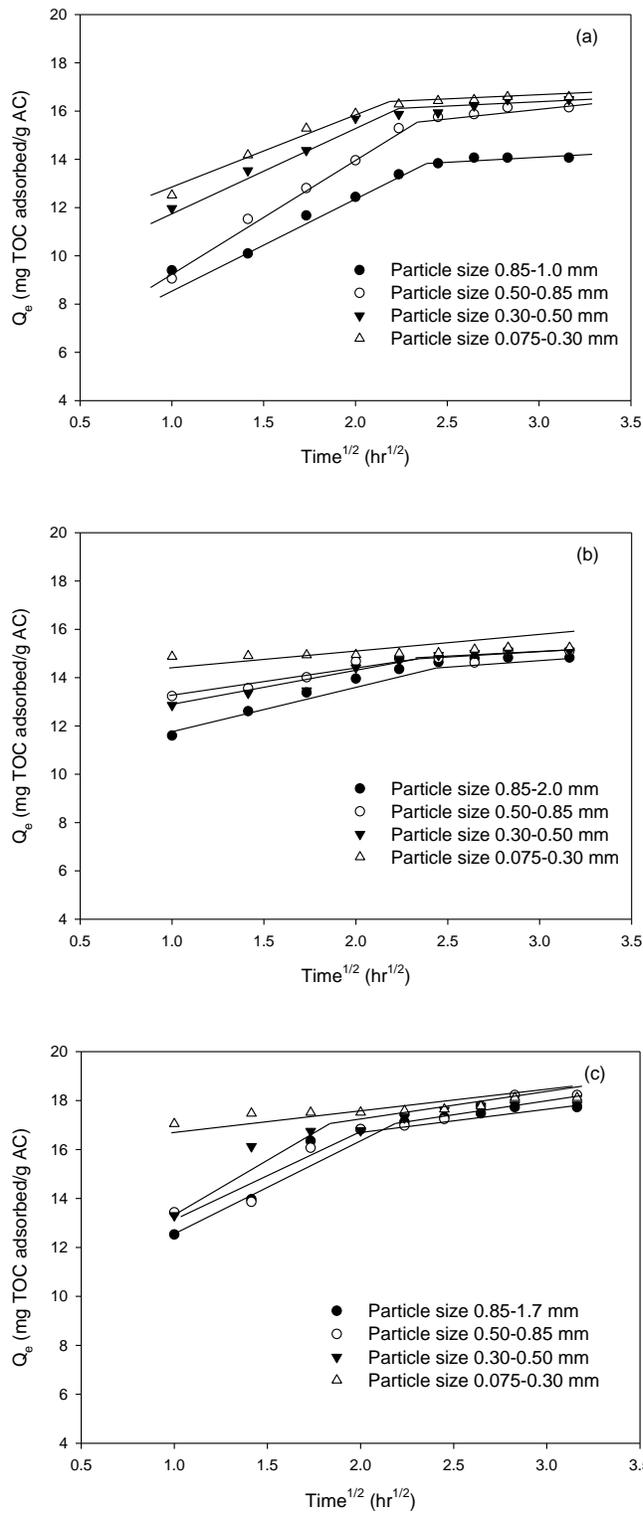


Figure 4-2. Weber and Moris intra-particle diffusion for removal of TOC using (a) Calgon F-300, (b) Norit HD-4000, and (c) Darco 12x40 AC. Data points were obtained using average of duplicate experiments in the model equations.

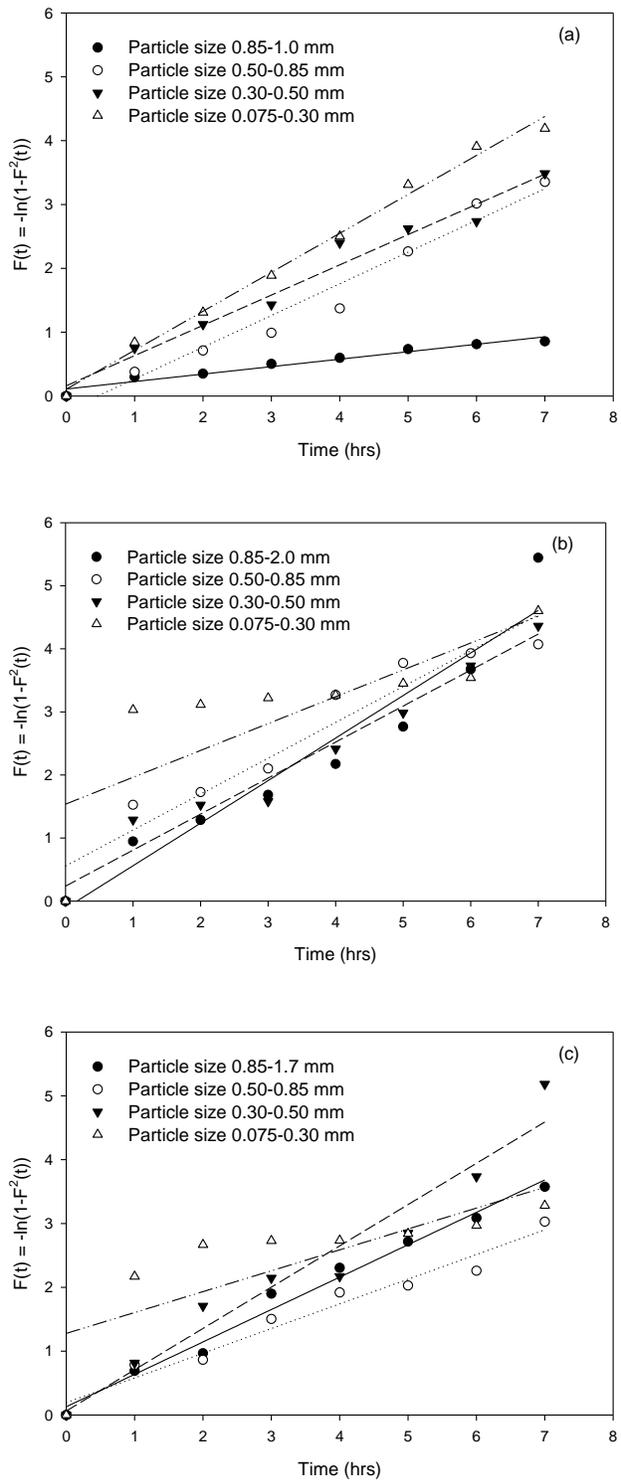


Figure 4-3. Homogeneous particle diffusion model for TOC removal in leachate using (a) Calgon F-300, (b) Norit HD-4000, and (c) Darco 12x40 AC. Data points were obtained using average of duplicate experiments in the model equations.

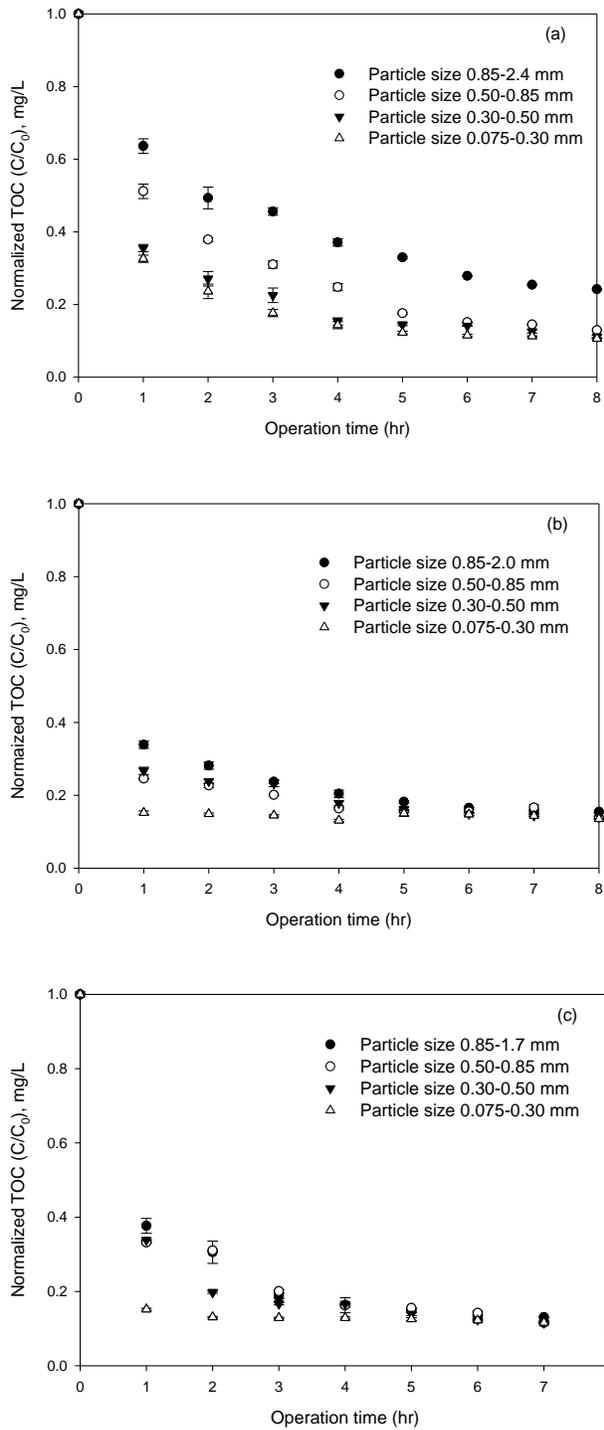


Figure 4-4. Adsorption kinetics of organic matter at different particle sizes (a) Calgon F-300, (b) Norit HD-4000, and (c) Darco 12x40 AC. Data points and error bars are average and standard deviation of normalized TOC obtained from duplicate experiments, respectively.

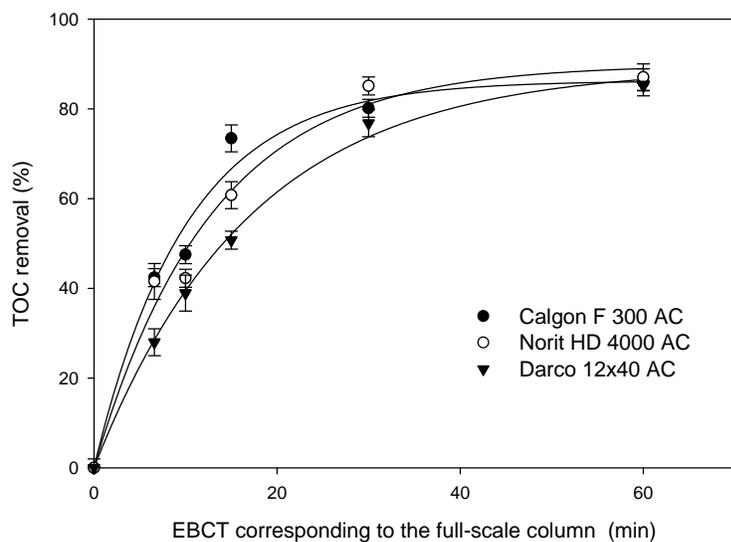


Figure 4-5. Effect of EBCT on the TOC removal of leachate using Calgon F-300, Norit HD-4000, and Darco 12x40 AC. Data points and error bars are average and standard deviation of percentage TOC removal obtained from duplicate experiments, respectively. Initial TOC =670 mg/L.

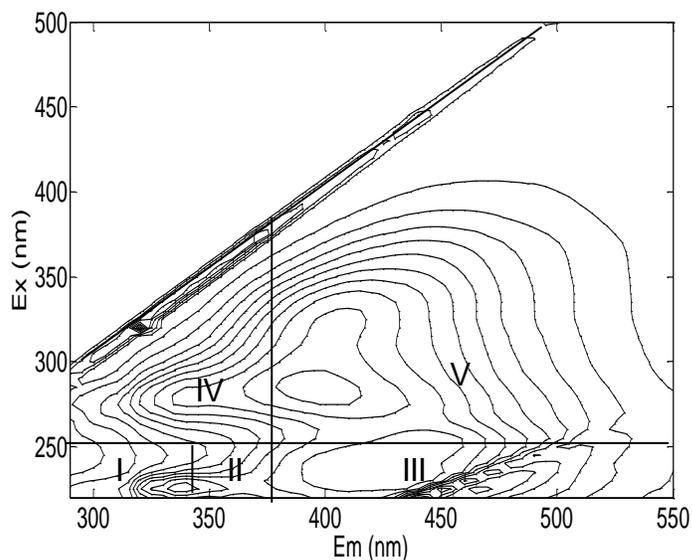


Figure 4-6. Fluorescence EEM of ACL leachate and operationally defined E_x - E_m boundaries for five EEM regions.

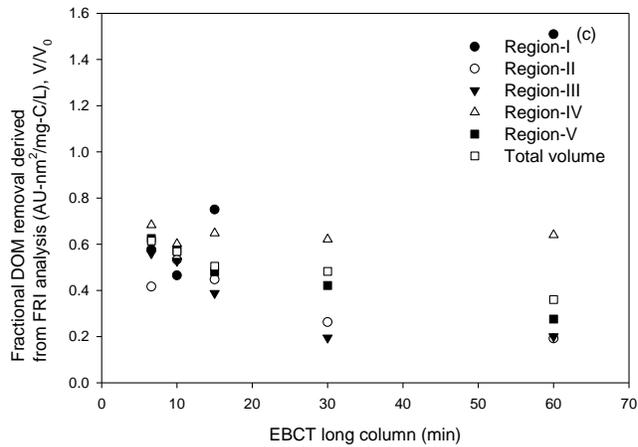
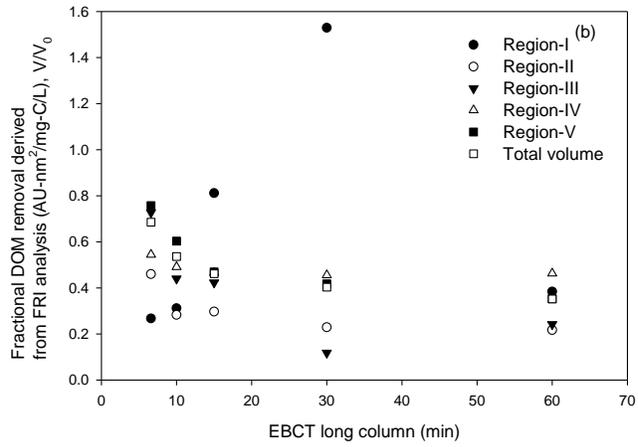
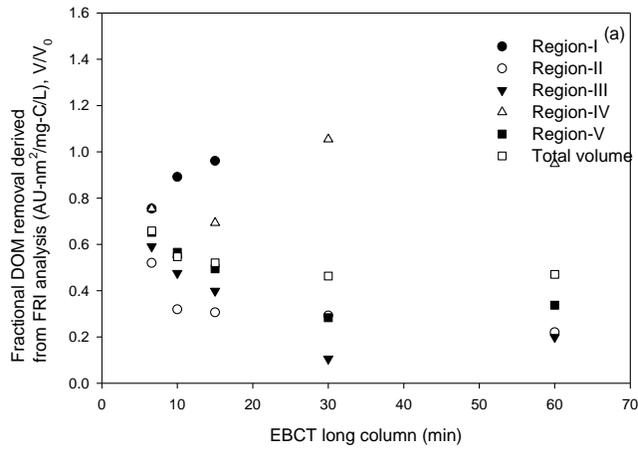


Figure 4-7. Effect of EBCT on DOM of each EEM region while leachate treatment using (a) Calgon F-300, (b) Norit HD-4000, and (c) Darco 12x40 AC. Volumes were derived from FRI analysis.

CHAPTER 5 SUMMARY AND CONCLUSIONS

5.1 Summary

Landfills are still the most accepted method for ultimate disposal of municipal and industrial solid waste due to their economic advantages. However, landfills face a major challenge of managing the leachate generated by the percolation of rainwater through the layers of waste. Traditionally, leachate treatment has been conducted by one or the combination of more than one treatment processes such as leachate recirculation, biological, and physico-chemical treatment methods. The characteristics of leachate have been found very heterogeneous and vary with the age of landfill. The biological treatment methods are effective for the young leachate, but as the landfill grows old, major presence of refractory organic matter in the leachate limits the effectiveness of these processes. However, physico-chemical treatment methods such as coagulation and flocculation, chemical oxidation, activated carbon adsorption and membrane systems have been found more effective for such old leachate. It has been observed that the use of a single treatment methodology does not produce effluent water that will meet water quality standards for direct discharge to groundwater or surface water, however, membrane filtration technologies such as nano-filtration (NF) and reverse osmosis (RO) have been found effective in this regard. Nevertheless, the membrane systems may not provide a cost-effective treatment due to excessive fouling caused by the presence of high concentrations of high molecular weight humic and fulvic-like organic matter.

The current research was divided into three major objectives. The first objective was to evaluate and compare the effectiveness of Fe (III) coagulation and MIEX anion

exchange processes for reducing the fouling of NF and RO membranes. The second objective was to study the effectiveness of oxidation of organic matter using ozone as a pretreatment step to reduce the membrane fouling. The third objective of the study was to evaluate the organic matter adsorption parameters for three different AC based on their pore sizes for stabilized leachate treatment.

In the first study, at first, batch coagulation and anion exchange experiments were conducted to determine their effectiveness of organics removal from stabilized leachates. All three leachate showed a variable amount of maximum DOC removal using the Fe(III) coagulant. A maximum of 70% DOC removal was observed in NCL leachate, which is in the similar range as suggested in the literature. The amount of DOC removed was correlated to the pH and alkalinity present in the leachate. Fluorescence regional integration (FRI) method as suggested by Chen et al. (2003) was used to determine the type of organics removed by the coagulant and approximately 80% removal of humic and fulvic-like organics were observed in all three leachate. An optimum coagulant dose of 22 mmol Fe(III)/L was selected for the membrane experiment because this dose generated optimum pH conditions for coagulation in all three leachate.

A maximum of 30% DOC was removed using MIEX; however, most of the DOC was removed at lower MIEX doses. Increase in MIEX doses did not remove additional DOC and the doses used in the study correspond to the doses typically used in drinking water treatments. There is no literature available to compare the results of leachate treatment using MIEX; hence this study is an important contribution for determining the MIEX doses for leachate treatment. MIEX removed 30 to 60% of negatively charged

humic and fulvic-like organics present in leachate. An optimum MIEX dose of 5 mL/L was selected for membrane experiments for membrane experiments.

The coagulation and MIEX pretreatment did not show any improved performance of NF and RO membranes in terms of contaminant rejection from leachate as compared to raw leachate treatment. Additionally, an increased fouling was observed for coagulated as well as MIEX pretreated leachate as compared to raw leachate in both membrane treatments. During the membrane operation, an increase in feed pH was observed in each condition, which might have caused an increased precipitation of alkalinity over the membrane surface, leading to increased fouling. Trebouet et al., (2001) also observed that leachate without any pre-treatment is the best way to use with NF while investigating coagulation as a pretreatment option for treating leachate with NF membranes. No literature was found to compare the results of MIEX treated leachate coupled with membranes; however, Cornelissen et al. (2010) used an anion exchange resin (Fluidized Ion Exchange (FIX)) to reduce fouling of NF membranes for surface water treatment but could not observe reduced fouling of NF membranes.

The second objective of the study was to investigate the effectiveness of ozonation as a pretreatment option for treating stabilized landfill leachate using RO and NF membranes. A fixed ozone dose of 70 mg/L was used at a feed gas flow rate of 3.5 L/min for 5 to 30 minutes to treat leachate from three different landfills. A maximum of 78% drop in UV-254 absorbance and 23% drop in DOC was observed. Faster ozone kinetics was observed at the start of experiments, which plateaued after 8 to 10 minutes of ozonation in all three leachate. The characterization of organic matter using fluorescence EEM and FRI analysis also showed that the ozone removed most of the

humic and fulvic-like organic matter at the start of ozonation. Landfill leachate literature contains several studies on the kinetics of ozonation, however, no studies has been reported on using ozonation as a pretreatment option for leachate treatment using membrane systems. An optimum ozonation time of 10 minutes was determined from the batch experiments and used to run the membrane experiment. RO and NF membranes rejected greater than 99% of DOM and 91% salts from all three leachate in the experiment duration. A faster flux decline was observed for the ozonated leachate treatment than raw leachate. Between RO and NF membranes, NF membranes showed a faster flux decline than RO membranes. Hermia's model predicted that the fouling was mainly caused by the particles blocking the membrane pores and not allowing the filtrate to pass through. Hence, in the applied experimental conditions, ozonation of leachate before membrane treatment did not reduce the fouling potential of membranes. However, selections of ozone dose that can further reduce the concentrations of humic and fulvic-like organic matter, thereby reducing the potential of complete blockage of membrane pores may reduce the fouling frequency of membranes.

Hence, the pretreatment options studied in this research were found effective in removing or transforming humic and fulvic-like organic matter from leachate. However, the pretreatments did not provide improved permeate flux in the applied experimental conditions as compared to raw leachate for NF as well as RO membranes.

The third objective of the study was to determine the adsorption profile of stabilized landfill leachate onto three different AC micro-porous Calgon F-300, meso-porous Norit HD-4000 and Darco 12x40 AC, which were selected based on their pore

sizes. AC has been generally studied in combination with other treatment methods for landfill leachate treatment, but a detailed study that determine the adsorption profile of organic matter removal using AC from the stabilized leachate, which helps in designing a AC treatment system has not been reported.

Each of the three AC showed almost similar organic matter adsorption capacity irrespective of their pore sizes. Among the adsorption isotherm model tested, three parameter model Redlich-Peterson gave the best fit to the experimental data. The Langmuir isotherm did not give a good fit for the experimental data. The Weber-Morris model equation of diffusivity showed that the overall diffusion of organic matter onto AC particles was controlled by the intra-particle diffusion process. The effect of AC particle sizes on the diffusion process showed that as the AC particle sizes were reduced, the overall diffusion rate constant also decreased and the boundary layer thickness across the adsorbent particles increased. Among all three AC, meso-porous Norit HD-4000 AC showed maximum rate of diffusion of organic matter onto AC. The RSSCT results showed that 30 minutes EBCT provides the maximum TOD removal and further increase in EBCT does not improve the TOC removal. Among all three AC, micro-porous AC showed slightly better TOC removal than other two meso-porous AC. The FRI analysis of fluorescence EEM showed greatest removal for fulvic-like organic compounds by each of the three AC. The protein like organic matter tends to adsorb at smaller EBCT and desorb at higher EBCT. The breakthrough study of meso-porous Norit HD 400 AC showed a rapid exhaustion of AC, making AC treatment as an expensive option for leachate treatment. This study provides an important contribution in selecting the type of AC for landfill leachate treatment.

5.2 Conclusions

Following specific conclusions were drawn from the research:

- A maximum of 70% removal of DOC was observed using Fe (III) salt as a coagulant at unadjusted leachate pH.
- Coagulation process was most effective at the pH range of 4.2 to 5.2. Highest DOC removal was observed in the same pH range for all three leachate.
- Approximately 80% of humic and fulvic-like organic matter was removed by coagulation.
- A maximum of 34% DOC removal was observed for leachate treatment using anion exchange resin MIEX for the applied doses.
- Most of the DOC was removed at lower MIEX doses. Additionally, most of the ion exchange process occurred within initial 20 minutes of experiment.
- Most of the organic matter removed by the MIEX was humic and fulvic-like compounds. A maximum of 60% humic like organic compounds were removed by MIEX.
- In the applied experimental conditions, an increased fouling was observed for coagulated as well as MIEX pretreated leachate as compared to raw leachate in both membrane treatments.
- MIEX treated leachate showed faster flux decline than Fe (III) salt treated leachate.
- A maximum of 78% reduction in UV-254 absorbance and 23% reduction in DOC was observed with the use of a fixed ozone dose of 70 mg/L at a feed gas flow rate of 3.5 L/min.
- Faster ozone kinetics was observed at the start of experiments, which plateaued after 8 to 10 minutes of ozonation, representing that initially ozone reacts quickly with the available unsaturated bond organic compounds but it does not react as quickly with the byproducts of initial reactions.
- Ozonation removed more than 80% of the humic and fulvic-like organic matter in initial 10 minutes of ozonation.
- RO and NF membranes rejected greater than 99% of DOM and 91% salts from all three ozone treated leachate in the experiment duration.
- A faster flux decline with RO and NF membranes for the ozone treated leachate than raw leachate showed increased fouling of membranes.

- Between RO and NF membranes, NF membranes showed a faster flux decline than RO membranes while treating ozone pretreated leachate with membranes.
- Hermia's model predicted that the fouling was mainly caused by the particles blocking the membrane pores and not allowing the filtrate to pass through. The standard and intermediate blocking mechanism also played a significant role in membrane fouling.
- Ozonation at high doses might increase the particle size by forming metal complexes, which might precipitate on the membrane surface and decreases the flux. Ozonation at lower doses might help in reducing the fouling frequency of membranes.
- Among the selected AC, all three AC showed almost similar adsorption capacity.
- Three parameter Redlich-Peterson isotherm model gave the best fit for the equilibrium experimental data.
- Weber-Morris model predicted that the intra particle diffusion is the main governing phenomenon of adsorption in all three AC.
- The diffusion rate constants were slightly dependent on the size of AC particles. As the size of AC particles reduces, the overall diffusion rate constant also decreases.
- Micro-porous AC showed a proportional diffusivity, however, meso-porous AC showed constant diffusivity of organic matter onto AC particles.
- The RSSCT results showed a slightly better performance of meso-porous AC than micro-porous AC in terms of TOC removal at high EBCT.
- All three AC showed a greater adsorption affinity towards fulvic-like organic compounds.

5.3 Future work

The results of the first study show that coagulant Fe(III) and anion exchange resin MIEX can effectively remove humic and fulvic-like organic matter from stabilized leachate. However, the selected doses of Fe (III) and MIEX for pre-treating leachate did not help improve the permeate flux of NF as well as RO membranes as compared to raw leachate. Further analysis should be conducted to study the cause of increased flux decline. Additional membrane fouling experiments should be conducted at fixed pH

conditions to determine the effect of pH on permeate flux. Additionally, the effect of pretreated leachate at variable coagulant and MIEX dose can be studied. A different coagulant (e.g. alum) can also be studied as a pretreatment option to avoid potential iron fouling.

Ozone helped reduce the concentration of humic and fulvic-like organic matter either by removing or transforming to other forms during stabilized leachate treatment; however, the selected ozone dose as a pretreatment option did not improve the permeate flux of NF as well as RO membranes as compared to that of raw leachate. Further membrane fouling experiments can be conducted for the pretreated leachate using variable ozone doses. Possibly, a lower ozone dose can be used as compared to the dose used in the current study to pre-treat leachate. Lower doses may cause lesser coagulation due to the divalent ions present in leachate. Anti-scalant can also be used as an additional pretreatment to reduce the possible coagulation caused by divalent ions.

The laboratory-scale adsorption study provided almost similar adsorption capacity of micro and meso-porous AC with higher organic matter adsorption rate in meso – porous AC. In the field-scale, all the studies have been conducted using micro-porous AC. It will be valuable to determine the effectiveness of meso-porous AC for stabilized leachate treatments using field scale design parameters. The performance of RSSCTs should also be validated with the field-scale study.

APPENDIX A EFFECT OF COAGULANT DOSE ON FILTRATE pH AND DOC

When the coagulant is added into a solution, the metal ion reacts with the hydroxide ion, a product of hydrolysis reaction and releases H^+ ion into the solution. The released H^+ ion reduces the pH of solution. As the coagulant dose increases, the concentration of H^+ also increases that further reduced supernatant pH. Similar trends of supernatant pH were observed in all three leachates with the increase in coagulant dose as shown in Figure A-1 (a). The NRL leachate showed faster decrease in pH as compared to ACL and NCL leachate with the increase in coagulant doses due to the presence of lower alkalinity in NRL leachate. The alkalinity of NRL leachate was 3000 mg/L as $CaCO_3$, however ACL and NCL leachate contained alkalinity of 6600 mg/L as $CaCO_3$ and 5400 mg/L as $CaCO_3$, respectively. At very high coagulant doses the hydrolysis product $Fe(OH)_4^-$ starts accepting available hydrogen ions and reducing free H^+ in the solution and thereby increasing the pH of supernatant solution (Letterman et al., 1999; O'Melia et al., 1999). At high coagulant doses, NCL and NRL leachate showed increase in pH, however, in ACL leachate, pH did not reach low enough to form $Fe(OH)_4^-$ that can accept H^+ ion from solution and increase the pH.

With the addition of coagulant, as the solubility product of metal hydroxides exceeds its limit, the particulate hydroxides start to precipitate. These hydroxides precipitates are stabilized by the coating of negatively charged natural organic matter (NOM). An increased reduction in DOC was observed in all three leachates with the increase in coagulant dose as shown in Figure A-1 (b). At lower coagulant doses in NRL leachate, faster drop in pH also caused higher concentrations of positively charged metal hydroxides. Higher concentrations of metal hydroxides lead to increased binding

or sorption of NOM to precipitating hydroxides and higher DOC reduction was observed as compared to ACL and NCL leachate. When the coagulant dose was further increased, the surface area of these metal hydroxides also increased and higher DOC removal was observed. At very high coagulant doses, the pH of the solution passes through the point of minimum solubility of metal hydroxides and the charges on the surface of precipitates becomes positive and this change tend to stabilize the particles and may release NOM into the solution as observed in NRL and NCL leachate (Letterman et al., 1999). The ACL leachate did not release NOM into the solution because pH of solution could not reach low enough at the applied coagulant doses such that the charges of precipitate become increasingly positive and release the adsorbed NOM to the solution.

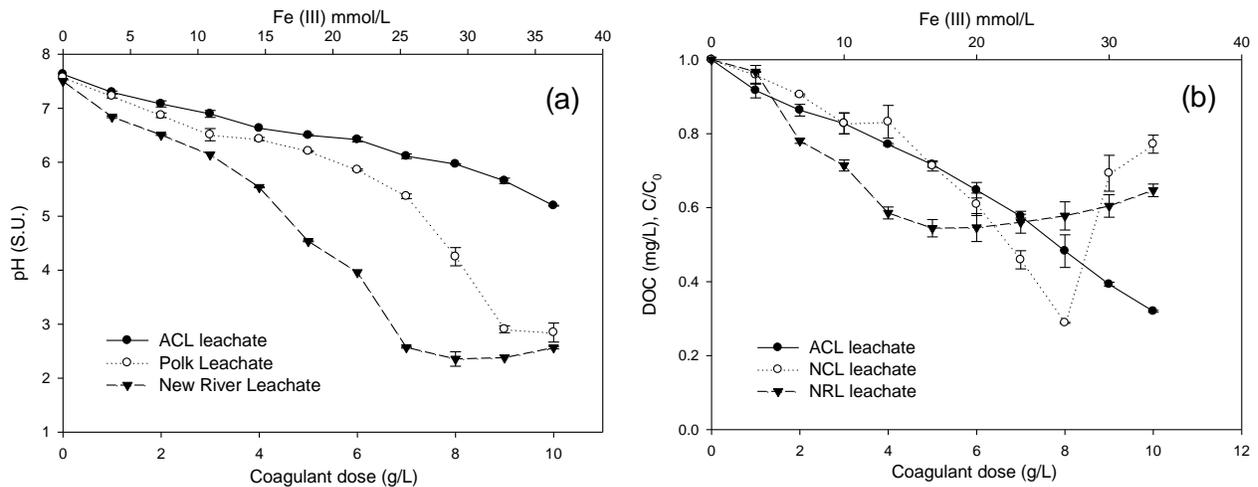
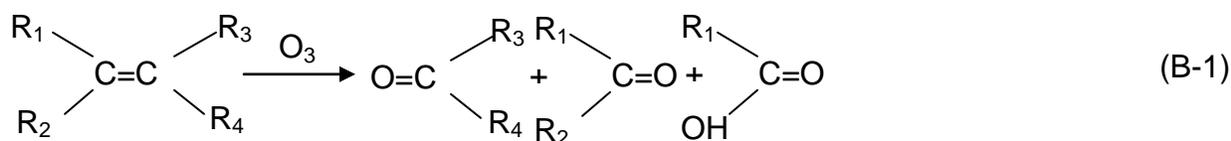


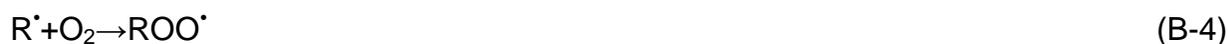
Figure A-1. Effect of coagulant dose on pH and DOC of ACL, NCL, and NRL leachate. The data points and error bars represent average and standard deviation of duplicate experiments, respectively.

APPENDIX B
REACTION MECHANISM OF OZONE AND HYDROXYL RADICALS TO ORGANIC
MATTER

Ozone has high oxidation potential ($E_0=2.07V$) and high reactivity and selectivity toward organic pollutants such as aromatic compounds. Ozone ruptures the C=C bonds or aromatic ring and produces ketones and esters. These intermediate products can be further transformed into organic acids through the oxidation process as shown in equation B-1.



At high pH conditions ($pH>8$), ozone produces hydroxyl radicals (equation B-2) that have even higher oxidation potential ($E_0=2.8V$) than ozone molecule, and accelerate the removal of recalcitrant organic matter from complex wastewater matrix. Hydroxyl radical mainly reacts with the organics via hydrogen abstraction or $\cdot OH$ radical addition (equation B-3). Hydroxyl radical can react with aromatic C=C structure and produces phenolic and ethers via addition reactions. It can also produce alcohols by reacting with C-C structures. These intermediates can be mineralized or transformed into small organic acids by ozone molecules and $\cdot OH$ radicals during ozonation. A typical pathway of $\cdot OH$ radical reaction can be given as equation B-4 to B-9.





Equations (B-3 to B-9) are adopted from Li et al. (2008).

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BIOGRAPHICAL SKETCH

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