Advanced Technologies for Resource Recovery and Contaminants Removal from Landfill Leachate

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ABSTRACT (Academic)

Landfill leachate contains valuable, recoverable organics, water, and nutrients. This project investigated leachate treatment and resource recovery from landfill leachates by innovative methods such as forward osmosis (FO), bioelectrochemical systems (BES), and advanced oxidation. In this study, a microbial fuel cell (MFC) removed 50-75% of the ammonia from a leachate through the electricity driven movement of ammonium to the cathode chamber followed by air stripping at high pH (> 9). During this process, the MFC system removed 53-64% of the COD, producing a net energy of 0.123 kWh m^{-3}. Similarly, an integrated microbial desalination cell (MDC) in an FO system recovered 11-64% of the ammonia from a leachate; this was affected by current generation and hydraulic retention time in the desalination chamber. The MDC-FO system recovered 51.5% of the water from a raw leachate. This increased to 83.5% when the FO concentrate was desalinated in the MDC and then recirculated through the FO unit. In addition, the project investigated humic acid (HA) recovery from leachate during the synergistic incorporation of FO, HA recovery, and Fenton's oxidation to enhance leachate treatment and to reduce Fenton's reagent requirements. This led to the investigation of harmful disinfection byproducts (DBPs) formation during Fenton's oxidation of landfill leachate. The removal of leachate UV-quenching substances (humic, fulvic, and hydrophilic acids) using an MFC and a chemical oxidant (i.e., sodium percarbonate) with a focus on energy production and cost efficiency were also studied. BES treatment can reduce leachate organics concentrations; lower UV absorbance; recover ammonia; and, in combination with FO, recover water. Although BES is promising, significant work is needed before its use in landfill leachate becomes practical. FO application to leachate treatment must consider the choice of an appropriate

draw solute, which should require minimal effort for regeneration. Resources like HA in leachate deserve more attention. Further efforts can focus on purification and application of the recovered products. The emerging issue of DBP formation in leachate treatment also requires attention due to the potential environmental and human health effects. The broader impact of this study is the societal benefit from more sustainable and cost-efficient leachate treatment.

Advanced Technologies for Resource Recovery and Contaminants Removal from Landfill Leachate

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ABSTRACT (General Audience)

On average, each of us produces 3 – 4 pounds of solid waste every day. In the U.S., the yearly generation of solid waste is 250 million tons, while the global generation is 1.1 billion tons. The global management cost of solid waste is around 200 billion dollars. About half of U.S. municipal solid waste ends up in landfills, in China, this number is 80%. Among the different municipal solid waste (MSW) management approaches, landfilling is the most common because of its low cost and relatively low maintenance requirements. In a landfill, the combination of precipitation and solid waste degradation produce leachate, a complex wastewater. A ton of municipal solid waste can generate 0.05–0.2 tons of leachate in its lifetime during the process of landfilling. Leachate contains a vast array of pollutants, which can result in major environmental impact and adverse human health risk if not contained and treated appropriately. At present, leachate is mostly treated biologically, without any resource recovery. Among the myriad recoverable resources in landfill leachates, water and ammonia are the most abundant. We applied innovative approaches such as, bioelectrochemical systems, forward osmosis, advanced oxidation to recover resources and remove contaminants from leachate simultaneously. We also incorporated these novel technologies to help each other. For instance, we recovered humic fertilizer from leachate prior to advanced oxidation (i.e., Fenton's oxidation) that helped the reduction of Fenton's reagent requirements. The next step of our study could be the pilot scale application of the proposed techniques so that it can be applied in field. The broader impacts of this study include improvements in sustainability and cost efficiency of leachate treatment that can benefit the society.

Dedication

This dissertation is dedicated to my mother, Rahena Akter, who unknowingly encourages me every moment to become a better human being; to my father, Md Gousul Azim, who loves to exaggerate my mere achievements; and my sister, Nusrat Tamanna, who always encourages me to pursue my dreams!

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Attribution

Dr. Zhen (Jason) He worked as the principal investigator, Dr. John T. Novak and Dr. Brian Brazil worked as the co-principal investigator of the project. Below is the list of the co-authors who are duly credited for their work.

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CHAPTER 1

Resource Recovery from Landfill Leachate Using Bioelectrochemical Systems: Opportunities, Challenges, and Perspectives

Abstract

Landfill leachate has recently been investigated as a substrate for bioelectrochemical systems (BES) for electricity generation. While BES treatment of leachate is effective, the unique feature of bioelectricity generation in BES creates opportunities for resource recovery from leachate. The organic compounds in leachate can be directly converted to electrical energy through microbial interaction with solid electron acceptors/donors. Nutrient such as ammonia can be recovered via ammonium migration driven by electricity generation and ammonium conversion to ammonia in a high-pH condition that is a result of cathode reduction reaction. Metals in leachate may also be recovered, but the recovery is affected by their concentration and values. Through integrating membrane process, especially forward osmosis, BES can recover high-quality water from leachate for applications in landscaping, agricultural irrigation or direct discharge. This review paper discusses the opportunities, challenges, and perspectives of resource recovery from landfill leachate by using BES.

Introduction

Landfilling is a widely applied method for disposing municipal solid waste (MSW) (Zhang et al., 2008). During the stabilization in a landfill, liquid waste – leachate is produced from the dynamic degradation of wastes and infiltration of water to landfill mainly from precipitation (Damiano et al., 2014; Ganesh & Jambeck, 2013). Leachate is a complex wastewater with high pollution potential resulting in major environmental problems such as soil and groundwater pollution and human health risks (Kjeldsen et al., 2002; Renou et al., 2008). Young landfill leachate can have a relatively high BOD_5/COD ratio (0.4-0.6) indicating good bioavailability (Ozkaya et al., 2014); however, this biodegradability decreases with time because of organic degradation within the landfill

(Calli et al., 2005; Renou et al., 2008). Leachate contains ammonium nitrogen with a concentration from 500 to 2000 mg L^{-1}, and a low amount of total phosphorous (Kjeldsen et al., 2002; Tatsi & Zouboulis, 2002). Due to the presence of high concentrations of inorganics and metal ions, leachate has a high electrical conductivity (Lin & Chang, 2000). Common metals present in the landfill leachate include Iron, Manganese, Zinc, Cadmium, Copper, Nickel, Silver, and Lead, but their prevalence is specific to the landfill (Deng et al., 2013; Harmsen, 1983; Kjeldsen et al., 2002) . The composition of leachate is affected by many factors including waste types, precipitation variation, soil condition of the landfill site, and landfill age (Christensen et al., 2001; Renou et al., 2008).

The methods/technologies for treating landfill leachate have been well reviewed before (Renou et al., 2008). Those methods/technologies can effectively treat leachate for removing some of the key contaminants. However, there are also challenges associated with those methods, especially to meet the need for sustainable leachate management that desires minimal input of energy and chemicals for treatment and maximized recovery of valuable resources. For example, physicochemical treatment processes (e.g. coagulation, flocculation, adsorption, membrane filtration, etc.) are energy and capital intensive because of costs of chemicals, oxidants, and membranes (Ahn et al., 2002; Kurniawan et al., 2006); biological treatment processes (e.g. activated sludge, trickling filter, ponding, etc.) are limited by treatment effectiveness, energy requirement, and a large amount of secondary sludge (Kargi & Pamukoglu, 2003; Loukidou & Zouboulis, 2001); and electrochemical treatment processes are electricity intensive (Deng & Englehardt, 2007; Fernandes et al., 2015). Leachate contains organic compounds that can be converted into electricity by anaerobic digestion, but this approach requires proper maintenance of generators and purification of biogas (Larson, 1993; Tafdrup, 1995).

Leachate has been studied as a substrate for bioelectrochemical systems (BES). BES employs biological and electrochemical reactions to generate electricity, remove contaminants, and recover resources from a wide range of substrates (Kelly & He, 2014; Pant et al., 2010). Among various BES that have been developed, microbial fuel cells (MFC) are most commonly studied. In an MFC, anaerobic degradation of organic matter releases electrons to an anode electrode, which transfers those electrons to a cathode electrode for reducing a terminal electron acceptor (e.g., O_2); to maintain charge neutrality, ions simultaneously migrate between the anode and the cathode (Logan et al., 2006; Rabaey & Verstraete, 2005). To overcome the thermodynamic barrier of certain reducing reactions (e.g., proton reduction), an external voltage can be applied to an MFC, which is then converted to microbial electrolysis cells (MEC) (Logan et al., 2008; Zhang & Angelidaki, 2014). When an additional chamber is added to the MFC to facilitate ion separation, a microbial desalination cell (MDC) can be created (Saeed et al., 2015; Sevda et al., 2015). More information about BES can be found in various review papers (Kelly & He, 2014; Sleutels et al., 2012; Wang & Ren, 2013).

Leachate has some characteristics that could give it a great potential for resource recovery using BES. For example, the high electrical conductivity of leachate (Lin & Chang, 2000) makes it favorable for electricity generation (energy recovery) in BES (Damiano et al., 2014). It contains a high concentration of ammonium nitrogen, which may be recovered for agricultural application. Landfill leachate also contains several metals, which can be recovered by employing BES. To reduce the leachate volume, water may be recovered by using osmotic processes (Dong et al., 2014). Therefore, resource recovery will help accomplish a sustainable leachate management system. Although BES have been studied for leachate treatment (Wu et al., 2015), resource recovery was not well addressed in the past research. The objectives of this review paper are to discuss the opportunities for resource recovery from leachate using BES, analyze the challenges associated with the recovery, and present the perspectives for future research and development.

Current status of landfill leachate treatment with bioelectrochemical systems

The previous studies of using BES to treat leachate have focused on the removal of organic matter and nitrogen and the generation of bioelectricity. The organic removal by BES varies from 40% to over 80% (Ozkaya et al., 2013; Zhang et al., 2015a), and the low bioavailability of landfill leachate appears to be a great challenge (Kjeldsen et al., 2002; Zhang & He, 2013). Proper pretreatment of leachate could significantly improve biodegradability of organics. For example, pretreatment using fermentation resulted in fifteen times increase in organics removal in an MEC treating landfill leachate (Mahmoud et al., 2014). A few studies have investigated nutrient removal from leachate such as ammonia nitrogen, nitrate, nitrite, and phosphorus. Ammonia removal was reported to be from 0% to over 90% , affected by insufficient retention time, absence of beneficial microorganisms, electricity generation, etc. (Ganesh & Jambeck, 2013; Kim et al., 2008; Zhang et al., 2015a). Substantial removal of phosphorus from leachate was reported in an air cathode MFC, but the removal mechanism was not clear (Damiano et al., 2014). With leachate as an anode substrate, BES produced a maximum power density as high as 12.8 Wm^{-3} (current density 41 Am^{-3}) (Zhang et al., 2008). Energy recovery is generally not reported, and only one study presented the energy production of 0.00190 kWh per kg of COD from landfill leachate (Zhang & He, 2013).

The BES performance treating landfill leachate is affected by many factors including, electrode surface area (Galvez et al., 2009), hydraulic retention time (HRT) (Greenman et al., 2009; Puig et al., 2011) , leachate dilution factor (Galvez et al., 2009; Puig et al., 2011), mode of operation (Ganesh & Jambeck, 2013; Greenman et al., 2009), electrode catalysts (Ganesh & Jambeck, 2013), organic loading rate (Zhang et al., 2008), reactor configuration (Wu et al., 2015), inoculation (Greenman et al., 2009), etc. More information about the past BES research treating leachate can be found in a recent review paper (Wu et al., 2015). Those prior studies have collectively demonstrated that landfill leachate can be used as a substrate for electricity generation in BES, and degradation of organic matter or nutrient removal occurs to a certain degree. However, they focused on the removal, instead of recovery that is important to sustainable leachate treatment. Despite the report of electricity generation, only one study has presented energy performance, which is critical to understanding energy recovery from leachate. As stated previously, leachate contains a wide range of resources such as energy, nutrients, metals, and water, which can be potentially recovered, thereby improving the sustainability of leachate treatment. In the following, the opportunities, challenges, and perspectives of recovering energy, nutrient, metals, and water from leachate using BES are discussed and analyzed.

Resource recovery from landfill leachate using bioelectrochemical systems

Energy recovery

Leachate contains many organic compounds that can be used to generate electricity in BES. The produced electrical energy may be used to offset the energy consumption by the treatment system, thereby realizing an energy-efficient method for leachate treatment. Although leachate can be treated by anaerobic digestion for biogas production, direct electricity generation in BES such as MFCs can avoid the issues associated with electrical generators and biogas purification. Thus, recovery of electrical energy from leachate in BES could be of strong interest. The prior studies reported electricity generation in the form of power and current density, but energy performance is usually not presented. Energy is expressed in either Joule, or kWh. A new parameter, normalized energy recovery (NER), has been proposed to present energy performance of BES; NER can be expressed in either kWh m^{-3} of wastewater treated or kWh per kg of COD removed (Ge et al., 2014). The unit of kWh m^{-3} is also commonly used in wastewater industry for energy consumption (Plappally & Lienhard, 2012), while the unit of kWh kg COD^{-1} can represent the conversion efficiency of organic matter into electrical energy. To understand how much energy can be produced from leachate, the data from some of the prior studies were converted to NER. Because most studies reported only the peak power data that cannot be used to calculate NER for the complete batch, only several studies were used for data presentation in Table 1-1. The NER obtained from leachate treatment in MFCs ranged from 0.00031 to 0.04866 kWh kg COD^{-1}. The NER value in terms of volume of leachate treated could be above 0.05 kWh m^{-3} leachate treated, but one study that used dilute leachate showed a significantly lower NER value. Compared to the NER reported from domestic wastewater, the leachate-generated NER values are generally higher, likely because of the higher COD content; however, they are lower than those reported from the industrial wastewater (Ge et al., 2014), possibly related to its low biodegradability which is also reflected by the low NER in kWh kg COD^{-1} from the leachate. The above comparison is not precise, because of significant difference in BES configuration, operation, inocula and approaches for data expression.

Table 1-1. Energy recovery (NER) from landfill leachate in BES in the literature.

BES configuration	**Leachate COD (mg/L)**	**Operational mode**	**COD removal (%)**	**NER (kWh/kg COD)**	**NER (kWh/m^3)**	**Reference**
Dual chamber	20,050	Continuous	89	0.04866	-	(Zhang et al., 2015a)
Dual chamber	50,000	Continuous	43	0.00251	0.05400	(Ozkaya et al., 2013)
Single chamber	12,300	Batch	72	0.01986	-	(Vazquez-Larios et al., 2014)
Single chamber	507 (Dilute)	Continuous	32	0.00031	0.0000506	(Puig et al., 2011)
Dual chamber	20,100	Continuous	86	0.00383	0.06648	(Zhang et al., 2015b)
Dual chamber	11,400	Continuous	87	0.00190	-	(Zhang & He, 2013)

The challenges to use leachate for energy recovery in BES lie in its complex composition and low biodegradability. Leachate contains four major groups of compounds: dissolved organic substances (e.g., BOD, COD, VFA, humic/fulvic acids), inorganic macro components (e.g., Ca^{2+}, Na^{+}, Mg^{2+}, SO_4^{2-}, Cl^{-} ,etc.), heavy metals (e.g., Cd^{2+}, Cr^{3+}, Cu^{2+}, Ni^{2+}, etc.), and xenobiotic organic compounds (e.g., phenols, cresols, aromatic hydrocarbons, polycyclic aromatic hydrocarbons, phthalates, and furans) (Kjeldsen et al., 2002; Renou et al., 2008). Volatile fatty acids (VFA) constitute a major fraction of the leachate in the acidogenic phase, and refractory organics such as humic and fulvic acids may dominate during the methanogenic phase (Kjeldsen et al., 2002). The presence of the recalcitrant compounds and heavy metals could decrease the biodegradability of leachate, and thus reduce electricity generation in BES. Most of the prior studies reported Coulombic efficiency (CE) lower than 10% (Ganesh & Jambeck, 2013; Puig et al., 2011), despite much removal of organic compounds, indicating that the removal was mostly conducted by non-electricity generating processes such as methane production and sulfate reduction (Ozkaya et al., 2013; You et al., 2006). High organic loading rates may also result in a low CE (Zhang & He, 2013). In addition, the toxic effect of some metals on electrochemically-active bacteria can lead to low energy recovery. Although most landfill leachates contain a trace amount of metals, some specific leachate could be rich in a certain type of metals that may inhibit electricity generation in BES.

To enhance energy recovery from leachate using BES, proper pretreatment will be necessary to break down the recalcitrant compounds and supply biodegradable organics to BES. Pretreatment like anaerobic digestion of leachate produces biogas, but it uses the bioavailable fraction of leachate and reduces its biodegradability for BES treatment. Fenton pretreatment of leachate was found to increase the biodegradability in terms of BOD_5/COD ratio, however, the increased concentration of iron after Fenton's treatment may retard the biological treatment possibly through a secondary effect such as a low pH (Lopez et al., 2004). Pre-fermentation under methanogenic inhibition has served this objective by increasing volatile fatty acids (VFA) fraction in the leachate substrate, resulting in increased electricity and CE (Fig. 1-1) (Ki et al., 2015; Mahmoud et al., 2014).

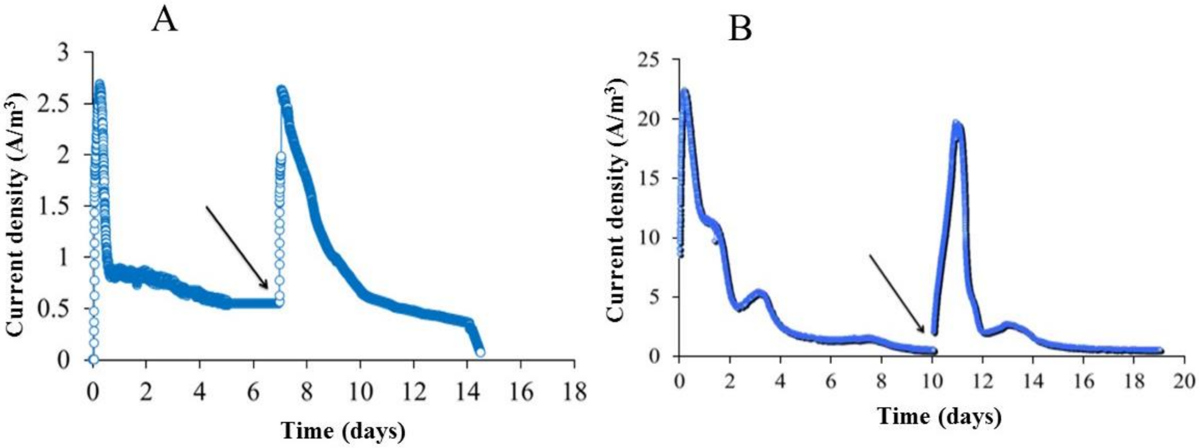

Figure 1-1. Current generation in a batch MEC fed with raw leachate (A) and fermented leachate (B). Reproduced with permission from (Mahmoud et al., 2014).

The produced energy must be efficiently extracted and then applied, and energy loss will occur during those processes. There have not been any studies that applied the energy produced from leachate for any application. Thus, there is a gap of knowledge about how much of the produced energy from leachate can be used. The prior experience with development of energy capturing and storing devices will help address such a question (Wang et al., 2015), and more research on energy application will certainly be needed. In addition to energy recovery, another key "energy" issue is energy consumption by the BES operation. In a BES, energy is mainly consumed by the pumping system that feeds the leachate into the BES and/or provides recirculation/mixing to facilitate the treatment, and aeration in the cathode if applicable. With the information of both energy recovery and consumption, it will be possible to establish an energy balance, which can be used to evaluate whether the BES treatment will be energy neutral or even positive. As additional treatments are required after BES, a calculation of the net energy requirement to meet the final discharge limit is of interest.

Nutrient recovery

Leachate is rich in ammonia and contains a certain amount of phosphorous. Because of the high concentration, ammonia removal is a key issue in leachate treatment. Conventional technologies for ammonia removal involve ammonia stripping and biological nitrogen removal (BNR). Ammonia stripping is an energy/chemical intensive process, and BNR requires delicate control of biological processes. BES have been employed to remove ammonia through multiple approaches: ammonia oxidation in the cathode, ammonia flux across ion exchange membrane driven by electricity generation, and/or denitrification in the anode (Kelly & He, 2014). The nitrogen removal efficiency ranged from nearly 100% (Zhang et al., 2015a) to very little removal (Ganesh & Jambeck, 2013). By coupling with anammox, BES could achieve 90% nitrogen removal with enhanced power generation because of the higher energy release in the nitrite coupled organic decomposition than the nitrate coupled decomposition (Lee et al., 2013). On the other hand, removal of phosphorous usually relies on precipitation that may occur in the high pH zone of the cathode compartment as a result of the cathode reducing reaction (Ichihashi & Hirooka, 2012; Kelly & He, 2014). The phosphorous removal could reach 80% in an air cathode MFC (Damiano et al., 2014). Simultaneous removal of both nitrogen and phosphorus is possible by forming struvite precipitation at the cathode (Ichihashi & Hirooka, 2012), or using both CEM (for ammonia migration) and AEM (for phosphate transport) in the same BES (Zhang et al., 2014).

Recovery of nutrients goes beyond removal and is of strong interest to sustainable leachate treatment. Ammonia recovery can be accomplished through integrating ammonium migration driven by electricity, ammonium conversion to ammonia under a high pH condition, and ammonia stripping (Fig. 1-2) (Kelly & He, 2014). Such a process has been realized in BES treating a synthetic solution, or actual wastes such as urine by employing a gas diffusion cathode in a dual chamber MFC (Kuntke et al., 2012). The stripped ammonia can be absorbed in dilute sulfuric acid to form ammonium sulfate, which has the potential to be used in agriculture as fertilizer, in industry for synthesis of valuable nitrogen polymers, or for food production (Matassa et al., 2015). If the absorption media - a sulfuric acid solution is pre-saturated with ammonium sulfate, ammonia can be collected as pure ammonium sulfate crystals that are valuable as laboratory chemical and fertilizer (Tao & Ukwuani, 2015). Stripped ammonia can also act as a draw solute for forward osmosis (FO). For example, a recent study demonstrated that the recovered ammonia from a synthetic wastewater by an MEC could form NH_4HCO_3 with a supply of carbon dioxide and this NH_4HCO_3 solution was used in an FO application (Qin & He, 2014). This MEC-FO system has been extended to leachate treatment with successful recovery of both ammonia and water (Qin et al., 2015).

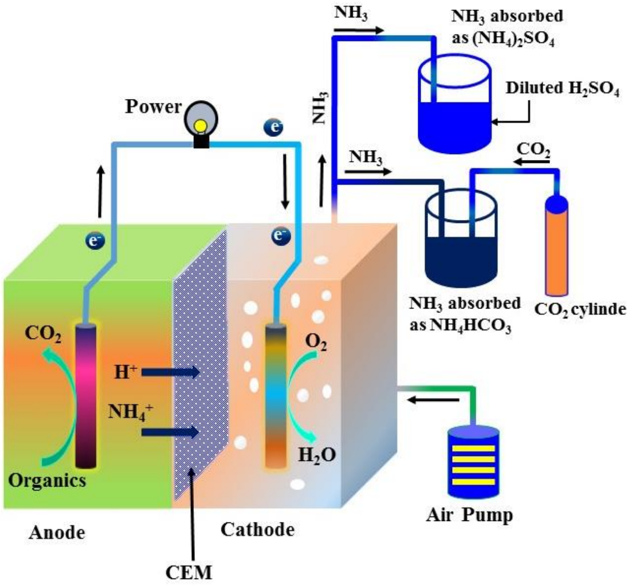

Figure 1-2. Ammonia recovery in BES through ammonium transport and conversion to ammonia. The stripped ammonia can be collected as either ammonium bicarbonate or ammonium sulfate.

Recovery of ammonia in BES can greatly affect the energy performance (production and consumption) of the system. In an MFC, recovering ammonia prefers an operation under high current generation, which will generate more electrons for driving the migration of ammonium ions but little power (or energy) production. To simultaneously recover ammonia and generate energy, MECs may be a better option because hydrogen production in MECs usually occurs under high-current condition. However, without aeration in the cathode compartment of an MEC, ammonia stripping out of the catholyte could be challenging. It was found that there was little ammonia recovery in the absence of aeration and the catholyte accumulated a high concentration of ammonium at 8,202 mg L^{-1}; supplying aeration was shown to significantly drive ammonia out of the cathode and resulted in recovery of ammonium at 0.77 M in the recovery bottle (Qin et al., 2015). Aeration could increase the energy consumption of BES, and thus development of an appropriate method to drive ammonia out of the cathode without significant energy input will be important to implement ammonia recovery in BES.

Phosphorous may also be recovered if it is present in a relatively high concentration in leachate, and its recovery is usually via precipitation (Kelly & He, 2014). Magnesium ammonium phosphate (MAP) or struvite can be formed at a high pH range (>9.2) and this has been practiced for phosphorous recover from high strength wastewater (Altinbas et al., 2002). Phosphorus recovery from leachate by BES has not been well studied, and challenges exist in maintaining the stoichiometry for struvite formation and the effect of precipitants on the electrode performance (or regeneration of electrodes for reuse).

Metals recovery

Leachate contains a wide range of metals such as iron, manganese, copper, zinc, and lead. The concentrations of those metals are usually low, for example below 1 mg L^{-1}, and highly dependent on the specific leachate (Wu et al., 2015). A medium aged landfill leachate in South Korea contained 76 mg L^{-1} of iron, 16.4 mg L^{-1} of manganese, 0.78 mg

L^{-1} of copper, 2.8 mg L^{-1} of zinc, 2.4 mg L^{-1} of chromium, and 0.72 mg L^{-1} of lead (Im et al., 2001). However, the maximum concentration of some metals in leachate can be higher. It was reported that some leachates contain 10 mg L^{-1} of copper, 5 mg L^{-1} of lead, 13 mg L^{-1} of nickel, 1000 mg L^{-1} of zinc, and up to 5500 mg L^{-1} of iron (Baun & Christensen, 2004; Kjeldsen et al., 2002).

Metal recovery from leachate using BES has not been investigated before, but prior studies have demonstrated that metals can be recovered from synthetic wastewaters by employing BES (Nancharaiah et al., 2015; Wang & Ren, 2014). Figure 1-3 shows general process of metal recovery in BES, and four types of metals recovery systems have been investigated by far using synthetic wastewaters as the metal source (Wang & Ren, 2014). First, metal can be recovered by the modified MFC, in which its cathode is in an anaerobic mode and metals with redox potential higher than the anode potential (e.g., Cu, Fe, etc.) can be reduced on the cathode electrode (Modin et al., 2012; Wang & Ren, 2014). Second, metal recovery is accomplished in an MEC, where an external power is supplied to drive electrons from an anode electrode to a cathode electrode for enhanced reduction of metals with low redox potentials (e.g., Cd, Pb, Ni, Zn, etc.) (Modin et al., 2012; Qin et al., 2012). Third, metal recovery is achieved by using bio-cathodes, which use specialized microbes to help reduce selective metals on the cathode surface (Tandukar et al., 2009). Fourth, metal recovery is enhanced on bio-cathodes enhanced by external power input as a driving force for electron flow (Huang et al., 2011).

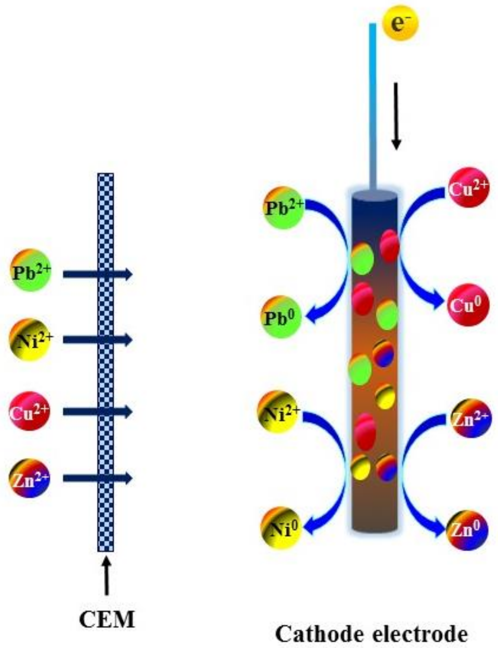

Figure 1-3. Possible metal recovery in the cathode of BES via metal ion transport across CEM driven by current generation and reducing reactions on a cathode electrode.

A great challenge for metal recovery from leachate is the low concentration of many metals, which can be affected by landfill age and type, and thus economic feasibility for recovery will need further analysis. The recovery should target those valuable metals that have relatively higher concentrations. Metals are more soluble at a low pH with a high concentration of volatile fatty acids (VFA) in the acidogenic phase, while they are less soluble in the leachate with a higher pH and lower organic content (Harmsen, 1983). These effects are specific to the type of metals; iron and lead can form complexes with high molecular weight compounds (methanogenic phase), while zinc is more available with low molecular weight compounds (acidogenic phase) (Harmsen, 1983). Different forms (i.e. colloidal and dissolved forms) of metals in leachate must be well understood to harness advantages form different metal forms in different aged leachate (Jensen et al., 1999).

Most of the studies of metal recovery from synthetic wastewater in BES took advantage of cathode reactions (Nancharaiah et al., 2015; Wang & Ren, 2014). However, leachate will need to be treated in the anode for organic removal, and direct use of the anode effluent in the cathode will introduce many organic compounds that can compete for oxygen with the cathode electrode and eventually cease the cathode reaction. A possible approach for metal removal/recovery is to drive metal ions across a cation exchange membrane in a similar way of ammonium removal. In that way, metals can be isolated from the anolyte without introducing undesired compounds into the cathode. Therefore, it is possible to have multiple tasks completed in a single process, ammonium and metal removal/recovery. In the cathode, ammonium will be converted to ammonia gas and collected in the gas phase; meanwhile, the high-pH condition of the catholyte can accelerate the precipitation of metals, which will be collected in solid phase. A successful operation of such a process will need to better understand the transport of multiple ions (and their competition) and develop effective methods for collecting different compounds. When biocathode is applied, the toxic effects of metals on microorganisms should be further investigated.

Because of the generally low concentrations of metals, recovery of target metals may not be a major goal for BES treating leachate. Instead, it can be a side effect of major processes such as ammonium removal/recovery. For instance, metal removal can occur concurrently with other biological processes such as denitrification in the BES (Watanabe et al., 2005). Recovered metals can be used for treating leachate or other applications. For example, during Fenton's pretreatment of leachate, captured Fe can be used as the catalyst with H_2O_2, which may also be generated in the cathode of a BES (Rozendal et al., 2009). Recovery/removal of metals may also help reduce toxic effects on microorganisms in BES, thereby improving leachate treatment.

Water recovery

Reducing the volume of leachate is critically important to sustainable leachate management and extracting high-quality water will accomplish such a goal. Membrane technologies such as microfiltration, ultrafiltration, nanofiltration, and reverse osmosis have been investigated to extract useful water from leachate (Renou et al., 2008). One problem with filtration treatment is that contaminants are not degraded, and the presence of organic matter can lead to serious fouling issues. Thus, proper treatment based on biological and/or chemical processes should be linked to filtration treatment. Such combination has been realized in BES that contains membrane filtration in two ways, internal integration in which membrane works as an integral part of the BES reactor (Fig. 1-4A), and external linkage that membrane units are separated from BES and linked through hydraulic connection (Fig. 1-4B) (Yuan & He, 2015). It was reported that synergistic application of hollow-fiber ultrafiltration membrane in the aerobic cathode chamber of an MFC could enhance performance in terms of organics removal, water purification, and power productions (Li et al., 2014). The resulting membrane bio-electrochemical reactor (MBER) succeeded to remove 90% of COD and 69% of inorganic nitrogen, and generated a high quality permeate of turbidity less than 2 NTU with inherent benefits of less energy requirements compared to membrane bioreactors (MBR) and less fouling due to aeration in the aerobic cathode compartment of the MBER (Li et al., 2014).

Forward osmosis (FO) is an emerging membrane technology for low-fouling operation (Zhao et al., 2012). It uses the natural osmotic pressure between the draw and the feed solutions to drive water to the concentrated draw solute side. FO has been integrated into BES to form osmotic BES (OsBES) for simultaneous organic removal, energy recovery, and water recovery through various synergistic combinations (Lu et al., 2015). A challenge in an FO process (including OsBES) is the selection of a draw solute that can be energy-efficiently regenerated. Ammonium bicarbonate is a very attractive draw solute for FO application, because it can be recovered by moderate heating (McCutcheon et al., 2005). An MEC-FO system has been developed to recover ammonium from synthetic wastewater and recovered ammonium in FO as a draw solute to recover water from the treated wastewater (Qin & He, 2014). This MEC-FO system has been applied to treat leachate (Qin et al., 2015). Although the system demonstrated poor COD removal (~ 35% with cathode aeration or ~6% without aeration in the final batch cycle) from leachate, ammonia recovery was significant (~ 65% with cathode aeration, or ~55% without aeration); when using treated leachate as the feed, the FO system was able to extract 51% water in 3.5 hours using 2 M NH_4HCO_3 as draw solution.

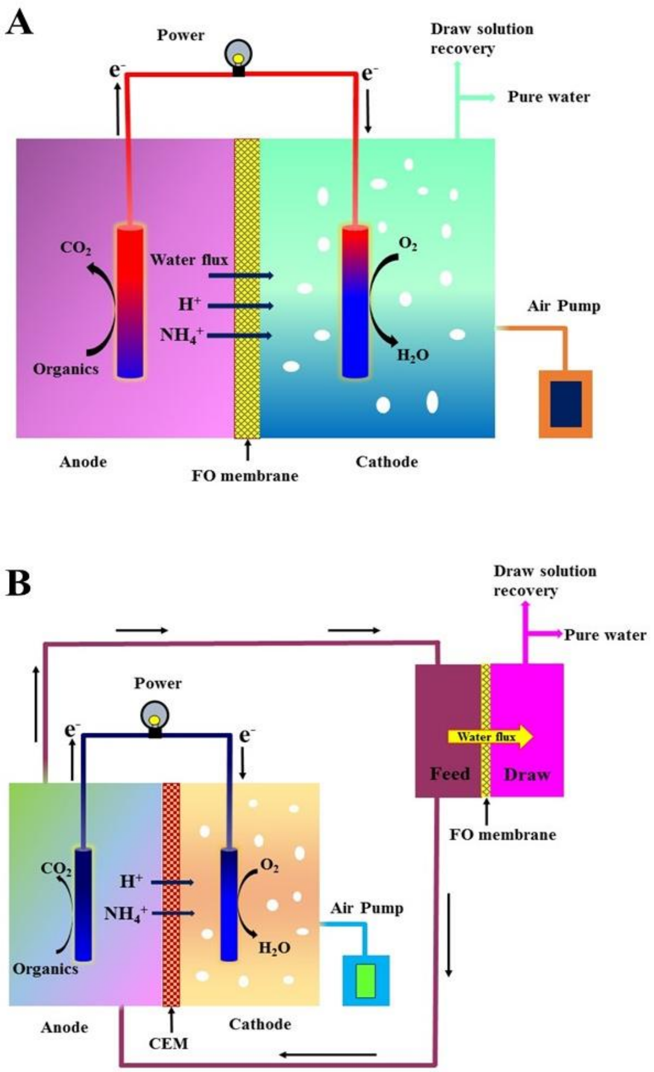

Figure 1- 4. Integrating FO with BES: (A) FO membrane functions as a separator between the anode and the cathode (internal integration); and (B) BES is linked to a FO process (external integration).

FO has advantages over micro/ultrafiltration processes, because it can reject a wide range of contaminants including heavy metals. Although nanofiltration and/or reverse osmosis (RO) can also achieve high-quality water extraction, those have not been reported in coupled application with BES. To apply BES-FO system (either internal or external linkage) for water recovery from leachate, there are several issues to address. First, fouling of FO membrane should be properly addressed. FO membranes are subject to biofouling and inorganic scaling by the contaminants presented in leachate. To alleviate fouling/scaling, BES may act as a pretreatment for removing a portion of contaminants and decreasing biodegradability of the remaining leachate (to avoid biofouling in the FO). Second, disposal of brine solutions should be studied. FO will concentrate the leachate by removing its water content, and thus the brine solution may need further disposal. Returning brine solution back to the landfill will be an option, and its effect on biological degradation within the landfill should be better understood. Third, application of the extracted water should be identified. Despite good reject of many contaminants, production of potable water may not be feasible. The quality of the produced water should be well analyzed, and possible applications include landscaping, agricultural irrigation, and direct discharge to surface water/groundwater. Fourth, selection of an appropriate draw solute will be critical to successful implementation of the FO process. Sodium chloride is widely used in FO research, but due to reverse salt flux and regeneration, its application in FO would be limited. The previously mentioned ammonium bicarbonate, especially using recovered ammonia from leachate, will be of strong interest.

Conclusions

BES is a viable approach for resource recovery from leachate. The recoverable resources include energy, nutrient, metals, and water. Laboratory studies demonstrate the feasibility of recovering some of those resources, and more research efforts are needed to further understand some fundamental and practical barriers in those recovering processes. Appropriate pretreatment is identified to be important for BES treatment of leachate, and this also indicates that resource recovery in BES should cooperate with other technologies such as forward osmosis. Resource recovery from leachate is challenging, but it will benefit sustainable leachate management and also create new application niche for BES development.

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CHAPTER 2

A Review of Landfill Leachate Induced Ultraviolet Quenching Substances: Sources, Characteristics, and Treatment

Abstract

Landfill leachate contains extremely diverse mixtures of pollutants and thus requires appropriate treatment before discharge. Co-treatment of landfill leachate with sewage in wastewater treatment plants is a common approach because of low cost and convenience. However, some recalcitrant organic compounds in leachate can escape biological treatment processes, lower the UV transmittance of waste streams due to their UV-quenching properties, and interfere with the associated disinfection efficacy. Thus, the leachate UV quenching substances (UVQS) must be removed or reduced to a level that UV disinfection is not strongly affected. UVQS consist of three major fractions, humic acids, fulvic acids and hydrophilics, each of which has distinct characteristics and behaviors during treatment. The purpose of this review is to provide a synthesis of the state of the science regarding UVQS and possible treatment approaches. In general, chemical, electrochemical, and physical treatments are more effective than biological treatments, but also costlier. Integration of multiple treatment methods to target the removal of different fractions of UVQS can aid in optimizing treatment. The importance of UVQS effects on wastewater treatment should be better recognized and understood with implemented regulations and improved research and treatment practice.

Introduction

Generation of solid waste is increasing globally due to both economic and population growth (Dang *et al*., 2016). A World Bank report predicted an increase of global waste generation from 1.3 to 2.2 billion tons by 2025, while the associated management cost was predicted to increase from $205.4 to $375.5 billion by 2025 (Hoornweg and Bhada-Tata, 2012). Among the different municipal solid waste (MSW) management approaches, landfilling is the most common because of its low cost and relatively low maintenance requirements (Deng and Englehardt, 2006). For instance, more than 80% and around 53%

of the solid waste is disposed of in landfills in China and the U.S., respectively (Chai et al., 2013; USEPA, 2016). During the process of stabilization, the landfilled solid waste produces liquid waste called leachate from the infiltration of water from precipitation into the landfill and the moisture in the waste (Damiano et al., 2014; Ganesh and Jambeck, 2013). A ton of municipal solid waste can generate 0.05 – 0.2 tons of leachate in its lifetime during the process of landfilling (Kurniawan and Lo, 2009; Maryana et al., 2014; Wang et al., 2016). This leachate is a complex wastewater containing a vast array of pollutants, which can result in major environmental impact and adverse human health risk if not contained and treated appropriately (Kjeldsen et al., 2002; Renou et al., 2008).

Because of the complexity and wide variation of leachate dissolved organic carbon (DOC), there is no single treatment process that works for all leachates (Comstock et al., 2010; Renou et al., 2008; Tatsi et al., 2003). In the U.S., more than 60% of the landfills discharge leachate to wastewater treatment plants (WWTPs) because of its low cost (~ \$0.04 per gallon) and convenience (Staley and Bolyard, 2018; Bolyard, 2016). About 29% (n = 258) of the landfills conduct treatment (e.g., aerated storage, solid separation, etc.) prior to disposal to WWTPs, and 22% (n = 60) are prohibited to discharge in WWTPs for several reasons (i.e., flow, COD, BOD_5, NH_3-N, sodium concentration) (Staley and Bolyard, 2018; Zhao et al., 2012). Biological treatment is suitable for removing biodegradable organics from leachates, with recalcitrant organic fractions left behind. Other methods, such as physicochemical (Gupta et al., 2014a; Jung et al., 2017), electrochemical (Shao et al., 2006; Xiao et al., 2013), and bioelectrochemical treatments (Iskander et al., 2017b; Zhang et al., 2015a) are being explored as well. Leachate DOC can vary with time with a concentration of 800 - 20000 mg L^{-1} (Huo et al., 2008; Huo et al., 2009; Kang et al., 2002; Mohammadzadeh et al., 2005). Over time, these organics can be converted from low molecular weight aliphatic compounds into high molecular weight aromatic compounds due to condensation and polymerization of byproducts from microbial degradation (Bolyard and Reinhart, 2017). The high molecular weight aromatic compounds are generally hydrophobic, consisting mainly of humic substances (e.g., humic and fulvic acids). The low molecular weight aliphatic compounds are mostly hydrophilic.

Both low and high molecular weight substances in municipal solid waste landfill leachates can strongly absorb UV light. Those substances are usually refractory in most treatment processes of WWTPs and can eventually interfere with the downstream UV disinfection process (Zhao et al., 2013a). Due to their UV quenching abilities, these substances are collectively called ultraviolet quenching substances (UVQS). UV quenching by leachate organics, which is synonymous with ‘to put out the UV light’, can have an adverse effect on disinfection, even if landfill leachate constitutes as low as 0.1% of the total flow into a municipal WWTP (Bolyard, 2016; Bolyard et al., 2018a; Reinhart and Bolyard, 2015). In addition, UV disinfection can become ineffective in removing antibiotic resistance genes (ARGs) as ARGs can be absorbed on humic acids surfaces during UV treatment (Yu et al., 2016). Leachate organics can also stimulate the production of carcinogenic disinfection byproducts (DBPs) (i.e., haloacetic acid, haloalkanes) if organics are present at a concentration over 2 mg L^{-1} during chlorination disinfection (Nikolaou et al., 2004).

Therefore, it is evident that the addition of complex landfill leachate into municipal wastewater treatment systems poses a serious challenge to wastewater treatment performance. It is imperative to develop effective treatment approaches to reduce UVQS to an acceptable level before routing it to wastewater treatment facilities. This requires a better understanding of properties and chemical characteristics of UVQS along with their behaviors in different treatment practices. The purpose of this review is to provide a detailed introduction of landfill leachate induced UVQS with respect to source, formation, and characteristics, a comprehensive evaluation of the current status of leachate treatment for UVQS removal, and in-depth discussion of the perspectives of UVQS control for wastewater treatment.

Characteristics of UVQS

Formation

The UVQS of leachate contain hydrophilic fraction (HPI) and hydrophobic humic substances (humic acids, HA and fulvic acids, FA). Hydrophilic aliphatic carbons are formed through the decomposition of organic solid wastes within a landfill, while humic substances are formed through complex biological and chemical reactions by a humification process (Castagnoli et al., 1990; Jones and Bryan, 1998). Several reaction pathways on humification involving lignin, polyphenols, and sugar amines condensation have been proposed (Jones and Bryan, 1998). Lignin is abundantly present in paper and paperboard, wood, leaves and other vegetation, and acts as a precursor for humic substances in landfills. According to a USEPA report, paper and paperboard (14.3%), yard trimmings (7.9%), wood (8.1%) accounted for approximately 30.3% of the total landfilled MSW in 2014, thereby serving as sources of lignin (USEPA, 2016). The process of humification may also be aided by proteins, carbohydrates, and fatty acids present in food wastes, which made up 21.6% of the disposed MSW into landfills in 2014 (USEPA, 2016). Because of the wide variety of precursors (e.g., lignin, proteins, carbohydrates, and fatty acids), source materials (e.g., paper and paperboard, wood, vegetation and food waste) and environmental conditions, humic substances in landfill leachate differ significantly in terms of chemical structures and properties (Castagnoli et al., 1990; Ratasuk and Nanny, 2007; Tahiri et al., 2016). Humic substances are structurally heterogeneous macromolecules, yellow to black in color, and acidic in nature. Specifically, they are covalently bonded agglomerates of aliphatic (i.e. hydrophilic fraction) and aromatic moieties that contain phenolic, carboxyl, alkoxy, and amido groups along with occasional presence of sulphate esters, phosphate esters, semiquinone and hydroquinone groups (Castagnoli et al., 1990; Jones and Bryan, 1998). The hydrophobicity of humic substances might also be enhanced by the presence of carboxyl rich alicyclic molecules and material derived from linear terpenoids (i.e., terpenoids contain five carbon isoprene units) (Lam et al., 2007). Humic substances grow in size by incorporating smaller fractions using –C – O –, –C – C –, van der walls, π-π, CH – π, and hydrogen bonds (Dec and Bollag, 2000; Freeman et al., 2001; Jones and Bryan, 1998; Piccolo, 2002; Piccolo et al., 2000).

Heterogeneity of humic substances in leachates and difficulty in characterizing them are largely attributed to their progressive change with age (Nanny and Ratasuk, 2002). It is believed that in a young leachate, FA are formed first and thus their concentration is higher than that of HA (Artiola Fortuny and Fuller, 1982; Kang et al., 2002; Nanny and Ratasuk, 2002). However, with humification, HA concentration increases with time and eventually decreases as landfills become stable and natural degradation and/or dilution takes place (Artiola Fortuny and Fuller, 1982; Nanny and Ratasuk, 2002). Considering the long exposure of the precursors to water, oxygen, and radiation (i.e. sunlight), humic substances are often considered the final products of the bio-degradative and oxidative pathway (Jones and Bryan, 1998). Due to this, humic substances are considered as 'old molecules' that are resistant to further biological treatment and susceptible to specific treatments (i.e., advanced oxidation) that they have not experienced before (Jones and Bryan, 1998). Additionally, the multiple redox states and reversibility of redox sites in humic substances increase its recalcitrance to microbial oxidation (Ratasuk and Nanny, 2007).

Biodegradable organic matter, including volatile fatty acids, is formed through the initial decomposition of organic solid waste, such as food scraps. They are usually aliphatic structures and fractionated as a part of HPI (Bolyard and Reinhart, 2017). Due to this simple carbon chained structure, they are susceptible to microbial degradation and contribute significantly to the readily biodegradable chemical oxygen demand (COD) and biochemical oxygen demand (BOD), especially in raw fresh leachates. However, they only contribute a small portion (10% on average) of the overall UV absorbance of leachates (Zhao et al., 2013a). In addition, this biodegradable organic matter can be easily removed in the biological treatment processes in WWTPs before entering the downstream UV disinfection system, and thus is usually not a significant issue for UV disinfection in WWTPs.

Composition

Leachate UVQS (measured as TOC) mainly consist of HA, FA and HPI fractions, the ratio of which is highly variable and depends on many factors, such as waste type, operating conditions, and landfill age. The percentages of HA, FA, and HPI fractions vary at 2.1 – 44%, 7 – 72%, and 24.9 – 70.1% of DOC, respectively (Table 2-1) (Gupta et al., 2014b; Nanny and Ratasuk, 2002; Zhang et al., 2009; Zhang et al., 2013). The molecular weight of humic substances ranges from low (less than 500 to 2,000 g mol^{-1} for

FA) to high (50,000 to 100,000 g mol^{-1} for HA), while the typical molecular weight of the HPI fraction is similar to that of FA (Amaral et al., 2015b; Kang et al., 2002; Zhang et al., 2009). Because of the wide distribution and the aggregation properties of humic substances, it is difficult to find the real size of a humic structure (Jones and Bryan, 1998). According to a previous study, hydrophobic humic substances are more polydisperse (polydispersity index >1), while hydrophilic fractions are more monodisperse (polydispersity index ~1) with the presence of homogeneous compounds in hydrophilic fractions and heterogeneous compounds in hydrophobic fractions (Table 2-1) (Seo et al., 2007).

Table 2-1. Physical and chemical properties of three types of dissolved organic carbons in landfill leachate.

Organic fraction	% of DOC	SUVA, L mg^{-1} m^{-1}	Polydispersity	Carboxylic acidity (meq g^{-1})	Phenolic acidity (meq g^{-1})	Total acidity (meq g^{-1})	C (wt %)	H (wt %)	O (wt %)	N (wt %)	S (wt%)	H/C	O/C	N/C
Humic acids	2.1 – 44.0	0.46 – 3.61	1.3 – 1.8	3.40 – 11.61	1.73 – 1.90	5.30 – 13.34	42.2 – 57.1	3.9 – 8.8	26.7 – 42.1	2.2 – 8.3	1.0 – 7.3	0.94 – 1.88	0.36 – 0.62	0.04 – 0.13
Fulvic acids	7.0 – 72.0	0.19 – 2.38	1.2 – 1.5	6.10 – 13.02	1.30 – 2.75	7.40 – 15.77	45.1 – 53.6	4.1 – 9.6	32.8 – 42.5	0.8 – 12.0	0.9 – 5.1	1.02 – 2.53	0.47 – 0.67	0.01 – 0.23
Hydrophilics	24.9 – 70.1	0.09 – 1.77	1.2 – 1.5	6.30 – 13.83	2.30 – 3.78	8.60 – 17.61	5.7 – 47.4	3.9 – 4.8	41.1 – 50.9	1.9 – 2.5	3.2 – 14.2	1.19 – 8.37	0.63 – 6.67	0.04 – 0.05

Leachate HA have a higher content of C, H, and N, and a lower content of O than those of FA and HPI fractions (Kang et al., 2002). In turn, the O/C ratio in FA is higher than that in HA, implying that FA have a higher proportion of O- alkyl and carboxylic acid functional groups (Table 2-1) (Huo et al., 2009). The carboxylic acidities of HA are lower than those of FA and HPI, while the phenolic acidities of HA are higher than those of FA (Christensen et al., 1998). Due to the presence of a relatively small amount of ionizable carboxylic acid groups along with a substantial amount of aliphatic and aromatic moieties, HA can easily agglomerate and precipitate upon charge neutralization at pH <2, while FA are soluble at all pH range (Jones and Bryan, 1998). Sometimes, HA show a high value of O/C ratio because of the presence of a higher carbohydrate content (Christensen et al., 1998). For this reason, the ratio of O/C can often be misleading if used to compare the carboxylic acid content in organic fractions. The N content of the organics typically follows a pattern of HA>HPI>FA, and HA and HPI can have doubled N content compared to FA (Huo et al., 2009). The low value of H/C (~1) suggests predominantly aromatic structures, and the order of the H/C ratio is HA<FA<HPI, indicating that hydrophilics are more aliphatic than hydrophobics (Table 2-1) (Christensen et al., 1998; Huo et al., 2008).

Separation and quantification of UVQS

The hydrophilic and hydrophobic fractions of leachate UVQS can be fractionated using different nonionic or ionic (cationic and anionic) resin adsorption methods. These fractionation procedures are time consuming and prone to cross contamination if not carefully handled (Imai et al., 2001). Most of the studies on fractionation of UVQS in landfill leachate focused on HA, FA and HPI fractions (Ma et al., 2001). A detailed speciation process is illustrated in Fig. 2-1. In this process, a leachate sample is firstly filtered to remove suspended particles. Membranes with pore sizes from 0.45µm to 1.5 µm have been employed for this purpose (Gupta et al., 2014b; Seo et al., 2007; Thurman and Malcolm, 1981). After that, a concentrated inorganic acid (i.e. sulfuric or hydrochloric acid) is added to precipitate the HA fraction at pH < 2 (Dia et al., 2017). The solution containing the precipitates is then centrifuged or filtered to separate the precipitated HA. The separated HA can be re-dissolved in a 0.1M NaOH solution for further analysis. The supernatant, after separating the precipitated HA, contains the FA and HPI fractions and is then passed through a XAD-8 resin column, where the FA fraction is adsorbed on the resin. More details about XAD-8 resin cleaning methods can be found in several previous studies (Leenheer, 1981; Ma et al., 2001; Thurman and Malcolm, 1981). The portion of the supernatant that passes through the resin column contains the HPI fraction. The adsorbed FA fraction can be back eluted by a 0.1M NaOH solution. The separated organic fractions are analyzed for water quality parameters, such as TOC, COD, UV absorbance, etc. Another study separated leachate organics into only hydrophobic and hydrophilic fractions by solid phase extraction (SPE) (Bolyard and

Reinhart, 2017). In SPE, a leachate is first filtered through a 0.45 µm filter to remove the suspended particles. The solution is then passed through a packed XAD-8 resin column to separate the hydrophobics and hydrophilics. The adsorbed hydrophobic fraction from the resin column is re-dissolved by back eluting with 0.1M NaOH solution, while the hydrophilic fraction passes through the resin column to be collected (Bolyard and Reinhart, 2017).

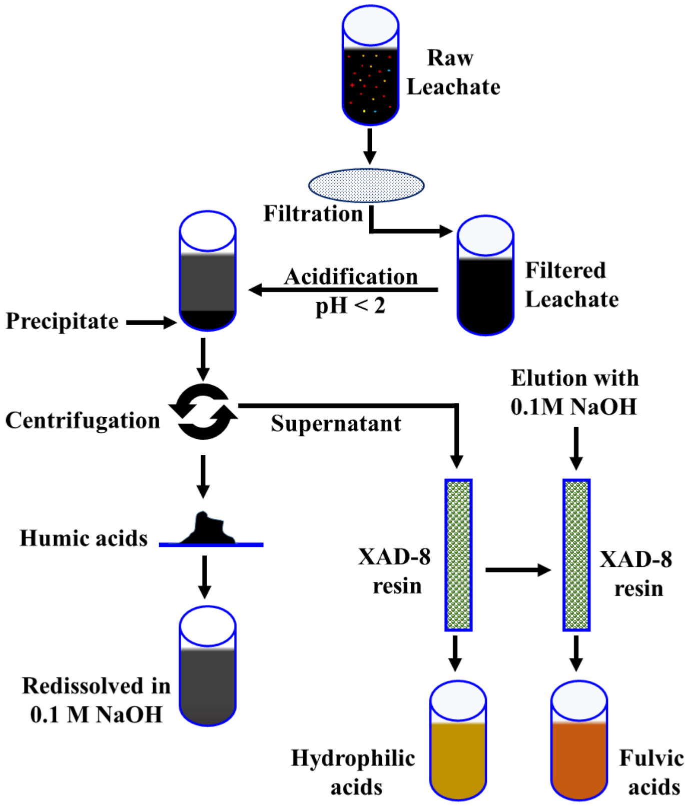

Figure 2-1. Fractionation protocol for the isolation of leachate UVQS (Christensen et al., 1998; Kang et al., 2002; Zhao et al., 2013a).

Several analytical techniques have been employed for characterizing UVQS in landfill leachates. Of those, size-based separation is performed with ultrafiltration or gel filtration chromatography (GFC) at different molecular weight cutoffs (MWCO) (Wang et al., 2016; Zhao et al., 2013a; Zhao et al., 2012). Elemental analysis is performed by using an elemental analyzer (Christensen et al., 1998; Kang et al., 2002). Spectroscopic properties are measured with a spectrophotometer (Chai et al., 2013; Cui et al., 2016). All these analyses are associated with different parameters for characterizing the organic fractions of leachate. In Table 2-2, the analytical techniques and associated parameters are described in detail for characterizing leachate UVQS.

Table 2-2. Measurement techniques and associated parameters for characterizing UVQS in landfill leachate.

Methods and description	Parameters and definition	Significance	References
Elemental composition analysis using elemental analyzers	H/C ratio	For highly aromatic structures, the typical value of H/C ratio clusters around 1, and a high value indicates the prevalence of aliphatic functional groups. The ratio of H/C less than 1 means that the organic chemical structure is composed predominantly by aromatic structures.	(Christensen et al., 1998; Kang et al., 2002)
	O/C ratio	Higher values of O/C ratio indicate the presence of O containing functional groups (i.e. carboxylic acid group).	
	N/C ratio	A high value of N/C ratio indicates the prevalence of N species (i.e. organic nitrogen) in the organic fraction. Typically, humic acids and hydrophilic fractions have higher N/C ratios than fulvic acids.	
UV absorbance measurement using UV/Vis Spectrophotometer at different wavelengths and organic carbon concentration measurement with a TOC analyzer	$SUVA_{254}$, the ratio of UV_{254} absorbance to DOC	$SUVA_{254}$ is the specific ultraviolet absorbance and positively correlated to the aromatic carbon content or percent aromaticity in organic carbon. A SUVA value > 2 L mg^{-1} m^{-1} indicates a predominantly aromatic organic structure.	(Weishaar et al., 2003)
	UV/DOC ratio, UV absorbance to DOC ratio	High value of UV/DOC ratio indicates recalcitrance of the organics. This can be SUVA if UV is UV_{254}.	(Imai et al., 2001; Imai et al., 2002)
	UV_{253}/UV_{203}, the ratio of UV absorbance at 253 to 203 nm wavelength	UV_{253}/UV_{203} is used as a measure of aromaticity. A high value indicates predominant presence of carbonyl group, carboxyl group, and ester group, while a lower value indicates the presence of aliphatic chains.	(Zhao et al., 2013b)
	UV_{250}/UV_{365} (E_2:E_3), the ratio of UV absorbance at 250 to 365 nm wavelength	This ratio decreases as the molecular weight of organics increases because the absorption at 365 nm increases with higher molecular weight.	(De Haan and De Boer, 1987)
	E_{465}/E_{665} or E_4/E_6, the ratio of UV absorbance at 465 to 665 nm	E_{465}/E_{665} value (indicator of aromaticity and humification) is inversely proportional to molecular weight and directly proportional to acidity. This parameter is used to get a rough idea about different organic fractions of leachate.	(Chin et al., 1994; Kang et al., 2002)
	e_{280} index, the ratio of UV_{280} absorbance and DOC	e_{280} is used as a measure of aromaticity. A strong correlation is observed among molar absorptivity at 280nm, total aromaticity and weight average molecular weight.	(Chin et al., 1994; Kang et al., 2002)
Ultrafiltration membrane with different cutoffs, gel filtration chromatography	Polydispersity index is calculated from weight averaged molecular weight and number averaged	Molecular weight size distribution is a good measure to have a complete scenario of the organic structures. To differentiate the organics based on molecular weight, ultrafiltration is an easy but time-consuming method. The polydispersity index gives an idea of the molecular	(Chin et al., 1994; Helms et al., 2008; Imai et al., 2002; Wang et al.,

(GFC) with different molecular weight standards, and high-pressure size exclusion chromatography (HPSEC) are used for finding the molecular weight distribution and polydispersity index	molecular weight data as follows: Polydispersity index, $D = \frac{Mw}{Mn}; D \geq 1$ Here, Mw is weight-averaged molecular weight and Mn is number-averaged molecular weight. The values for Mn and Mw can be calculated from the GFC or HPSEC data according to the following equations - $Mn = \frac{\sum CiMi}{Ci}$ $Mw = \frac{\sum CiMi^2}{Ci}$ where Mi is the molecular weight, Ci represents the area or number of specific Mi from chromatography data.	weight distribution of an organic fraction. The higher the value, the more polydisperse the distribution is. Typically, HA have the highest polydispersity index, followed by FA and then HPI.	2016; Zhang et al., 2009; Zhao et al., 2013a)
Fourier transforms infrared (FTIR) spectroscopy with spectrophotometer	Different peaks of the spectra qualitatively indicate the presence of different functional groups and chemical composition.	By comparing the absorbance bands at different wavenumbers, the chemical composition and structural characterization can be predicted. Different functional groups can be predicted from the absorbance peaks at different wave numbers. By comparing the ratio of the fluorescence peaks at longer wavelength (400 nm) to shorter wavelength (360 nm), it can be concluded that humic acids have highly condensed aromatic rings compared to fulvic acids.	(Bu et al., 2010b; Chai et al., 2013; Kang et al., 2002; Liu et al., 2015; Wang et al., 2016; Zhao et al., 2013a)
Mean oxidation state (MOS) measured from the COD and TOC values of different organic fractions	Mean Oxidation State, $MOS = \frac{4\,(TOC - COD)}{TOC}$; TOC in mol C L^{-1} and COD is in mol O_2 L^{-1}.	Mean oxidation state can be used for characterizing organic fractions based on their oxidation state. It can be used to indirectly predict the oxygen content of an organic fraction, the more positive, the higher the presence of oxygen containing functional groups. A negative MOS is indicative of a higher content of polycyclic aromatics or humic substances.	(Wang et al., 2016; Zhang et al., 2005)

Excitation-emission matrix fluorescence spectroscopy (EEM) with fluorescence spectrophotometer at different emission wavelength by changing the excitation wavelengths	Humification index is calculated from the EEM data as follows: $\mathrm{HIX_M} = \frac{\sum_{\mathrm{Ex}=200}^{450} 0 \sum_{\mathrm{Em}=435}^{480} \mathrm{Int}}{\sum_{\mathrm{Ex}=200}^{450} 0 \sum_{\mathrm{Em}=300}^{345} \mathrm{Int}}$ Here, Em (nm) is the emission wavelength, Ex (nm) is the excitation wavelength and Int. is the fluorescence intensity at these wavelengths. Another form of humification index is also used in literature: $\mathrm{HIX_M} = \frac{\sum_{\mathrm{Em}=435}^{480} 0 \sum_{\mathrm{Ex}=255} A}{\sum_{\mathrm{Em}=300}^{345} 0 \sum_{\mathrm{Ex}=255} A}$ Here, A is the area under the emission spectra at the wavelengths.	Fluorescence can be used as a sensitive and rapid shortcut for measuring DOM composition of leachate based on the distinct peaks at different excitation and emission wavelengths (Ex/Em). Different peaks at different Ex/Em wavelength are assigned to different compounds and any shift of the peak location or intensity qualitatively identify the change of the structural pattern of the organics. By calculating $\mathrm{HIX_M}$ before and after treatment for a sample, the removal percentage of humic like substances can be determined. $\mathrm{HIX_M}$ can be used as a surrogate for degree of structural condensation and aromaticity in organics. A high value of it indicates greater aromaticity.	(Cui et al., 2016; Hansen et al., 2016; Huo et al., 2008; Leenheer and Croué, 2003; Wang et al., 2016; Xiao et al., 2013; Lee and Hur, 2016; Zheng et al., 2009)
Solid-state ^{13}C nuclear magnetic resonance (^{13}C-NMR) using spectrometer	Different functional groups and % aromaticity can be calculated from different spectra.	^{13}C-NMR spectra could be divided into different regions that depict different functional groups in the organic fraction. Based on the NMR spectra, % aromaticity can be calculated by dividing the peak area of the aromatic C by the total peak area of aliphatic and aromatic carbon.	(Kang et al., 2002; Tong et al., 2015a; Tong et al., 2015b; Weishaar et al., 2003)
^{1}H nuclear magnetic resonance (NMR) spectra using spectrometer	Different functional groups and % proton in different organic fractions can be calculated from different spectra.	Based on the spectra, of which different peaks are contributed by different functional groups, ^{1}H-NMR can be used for characterizing organics. By analyzing the peaks, proton percent in different organic fractions could be calculated.	(Kang et al., 2002)

Effects of UVQS

Because of the complex chemical structure and continuous evolution with time (Section 2.1 – 2.2), UVQS are recalcitrant and can strongly absorb UV light. The strong UV absorbance by leachate UVQS is attributed to the presence of different aromatic moieties (e.g., phenolic, benzoic, aniline, etc.) that absorb UV light because of the $\pi - \pi^*$ electron transitions in the range of 200 – 380 nm (Chin et al., 1994; Weishaar et al., 2003). Among the different UVQS, HA have the highest specific UV absorbance (SUVA) followed by FA and HPI (Fig. 2-2) (Baccot et al., 2017; Gupta et al., 2014b; Zhao et al., 2013a). Although HA and FA possess the highest SUVA, HPI contribute slightly more than half to the total UV absorbance owing to their higher concentration (Gupta et al., 2014b; Zhao et al., 2013a). Metals (e.g., especially Fe) associated with humic substances can also contribute to the UV absorbance of leachate (Martensson et al., 1999; Qu et al., 2008; Xi et al., 2012). Because of this UV absorption by leachate, the effectiveness of UV disinfection is diminished due to the decreased UV transmittance (UVT). For effective disinfection, the UVT of a wastewater stream entering an UV disinfection process should be in the range of 60-65% or higher, and the UV absorbance (UVA) needs to be less than 0.187 cm^{-1} [UVT (%) = 10^{-UVA} × 100] (NWRI, 2012). As most UVQS will pass through biological treatment processes without being removed (Huo et al., 2009), they can interfere with the downstream UV disinfection process causing ineffective disinfection (Bolyard, 2016; Bolyard et al., 2018a; Reinhart and Bolyard, 2015; Zhao et al., 2013a).

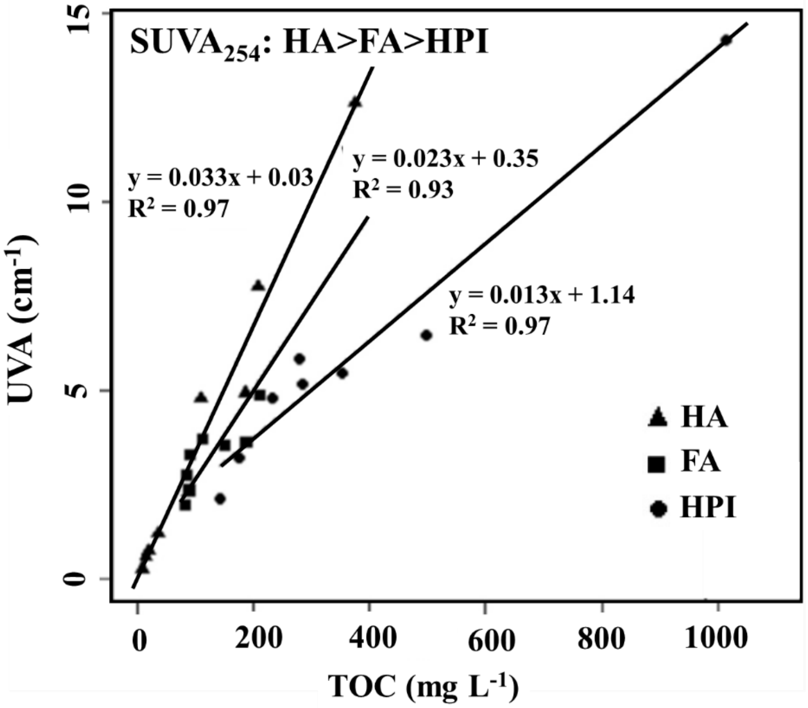

Figure 2-2. The correlation between UV_{254} absorbance (UVA, cm^{-1}) and TOC (mg L^{-1}) of the HA, FA and HPI fractions of multiple leachates (Zhao et al., 2013a).

This UV quenching by leachate may also affect ARGs removal by UV disinfection during co-treatment. Previous studies have shown significantly positive correlations among HA, metals (Co, Cu, Zn), ARGs, and mobile genetic elements (MGEs) because of ARG sorption on HA surface (Wu et al., 2017; Xu et al., 2016; Yu et al., 2016). The association of ARGs with leachate organics would make leachate treatment challenging as leachate organics can quench UV light and result in ineffective ARGs removal. In addition, the presence of leachate organics, especially humic substances, during chlorination disinfection can create issues such as disinfection by-products (DBPs) formation (Nikolaou et al., 2004). Molecular weight and the degree of aromaticity of aquatic humic substances determine the amount of DBPs formed during chlorination (Reckhow et al., 1990). Because UVQS are aromatic and contain nitrogen, the potential of carbonaceous and nitrogenous DBPs formation is high (Bhatnagar and Sillanpää, 2017; Mitch and Sedlak, 2004; Westgate and Park, 2010).

Treatment of UVQS

Biological treatment

Biological treatment of landfill leachate can be conducted in either aerobic or anaerobic reactors, and the effectiveness of biological treatments largely depends upon the type and composition of leachate (Driskill et al., 2015). Young leachates, which are high in volatile fatty acids and biodegradable organics, are more suitable for biological treatment compared to mature leachates that are mostly comprised of the recalcitrant portion of the organics (Kjeldsen et al., 2002; Renou et al., 2008). Aerobic biological treatment mainly includes activated sludge and fixed film bioreactors. The decrease of UV absorbance and UVQS (as TOC) after aerobic biological treatment can vary from 2.5 to 55% and 26 to 60% with an average of 22.7 and 44%, respectively (Fig. 2-3). The average decrease of HA, FA and HPI concentrations (in terms of TOC) after biological treatments is found to be 50.2, 53.9 and 50.1%, respectively, while the removals of UV absorbance for the respective fractions were 43.5, 23 and 19.5% (Fig. 2-3). Biological treatment is less effective in reducing UV absorbance than in reducing TOC, likely related to the ineffectiveness of biological treatment for recalcitrant organics (mainly humic substances); this could result in a rise in the SUVA value (Driskill et al., 2015; Zhao et al., 2013a). For example, after biological treatment, the SUVA values of HA, FA, HPI, and raw leachate increased from 2.77 to 4.40 L mg^{-1} m^{-1}, 1.92 to 3.25 L mg^{-1} m^{-1}, 1.55 to 2.05 L mg^{-1} m^{-1}, and 2.51 to 3.15 L mg^{-1} m^{-1}, respectively (Bolyard et al., 2018b; Zhao et al., 2013a). The increase of SUVA/aromaticity in a sequential batch reactor (SBR) could be caused by the condensation of simple aromatics into polycondensed aromatic structures (Jouraiphy et al., 2005) and generation of complex soluble microbial products (SMPs) with high molecular weights (Westerhoff and Pinney, 2000). However, polydispersity ($d = M_w/M_n$) (Gellerstedt, 1992) decreased for the organic fractions after SBR treatment because of the consumption of lower molecular weight organics (i.e. volatile fatty acids, amino acids) by bacteria and absorption of higher molecular weight organics to activated sludge solids (Bolyard et al., 2018b; Bu et al., 2010a). Anaerobic biological treatment of leachate has a limited ability to remove organics and UV absorbance. For example, a two-stage anaerobic membrane bioreactor consisted of thermophilic (55± 2 °C) and mesophilic (37 ± 1 °C) phases removed 39% of HA, 37% of FA, and 55% of HPI fraction from a landfill leachate, while the removal of TOC was slightly over 50% and UV absorbance removal was 46% (Pathak et al., 2018). In an Anammox process, of the total reduction of DOC (from 288 to 136 mgL^{-1}), 33% was contributed by HA and 57% by FA, suggesting the susceptibility of FA over HA in this treatment (Liang et al., 2009).

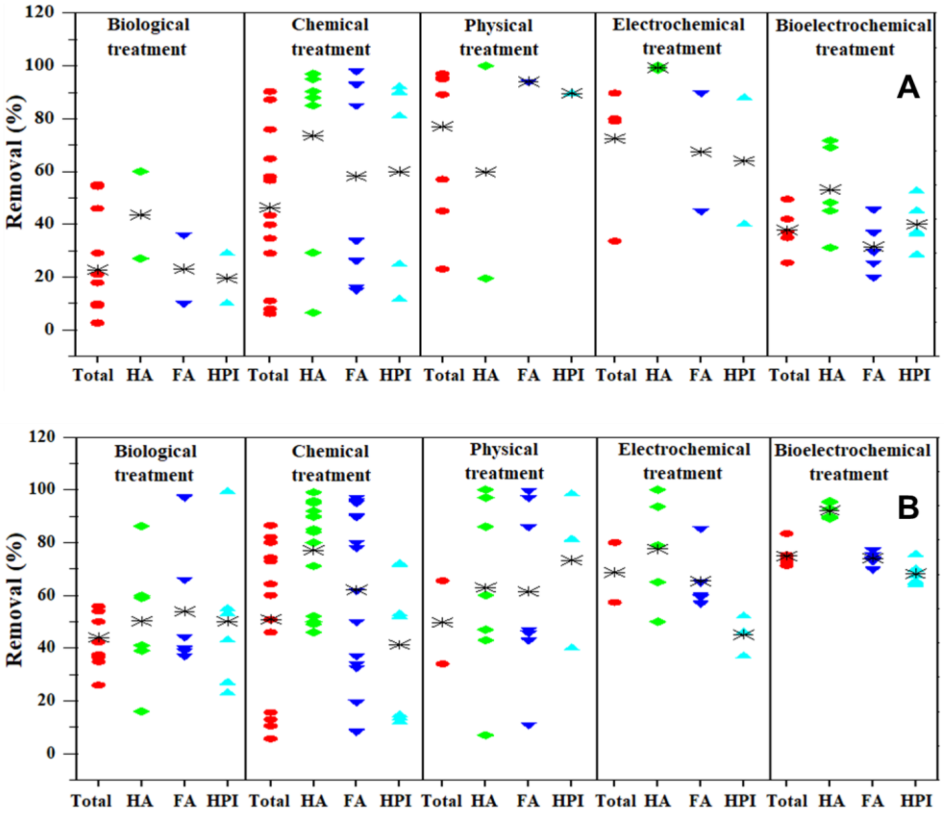

Figure 2-3. Collection of removal data values for UV absorbance (A) and UVQS as TOC (B) from landfill leachate after different treatments. '*' indicates the mean of the values. Figure was plotted with data from 42 papers.

Because of the ineffectiveness of standalone biological treatments, combined biological and physicochemical treatments have been investigated to enhance the removal of UVQS. For example, incorporation of powdered activated carbon (PAC) with an activated sludge process improved the organics removal for HA from 41% to 59.8%, FA from 40% to 44.2%, and HPI from 27% to 53.1% (Zhao et al., 2013a). Membrane separation is an effective post-treatment method to lower the UV absorbance of landfill leachates (Zhao et al., 2013a). Due to the higher average molecular weight of HA and FA, nanofiltration (NF) following biological treatment was able to elevate the UV transmittance of leachate-sewage blended streams from 35% to 62% when leachate constituted 5% of the total volumetric flow (Zhao et al., 2013a; Zhao et al., 2012). Although biological treatment processes are generally low cost and environmentally compatible, their treatment efficiency for UVQS is limited. The UV absorbance decrease in a leachate after biological treatment is always lower than the decrease of the UVQS concentration (in terms of TOC). As a result, recalcitrant leachate organics can penetrate through biological treatment and pose negative effects on the subsequent disinfection process. Appropriate incorporation of chemical, physical, and/or physicochemical treatment with biological treatment should offer a feasible solution to control UVQS.

Chemical treatment

Chemical treatment of leachate UVQS can be conducted by chemical oxidation (e.g., Fenton, Ozone, Percarbonate) and/or coagulation-flocculation. On average, chemical treatments have demonstrated the UV absorbance decrease of 46% and UVQS removal of 51% in term of TOC (Fig. 2-3). Chemical treatments such as Fenton's oxidation are very effective and could achieve an average removal of 84.5% UV absorbance and 67.4% UVQS (in term of TOC) from leachate (Gupta et al., 2014a; Jung et al., 2017; Moravia et al., 2013; Wu et al., 2011). While treatments such as Ozone can achieve a 65% UV absorbance decrease, only 5.6 - 30% of UVQS removal in term of TOC was achieved, mainly because of its selective reaction with hydrophobic compounds, which subsequently transform to hydrophilic smaller molecular weight fraction after ozone treatment (Fig. 2-4) (Jung et al., 2017; Wang et al., 2016; Wu et al., 2004). For example, 100% decrease of HA, 16.2% decrease of FA, and 78% increase of HPI fraction was observed after ozone treatment (Wang et al., 2016). Likewise, as demonstrated in Fig. 2-5, the UV absorbance of the HPI fraction after ozone treatment did not change, possibly because of the recalcitrance of the HPI to ozone or interconversion of the hydrophobic fractions to the hydrophilic fraction. Due to this, the contribution of the HPI to the total UV absorbance increased from 41% to 93% after ozone treatment (Fig. 2-5). Also, the polydispersity index increased from 2.9 to 15.6 after ozonation of leachate, indicating a broader molecular weight distribution of leachate organics with ozonation (Wang et al., 2016). To improve the performance of ozone treatment, combination of ozonation with other treatments (e.g., ozone/UV, ozone/H_2O_2, ozone/persulfate) has been investigated and exhibited improved UVQS removals, for instance, from 8 to 23% with ozone/UV treatment (Soubh and Mokhtarani, 2016; Wang et al., 2017). A disadvantage of ozone-based treatment is the large consumption of electricity during ozone generation.

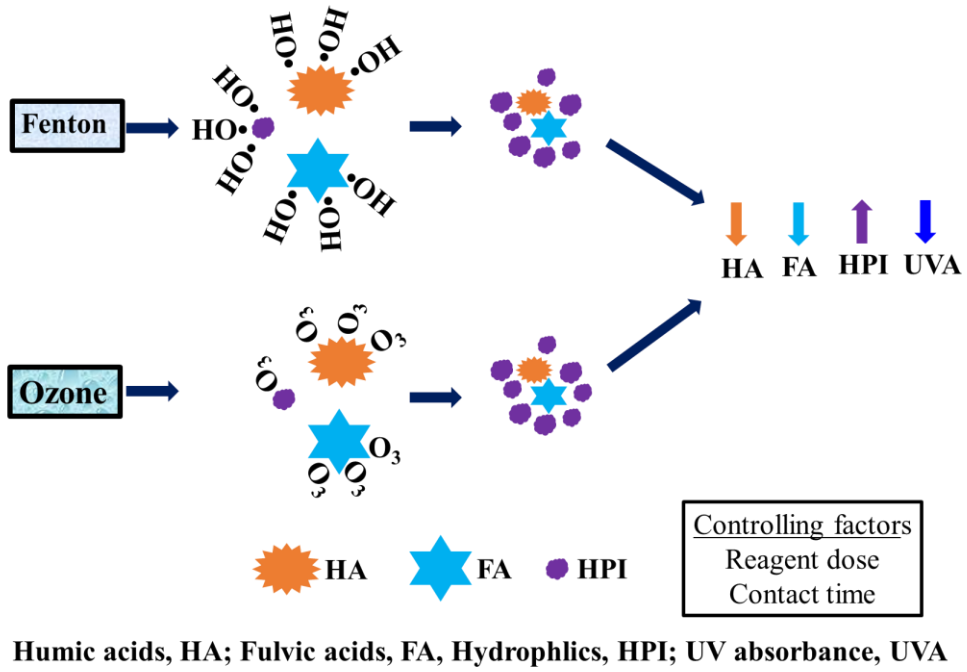

Figure 2-4. A schematic of two common chemical oxidation treatments of landfill leachate, Fenton and Ozone, and their general interaction mechanisms with leachate organics (HA, humic acids; FA, fulvic acids; HPI, hydrophilics, and UVA, UV absorbance).

Chemical oxidation mainly works on the principle of interconversion of leachate UVQS during treatment. For example, Fenton removes most of the hydrophobic HA and FA by converting them into the HPI fraction (Jung et al., 2017; Xu et al., 2017; Zhao et al., 2013b). The possible pathway of such conversions is via the nonselective reaction of •OH radicals with both hydrophobic and hydrophilic compounds (Fig. 2-4) (Cataldo and Angelini, 2012; Jung et al., 2017). The total TOC removal after Fenton treatment was reported to be less than the COD and humic substances removal, indicating that some of the organics were converted into intermediates after Fenton treatment (Wu et al., 2010a; Wu et al., 2010b). These smaller sized intermediates with fewer carboxylic groups than initial humic substances are more susceptible to oxidation than original molecules and exert less COD after treatment (Wang et al., 2016). A broad range of intermediates during the degradation of HA and FA can be utilized as a carbon source for bacteria, as a result of increased biodegradability of leachates by Fenton treatment (Wang et al., 2017). To improve the performance, different types of Fenton processes such as solar photo-Fenton and iron oxide coated GAC assisted Fenton (FeGAC/H_2O_2) have been investigated for removing leachate UVQS and were able to achieve the removal of 80 - 85% humic substances (Fan et al., 2007; Silva et al., 2013). Fenton was also coupled with SBR for leachate treatment, and in this system Fenton removed high molecular weight aromatic rings and conjugated moieties, while the SBR removed low molecular weight fractions, carboxylic acids, and proteins (Liu et al., 2015). Fenton treatment, though a strong and effective chemical oxidation process for UVQS removal, has issues such as high reagent cost, sludge production, and foaming during the initial pH adjustment.

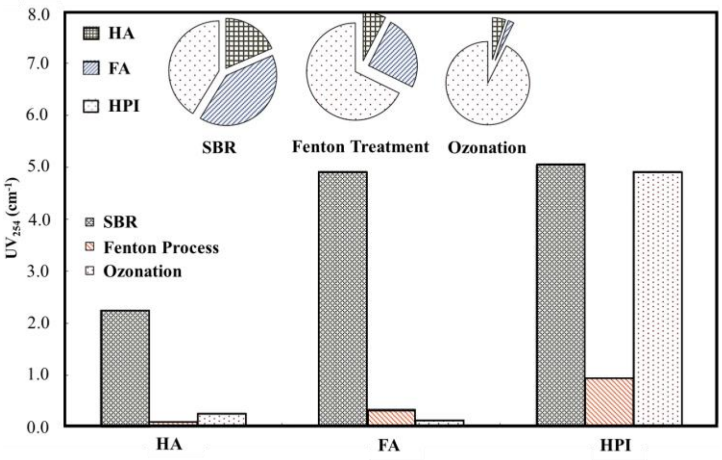

Figure 2-5. UV_{254} absorbance (cm^{-1}) of different organic fractions (HA, FA and HPI) of a leachate in a sequential batch reactor (SBR), Fenton treatment, and Ozonated treatment (Jung et al., 2017).

Other chemical oxidation processes have also been studied for treating landfill leachate UVQS with varied performances. For example, sodium percarbonate oxidation of leachate was able to remove 8 - 43.4% UV absorbance and 15.1 - 15.6% UVQS (as TOC) (Iskander et al., 2017a). Microwave assisted persulfate oxidation was ineffective to remove recalcitrant aromatics, resulting in the increase of the SUVA value from 1.5 to the range of 2.3 - 14.7 L mg^{-1} m^{-1} (Kim and Ahn, 2017). Coagulation-flocculation and lime treatment could achieve the removal of some UVQS: 21 - 71.1% of HA, 21 - 37% of FA, and ~ 53% of HPI fraction (Amokrane et al., 1997; Liao and Randtke, 1986; Wu et al., 2011; Zheng et al., 2009). In addition, several unconventional technologies have been investigated for leachate treatment. For instance, a bioflocculant successfully removed 85% of HA and produced less sludge than conventional chemical coagulant ($Al_2(SO_4)_3$) (Zouboulis et al., 2004). The combination of a collector (70 mg L^{-1} N-cetyl- N, N, N-trimethylammonium-bromide), a frother (1% ethanol), and flotation was able to remove 99% of HA from a simulated landfill leachate (Zouboulis et al., 2003). Subcritical water catalytic oxidation (Zhai et al., 2016), catalyzed wet air oxidation (Wang et al., 2014), and photocatalytic degradation (Wiszniowski et al., 2004) also showed promising performance of leachate UVQS treatment with removal of 49 - 93% of HA and 75 - 87% of TOC. In general, the potential applications of those treatment methods are limited by the high chemical cost.

Physical treatment

Physical treatments are mostly membrane separation and sorption-based techniques such as resin separation. In general, physical treatments have exhibited removals of 23 - 97% (average 77%) UV absorbance and 34 - 98% (average 65.8%) UVQS in terms of TOC (Fig. 2-3). Membrane separation that works on the size exclusion principle includes reverse osmosis (RO), forward osmosis (FO), nanofiltration (NF), ultrafiltration (UF), and microfiltration (MF) (Amaral *et al.*, 2015b; Huo et al., 2009; Iskander et al., 2017c; Zhao et al., 2013a; Zolfaghari et al., 2017). Huo et al. (2009) reported that an RO process was able to remove 100% HA, 99.7% FA, and 98.4% HPI from a biologically treated leachate. FO could remove ~98% UVQS (in terms of TOC) from landfill leachate during water recovery (Iskander et al., 2017c). A removal efficiency of 43% for TOC by combined lime precipitation (8 g L^{-1} lime) and MF was reported for humic substances from landfill leachate, while NF increased the removal to 86% (Amaral et al., 2015b). This removal corresponded to 23% UV absorbance reduction by the MF treatment and 74% reduction of UV absorbance by the NF treatment (Amaral et al., 2015b). In a UF-based membrane bioreactor, a removal of 60% HA, 11% FA and 40% HPI was obtained (Zolfaghari et al., 2017). Another study on UF demonstrated a removal of 15 - 19% UV absorbance after filtration of biologically treated leachates with 100 kDa (~0.7 µm) MWCO, while the removal increased to 54 - 65% with a MWCO of 1 kDa (~0.007 µm). The improved overall removal of UV absorbance from 100 kDa to 1 kDa UF was largely contributed by the reduction of HA and FA (Fig. 2-6). When 0.5 kDa (~0.004 µm) MWCO was employed, further overall UV absorbance removal was mainly contributed by the removal of HPI (Fig. 2-6), and this demonstrated the susceptibility of HA and FA to membrane separation because of their larger MW than that of the HPI fraction (Gupta et al., 2014b; Zhao et al., 2013a). Thus, the performance of UF largely depends on the MWCOs used during treatment. Although most membrane separation technologies are effective for removing leachate UVQS, there are concerns due to membrane fouling along with the concentrated brine handling and disposal (Amaral et al., 2015a; Tang et al., 2007). The presence of UVQS can increase membrane fouling. It was reported that a decrease of 18% water flux was observed in a RO unit after an addition of 50 mgL^{-1} HA in the feed stream (Sir et al., 2012).

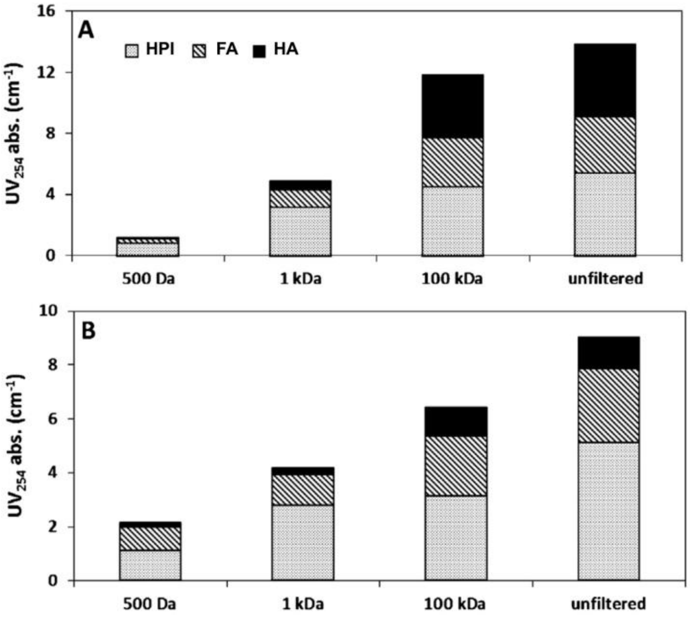

Figure 2-6. UV_{254} absorbance (cm^{-1}) distribution of different UVQS after ultrafiltration with different molecular weight cutoffs of biologically treated leachates (A and B are for two different leachates) (Zhao et al., 2013a).

Among emerging physical separation methods, magnetic ion (anion) exchange resin (MIEX) has demonstrated a removal of 57% UV absorbance from landfill leachate at a dose of 40 mL L^{-1} of MIEX-Cl for 20 min mixing (Boyer et al., 2011). Carbon nanotubes (CNTs) exhibited preferential absorption of HA in the molecular weight range of 0.5 - 2 kDa and FA in the molecular weight range of 1 - 3 kDa (Ateia et al., 2017). GAC could achieve good removal of UVQS, for example, a removal of 89.1% UV absorbance and 65.5% TOC from a microbial fuel cell (MFC) treated leachate effluent using 40 gL^{-1} GAC for 6 hours was observed (Iskander et al., 2017b). Similarly, powdered activated carbon (PAC) demonstrated a high UV absorbance removal (92%) as GAC with a preferential adsorption of hydrophobic fractions (HA and FA) (Deng et al., 2018). The application of sorption based physical separation is limited by the regeneration of adsorbents. In addition, the UVQS removed by physical treatment methods are not destroyed (but separated).

Electrochemical treatment

Electrochemical treatments mainly consist of electrocoagulation, electro-oxidation, and electron beam radiation, and can have an average removal of 72.5% (33.5 to 89.5%) UV absorbance and 68.5% (57 to 80%) UVQS in terms of TOC (Fig. 2-3). Electrocoagulation involves the production of metal cations from a sacrificing anode electrode under an external electric field (current or voltage). Cations are subsequently hydrolyzed and polymerized with increased surface area, and aggregate or absorb organics to be removed as a settled or floated sludge (Fig. 2-7) (Song et al., 2017). Direct electro-oxidation of leachate UVQS happens on an anode electrode, while in indirect electro-oxidation, anodically created oxidants (e.g., chlorine, hypochlorite) are responsible for oxidizing leachate UVQS (Deng and Englehardt, 2007). Electro-oxidation and electrocoagulation are most effective in removing larger molecular weight humic substances (Dia et al., 2017; Shao et al., 2006). For example, electrocoagulation removed 100% HA from a landfill leachate and benefited from the electrostatic attraction between positively charged metal hydroxides and negative functional groups (hydroxyl and carboxylic groups) of humic substances (Fig. 2-7) (Dia et al., 2017). Although the removal of the HPI fraction is less (37%), electrocoagulation is effective in removing smaller colloidal particles because of the external electric field that puts the particles in motion and increases the coagulation removal by forming flocs (Kliaugaite et al., 2013). The effectiveness of electrochemical methods largely depends on the intensity of the applied current or voltage. For example, increasing the current density from 450 to 600 Am^{-2} during electro-oxidation of leachate resulted in an increase of UVQS removal from 75 to 95% in eight hours (Anglada et al., 2009). A potential difference between chemical oxidation and electrochemical methods (e.g., electrocoagulation and electro-oxidation) is that the HPI fraction may increase after chemical oxidation (Section 3.2), but decreases after electrochemical treatment, likely because the HA and FA fractions do not degrade to smaller molecular weight HPI fraction during electrochemical treatments (Dia et al., 2017).

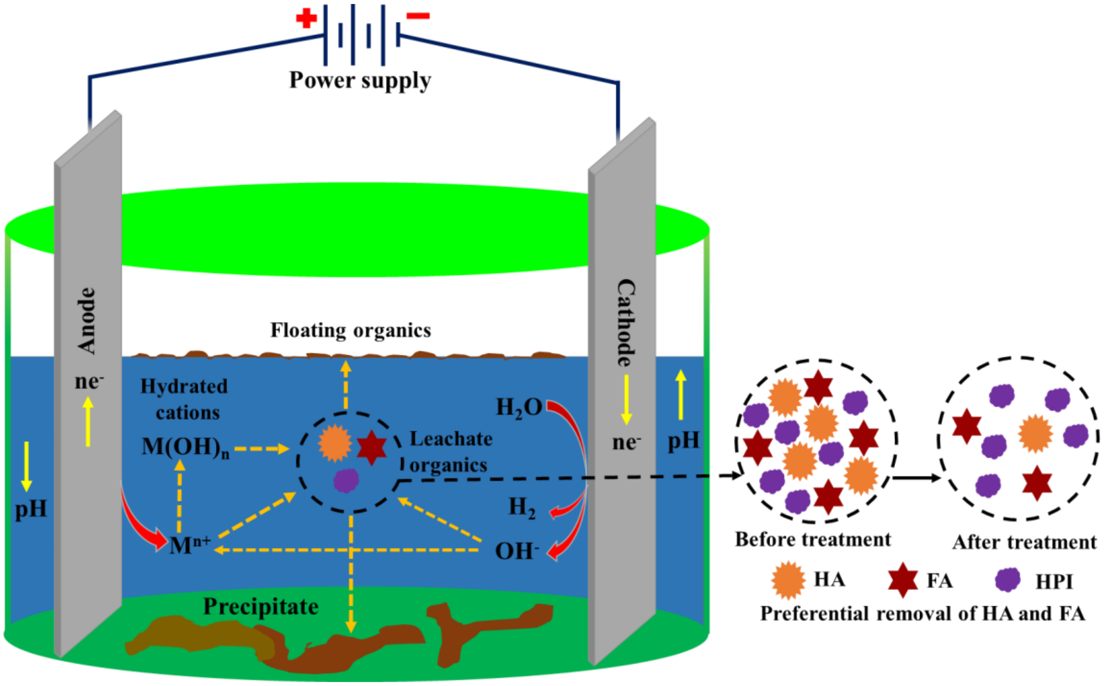

Figure 2-7. A schematic showing the removal mechanism of leachate UVQS during an electrocoagulation treatment (adapted from (Song et al., 2017)).

Several new electrochemical treatments have been reported. High voltage pulsed discharge (HVPD) combined with TiO_2 (Zhang et al., 2017) and electron beam radiation (Bae et al., 1999) have demonstrated excellent performance in reducing UV absorbance and UVQS. Electrolytic reduction can help downstream activated carbon treatment of HA as it reduces the surface tension (became more hydrophobic) and makes them susceptible to adsorption (Satyawali et al., 2007). Electrochemical processes have also been applied with UV irradiation to achieve the removal of 65% humic substances from biologically treated landfill leachate after 30 min of treatment (Xiao et al., 2013). Bioelectrochemical systems (BES), which operate on the principal of anaerobic degradation of organics, were studied for leachate treatment (Iskander et al., 2016). The studies reported 25.5 to 49.5% of UV absorbance decrease after BES treatment, and the UVQS decrease ranged from 71 to 83% in terms of TOC (Fig. 2-3) (Iskander et al., 2017b; Zhang et al., 2015b). Higher HRT and higher current density could facilitate UVQS removal in BES (Fig. 2-8A) (Iskander et al., 2017b), and this improvement was related to reduced organic loading rate and increased bioelectrochemical oxidation. UV absorbance reduction by BES for the HA, FA, and HPI fractions was less than the corresponding TOC concentration decrease, and in turn, the SUVA increased. For example, the HA fraction showed a SUVA increase from 0.46 to 4.99 L mg^{-1} m^{-1} (Fig. 2-8B) (Iskander et al., 2017b; Zhao et al., 2013a). Along with UVQS removal, BES produced 0.123 kWhm^{-3} energy during leachate treatment (Iskander et al., 2017b). BES treatment of UVQS is still in its infancy and much understanding of the fate and transformation of UVQS during BES treatment is still to be obtained.

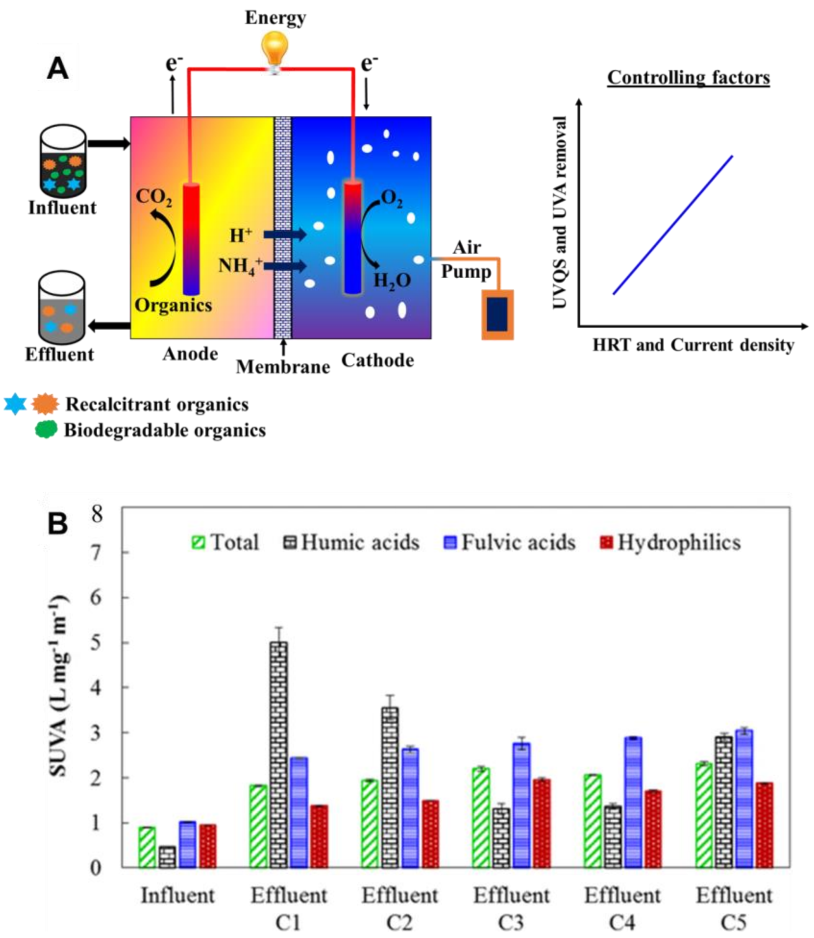

Figure 2-8. Bioelectrochemical treatment of UVQS in a landfill leachate: (A) system schematic and effects of hydraulic retention time and current density on UVQS removal; and (B) specific UV absorbance (SUVA) of different organic fractions of leachate UVQS at different operating conditions after an MFC treatment (Iskander et al., 2017b).

Perspectives

The fractions of leachate UVQS exhibit different removal efficiencies. Humic substances (HA and FA) are easier to remove by physical and chemical methods because they are macromolecules with higher MW. However, the HPI fraction can contribute more than half of the total UV absorbance in leachate and is relatively difficult to remove; little is known about their characteristics or composition. Those low MW and bio-refractory HPI organics may be better removed by chemical treatment (e.g., Fenton) if the high MW humic substances are removed beforehand. Because chemical treatment (e.g., Fenton, Ozone) can increase the smaller MW HPI fraction due to interconversion of high MW

HA and FA, chemical treatment could be used as a pretreatment prior to electrochemical treatments such as electrocoagulation and electro-oxidation, which are effective in removing the HPI fraction. Chemical treatment could be performed prior to adsorption based treatments (e.g., activated carbon) to reduce the organic load on adsorbent materials, thereby increasing their lifetime. Incorporating membrane as a post-treatment method, for example after chemical or electrochemical treatments, could also increase membrane performance and extend the cycle times because of the potential for low fouling due to a lower organic loading. Nevertheless, more investigations on leachate UVQS are needed for characterizing HPI and its behavior in biological and physicochemical treatment processes.

UV absorbance by recalcitrant leachate organics lingering in WWTP effluents can have disastrous consequences for disinfection. A prime example occurred at a WWTP in Richmond, VA, which was incapacitated in 2016 by receiving 0.2 – 0.4 MGD leachate (~1% of daily wastewater flow) collected by a third party from several landfills (Zhao et al., 2016). A dilution of the leachate of 100 times or more with conventional influent was required to bring the UV transmittance of the final effluent within the acceptable range (> 65%) for UV disinfection. As a result, the WWTP was penalized with noncompliance of its permit in terms of fecal coliform counts. Ultimately, the Richmond WWTP had to terminate leachate flow from all nine landfills to restore operation, requiring the landfills to seek out alternative disposal options with little warning. Thus, interference of UV disinfection by landfill leachate is a real and present problem, for which awareness is emerging and consequences could be very serious if not addressed properly.

The UV quenching by leachate UVQS could be more prominent at small WWTPs if they receive indirect leachate discharge (i.e., leachate discharged to WWTPs for treatment), because of insufficient dilution during leachate/sewage co-treatment. Hence, UV absorbance of leachate should be considered carefully along with nutrient content. Pretreatment is more desirable for reducing the effects of UVQS in WWTPs. For example, onsite biological treatment may be considered because of relatively low cost compared to chemical/physical treatments, though limited treatment efficiency would be expected. There is no standalone cost effective UVQS removal technology available, and thus incorporation of multiple treatments would be necessary to meet the 60-65% UV transmittance requirement in WWTPs. Because complete leachate treatment by chemical and electrochemical processes are limited by cost, the incorporation of these with the widely practiced biological treatment to attain enhanced removal of UVQS needs further exploration. The source separation of humic substance precursors can significantly improve the biodegradability of leachate in the cells/landfills receiving an insignificant amount of lignocellulose. For instance, enhanced recycling of lignin rich waste (yard waste, wood or paperboard) can help reduce the UVQS concentration in leachates. Biological treatment could be more effective and implemented for leachate from cells/landfills with low UVQS concentrations because of higher biodegradability. To facilitate data collection and improve our understanding of UVQS, the studies of leachate UVQS should report data on key parameters such as UV absorbance, TOC concentration, and SUVA for the unfractionated and fractionated samples (i.e. HA, FA. HPI).

Currently, there is no pretreatment standard for indirectly discharged leachate from landfills in the nonhazardous subcategory. Although US EPA is authorized by the Clean Water Act (CWA) to create regulation/standards on pollutants that interfere with or are incompatible with publicly owned treatment works, it does not have any Pretreatment Standards for Existing Sources (PSES). Thus, besides imposing pretreatment standards for existing facilities, it is important to consider imposing Pretreatment Standards for New Sources (PSNS), as newly constructed facilities would be able to incorporate best available treatment technologies to attain imposed pretreatment standards. If a pretreatment standard can be incorporated for leachate, the nonconventional pollutant TOC and non-listed pollutant UV absorbance should be considered along with the existing conventional pollutants (BOD_5, TSS, and pH). In the absence of regulations, professionals and experts should use their best professional judgment and the impacts of leachate UVQS on UV disinfection in WWTPs to come up with a standard for landfills discharging leachate to WWTPs. The regulation on new parameters may negatively affect the small operating landfills, which may not be able to upgrade to attain the pretreatment discharge requirements. This will demand subsidy for small operating landfills for technology upgrade.

Conclusions

Due to the UV quenching properties, the leachate UVQS are found to reduce the efficacy of UV disinfection in WWTPs. Thus, it is important to understand the detailed effects of UVQS and develop cost-effective treatment approaches. The following conclusions can be made.

- Leachate organics (HA, FA, and HPI) can strongly absorb UV light and thus severely interfere with UV disinfection. Hence, co-treatment of landfill leachate along with sewage in WWTPs can be affected by leachate induced UVQS during UV disinfection.
- Among the three organic fractions of landfill leachate, the HPI contributes slightly more than half of the overall leachate UV absorbing capacity, and the rest is by humic substances (HA and FA). However, humic substances exhibit higher SUVA than HPI because of their complex polymeric structures. The order of SUVA for the three organic fractions follows the trend of $SUVA_{HA} > SUVA_{FA} > SUVA_{HPI}$.
- Biological treatment has limited effectiveness for UVQS removal because those compounds are resistant to biodegradation and would require process optimization to be applied successfully, while, physical separation such as membrane separation can effectively remove UVQS. The performance of membrane separation of UVQS is dictated by the pore size of the membrane. The smaller the pore size, the more removal of UVQS. The application of adsorption-based treatment is limited by regeneration of the adsorbents once it is spent.
- Chemical treatment such as advanced oxidation (e.g., Fenton) can be effective in reducing UVQS. However, it may increase the HPI fraction due to the conversion of humic substances (HA+FA) to HPI. The biodegradability of leachate may be increased after chemical treatment and thus benefits the subsequent biological treatments. Chemical treatments often have a high cost and complexity of operation.
- Electrocoagulation and electro-oxidation can be effective in removing UVQS without increasing the HPI fraction. The application of electrocoagulation is

limited by the cost of electricity. Bioelectrochemical systems have shown some promise in leachate UVQS treatment.

- A consensus is required among researchers about mandatory parameters that should be included in leachate studies. UV absorbance and UVQS concentrations should be considered as a critical wastewater parameter. The key parameters including HA, FA, and HPI concentrations and their respective UV absorbance need proper reporting in literature.
- UV quenching by leachate organics is an issue that has not received the level of attention that it deserves, as it could become a serious problem if not conceived with care. Landfills need appropriate provisions for alternative treatments if WWTP effluent UV disinfection is problematic, potentially requiring onsite treatments prior to discharge in WWTPs. Going into the future, it is important to environmental and public health for WWTPs to be aware of the UV transmittance issue exerted by leachate organics.

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CHAPTER 3

Energy Consumption by Forward Osmosis Treatment of Landfill Leachate for Water Recovery

Abstract

Forward osmosis (FO) is a potential approach for treating landfill leachate with advantages of reducing leachate volume and recovering high quality water for direct discharge or reuse. However, energy consumption by FO treatment of leachate has not been examined before. Herein, the operational factors such as recirculation rates and draw concentrations were studied for their effects on the quantified energy consumption by a FO system treating actual leachate collected from two different landfills. It was found that the energy consumption increased with a higher recirculation rate and decreased with a higher draw concentration, and higher water recovery tended to reduce energy consumption. The highest energy consumption was 0.276 ± 0.033 kWh m^{-3} with the recirculation rate of 110 mL min^{-1} and 1-M draw concentration, while the lowest of 0.005 ± 0.000 kWh m^{-3} was obtained with 30 mL min^{-1} recirculation and 3-M draw concentration. The leachate with lower concentrations of the contaminants had a much lower requirement for energy, benefited from its higher water recovery. Osmotic backwashing appeared to be more effective for removing foulants, but precise understanding of membrane fouling and its controlling methods will need a long-term study. The results of this work have implied that FO treatment of leachate could be energy efficient, especially with the use of a suitable draw solute that can be regenerated in an energy efficient way and/or through combination with other treatment technologies that can reduce contaminant concentration before FO treatment, which warrants further investigation.

Introduction

Landfilling is the most common method for disposing municipal solid waste because of low cost and low maintenance (Renou et al., 2008). During landfill waste stabilization, liquid waste or leachate, is produced from the dynamic degradation of waste and from water infiltration (primarily rainwater) (Damiano et al., 2014; Ganesh & Jambeck, 2013). Leachate includes four major groups of compounds: dissolved organic substances, inorganic macro components, heavy metals, and xenobiotic organic compounds (Kjeldsen et al., 2002; Renou et al., 2008). In addition, leachate contains a substantial amount of water that could be recovered and reused (Iskander et al., 2016). The widely practiced leachate treatment processes include physicochemical treatment (e.g., coagulation, flocculation, GAC treatment, etc.), biological treatment (e.g., activated sludge, aerated lagoon, etc.), and electrochemical treatment (Deng & Englehardt, 2007; Renou et al., 2008).

Extraction of high-quality water from leachate will greatly reduce the volume of leachate, accomplish water reuse or direct discharge, and thus help to achieve sustainable leachate management. Membrane technologies including microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) have been studied and applied for leachate treatment (Di Palma et al., 2002; Renou et al., 2008), and among them RO can recover high quality water from leachate (Dong et al., 2014). For example, a study showed that the treatment of pre-filtered leachate by a pilot scale RO unit attained 93.4 % recovery with 79.2 % COD and 69.8% of ammonia rejection (Cingolani et al., 2016). Water flux in a RO system depends on the conductivity of leachate: the higher the conductivity of leachate, the lower the water flux (Linde et al., 1995). The RO treatment is prone to irreversible membrane fouling that demands periodical chemical cleaning, and due to this the cost and energy requirement for RO treatment is high (Lee et al., 2010). A study reported an average energy requirement of 1.2 - 1.5 kWh m^{-3} to treat pretreated wastewater by a RO system (Pearce, 2008).

Forward osmosis (FO) is a membrane process that extracts water utilizing the osmotic pressure difference between a concentrated draw solution and a feed solution (Cath et al., 2006). In FO, water molecules move through a semipermeable membrane from a region of high water chemical potential (i.e. low osmotic pressure) to a low water chemical potential (i.e. high osmotic pressure) due to an osmotic gradient (Cath et al., 2006). FO is susceptible to less fouling compared to RO (Lee et al., 2010), and may be more energy efficient if a proper draw solute (e.g., no need for regeneration) is applied. FO has been studied for seawater desalination, wastewater treatment, and leachate treatment, and can reject a wide range of contaminants such as organic compounds, nutrients, heavy metals, and ammonia nitrogen (Cath et al., 2006; Elimelech & Phillip, 2011; Linares et al., 2014). By linking to a membrane reactor as a post-treatment process, a FO system using NaCl as a draw solute could reject 96.6 % total phosphorus, 98.6% COD, and 76.9% ammonium (Dong et al., 2014). Another study extracted water from a membrane bioreactor treated leachate by employing NH_4HCO_3 draw that was subsequently used as liquid fertilizer without further treatment (Li et al., 2017). FO has also been connected to a microbial electrolysis cell (MEC) for treating leachate, and it was reported that the FO recovered about 50% of the water from the MEC effluent using 2-M ammonium bicarbonate as a draw solution (Qin et al., 2015). The commercial-scale application of FO for treating leachate has been investigated by using 9% NaCl as a draw solution, and this facility located in Corvallis, Oregon having 2500 m^2 FO membrane was able to extract water from leachate at a rate of 95 cubic meter per day at a cost of $132.0 per cubic meter (HTI, 2010). Clearly, using FO to treat leachate is of interest and there is more to explore towards practical applications.

The operation of a FO system requires continuous recirculation of draw and feed solutions for improving water flux and reducing fouling on the feed side of the FO membrane. However, this recirculation also results in a significant demand for energy (Zou et al., 2016). Energy requirement by recirculation in FO has not been well investigated until recently. A very recent study on a submerged FO system using commercial fertilizer as draw solute has demonstrated a reduction of energy consumption from 1.86 to 0.02 kWh m^{-3} by reducing the recirculation flow rate from 100 to 10 mL min^{-1} (Zou & He, 2016). Despite the prior efforts of studying FO treating leachate, the operating energy of such treatment has not been reported before. This study focused on the energy perspective of a FO system treating landfill leachate, with specific objectives for: (1) investigation of the effects of the draw solution concentration on FO performance and energy consumption; (2) examination of the recirculation rates and its influence on energy consumption; (3) comparing the treatment performance and energy consumption when treating different leachates; and (4) a preliminary study of membrane fouling and its effects on energy consumption.

Materials and Methods

FO cell and operating conditions

A cellulose triacetate membrane (Hydration Technology Innovations, Albany, OR, USA) with a surface area of 139 cm^2 was used in a SEPA CF Cell (Sterlitech Corporation, Kent, WA, USA) with its active layer facing the feed solution (Fig. 3-1). The FO system was operated in batch mode. The feed solution (leachate) was maintained at 550 mL and the initial volume of the NaCl draw solution was 200 mL. Three draw solute concentrations, 1 M, 2 M, and 3 M, and three recirculation flow rates, 30 mL min^{-1}, 70 mL min^{-1}, and 110 mL min^{-1}, were studied. Duplicate experiments were performed for each parameter.

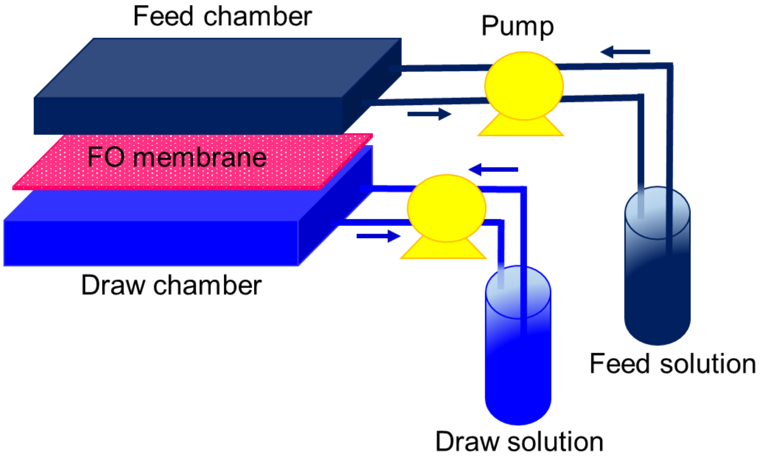

Figure 3-1. Schematic of the FO system setup for water extraction from landfill leachate.

FO membrane cleaning

Fouling experiments were conducted for 12 hours each batch. Three types of membrane cleaning method were investigated – simple *in situ* washing, osmotic backwashing, and chemical cleaning. Simple *in situ* washing was conducted by recirculating tap water in the both draw and feed chamber at a recirculation rate of 30 mL min^{-1}. Osmotic backwashing was conducted with 3-M draw solute at 30 mL min^{-1} recirculation rate for

30 min. During osmotic backwashing, draw solute was replaced by DI water, while the feed was replaced by 3-M draw solution. Chemical cleaning was conducted in three 30-min steps: acid (HCl, pH = 3), base (NaOH, pH= 11), and oxidant (NaOCl, 5% v/v). At each step, respective solution was recirculated at 30 mL min^{-1} for 25 mins followed by 5 mins washing with DI water.

Landfill leachate

The leachates were collected from two different landfills located in Virginia, USA, and used as the feed solution. After collection, leachates were stored at 4 °C and used for the experiment without modification. The first leachate, named as "Leachate A", was dark brown in color and had the following characteristics: 11,647 ± 109 mg COD L^{-1}, 4,733 ± 33 mg NH_3-N L^{-1}, pH 8.05, and conductivity of 31.11 mS cm^{-1}. The second leachate, "Leachate B", was light brown in color and had the following characteristics: 730 ± 67 mg COD L^{-1}, 101 ± 11 mg NH_3-N L^{-1}, pH 7.64, and conductivity of 3.08 mS cm^{-1}. The chemical characteristics of the leachates are summarized in Table 3-1.

Table 3-1. Properties of the leachates used in this study.

Parameters	Leachate A	Leachate B
pH	8.05 ± 0.02	7.64 ± 0.02
Conductivity, mS cm^{-1}	31.11 ± 0.01	3.08 ± 0.01
COD, mgL^{-1}	11647 ± 109	730 ± 67
TOC, mgL^{-1}	3075 ± 62	67 ± 9
NH_3-N, mgL^{-1}	4733 ± 33	101 ± 11
NO_3^- - N	-	-
NO_2^- - N	-	-
Na^+, mgL^{-1}	3879 ± 78	539 ± 45
Cl^-, mgL^{-1}	5243 ± 78	725 ± 65
K^+, mgL^{-1}	1340 ± 78	72 ± 6
Mg^{2+}, mgL^{-1}	141 ± 12	12 ± 9
Ca^{2+}, mgL^{-1}	54 ± 11	-

Measurements and analysis

The concentrations of chemical oxygen demand (COD) and NH_3-N were measured using a spectrophotometer according to the manufacturer instructions (DR 890, HACH Company, USA). Conductivity was measured by using a benchtop conductivity meter (Mettler-Toledo, Columbus, OH, USA). The solution pH was measured using a benchtop pH meter (OAKTON Instruments, Vernon Hills, IL USA). The concentrations of sodium (Na^+) and chloride (Cl^-) ions were measured by ion chromatography (Dionex LC20 ion chromatograph, Sunnnyvale, USA) in combination with an ED40 electrochemical detector. Water flux was measured by taking the difference of draw solution weight recorded in an electronic balance (Scort Pro, Ohous, Columbia, MD, USA), according to a previous study (Yuan et al., 2016). Total organic carbon (TOC) in draw solution was measured with TOC- Vcsn (Shimadzu, Japan).

It was assumed that the major energy consumption by the present FO system was due to the recirculating pump, P_{pump} (kW). Thus, the power consumption from the pump was equal to the power consumption of the FO system, P_{system} (kW). The specific energy consumption (SEC, kWh m^{-3}) was calculated according to the following equation (Shaffer et al., 2012).

$$E = \frac{P_{system}}{Q} \approx \frac{P_{pump}}{Q} = \frac{P_{pump} \cdot \rho}{m_{t,D} - m_{t-1,D}}$$

Where, Q ($m^3\ h^{-1}$) is the recovered water flow rate. $m_{t,D}$ and $m_{t-1,D}$ are the mass of draw solution at a specific time t and $t-1$ (h), respectively. ρ is the density of the permeate, water. Besides energy requirement for pump recirculation during FO batch operation, energy requirement during membrane cleaning from pump use was also considered in total energy calculation. Maximum and minimum specific energy requirement for membrane cleaning was calculated by dividing the pump energy (during cleaning) with minimum and maximum recovered water amount respectively.

Reverse salt flux (RSF), the movement of salt ions from the draw side to the feed side during FO operation, was calculated according to the following equations. This movement is against the direction of water flux and is due to salinity gradient across the FO membrane. The concentrating effect in the feed side was considered and excluded during the RSF calculation (Zou & He, 2016):

$$RSF = \frac{V_F \times C_{f,F} - (V_F + V_{recovered}) \times C_{i,F}}{S \times t}$$

$$Concentrating\ Effect = \frac{V_{recovered} \times C_{i,F}}{S \times t}$$

where, V_F is the feed volume (mL), $V_{recovered}$ is the volume of the recovered water in the draw side, $C_{f,F}$ is the final solute concentration in the feed, $C_{i,F}$ is the initial solute concentration in the feed, S is the surface area of the membrane, and t is the total batch time.

Results and Discussion

Effects of the draw solute concentration

The effects of the draw solute concentration on water recovery and energy consumption were investigated with Leachate A at a recirculation rate of 110 mL min^{-1}. In general, water recovery increased with the increased draw solute concentration due to a higher osmotic pressure difference. The highest volume of the recovered water was 277.3 ± 3.8 mL, achieved with the 3-M draw solution, while the lowest of 63.8 ± 7.7 mL was obtained with the 1-M draw (Fig. 3-2A). RSF also increased with the increase in the draw solute concentration (Fig. 3-2B). The 3-M draw resulted in the highest RSF of 4.70 ± 0.20 gMH, and the 1-M draw led to the lowest RSF of 2.27 ± 0.34 gMH. This was mainly because that a higher initial draw solute concentration could create a larger salt concentration gradient across the FO membrane, which promoted the driving force for RSF. Despite a great rejection ability of FO membranes for many compounds, some contaminants can still move through the membrane and enter the draw solution because of intrinsic limitations of the membrane. Both TOC and ammonia nitrogen were detected in the draw solution, however, there was no clear relationship between the draw solute concentration and TOC/ammonia movement (Fig. 3-2C). Their movement was due to the concentration gradient that is dictated by their concentrations in the feed leachate, not the draw solute concentration. The TOC concentration in the draw solution was 2.3-2.8 % of the raw leachate's TOC content (3075 ± 62 mgL^{-1}). The movement of ammonia nitrogen was significantly higher than that of TOC, likely related to its low molecular weight and small hydrated radius (0.331 nm), and more than 900 mg L^{-1} of ammonia nitrogen was detected in the draw solution (Howitt & Udvardi, 2000). Rejection of TOC by the FO membrane (~98%) is much better than that of a previous study that reported about 79.2% COD rejection by a RO membrane treating pretreated leachate, and the rejection of ammonia (~80%) by the present FO system also exceeds the same RO system (69.8%) (Cingolani et al., 2016). However, it should be noted that RO systems usually have much higher water flux and thus a lower retention time than FO systems (Altaee et al., 2014). Because of this, a FO unit must have a higher membrane area compared to an RO unit to maintain a comparable water recovery.

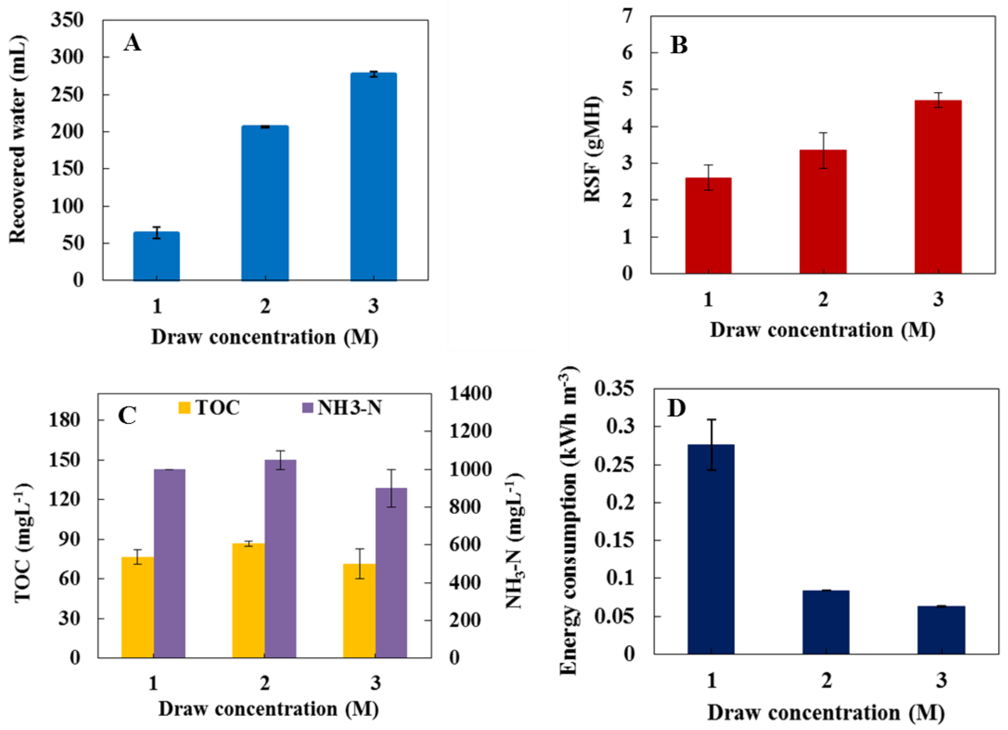

Figure 3-2. The performance of the FO system treating Leachate A affected by the draw solute concentration (recirculation rate of 110 mL min^{-1}): (A) the volume of the recovered water; (B) reverse salt flux (RSF); (C) TOC and ammonia nitrogen concentration in the draw solution; and (D) energy consumption.

Energy consumption by the FO system was calculated as kilowatt hour normalized over the volume of the recovered water over a period of 12 h, and the results exhibited an opposite trend to that of the increased draw concentration (Fig. 3-2D). At the recirculation rate of 110 mL min^{-1}, the highest energy consumption was 0.275 ± 0.033 kWh m^{-3} with the 1-M draw, more than four times that with the 3-M draw (0.063 ± 0.001 kWh m^{-3}). This was related to the much lower volume of the recovered water with the 1-M draw within the same time period of 12 h. When the draw increased to 2 M, the recovered water of 206.5 ± 0.8 mL was close to that with the 3-M draw, resulting in much lower energy consumption of 0.084 ± 0.000 kWh m^{-3} than that of the 1-M draw. The highest energy requirement of the present FO system (0.276 ± 0.033 kWh m^{-3}) is much lower than a typical RO treatment (1.2 to 1.5 kWh m^{-3}) (Pearce, 2008). When the energy required to regenerate the draw solute from the diluted draw by using RO is considered, the overall energy consumption of the FO- RO based treatment will be much higher than FO alone. On the other hand, using FO as a pretreatment step for treating high strengthen wastewater by RO can reduce energy consumption compared to a standalone RO system, because of the less susceptibility and high reversibility of the FO membrane towards fouling compared to RO membrane (Shaffer et al., 2015).

Effects of the recirculation flow rate

Recirculation of the draw and feed solutions is an important factor that is strongly relevant to energy consumption. To examine its effects, the 3-M draw solution was used and three recirculation rates, 30, 70, and 110 mL min^{-1} were applied to extract water from Leachate A. The relatively higher recirculation rates of 70 and 110 mL min^{-1} resulted in more water recovery than that with 30 mL min^{-1} (Fig. 3-3A). This was due to the reduction of external concentration polarization (ECP) at a relatively higher recirculation rate (Zou & He, 2016). The values of RSF were comparable among three recirculation rates, varying from 4.60 ± 0.59 to 5.37 ± 1.15 gMH for the recirculation flow rate of 30 to 110 mL min^{-1} (Fig. 3-3B). The insignificant difference in RSF was due to that RSF is governed by a concentration gradient (Phillip et al., 2010) and the draw concentration was the same with all the recirculation rates (thus resulting in similar concentration gradients). The decreasing concentration pattern of TOC with the increase of the recirculation rate was observed (Fig. 3-3C), likely related to the relatively higher water recovery at a higher recirculation rate that rendered a lower concentration of TOC (dilution effect). Ammonia movement was significantly higher for all the conditions and it did not follow any pattern (Fig. 3-3C). Energy consumption was clearly affected by the recirculation rate and a higher recirculation rate led to more energy demand (Fig. 3-3D). The energy consumption at 30 mL min^{-1} (0.005 ± 0.000 kWh m^{-3}) was smaller than 10% of that with 110 mL min^{-1} (0.063 ± 0.001 kWh m^{-3}). The lowest energy consumption was even lower than the previous reports of an MEC+FO system treating leachate (0.10 kWh m^{-3}) and a submerged FO system using commercial fertilizer as a draw (0.02 ± 0.01 kWh m^{-3}) treating domestic wastewater (Qin et al., 2015; Zou & He, 2016).

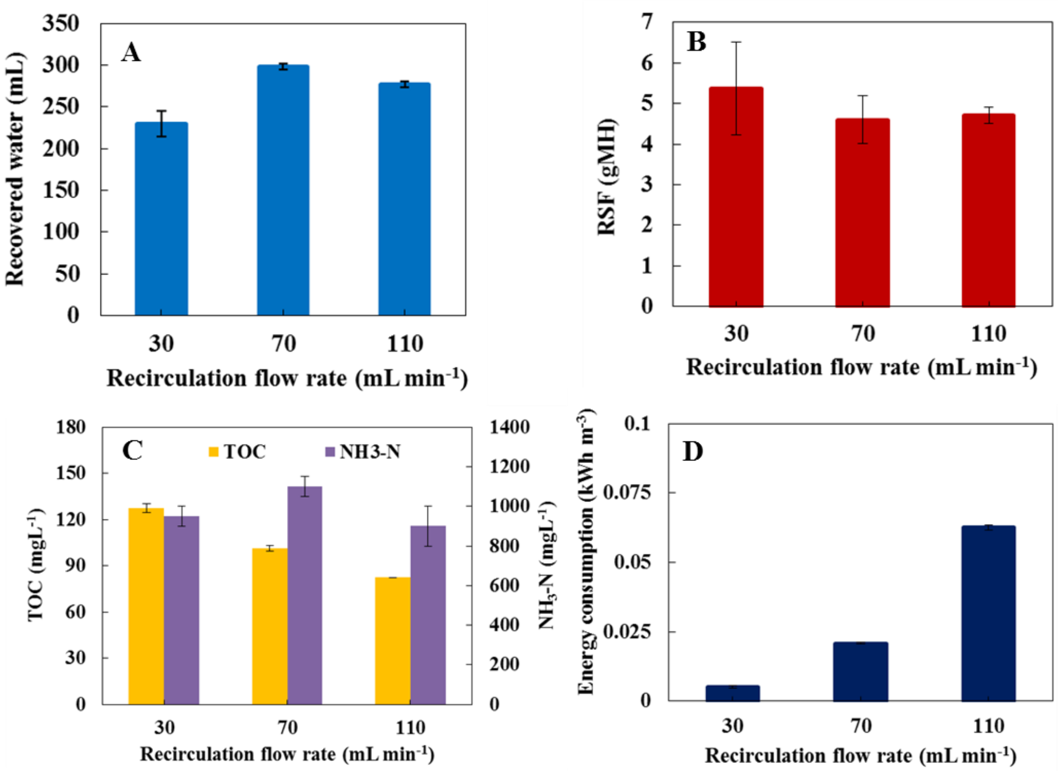

Figure 3-3. The performance of the FO system treating Leachate A affected by the recirculation rate (draw solute concentration of 3 M): (A) the volume of the recovered water; (B) reverse salt flux (RSF); (C) TOC and ammonia nitrogen concentration in the draw solution; and (D) energy consumption.

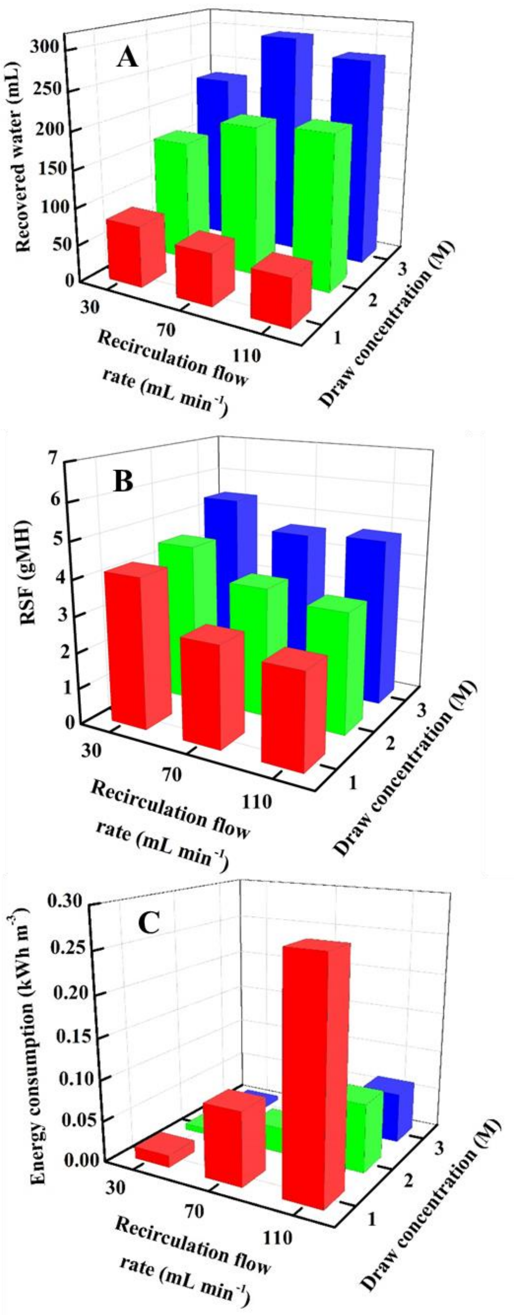

Figure 3-4. The FO performance treating the Leachate A affected by both the draw solute concentration and the recirculation rate: (A) the volume of the recovered water; (B) reverse salt flux (RSF); and (C) energy consumption.

To further understand the effects of the recirculation rate and draw concentration on the FO treatment performance and energy consumption, we examined nine combinations of recirculation rates and draw concentrations using Leachate A (Fig. 3-4). The results confirmed the findings described in the previous sections that water recovery was mainly governed by the draw concentration, and the recirculation rate enhanced water recovery at a higher rate (Fig. 3-4A). RSF also increased with the increased draw concentration due to the higher salt gradient; however, a lower recirculation rate tended to result in a higher RSF, likely related to the lower water flux that led to less dilution/concentration effects and helped to maintain a relatively larger salt gradient (Fig. 3-4B). The data of energy consumption supported the previous conclusions that a higher recirculation rate or a lower draw concentration would result in higher energy consumption (Fig. 3-4C). The lowest energy consumption was 0.005 kWh m^{-3} under the condition of 30 mL min^{-1} and 3-M draw; while the highest energy consumption of 0.276 kWh m^{-3} occurred with 110 mL min^{-1} recirculation and 1-M draw.

Leachate from different landfills

In addition to Leachate A, Leachate B was also examined for water recovery by the same FO system with a recirculation rate of 30 mL min^{-1} and the 3-M draw solution. These two leachates had very different characteristics as described in the section 2.2, and such difference resulted in different FO performance. It is evident that Leachate B as a feed solution showed much higher water flux compared to Leachate A (Fig. 3-5A), due to its lower conductivity (3.08 vs. 31.11 mS cm^{-1}) that increased the osmotic gap. This is in accordance with a recent study that demonstrated higher water recovery from the MEC treated leachate compared to the raw leachate using an FO, because of the lower conductivity of the MEC treated leachate (17.4 mS cm^{-1}) than the raw leachate (28.1 mS cm^{-1}) (Qin et al., 2015). The total volume of the recovered water from Leachate B was 613.8 ± 9.4 mL in 12 hours, 2.6 times higher than that from Leachate A under the same operating conditions (Fig. 3-5B). However, RSF with Leachate B was also higher than that with the Leachate A because of its lower conductivity and thus a larger salt concentration gradient across the FO membrane (Fig. 3-5C). The concentrations of both TOC and ammonia nitrogen in the draw solution were much lower with Leachate B than those with the Leachate A (Fig. 3-5D), because of their low concentrations in Leachate B. With higher water recovery, the energy consumption of the FO system treating Leachate B (0.002 kWh m^{-3}) was much lower than that of Leachate A (0.005 kWh m^{-3}) (Fig. 3-5E).

Preliminary study of Membrane fouling

Membrane fouling is an important issue for FO applications in treating landfill leachate. Herein, we have conducted a preliminary study of FO membrane fouling using Leachate A with the 30 mL min^{-1} recirculation rate and the 1-M draw solute concentration. Several cleaning methods were performed, and water flux was examined. As shown in Fig. 3-6, the Batch 1 was the start of the fouling experiment; following the Batch 1, the Batch 2 was conducted without any membrane cleaning; then, the Batch 3 was continued after 30 min *in situ* washing with tap water; the Batch 4 was conducted after osmotic backwashing; and finally, the Batch 5 was conducted after 90 min *in situ* chemical cleaning (Fig. 3-6). It is obvious that cleaning could enhance water flux, indicating the presence of fouling, but the enhancement was different with different cleaning methods. The *in situ* washing with tap water (Batch 3) had limited improvement on water flux, compared to that of the Batch 1 & 2. The osmotic backwashing (Batch 4) exhibited the best effect with the highest water flux, indicating that in the present FO system the cross flow of water through the FO membrane could be more effective to remove foulants than sheer flow of water on the sides of the FO membrane (Batch 3).

It was unexpected that chemical cleaning of the FO membrane (Batch 5) did not result in a higher water flux than the osmotic backwash (Batch 4), though it was better than tap water washing (Batch 3). This could be related to the recalcitrance of the foulants that were resistant to the chemicals used, but the exact reasons warrant further investigation. Energy consumption was strongly related to the duration of the fouling experiment. As discussed earlier, normal *in-situ* washing and osmotic backwashing (batch 3 and 4, respectively) was conducted for 30 mins each, while chemical cleaning was conducted for 90 mins, all of which were much shorter as compared to the operation length. The estimated energy consumption for membrane cleaning was in the range of 0.00016 (by crossflow cleaning and osmotic backwashing) to 0.00221 kWhm^{-3} (by chemical cleaning). This cleaning energy has been included in total energy estimation. In general, there was no serious fouling during the course of this study, benefited from the short testing period of the batch and periodical cross washing. This also confirms that most of the FO fouling is highly reversible (Shaffer et al., 2015). However, a long-term operation of FO treating leachate will inevitably face fouling issues, and frequent membrane cleaning would increase the operational energy/expense and therefore result in more demand for system maintenance.

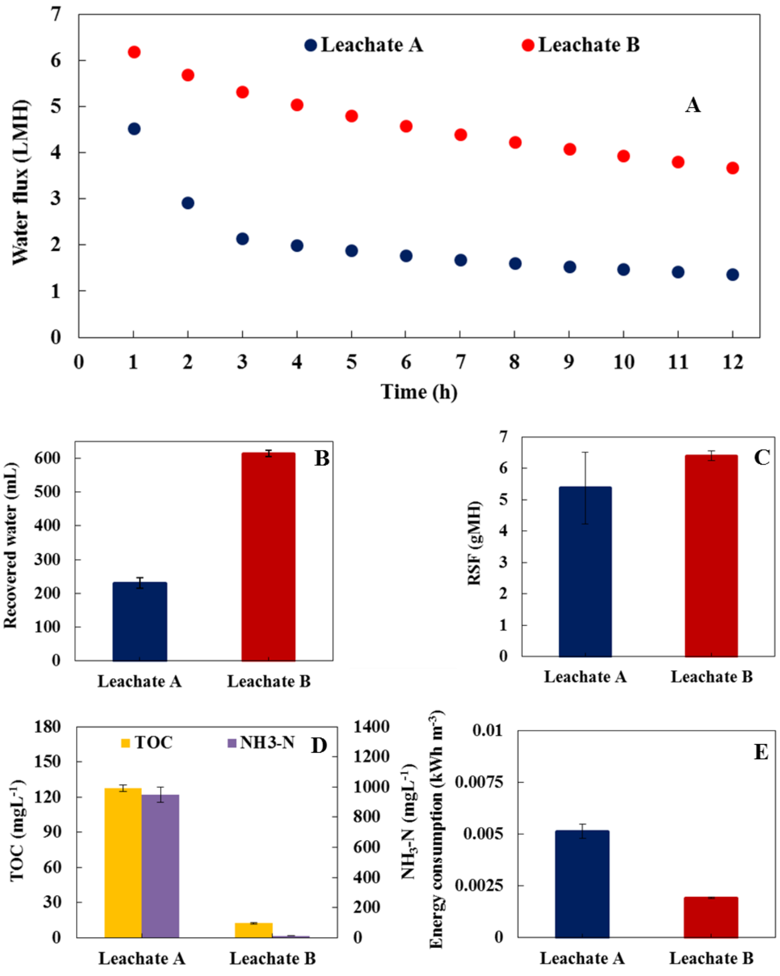

Figure 3-5. The FO treatment of two different leachates with the recirculation rate of 33 mL min^{-1} and 3 M draw solute concentration: (A) water flux as a function of time; (B) the volume of the recovered water; (C) reverse salt flux (RSF); (D) TOC and ammonia nitrogen concentration in the draw solution; and (E) energy consumption.

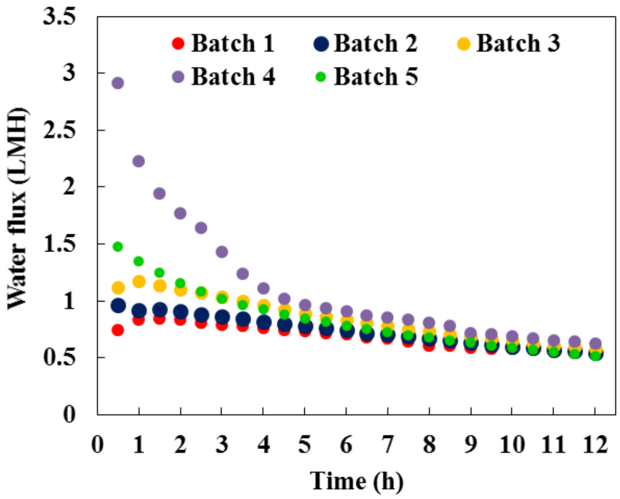

Figure 3-6. Water flux of the FO system treating Leachate A after different cleaning methods. Batch 1: the first run. Batch 2: the operation following the Batch 1 without any cleaning. Batch 3: after 30-min *in situ* washing with tap water. Batch 4: after 30-min osmotic back washing. Batch 5: after 90-min chemical cleaning.

Perspectives

Applications of FO technologies to treat landfill leachate have several potential advantages such as high quality of the extracted water (which may be directly discharged or reused after draw solute regeneration) and low energy requirement compared to RO. The quality of the recovered water in a FO has been examined in numerous studies, and the present study has provided the support to low energy consumption. However, the movement of ammonium and organics to the draw solution demands further treatment before discharging the recovered water. The reject, or brine, although much less in volume, will need further disposal, such as being returned to landfill, further treatment by biological/chemical methods, or being solidified (HTI, 2010; Cingolani et al., 2016). Energy consumption is strongly related to water flux, and thus the factors that would affect water flux will influence energy requirement. A high recirculation rate, which is usually applied in a FO system, seems unnecessary because of its high energy demand offsetting its benefit of improving water flux.

The comparison between two different leachates shows that the lower concentrations of the contaminants would lead to lower energy consumption. This suggests that when treating a complex leachate such as Leachate A, FO should be linked to other treatment processes, for example, biological and/or chemical oxidation of leachate, and act as a final polishing step to produce high-quality effluent. This is because that a filtration process does not degrade any contaminants, unless biological/chemical treatment is integrated within FO, such as osmotic membrane bioreactors (Lu & He, 2015; Wang et al., 2016). Such integration can save the footprint of a treatment system but could create challenges for *in situ* cleaning of FO membrane (that could affect biological processes). Biological/chemical treatment can also be connected with FO externally, and an example is anaerobic digestion linked to FO for treating leachate. Chemical treatment such as advanced oxidation processes is very effective to treat landfill leachate (Umar et al., 2010), and when linked to FO, its effects on elevating the conductivity of the treated leachate (feed solution) need to be better understood. Adding pretreatment will generally increase the demand for energy for overall leachate treatment due to more unit operation, but some processes such as anaerobic digestion can produce bioenergy to offset energy consumption. Pretreatment will undoubtedly benefit the FO and decrease energy consumption by FO alone through removing contaminants, increasing osmotic pressure (and thus increasing water flux), and reducing membrane fouling.

It should be noted that this study is an early attempt to understand energy consumption by FO treating leachate, and it does not give a complete picture of energy requirement. Using NaCl as a draw solute will require regeneration after FO treatment, and the regeneration is usually conducted by using RO. Such a regeneration method will require additional energy input and thus lower the energy benefit of FO treatment; while, fouling of RO membrane will be greatly reduced after FO treatment (Shaffer et al., 2015), which may result in lower energy requirement in RO when comparing to direct treatment of leachate by RO. Therefore, an appropriate draw solute with energy-efficient regeneration will be critically important to FO applications to leachate treatment. A potential draw solute is ammonia bicarbonate, which can be regenerated with low heat (McCutcheon et al., 2006), for example the heat produced by anaerobic digesters or landfill biogas combustion. Ammonia draw solute is of interest to leachate treatment, because leachate contains a large amount of ammonia that can be recovered and used as the draw solute.

This has been demonstrated in a previous study that employed an MEC to recover ammonia from leachate and used the recovered ammonia to extract water from the MEC treated leachate (Qin et al., 2015). This draw solute has also been used in a regular FO system to treat landfill leachate with satisfied performance of contaminant rejection (Li et al., 2017). As explained earlier, the precise estimate of energy requirement during periodical membrane cleaning demands the determination of cleaning methods (e.g., simple wash, osmotic backwash, chemical cleaning, or combination of two or more methods) and frequency of cleaning during long term operation. This will require a long-term study of FO treatment of leachate.

Conclusions

In this study, the effects of recirculation rates, draw concentrations, and leachates properties on energy consumption by FO treatment have been examined. A lower recirculation rate will have less energy consumption, because of lower power consumption by the recirculation pump. A higher draw concentration can greatly reduce energy consumption, due to the higher water flux. A leachate with lower concentrations of contaminants results in more water flux and lower energy consumption. The preliminary study of membrane fouling suggests that osmotic backwashing could be an effective method for controlling membrane fouling and decreasing energy consumption. Those results indicate that FO treatment of leachate could be a low energy process, if an appropriate draw solute with low-energy regeneration can be applied. A long-term study of FO treatment of leachate will be necessary to provide a complete picture of energy consumption.

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CHAPTER 4

Enhancing Forward Osmosis Water Recovery from Landfill Leachate by Desalinating Brine and Recovering Ammonia in a Microbial Desalination Cell

Abstract

Minimizing leachate volume via forward osmosis (FO) can benefit its sustainable management practice. In this work, a microbial desalination cell (MDC) was employed to desalinate the FO treated leachate for reduction of both salinity and chemical oxygen demand (COD). The FO recovered 51.5 % water from a raw leachate and the recovery increased to 83.5% from the concentrated leachate after desalination in the MDC fed with either acetate or another leachate as an electron source and at a different hydraulic retention time (HRT). Easily-degraded substrate like acetate and a long HRT resulted in a low conductivity desalinated effluent. Ammonia was also recovered in the MDC cathode with a recovery efficiency varying from 11 to 64%, affected by current generation and HRT. Significant COD reduction, as high as 65.4%, was observed in the desalination chamber and attributed to the decrease of both organic and inorganic compounds via diffusion and electricity-driven movement.

Introduction

Landfill leachate is a complex wastewater that contains dissolved organic substances, inorganic macro components (i.e. Na^+, NH_4^+, K^+, Mg^{2+}, Cl^-, PO_4^{3-}, SO_4^{2-}), heavy metals (i.e. Fe, Hg, Zn, Cu, Cd, Pb), xenobiotics (i.e. aromatics), and a substantial amount of water (Christensen et al., 1998; Jensen & Christensen, 1999; Kjeldsen et al., 2002). Thus, it must be properly treated to reduce its impact on the environment, and various treatment methods have been employed or investigated, including biological, physicochemical, and electrochemical treatments (Renou et al., 2008). These processes can be effective in reducing the concentrations of contaminants to a certain degree, but in general, leachate management is very challenging (Bohdziewicz et al., 2001; Welander et al., 1998). In addition to contaminant removal, reducing the volume of leachate could also help with its treatment and management, for example, decreasing the use of external chemicals or the size of the treatment systems. Volume reduction could also recover high quality water that may be directly discharged or used for other purposes. Membrane technologies, especially pressure driven filtrations (e.g. ultra, micro, nano, reverse osmosis), have been employed for leachate treatment to separate contaminants from the final effluent and because of the need for external pressure, those membrane treatments are usually energy intensive (Chianese et al., 1999; Di Palma et al., 2002; Renou et al., 2008).

Forward osmosis (FO) is an emerging separation technology that uses an osmotic gradient between a draw solution and a feed solution to drive water molecules through the semipermeable membrane (Cath et al., 2006). FO has been investigated for water recovery from sea water, municipal wastewater, and landfill leachate with simultaneous volume reduction, and can reject contaminants such as heavy metals, organics, ammonia nitrogen, etc. (Elimelech & Phillip, 2011; Iskander et al., 2017; Linares et al., 2014). In the absence of an external pressure, FO treatment is potentially energy efficient. For example, a recent study reported an energy consumption of 0.005 $kWhm^{-3}$ for treating landfill leachate with 30 mL min^{-1} recirculation and a 3-M NaCl draw (Iskander et al., 2017). In a submerged FO system, 621.5 mL water was recovered from 1700 mL leachate in 59 hours by using the 4-M NaCl draw (Wu et al., 2018). The use of a 2-M NH_4HCO_3 draw solution achieved a higher water recovery of 51 % with pretreatment of leachate by a microbial electrolysis cell that decreased the conductivity of leachate and thus benefited FO treatment (Qin et al., 2016). The FO treatment could effectively separate polycyclic aromatic hydrocarbons in the leachate from the final effluent, which may be used for direct fertigation when using NH_4HCO_3 as a draw (Li et al., 2017). FO has also been incorporated with a membrane distillation (MD) unit for recovering water and removing contaminants (i.e. TOC, NH_4^+-N) from landfill leachate (Zhou et al., 2017).

During FO treatment, the feed (leachate) becomes highly concentrated and this brine creates more resistance for the water flux that is controlled by the salinity gradient across an FO membrane. For example, it was found that the water flux decreased from 4.5 LMH to 1.5 LMH after 12 hours treatment or from 2.9 LMH to 0.1 LMH after 59 hours treatment, which was related to the conductivity increase of the feed side with time (Iskander et al., 2017; Wu et al., 2018). In addition, because brine has a high concentration of dissolved solids, inorganic fouling may be promoted and subsequently affect the FO membrane (Afrasiabi & Shahbazali, 2011). To minimize the volume of the treated leachate using FO technology, the brine should be treated to facilitate further water extraction. Proper brine management is both environmentally and economically important (Pramanik et al., 2017). Conventional processes of brine management include deep well injection, land application, evaporation ponds, conventional crystallizers, and landfilling, and the advanced processes such as electrodialysis, membrane distillation, and capacitive deionization are still under development (Afrasiabi & Shahbazali, 2011; Pramanik et al., 2017).

In this study, a microbial desalination cell (MDC) was proposed to act as a brine control unit to help with FO water extraction from landfill leachate. MDCs are bioelectrochemical systems that use bioelectricity to accomplish desalination (Cao et al., 2009; Kim & Logan, 2013; Sevda et al., 2015). In the proposed system, the brine from the FO treatment was desalinated in the MDC, driven by electricity generation from organic oxidation (e.g., the waste organic matter), and thus the desalinated brine could be further treated by FO for water extraction. Meanwhile, cation movement in the MDC would help to recover valuable compounds such as ammonia in its cathode. This is different from a prior study of FO-MDC system, in which the MDC was used to treat the diluted draw solution from the FO (Yuan et al., 2015). The specific objectives of this study were to: 1) demonstrate the feasibility of the proposed system for enhancing water recovery in the FO; 2) examine the effects of organic loading rates in the anode and salt loading rates in the desalination chamber on the performance of the FO – MDC system; and 3) investigate the recovery of ammonia in the MDC.

Materials and Methods

Leachate

Two types of leachates were studied, Leachate A and Leachate B. Leachate A was low in biodegradability ($BOD_5/COD = 0.07$), while Leachate B ($BOD_5/COD = 0.19$) was higher. Hence, physicochemical treatment would be more effective for Leachate A, while biological treatment was chosen for Leachate B. For this reason, Leachate A was used in the FO treatment followed by the MDC desalination, while leachate B was used in the later stage of the study for electricity generation in the MDC anode. The leachates were collected from two different cells of a landfill in Virginia, USA. After collection, leachates were stored at a 4°C temperature until use. The chemical properties of the leachates are given in Table 4-1.

Table 4-1. Chemical properties of the two leachates. Leachate A was used for water recovery and desalination. Leachate B was used as an anode substrate in the MDC.

Parameters	**Leachate A**	**Leachate B**
pH	8.05 ± 0.02	7.81 ± 0.03
Conductivity, mS cm^{-1}	31.11 ± 0.01	27.1 ± 0.1
COD, mg L^{-1}	11650 ± 109	4740 ± 30
TOC, mg L^{-1}	3353 ± 89	1771 ± 44
BOD_5/COD	0.07	0.19
NH_3-N, mg L^{-1}	2000 ± 80	1897 ± 6
Na^+, mg L^{-1}	5691 ± 81	3837 ± 45
Cl^-, mg L^{-1}	4923 ± 78	5273 ± 67
K^+, mg L^{-1}	1771 ± 98	993 ± 54
Mg^{2+}, mg L^{-1}	141 ± 12	219 ± 29
Ca^{2+}, mg L^{-1}	54 ± 11	59 ± 11

Forward osmosis – Microbial desalination cell system setup and operation

The FO-MDC system is shown in Fig. 4-1. Leachate A was used for the main experiment in the FO for water recovery and in the MDC for brine desalination. The FO unit was operated in a batch mode for 10 hours with the initial feed (leachate) volume of 500 mL and a draw solution volume of 200 mL containing 3-M NaCl. Then, the concentrated leachate feed was fed into the desalination chamber of the MDC for desalination. A SEPA CF Cell (Sterlitech Corporation, Kent, WA, USA) was used as the FO unit with an Aquaporin embedded flat-sheet FO membrane (Aquaporin A/S, Lyngby, Denmark) that had a surface area of 139 cm^2. The active layer of FO membrane was facing the feed (leachate), while the support layer was in contact with the draw solution. Both draw and feed solutions were recirculated at 40 mL min^{-1}, respectively. A tubular MDC was constructed according to a previous study (Jacobson et al., 2011). Ion exchange membranes (Membranes International, Inc., Ringwood, NJ, USA) were used to create an anode chamber of 330 mL and a desalination chamber of 110 mL. The membrane tubes were installed in a plastic tube which provided a cathode chamber of 750 mL with continuous aeration of 60 mL min^{-1}. A 50-cm carbon brush (Gordon Brush Mfg. Co., Inc.) was used as the anode electrode, while a piece of 450-cm^2 carbon cloth (coated with 5 mg cm^{-2} activated carbon) was used as the cathode electrode. The anode and cathode electrodes were connected across a 1-Ω external resistor for high current generation. To start the MDC, its anode was inoculated with anaerobic sludge from a local wastewater treatment plant (Christiansburg, VA). Ammonia that migrated from the desalination chamber into the cathode chamber was stripped out of the catholyte by aeration and collected in a 1-M sulfuric acid solution.

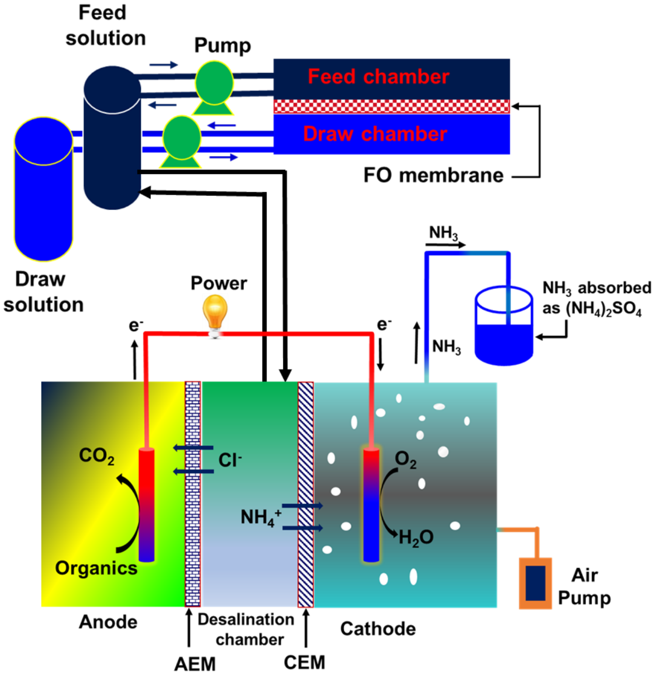

Figure 4-1. Experimental setup of a forward osmosis (FO) unit with a microbial desalination cell (MDC).

Four operating conditions were studied for treating Leachate A in both FO and MDC (Table 4-2), with C1 and C2 using 5 g L^{-1} sodium acetate in the MDC anode, and C3 and C4 using Leachate B as the MDC anode substrate. The use of synthetic organic compounds in C1 and C2 was to start the MDC and demonstrate the feasibility of the proposed system. In addition to substrate, the hydraulic retention time (HRT) of the anode solution and the desalination stream in the MDC were also varied to examine the effects of organic loading and salt loading on the system performance. After the MDC treatment, the desalination effluent was stored for the following FO operation. Because the HRT of the MDC (desalination chamber) was longer than that of the FO, a single FO batch operation could treat the effluent from several batches of the MDC effluent as stated in the paper.

Measurement and analysis

The concentrations of ammonia nitrogen (NH_3-N) and chemical oxygen demand (COD) were measured by using a spectrophotometer according to manufacturer's instructions (DR 890, HACH Company, USA). Five-day biochemical oxygen demand (BOD_5) was measured following a standard procedure (APHA, 2005). The conductivity and pH of solution were measured by a benchtop conductivity meter (Mettler-Toledo, Columbus, OH, USA), and a benchtop pH meter (OAKTON Instruments, Vernon Hills, IL USA), respectively. Ion chromatography (Dionex LC20 ion chromatograph, Sunnnyvale, USA) in combination with an ED40 electrochemical detector was used to measure the concentration of different ions. A TOC- Vcsn (Shimadzu, Japan) analyzer was used to measure total organic carbon. Voltage across the external resistance of the MDC was measured using a digital multimeter (2700, Keithley Instruments Inc., Cleveland, OH, USA). Total Coulombs were calculated according to a previous study (Qin et al., 2016). Water flux was measured by monitoring the weight difference of the draw solution recorded every 2 min by an electronic balance (Scort Pro, Ohous, Columbia, MD, USA) according to a previous study (Yuan et al., 2016). The desalination rate in the MDC desalination chamber was calculated according to a previous study (Luo et al., 2012). Ammonia recovery rate was calculated by dividing the recovered ammonia amount by the total loaded ammonia in the system in a certain time. Reverse salt flux (RSF), which is the movement of salts from the draw to the feed solution due to a concentration gradient was calculated according to the following equation (Zou & He, 2016).

$$\mathrm{RSF} = \frac{V_F \times C_{f,F} - V_i \times C_{i,F}}{S \times t}$$

where V_F is the final feed volume (L), V_i is the initial feed volume (L), $C_{f,F}$ is the final solute concentration in the feed (g L^{-1}), $C_{i,F}$ is the initial solute concentration in the feed (g L^{-1}), S is the surface area of the membrane (m^2), and t is the total batch time (h).

Results and discussions

Enhanced water recovery

Water recover from Leachate A was examined in the FO treating raw leachate and four desalinated leachate effluents (Table 4-2) using two different electron sources, acetate and Leachate B. With 3-M NaCl draw solution, the FO reduced 51.5 % of the feed volume of raw leachate with an initial water flux of 2.84 LMH (Fig. 4-1A). Because of water extraction and the associated concentration effect, the COD of the feed leachate increased from 11,650 ± 109 to 20,700 ± 600 mg L^{-1}, TOC increased from 3,353 ± 89 to 5,671 ± 78 mg L^{-1}, and the ammonia nitrogen concentration increased from 2,000 ± 80 to 2,400 ± 50 mg L^{-1}. Both TOC and ammonium migrated from the feed into the draw, resulting in 189± 14 mg L^{-1} of TOC and 1,450 ± 40 mg L^{-1} of ammonia nitrogen in the diluted draw. The accumulated ammonium in the draw solute will need further treatment during regeneration of draw solute using a separation system such as reverse osmosis or electrodialysis, or to be removed by air stripping once the concentration reaches a suitable level. If a fertilizer-based draw solute is used in the present system, then there may not be the need to deal with the accumulated ammonium, because it is a key component of fertilizer and can be used for agricultural applications (Zou & He, 2016). The conductivity of raw leachate increased from 31 to 61 mS cm^{-1}, and this increase resulted in a decreased water flux. Meanwhile, the RSF was 12.36 ± 0.46 gMH.

Table 4-2. Four operating conditions with different anode substrates and/or HRT.

Operating conditions	Anode feed	Anode HRT (d)	Desalination HRT (d)
C 1	Acetate	9	6
C 2	Acetate	6	2
C 3	Leachate B	12	4
C 4	Leachate B	6	2

The leachate brine from the FO treatment was then desalinated in the MDC and the effluent was returned to the FO for further water recovery. The MDC desalination performance is described in detail in the next section. The effluent from the acetate-fed MDC with a long desalination HRT (C1) had the highest water flux of 7.28 LMH and recovery efficiency (417.5 mL, 83.5%) in a period of 10 hours and benefited from the lowest conductivity because of better desalination (Fig. 4-2A). The water recovery from the C2 and C3 effluents, which had similar conductivities (22.2 vs. 22.6 mS cm^{-1}), was comparable at 311.3 and 324.6 mL, respectively. The C4 effluent had the highest conductivity of 30.4 mS cm^{-1} among the tested conditions, and thus its maximum water flux of 4.14 LMH was the lowest. The reverse salt flux of C1, C2, and C3, which was 16.02 ± 0.79, 14.05 ± 1.28, and 14.25 ± 0.86 gMH, respectively, became higher than 12.36 ± 0.46 gMH of raw Leachate A, because of a higher salt gradient across the FO membrane due to the lower conductivity of the feed (desalinated brine). After water extraction from the MDC treated Leachate A concentrate, the final concentration of COD ranged from 16000 to 30500 mg L^{-1}, TOC 2400 to 5650 mg L^{-1} and ammonia 670 – 840 mg L^{-1} for C1 – C4 in the final Leachate A effluent.

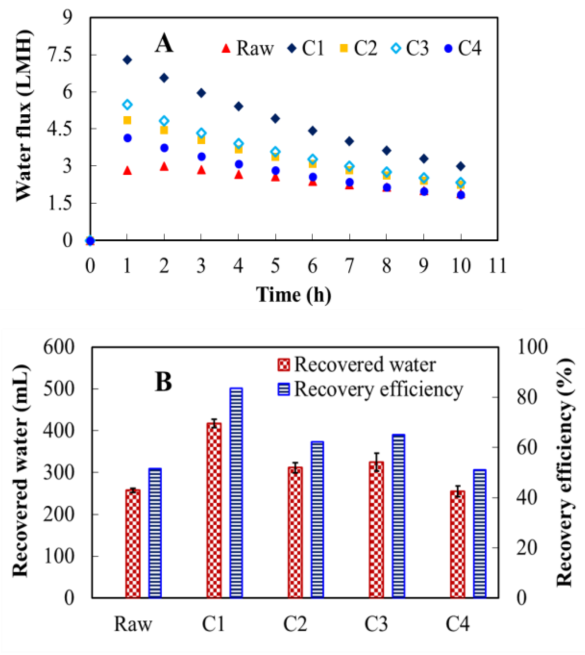

Figure 4-2. Water recovery from Leachate A under different operating conditions: (A) water flux; and (B) recovered water volume along with recovery efficiency (%).

Desalination of forward osmosis brine in the microbial desalination cell

The desalination of the FO brine in the MDC was studied for current generation and salt removal affected by the type of the anode substrates and HRT. It was obvious that acetate as an anode substrate led to much higher current generation than that of the Leachate B-fed MDC (Fig. 4-3). A shorter HRT in both the anode and the desalination chambers resulted in a higher organic loading rate (more electrons available) and a higher salt loading rate (lower electrolyte resistance), both of which benefited current generation and led to a higher current density of 56.9 A m^{-3} and total Coulomb of 1,833 ± 75 C in the C2, compared to those of the C1 (47.3 A m^{-3} and 1,063 ± 68 C). The same phenomenon was observed with the leachate-fed MDC, which had higher coulomb production in the C4 than that in the C3, due to the lower HRT of C4.

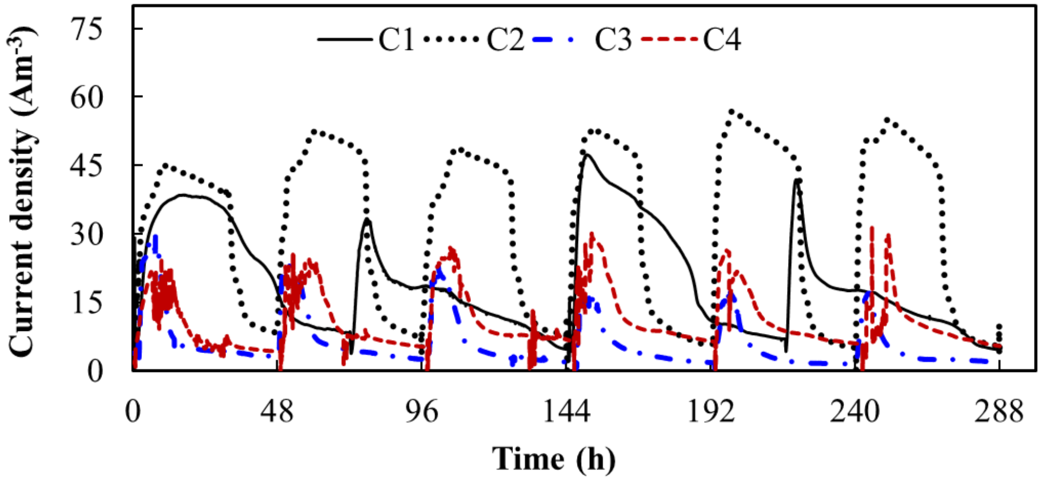

Figure 4-3. Current density (Am^{-3}) profile of the MDC under different operating conditions.

The performance of salt removal was first examined by monitoring the conductivity change in the FO brine. All four testing conditions (C1 – C4) effectively reduced the conductivity of the brine, and this reduction is more significant as the conductivity of raw Leachate A increased due to the concentrating effect after FO treatment (Fig. 4-4A). The conductivity reduction was affected more by HRT, because a longer HRT allows more time for desalination. Between the two acetate-fed MDCs, the C1 had a higher reduction efficiency of 85.9 % (decreased from 61 to 8.6 mS cm^{-1}) than that of the C2; likewise, the leachate-fed MDC exhibited a higher conductivity reduction efficiency of 63% in the C3, which had a longer HRT. Although the C2 and C3 had the similar reduction efficiencies of ~63%, their desalination rates (including the factor of time) differed significantly, 0.81 mS cm^{-1} h^{-1} for the C2 and 0.40 mS cm^{-1} h^{-1} for the C3. The desalination rate is influenced by current generation and thus the higher current output of the C2 resulted in a higher desalination rate. Surprisingly, the C1 exhibited the lowest desalination rate of 0.36 mS cm^{-1} h^{-1}, despite its higher current generation than the C3 and C4. This result was likely related to its longest HRT of 6 days in the desalination chamber: a high desalination rate could have occurred during the initial period and with a great conductivity reduction (the best among the four conditions), the desalination rate decreased dramatically in the later phase of the test, resulting in a low overall desalination rate across the whole desalination period. Prior studies have reported various desalination rates ranging from 0.03 to 0.22 mS cm^{-1} h^{-1}, which are affected by many factors including anode feed, initial conductivity, hydraulic retention time, and system configuration (Luo et al., 2017; Luo et al., 2012). The desalination rate obtained in the present study is significantly higher than many prior MDC studies, because of the high conductivity of the brine that provided more salt for desalination and decreased the electrolyte resistance.

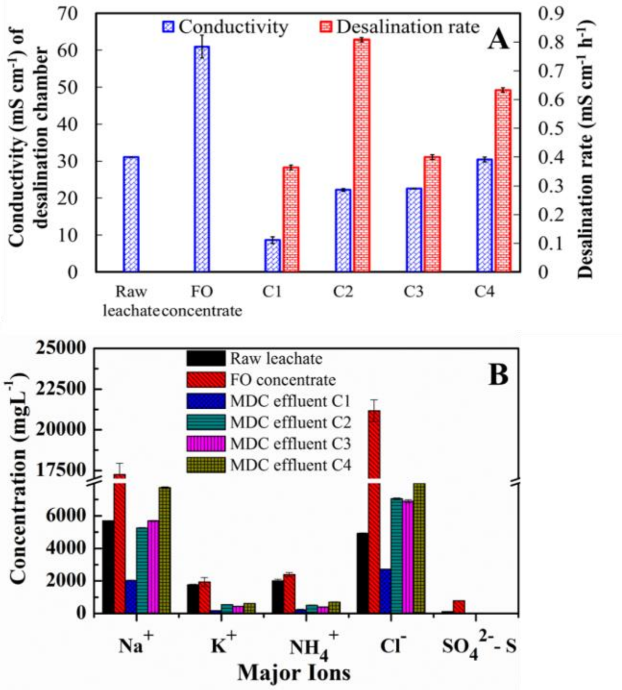

Figure 4-4. The desalination performance of the MDC: (A) Conductivity and desalination rate; and (B) distribution of major cations and anions.

The salt removal was further investigated by examining the concentrations of major ionic species (Fig. 4-4B). The decrease in ionic concentrations followed the trend of conductivity decrease. The MDC effluent of the C1 showed the lowest concentrations of the dominant ions including 2,033.9 mg L^{-1} Na^+, 183.9 mg L^{-1} K^+, 233.3 mg L^{-1} NH_4^+, 2723.7 mg L^{-1} Cl^-, and 0 mg L^{-1} SO_4^{2-}-S, which corresponded to 90.0, 90.5, 90.3, 87.8 and 100 % removal for those species, respectively (Fig. 4-4B). The movement of ions from the desalination chamber to the anode and cathode chambers through AEM and CEM are dictated by ionic charge and hydrated radius (Van der Bruggen et al., 2004). The hydrated radius of Na^+, K^+, and NH_4^+ are 0.358, 0.331, and 0.331 nm, respectively (Howitt & Udvardi, 2000). Thus, the removal efficiency of these three ions was similar at ~90%. For anions, the hydrated ionic radius of Cl^- and SO_4^{2-} are 0.347 and 0.380 nm, respectively (Firdaous et al., 2004). Although the multivalent ions are more susceptible to stay on the membrane material and move slowly, the low concentration of sulfate in the FO brine (789 mg L^{-1}) benefited its complete removal. Despite a lower removal efficiency of Cl^- than SO_4^{2-}, its removal rate of 14.1 mg h^{-1} was much higher than that of SO_4^{2-} (0.6 mg h^{-1}). When using actual leachate (Leachate B) as an anode substrate (C3 and C4), the presence of similar ions in high concentrations in Leachate B would decrease concentration gradients across the AEM and create some resistance to ion movement. As described by previous research, along with electricity driven movement, concentration gradient driven movement is also responsible for desalination in an MDC (Cao et al., 2009).

Ammonia removal and recovery

One of the major cations in leachate is ammonium (NH_4^+), which can move to the cathode chamber via CEM in the MDC. This movement allows the separation of ammonium from the brine and concentrate it in the catholyte for further separation and recovery as ammonia. Such a method for ammonia recovery has been demonstrated in either microbial fuel cells or microbial electrolysis cells (Kelly & He, 2014). Because of oxygen reduction reactions, the catholyte pH in the MDC increased from 5.60 to 9.61, 9.36, 9.30, and 8.04 at the end of the operating cycle in the C1, C2, C3, and C4, respectively. This alkaline pH helped to convert NH_4^+ to NH_3. Aeration then provided a stripping function to drive ammonia out of the catholyte to be collected as ammonium sulfate in the recovery bottle containing 1-M H_2SO_4 solution. The distribution of ammonium/ammonia in the absolute amount (mmol) was analyzed in four locations, the anode chamber, the desalination chamber, the cathode chamber, and the recovery bottle (Fig. 4-5). It was observed that ammonium moved from the desalination chamber into the anode chamber, despite the use of AEM as a barrier that is thought to prevent cation movement. In the acetate-fed MDC, the average ammonium nitrogen concentration in the anode was 65 mg L^{-1} for C1 (or an absolute amount of 1.5 mmol) and 237 mg L^{-1} for C2

(5.8 mmol), much higher than that of the fresh anode feeding solution. When using Leachate B as the anode feeding solution that had an ammonia nitrogen concentration of 1,897 mg L^{-1}, the anodic ammonium concentration was 1,233 mg L^{-1} for C3 (29.1 mmol) and 1,992 mg L^{-1} for C4 (47.0 mmol). One can see that ammonium movement into the anode was weak with Leachate B as the anode substrate because of a high ammonium concentration in Leachate B. The anodic ammonium concentration in C3 became lower than its original concentration, likely due to its long anode HRT (12 h) that allowed ammonium to move into the desalination chamber where the ammonium concentration decreased because of desalination (ammonium moving into the cathode chamber). The ammonium concentration in the cathode chamber was low, at 23 mg L^{-1} for C1 (1.2 mmol), 88 mg L^{-1} for C2 (4.7 mmol), 80 mg L^{-1} for C3 (4.3 mmol), and 72 mg L^{-1} for C4 (3.8 mmol). This is because continuous aeration stripped ammonia out of the catholyte. The ammonium concentration in the desalination chamber decreased from an initial value of 2,400 mg L^{-1} (18.9 mmol) to 233 mg L^{-1} for C1 (1.8 mmol), 510 mg L^{-1} for C2 (4.0 mmol), 400 mg L^{-1} for C3 (3.1 mmol), and 697 mg L^{-1} for C4 (5.5 mmol), representing removal efficiencies of 90.5, 78.9, 83.6, and 70.9 %, respectively. The reduced ammonium concentration in the desalination effluent would benefit the subsequent FO treatment by lowering ammonium movement into the draw solution. It was found that ammonium movement was 95 ± 12, 290 ± 40, 200 ± 10, and 490 ± 40 mgL^{-1} in the draw for the C1, C2, C3, and C4, respectively, much lower than 1,450 ± 40 mgL^{-1} with raw Leachate A as the feed. The total amount of ammonia recovery was 24.3, 15.6, 15.7, and 13.0 mmol in the C1, C2, C3, and C4, representing recovery efficiencies of 64.3, 13.7, 27.7, and 11.5 %. The higher recovery of ammonium in C1 and C3 were related to their relatively higher desalination chamber HRT, which resulted in more ammonium movement (Table 4-2).

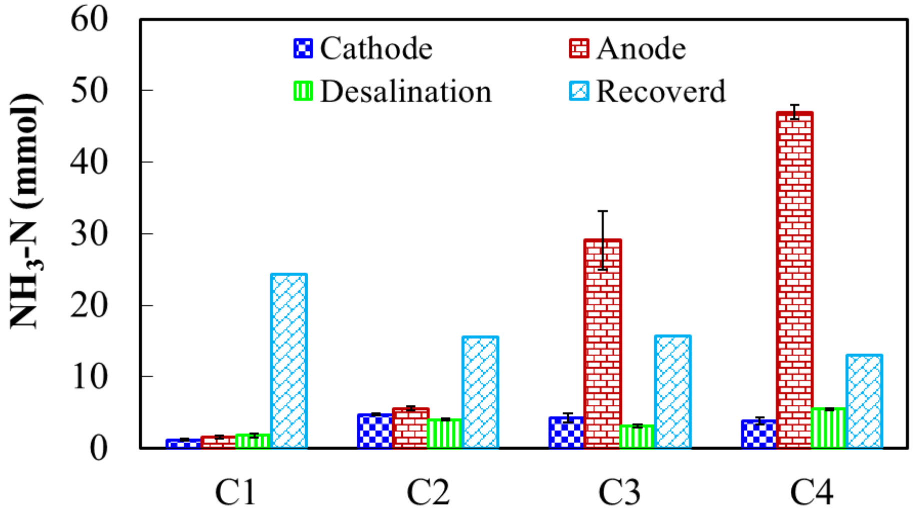

Figure 4-5. Ammonia nitrogen distribution in different locations of the MDC (and the recovery bottle) under four operating conditions.

Microbial desalination cell chemical oxygen demand removal

COD removal occurs in two locations of the MDC, the anode chamber (anode substrate degradation) and the desalination chamber. Interestingly, the desalination chambers COD decreased after each batch cycle. The COD concentration decreased from 20,700 mg L^{-1} to 7,170 in C1, to 10,170 in C2, to 8,250 in C3, and 9,550 mg L^{-1} in C4, representing removal efficiencies of 65.4, 50.9, 60.2, and 53.9%, respectively (Fig. 4-6A). This decrease was proportional to the HRT in the desalination chamber; the longer the HRT, the higher the COD removal efficiency. The COD of a landfill leachate could include both organic and inorganic compounds (e.g. sulfide, reduced metal species, ammonia, chloride can exert oxygen demand), and it was reported that up to one third of leachate COD could be from the inorganics (Kylefors et al., 2003). In the present study, the COD of raw Leachate A was 3.47 times the TOC and the COD of the FO brine (concentrated Leachate A) was 3.65 times the TOC, indicating that COD was contributed largely by the inorganics. Although the TOC removal efficiencies (69.7, 58.3, 64.6, and 61.2%) were higher than that of the COD removal efficiencies under the four conditions, the actual concentration decrease of TOC (2,336, 1,890, 2,168, and 2,053 mg L^{-1}) was much lower than the COD decrease (13,532, 10,533, 12,457 and 11,155 mg L^{-1} for C1, C2, C3, and C4, respectively). This suggests that the COD decrease was dominated by the movement of inorganics from the desalination chamber to the anode and cathode chambers. In addition, the anaerobic condition in the desalination chamber might have facilitated the anaerobic degradation of organics. The diffusional movement of organics to both the anode and cathode chambers might also happen, especially for organic acids as a result of anaerobic degradation. Because the TOC concentration in the cathode chamber was only ~ 1 mg L^{-1}, it is more likely that the movement of anionic organic acids (e.g. butyrate, propionate) to the anode chamber was the major process for organic movement.

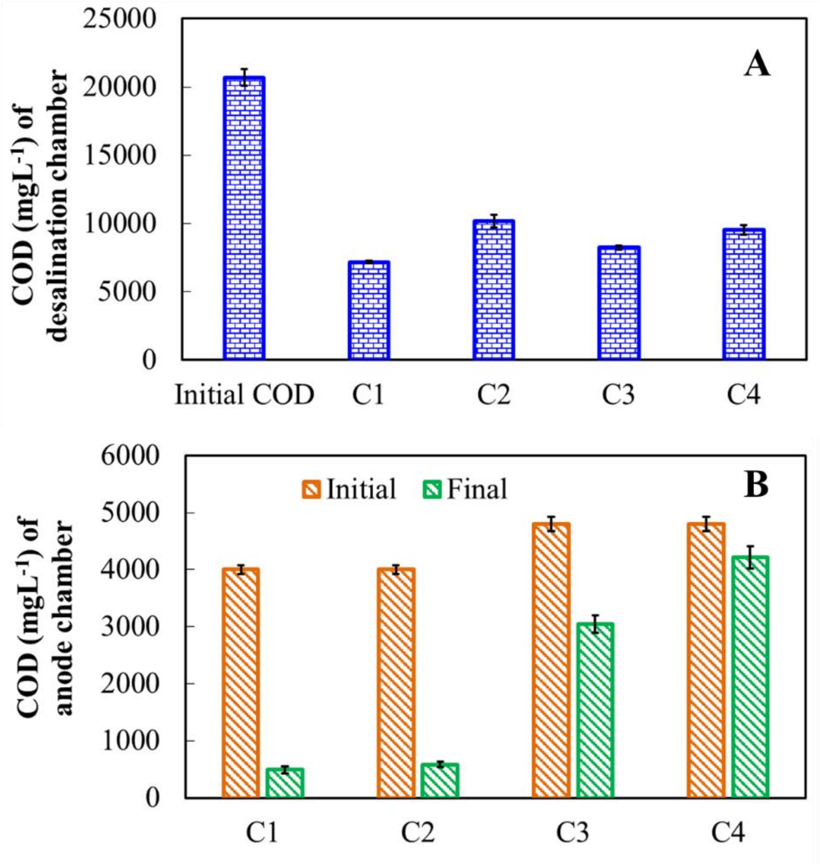

Figure 4-6. COD removal in the MDC under different operating conditions: (A) COD concentration in the desalination chamber; and (B) COD concentration in the anode chamber.

The anode COD removal was much higher in the acetate-fed MDC (87.7 % in the C1 and 85.4 % in the C2) than that in the leachate-fed MDC (36.5 % in the C3 and 12.1 % in the C4). The remaining COD in the leachate-fed MDC anode was 3,050 and 4,220 mg L^{-1} for C3 and C4, respectively (Fig. 4-6B). This result is expected because of the recalcitrance of leachate to biodegradation. The movement of anionic organic acids and inorganics (which could contribute to COD) would complicate COD quantification in the anode chamber. Thus, the actual removal might be higher than the measurement, but this needs further investigation. There have not been any studies of leachate treatment in the anode of an MDC, but leachate has been used in the anode of other BES like MFCs. A wide range of organic removal efficiencies, from 40 % to over 80%, has been reported in BES treating leachate and the treatment performance was highly affected by the bioavailability of organic compounds in the leachate (Ozkaya et al., 2013; Zhang et al., 2015). Although the COD removal in the present study was in the lower regime, current density of the MDC (31.4 A m^{-3}) was higher than that of the previous studies with leachate in BES, for example 21 A m^{-3} from fermented leachate (Mahmoud et al., 2014). The presence of a desalination chamber containing high-salinity brine in the MDC could greatly decrease the internal resistance of the system, thereby benefiting current generation. This was demonstrated in the recent study that current generation increased dramatically with a higher NaCl concentration in the desalination chamber of an MDC (Yuan et al., 2017).

Perspectives

A landfill often has multiple cells with different ages, resulting in the production of very different leachates. The proposed system was designed to take advantage of the difference in leachates produced in the same landfill, and use “one waste” - a “newer” leachate that is more biodegradable to help treat “another waste” - an “older” leachate that is less biodegradable. This system involves both biological and physicochemical treatment, and delivers multiple products including treated leachate, water, ammonia, and possibly electricity (depending on how the MDCs are operated). To further explore the potential of this system, several challenges must be addressed. First, the treatment capacity between FO and MDCs must be well coordinated. This is because FO treatment is usually fast, while MDCs will be much slower due to their biological processes. Such differences create a situation that FO units should be much smaller than MDCs. Second, energy consumption of this system should be properly evaluated. FO or MDCs have been evaluated for energy consumption separately, but the cooperative system treating a specific wastewater needs to be examined for energy input. Third, the residue from the system (after water extraction/desalination in FO/MDC and biological treatment in MDC) still needs further management. A treatment system cannot decompose a waste completely, but volume reduction by the proposed system could benefit the next management step. After the MDC treatment, the treated Leachate B becomes less biodegradable and may be further treated for volume reduction like that of Leachate A, with assistance of more biodegradable leachate that is continuously generated in a landfill. Finally, membrane fouling, especially FO membranes during a long-term operation with leachate, warrants further investigation.

Conclusions

It has been demonstrated that MDCs can be used to desalinate FO treated leachate and reduce the concentrations of both salts and COD. This would enhance water recovery in FO when treating the MDC desalinated effluent, towards maximizing water extraction and minimizing the leachate volume. Additional products such as electricity and ammonia may be recovered during the MDC treatment. This FO-MDC system aims to treat the leachates with different biodegradabilities in the same landfill, especially for volume reduction. Several challenges such as system coordination, energy consumption, residue disposal, and membrane fouling must be addressed toward further development of this system.

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CHAPTER 5

Reduction of reagent requirements and sludge generation in Fenton's oxidation of landfill leachate by synergistically incorporating forward osmosis and humic acid recovery

Abstract

Application of Fenton's oxidation of landfill leachate is limited by both high reagent requirements and a large amount of sludge generation. To address those issues, forward osmosis (FO) and humic acid (HA) recovery were incorporated with Fenton's treatment. In the FO, leachate was concentrated by 3.2 times in 10 hours using a 5-M NaCl draw solution. The HA recovery increased from 1.86 to 2.45 g L^{-1} at pH 2 after FO concentration, mainly because of the replacement of O in the HA structure by other inorganics (i.e., Cl, Na, K) with higher molecular weight. Due to the movement of alkalinity causing species (i.e., HCO_3^-, CO_3^{2-}) to the draw side driven by a concentration gradient, the H_2SO_4 requirement per g of recovered HA and per g of removed COD decreased by 46.4% and 17.1%, respectively. The HA recovery also decreased sludge generation by 29.1%. At a dimensionless oxidant dose of 0.5, the proposed system reduced the overall requirement of H_2SO_4 by 25.2%, NaOH by 34.6%, and both $FeSO_4.7H_2O$ and H_2O_2 by 35.1%, compared to the Fenton's treatment of raw leachate alone. Those results have demonstrated that the proposed system could greatly decrease the leachate volume, lower the reagent requirements, and reduce the sludge production towards sustainable leachate treatment.

Introduction

Landfill leachate contains recalcitrant organics such as humic acid, fulvic acid, and hydrophilics (Kang et al., 2002; Kjeldsen et al., 2002; Zhao et al., 2013a). In addition, the presence of inorganics (i.e., ions such as Mg^{2+}, Na^+, Cl^-, etc.), xenobiotics (i.e., aromatic compounds), and metals (i.e., Fe, Ni, Co, etc.) have labeled leachate as a "complex wastewater" (Kjeldsen et al., 2002). The recalcitrance and complexity of leachate have triggered a wide array of treatments including biological, physical, chemical, and electrochemical treatments (Renou et al., 2008; Li et al., 2017). Among those, biological treatment is widely practiced (though limited by treatment efficiency) (Kurniawan et al., 2010). Chemical treatments, particularly, advanced oxidation processes (AOP) such as UV+H_2O_2, ozone+H_2O_2, and Fenton, have been implemented for leachate treatment by taking advantages of the reaction of hydroxyl radical (•OH), a very strong oxidant, with the organics (Deng & Englehardt, 2006; Renou et al., 2008). As a well-known AOP, Fenton oxidation is considered the most effective for leachate treatment (Deng & Englehardt, 2006). It has been reported that Fenton treatment of leachate could achieve up to 90% COD removal, 82% TOC removal, 92% decolorization, and a significant increase in biodegradability (BOD_5/COD) (Deng & Englehardt, 2006; Jung et al., 2017; Zhang et al., 2005; Zhao et al., 2013b).

Fenton's is a reaction of Fe (II) and H_2O_2 that produces hydroxyl radical (•OH) to oxidize organics (Walling, 1975). Despite its efficacy, Fenton oxidation possesses a few inherent drawbacks. For the effective application of Fenton oxidation, the optimum pH range is 2 – 4 (Deng & Englehardt, 2006; Hermosilla et al., 2009), which demands the addition of inorganic acid (e.g., H_2SO_4, HCl). Foaming could occur in leachate at such a low pH because of the production of CO_2 from the conversion of HCO_3^- and CO_3^{2-}, resulting in the requirement of a large reactor volume (Deng & Englehardt, 2006). At the end of Fenton reaction, base (e.g., NaOH, Lime) is added to neutralize the system, with the production of a large amount of ferric based sludge (Benatti et al., 2006; Wu et al., 2010). Disposal of this sludge is one of the major costs for Fenton applications (Umar et al., 2010). Another key cost of Fenton treatment comes from the reagents (i.e., $FeSO_4$ $7H_2O$ as a source of Fe (II) and H_2O_2) that are highly related to the concentrations of organic matter in a leachate (Vilar et al., 2013). Therefore, it is of strong interest to reduce the reagent dosage and sludge production towards enhancing cost efficiency of Fenton oxidation technology for leachate treatment.

Herein, we hypothesized that reducing leachate volume and organic contents would help accomplish the reduction of both reagent dosage and sludge generation, and this may be realized by incorporating two additional processes, forward osmosis (FO) and recovery of humic acid (HA). Forward osmosis is a membrane-based separation technique that utilizes an osmotic gradient between a draw solution and a feed solution for extracting water, (Cath et al., 2006; Shaffer et al., 2015) and has been investigated for recovering water from landfill leachate (Iskander et al., 2018; Iskander et al., 2017b). It was reported that FO treatment could recover 12.3 – 51.5 % water from landfill leachates and this recovery was dictated by the leachate properties (e.g., organics content, conductivity, etc.) and FO operating conditions (e.g., draw solute type and concentration, recirculation rate, etc.) (Iskander et al., 2018; Qin et al., 2016; Wu et al., 2018). HA consists of a substantial amount of aliphatic and aromatic moieties containing phenolic, carboxylic, and alkoxy groups along with the occasional presence of esters and quinones (Castagnoli et al., 1990; Jones & Bryan, 1998). It has several useful applications in agriculture such as a highly efficient organic fertilizer or a key fertilizer component (Li et al., 2009; Li et al., 2014; Morozesk et al., 2017). HA can also be used to remove aqueous phosphorus, nitrogen, heavy metals, and chlorinated solvents by forming stable complexes followed by precipitation (Zanin & Boetti, 1995). Furthermore, it can improve the aggregation capability of soils and be used as a soil stabilizer (Piccolo & Mbagwu, 1999). Thus, HA could be a potentially valuable resource and recovery of HA from a leachate, in which the HA concentration increases with time because of humification (Artiola Fortuny & Fuller, 1982; Nanny & Ratasuk, 2002), may make leachate treatment more sustainable (Jones & Bryan, 1998).

In the proposed system, FO is used to concentrate the leachate by extracting water, followed by HA recovery. Because of the low pH (~2) requirement for HA recovery, the leachate after HA recovery would still have a low pH that can be utilized by subsequent Fenton oxidation. In addition, HA recovery would decrease the organics concentration and thus benefit the subsequent Fenton oxidation with a lower reagent requirement (Fe (II) and H_2O_2) and less sludge production. In this way, the drawbacks of Fenton (i.e., initial pH adjustment, reagent requirement, sludge generation) for leachate treatment can be addressed or alleviated. In the present study, we have experimentally investigated the proposed system for treatment of organic contaminants in an actual landfill leachate. Experiments were performed to understand the effects of FO treatment and/or HA recovery on Fenton oxidation. HA recovery and associated inorganic acid (H_2SO_4) requirement were quantified, and the recovered HA was characterized and compared with a commercial HA. Fenton oxidation of raw leachate or the leachate pre-treated by different methods was conducted to compare the treatment performance in terms of organics removal, reagent requirement, and sludge generation.

Materials and Methods

Experimental procedures

Three experiments (Cases A-C) were performed for comparison and analysis (Fig. 5-1). Two of them were without HA recovery (Case A and B) and one was with HA recovery (Case C). Case A was the direct application of Fenton's oxidation of raw leachate at pH 3, providing a bottom line for comparison. As pH 2-4 has been described as the optimum pH for Fenton's application, pH 3 was chosen as the midpoint of the range (Deng and Englehardt, 2006). FO treatment was performed in Case B to concentrate the leachate prior to Fenton's oxidation. In Case C, after FO concentration, HA was recovered at pH 2 followed by Fenton's oxidation of the remaining organic fractions at pH 3. The dimensionless oxidant doses (DODs) investigated were 0.25, 0.5, 1. Considering the different initial COD in different cases, the application of DOD, which is the ratio of chemical equivalent of oxidant to chemical equivalent of initial COD (Eqn. 5-1 and 5-2), would facilitate comparison of the Fenton's oxidation performance among different cases (Jung et al., 2017; Singh et al., 2013).

$$\text{Dimensionless oxidant dose, DOD} = \frac{\text{Chemical equivalent of oxidant}}{\text{Chemical equivalent of } COD_0} \qquad (5\text{-}1)$$

$$\text{DOD in Fenton oxidation} = \frac{0.471 * H_2O_2}{COD_0} \qquad (5\text{-}2)$$

Because of the comparable organics removal at DOD 0.5 and 1 at different cases, DOD 0.5 was chosen for the analysis of reagents requirement (less reagents requirement at DOD 0.5 than DOD 1.0) change and sludge generation in different cases.

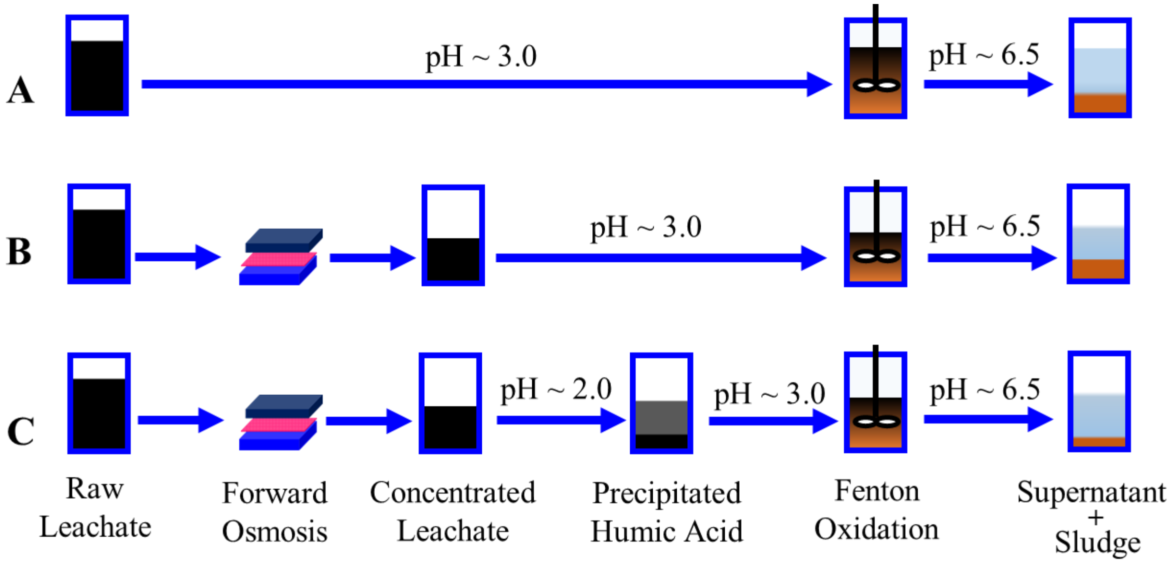

Figure 5-1. Three different experimental cases: (A) Fenton's oxidation of raw leachate at pH 3; (B) Fenton's oxidation of the FO concentrate at pH 3.0; and (C) HA recovery from the FO concentrate at pH 2 followed by Fenton's oxidation of the FA+HPI fraction at pH 3.0.

Leachate sample

The leachate was collected from a municipal solid waste landfill in Virginia, USA. After collection, the leachate was stored at 4 °C and used for the experiment without modification. The stable leachate was dark brown in color indicating the presence of humic substances and had the following characteristics: 10750 ± 520 mg COD L^{-1}, $BOD_5/COD = 0.08$, 2900 ± 115 mg NH_3-N L^{-1}, 8.46 ± 0.01 pH and a conductivity of 30.63 ± 0.19 mS cm^{-1}. Chemical properties of the leachate are listed in Table S5-1.

Forward osmosis

Forward osmosis was set up as shown in Fig. S5-1 by using a SEPA CF Cell (Sterlitech Corporation, Kent, WA, USA). An aquaporin embedded flat-sheet FO membrane (Aquaporin A/S, Lyngby, Denmark) with a 139 cm^2 active membrane surface area was used with its active layer facing the feed side (leachate). FO test was conducted by using 200 mL 5-M NaCl as draw solution and with an initial feed leachate volume of 500 mL in a batch mode of 10 hours/each batch. To reduce the concentration polarization effect, a 40 mL min^{-1} (3.5 cm sec^{-1}) recirculation flow rate was applied to both the draw and feed chambers. To ensure consistent water recovery in FO, after each batch, the FO membrane was cleaned via osmotic backwashing with the same concentration of draw solution for 2 hours.

Recovery of humic acid

HA was recovered by precipitation at a pH of either 1.5 or 2. The leachate sample, either raw or FO concentrated, was filtered through a 1.5 µm DSC – Grade TSS Borosilicate Glass Fiber Filter (LabFilterz, P. City, CA) to remove suspended particles. The pH adjustment was conducted by using a 0.25-M H_2SO_4 solution (Fisher Scientific, Hampton, NH). The acid addition was conducted slowly by controlling foaming from carbon dioxide generation. The precipitated HA was separated by using centrifugation at 8000 rpm for 30 min (Beckman Coulter, Brea, CA) and then filtration through 1.5µm filter. To quantify the recovered HA, the mass of the filter was subtracted from the mass of the filter + HA (after heating at 70°C for 24 hours), and the difference in mass was then normalized over the initial leachate/FO concentrate volume (100 mL). After HA recovery, the filtrate containing fulvic acid (FA) and hydrophilics (HPI) was collected for further analysis and Fenton's oxidation. The FA+HPI fraction was further separated into FA and HPI by using an ion exchange resin column (Amberlite® XAD-8 ion-exchange resin, Sigma Aldrich, St. Louis, MO) according to a literature (Iskander et al., 2017a). A schematic of the fractionation protocol is demonstrated in Fig. S5-2.

Fenton's oxidation

Fenton's oxidation was performed on raw leachate or pre-treated leachate at five different DODs and at a fixed molar ratio of Fe^{2+}: H_2O_2 = 1: 1.5, an optimal ratio reported for batch operations of Fenton's oxidation of leachate (Hermosilla et al., 2009; Zhang et al., 2005). All the reactions were conducted in triplicates in 220-mL snap cap plastic bottles (Weber Scientific, Hamilton, NJ) with a 50 mL volume of the leachate. In this study, 30% (wt.%) H_2O_2 (Fisher Scientific, Hampton, NH) and ferrous sulfate heptahydrate ($FeSO_4.7H_2O$, Fisher Scientific, Hampton, NH) were used as the sources of H_2O_2 and Fe^{2+}. In Cases A and B, the raw or concentrated leachate was adjusted to an initial pH of 3 with 0.25-M H_2SO_4, while in Case C, the pH of the leachate after HA recovery was increased to 3 with 10-M NaOH (Fisher Scientific, Hampton, NH) (Fig. 5-1). After pH adjustment, $FeSO_4.7H_2O$ was added and mixed at 500 rpm for 5 minutes followed by the slow addition of H_2O_2 to avoid spill of the reactants due to vigorous reactions. The solution was further mixed at ~ 800 rpm for 2.5 hours, and its final pH was adjusted to 6.5 with the addition of 10-M NaOH and gentle mixing for 30 min. Then, a settling period of 30 minutes was allowed, and the supernatant was filtered through a 1.5 μm filter for further analysis.

Measurement and analysis

The concentrations of COD and NH_3-N were measured by using a spectrophotometer according to the manufacturer's instruction (DR 890, HACH Company, USA). Conductivity was measured with a benchtop conductivity meter with a temperature sensor (Mettler-Toledo, Columbus, OH, USA) and pH was measured using an Oakton pH 700 meter (OAKTON Instruments, Vernon Hills, IL USA). Hydrogen peroxide concentration was measured using iodometric titration (Schumb et al., 1955). Alkalinity and acidity were measured by titration with 0.1-M HCl and 0.1-M NaOH, respectively (APHA, 2005). For acidity measurement, the recovered HA was dissolved in a 1-M $NaNO_3$ solution to have the same concentration of HA in either the raw leachate (1.86 g L^{-1}) or FO concentrate (7.78 g L^{-1}) according to a previous literature (Christensen et al., 1998). Alkalinity was measured as total alkalinity (up to pH 4.5), carbonate alkalinity (up to pH 8.3) and bicarbonate alkalinity (from pH 8.3 to 4.5), while acidity was measured as total acidity (pH 3 – 11), carboxylic acidity (pH 3 – 8), and phenolic or weak acidity (pH 8 – 11) (Christensen et al., 1998). Scanning electron microscopy/ energy dispersive spectroscopy (SEM/EDS) of HA was performed by coating (5 nm coating) with 6:4 (wt.%) of Au: Pd to quantify the elemental composition. For the sludge volume determination experiment, the plastic reactor containing the Fenton sludge were dried at 70ºC for a consecutive five-day period to attain complete removal of the moisture. Commercial HA was purchased from Alfa Aesar, Haverhill, MA. Minitab® 18 was used for performing statistical analysis (two sample t test and one-way ANOVA) using a confidence interval of 95%.

Water flux was measured by measuring the change of mass of the draw solution in every 0.5 min using an electric balance (Scort Pro, Ohous, Columbia, MD, USA). Concentration factor ($C_f = V_f/V_c$) was calculated by dividing the feed volume (V_f) with the concentrate volume (V_c) (Xu et al., 2017). Reverse salt flux (RSF), which is the movement of salts from the draw to the feed solution due to a concentration gradient, was calculated according to the following Eqn. 5-3 (Zou & He, 2016).

$$\mathrm{RSF} = \frac{V_F \times C_{f,F} - V_i \times C_{i,F}}{S \times t} \qquad (5\text{-}3)$$

Here, V_F is the final feed volume (L), V_i is the initial feed volume (L), $C_{f,F}$ is the final solute concentration in the feed (g L^{-1}), $C_{i,F}$ is the initial solute concentration in the feed (g L^{-1}), S is the surface area of the membrane (m^2), and t is the total batch time (h). UV_{254nm} absorbance was measured using a spectrophotometer (Beckman Coulter, Brea, CA). Total organic carbon (TOC) was measured with a TOC- Vcsn (Shimadzu, Japan). Specific UV absorbance (SUVA) was measured by dividing UV absorbance with the corresponding TOC concentration according to Eqn. 5-4 (Iskander et al., 2017a).

$$\mathrm{SUVA}\ (\mathrm{L\,mg^{-1}m^{-1}}) = \frac{\text{UV absorbance at 254 nm}\ (\mathrm{cm^{-1}})\ \text{x}\ 100}{\text{Total organic carbon}\ (\mathrm{mg\,L^{-1}})} \qquad (5\text{-}4)$$

Results and discussion

Forward osmosis treatment

The FO treatment has concentrated the feed leachate (volume 500 mL) by a factor of 3.18 ± 0.06 in 10 hours. Previous studies on FO of leachates demonstrated a concentration factor (CF) of 1.14 – 2.06, which was dictated by leachate properties and FO operating conditions (Iskander et al., 2018; Qin et al., 2016; Wu et al., 2018). These studies used both NaCl (3 – 4 M) and NH_4HCO_3 (0.5 – 4 M) draw solutions at recirculation rates varying from 40 to 125 mL min^{-1}. The higher CF (3.18) in this study could be because of the high draw solute concentration (5-M NaCl). The recovered water from FO in the diluted draw form needs a post-treatment to recover draw solute and produce reusable water. Due to the low organics and contaminants concentration, FO followed by reverse osmosis could be a viable option. The highest water flux was 5.23±0.20 LMH, which decreased to 2.46±0.02 LMH in 10 hours (Fig. 5-2A), mainly because of the dilution of the draw solution, fouling of the membrane, and reverse solute flux (10.35 ± 0.50 gMH) of the draw solute (Table S5-2). Because of leachate concentration, the HA, FA, HPI and total TOC concentrations increased from 763 to 1789 mg L^{-1}, 739 to 1091 mg L^{-1}, 1857 to 5251 mg L^{-1}, and 3360 to 8131 mg L^{-1} in the feed side, respectively (Fig. 5-2B). Because of the forward substrate flux, the diluted draw contained 119 ± 2 mg L^{-1} HA, 166 ± 2 mg L^{-1} FA, 152 ± 2 mg L^{-1} HPI, and 437 ± 5 mg L^{-1} total TOC, which was 16.9, 24.4, 8.9, and 14.1% of the initial absolute amount (in mg) of the respective organic fractions in the raw leachate (Table S5-2). The concentrated feed solution contained 73.7% HA, 46.4% FA, 88.9% HPI, and 76.1% total TOC of the initial absolute amount in the raw leachate. The unaccounted portion (9.4% HA, 29.2% FA, 2.2% HPI, and 9.8% total TOC) was lost either in the degradation process or during separation (e.g., FA can be lost in the ion exchange resin column). The total COD concentration of the leachate in the feed solution increased significantly by 219.3%, from 10750 mg L^{-1} to 34340 mg L^{-1}. Meanwhile, the NH_3-N concentration increased by 31% (from 2900 to 3800 mg L^{-1}). The diluted draw contained 1367 mg L^{-1} NH_3-N, which was 51.2 % of the absolute amount (in mg) in the raw leachate, while the FO concentrate contained 41.2 % and the remaining 7.6 % was unaccounted for which might have lost during the measurement. The higher movement of NH_3-N (51.2%) compared to TOC (9.8%) to the draw side is because of the smaller hydrated radius (0.331 nm) and low molecular weight of ammonia compared to the wide array of organic compounds (Howitt & Udvardi, 2000).

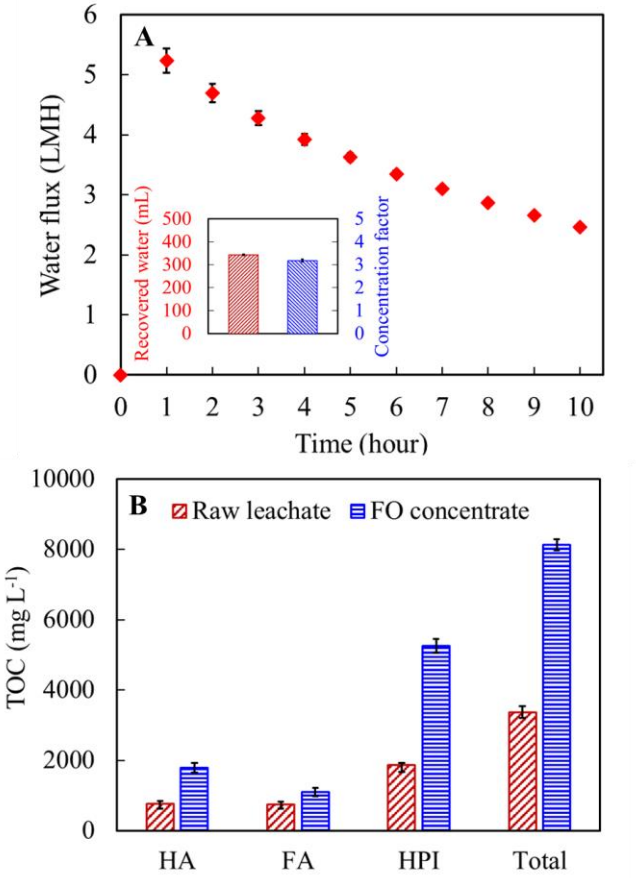

Figure 5-2. The performance of forward osmosis treatment of leachate with a 5-M NaCl draw solution: (A) water flux, recovered water, and concentration factor; and (B) Change in the different organic fractions (HA, humic acid; FA, fulvic acid; and HPI, hydrophilics) of leachate after forward osmosis concentration.

Humic acid recovery

HA was recovered from both raw and FO concentrated leachates at two pH, 1.5 and 2.0. The recovered HA from 1-L raw leachate at pH 1.5 and 2 was 1.85±0.03 g and 1.86±0.05 g, respectively (Fig. 5-3). This amount increased by 28.4 % to 2.37±0.26 g and 31.7 % to 2.45±0.32 g at pH 1.5 and 2 from 0.31-L FO concentrated leachate (which was generated from 1 L of raw leachate) (Fig. 5-3). Because of the insignificant difference between the recovered HA at pH 1.5 and 2.0 ($p > 0.05$), pH 2 was used in the rest of the study for HA recovery to reduce the inorganic acid consumption. Given that pH adjustment is a critical cost factor in treatment, more studies on the optimum pH for HA recovery from leachate, which can be specific to a leachate, are required.

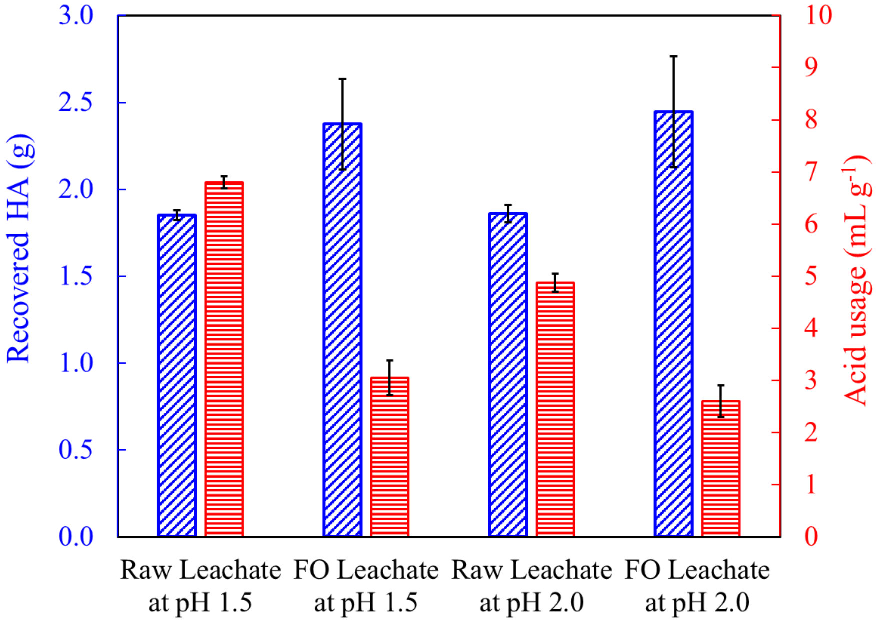

Figure 5-3. Absolute amount of recovered humic acid from leachate (1L of raw leachate and equivalent volume of FO concentrate) at pH 1.5 and 2.0 and corresponding inorganic acid (0.25-M H_2SO_4) usage.

After FO, the normalized mass percent increased for Na (1.25 to 2.95%), Mg (0.01 to 0.17%), Cl (3.49 to 9.54%), and K (0.63 to 1.62%) in the recovered HA. But, the mass percent of C stayed relatively stable and the mass percent of O decreased from 47.50 to 35.99%. The replacement of O with higher molecular weight elements such as Na, Cl, K, and Mg (Table 5-1) might have led to increased HA recovery. Some of those elements, such as K and Mg, are important nutrients for plant growth, and thus their increase after FO could be beneficial (Malhi et al., 2005). The O/C ratio in the recovered HA after FO decreased from 1.08 to 0.81; meanwhile, the absolute phenolic acidity decreased by 44.3% (7.0 to 3.9 meq) (Table S5-3). Those results indicate that the replacement of O by other elements might have happened in the weak acidity zones (i.e., phenolic acidity). Compared to a standard HA (Alfa Aesar), the C content of the recovered HA is almost twice; in addition, other elements such as Mg, P, S and K become higher. The higher carbon content is beneficial to improving soil stability because humic substances are central to enhanced soil aggregation (Haynes & Naidu, 1998).

Table 5-1. Elemental composition of a standard humic acid (Alfa Aesar) and the leachate humic acids.

Normalized Mass %	C	O	Na	Mg	Al	P	S	Cl	K
Standard HA	22.29	40.81	0.54	0.08	3.85	0.01	0.68	0.00	22.61
Leachate HA	44.15	47.50	1.25	0.01	0.09	0.24	4.22	3.49	0.63
FO Leachate HA	44.44	35.99	2.95	0.17	0.12	0.21	4.96	9.54	1.62

The inorganic acid requirement, normalized over the recovered HA, decreased after the FO treatment (Fig. 5-3). The acid usage decreased significantly from 6.80 to 3.05 mL g^{-1} (55.1% decrease, $p < 0.05$) at pH 1.5 and from 4.87 to 2.61 mL g^{-1} (46.4% decrease, $p < 0.05$) at pH 2.0. Such a decrease could be related to the decrease in the absolute alkalinity (266.0 to 177.6 meq) after FO, likely caused by the movement of the alkalinity causing species (i.e. HCO_3^-, CO_3^{2-}) from the feed (leachate) into the draw driven by a concentration gradient (Table S5-4). This movement resulted in 51.3±0.7 meq bicarbonate alkalinity in the draw solution. The pH of the draw solution increased from 5.74±0.03 to 8.35±0.01, at which bicarbonate species would dominate the alkalinity.

Fenton's oxidation of leachate

The removal of both COD and TOC by Fenton's oxidation, in each of the three Cases, has demonstrated similar behavior in terms of DOD effects and became less responsive to the increased DODs (i.e., increased reagent dose), probably because of the recalcitrance of the remaining organics (Jung et al., 2017; Wang et al., 2016). However, there are differences among those Cases and the overall COD and TOC removal performance were enhanced by HA recovery prior to Fenton's oxidation. The maximum COD removal in Case C with HA recovery was 80.3%, significantly higher ($p < 0.05$) than that in Case A

(75.2%) or B (74.0%) (Fig. 5-4A). The TOC removal in Case C at DODs 0.5 and 1.0 were significantly higher ($p < 0.05$) than that of Case B (Fig. 5-4B); however, at DOD 0.25 it was not significantly different, possibly because at this DOD, the ultimate degradation (i.e., conversion to CO_2) of the FA+HPI fraction in Case C was significantly lower than that at higher DODs. For instance, the removal of the FA+HPI fraction was 63.4 % at DOD 0.25, while it was higher at 75.6 % at DOD 0.5. Usually, HA can be converted into lower molecular weight organic fractions after oxidation (i.e., Fenton's), and those fractions exert lower COD than the initial (Jung et al. 2017, Wang et al. 2016). However, the recovery of HA prior to Fenton's oxidation has reduced the possibility of such conversion. Because of the interconversion of larger molecular weight organics, the decrease of TOC is always lower than the decrease of COD (Wang et al. 2016). For example, at DOD of 0.5, Case B had 74.0% COD decreased and 63.8% TOC decreased.

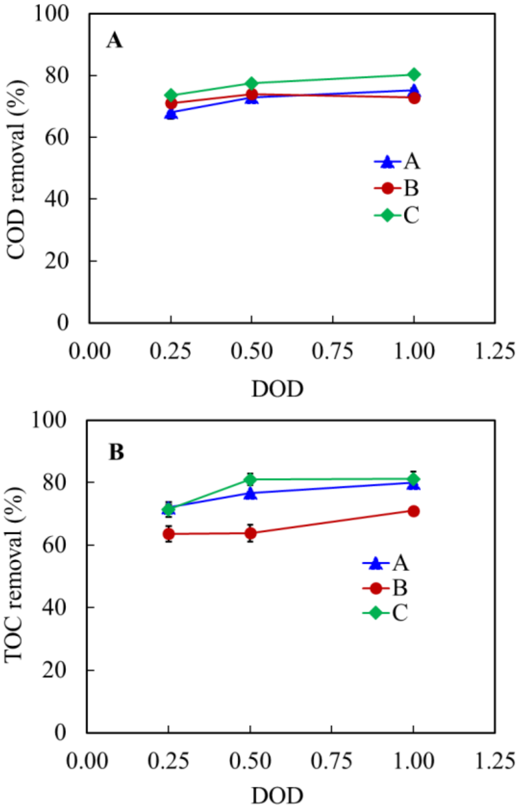

Figure 5-4. Chemical oxygen demand (COD) and total organic carbon (TOC) removal performance in three different experimental cases (A – C) at different dimensional oxidant doses (DODs) (Case A – Standalone Fenton's oxidation; Case B – FO + Fenton's oxidation; Case C – FO + HA recovery + Fenton's oxidation).

The removal of UV absorbance and NH_3-N were also enhanced by HA recovery prior to Fenton's oxidation. The UV absorbance removal in Case C (93.2 %) was higher than that in other two cases because the recovery of HA decreased the amount of UV quenching compounds that could have contributed around 47.5% of the total UV absorbance (Table S5-5). Due to the reduction of HA (SUVA = 5.15 ± 0.47 L mg^{-1} m^{-1}) prior to Fenton's oxidation, the final effluent SUVA was lower in Case C than other cases (Table S5-6). In all three cases, SUVA value decreased below 2 L mg^{-1} m^{-1} at all the DODs, proving that Fenton's oxidation has removed or converted most of the aromatic organic structures into aliphatic structures (Gupta et al. 2014, Wang et al. 2016). Like UV absorbance, NH_3-N removal was higher in Case C (55.5%) than that in Cases A and B, because of the removal of 1270 ± 90 mg L^{-1} NH_3-N (in HA) prior to Fenton's application (Table S5-7). The overall NH_3-N removal in Cases A and B was 11.0 to 31.6% (Table S5-7), indicating that hydroxyl radicals generated during Fenton's was not highly reactive to ammonia (Deng and Englehardt 2006). These results have clearly demonstrated that the recovery of HA prior to Fenton's oxidation can help enhance the removal of organics, UV absorbance, SUVA, and NH_3-N from leachate. The enhanced removal of UV absorbance and ammonia nitrogen prior to any biological co-treatment of leachate with conventional wastewater would help in terms of UV disinfection effectiveness and biological nitrogen removal (Reinhart and Bolyard 2015, Zhao et al. 2013a).

Reduction of reagent requirements and sludge production

Assuming the reagents requirement in Case A as "100%", the major reagents including $FeSO_4\,7H_2O$, H_2O_2, H_2SO_4, and NaOH have shown a generally decreasing trend in Cases B and C, though behaving differently (Fig. 5-5A). The volume of inorganic acid or base requirement normalized over g COD removed decreased after FO treatment and/or HA recovery. For example, at DOD 0.5, Case A consumed 1.05 mL 0.25-M H_2SO_4 per g of COD removed, which decreased to 0.72 mL 0.25-M H_2SO_4 per g of COD in Case B, and to 0.87 mL 0.25-M H_2SO_4 per g of COD in Case C (Fig. 5-5B). This corresponded to 38.4% and 25.2% decrease in H_2SO_4 requirement in Cases B and C compared to Case A (Fig. 5-5A). The possible reason was the decrease in absolute alkalinity of the raw leachate after FO treatment as discussed previously. A higher acid consumption in Case

C than that in Case B was due to the pH adjustment for HA recovery, although this consumption also served the purpose of initial pH adjustment for the subsequent Fenton's oxidation. Likewise, the consumption of base solution also decreased, from 5.92 mL 10-M NaOH per g COD removed in Case A to 5.53 mL 10-M NaOH per g COD in Case B, and to 4.19 mL 10-M NaOH per g COD in Case C (Fig. 5-5B). This decrease corresponded to 13.9% and 34.6% base decrease in Cases B and C compared to Case A (Fig. 5-5A). This decrease was mainly because of the lower $FeSO_4$ $7H_2O$ dose in Cases B and C than Case A attributed to the lower organics concentration after FO and HA recovery as the major base requirement in Fenton's comes from neutralization of residual Fe species into ferric-hydroxo complexes for effective coagulation removal of organics (Deng and Englehardt 2006, Kang and Hwang 2000, Neyens and Baeyens 2003). Besides, the decrease in base requirement was enhanced by the absolute acidity decrease of the FA+HPI fraction from 219±0.6 meq (raw leachate) to 89.1±1.1 meq after FO treatment and a reduction of 12.2 ± 0.1 meq absolute acidity from FO concentrate because of HA recovery (Table S5-3). The significantly higher COD removal in Case C compared to Cases A and B contributed as another factor for the significantly lower base requirement normalized over COD removed in Case C than Cases A and B. The consumption of $FeSO_4$ $7H_2O$ and H_2O_2 decreased by ~10% each for Case B and ~35% each for Case C compared to Case A, benefited from the lower COD concentrations attributed to the substrate movement to the FO draw side and HA recovery, respectively. These results demonstrate that the applications of FO and HA recovery can reduce the overall reagents requirement for Fenton's oxidation of leachate.

Another benefit of the HA recovery was the significant reduction of sludge generation from Fenton's oxidation. The absolute mass of generated sludge in Cases A and B at DOD 0.5 was 83.9±1.7 g and 76.4±1.4 g, respectively; this has significantly decreased to 59.5±1.2 g in Case C that had the HA recovery (Fig. 5-6). Sludge generation in Case B was 8.9 % lower ($p < 0.05$) than that in Case A (Fig. 5-6), likely because of the loss of organics during FO concentration, as demonstrated by 440 mg L^{-1} TOC in the FO draw solution (Table S5-2) which reduced the reagents dose requirements. The ~30% reduction in Fenton's sludge after FO treatment and HA recovery in Case C, which was also because of the lower Fenton's reagents dose, would greatly decrease the expense associated with sludge disposal.

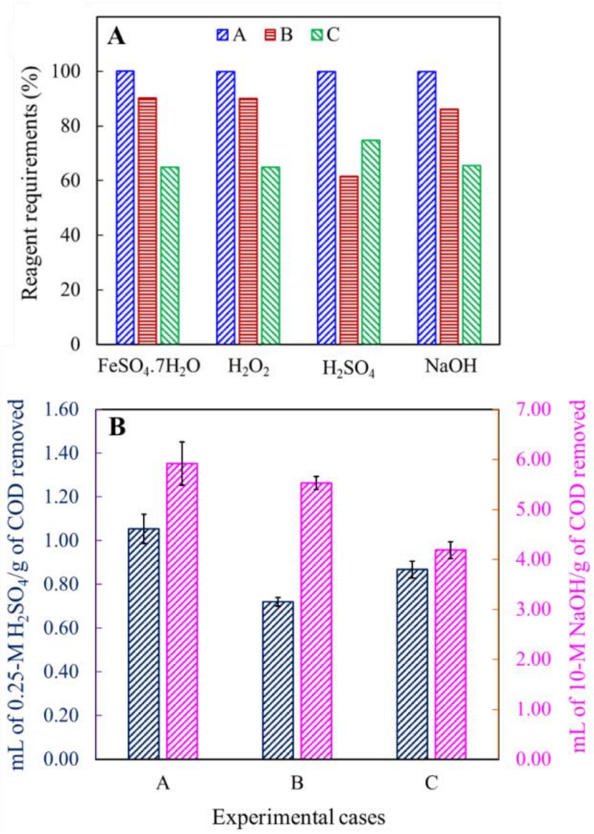

Figure 5-5. Reagent requirements at DOD = 0.5 in different experimental cases: (A) change in regent requirements (the reagent requirements for 1-L raw leachate was treated as "100%"): and (B) normalized requirement of acid and base (the volume of 0.25-M H_2SO_4 and 10-M NaOH required per g of COD removed) in three different experimental cases (Case A – Standalone Fenton's oxidation; Case B – FO + Fenton's oxidation; Case C – FO + HA recovery + Fenton's oxidation).

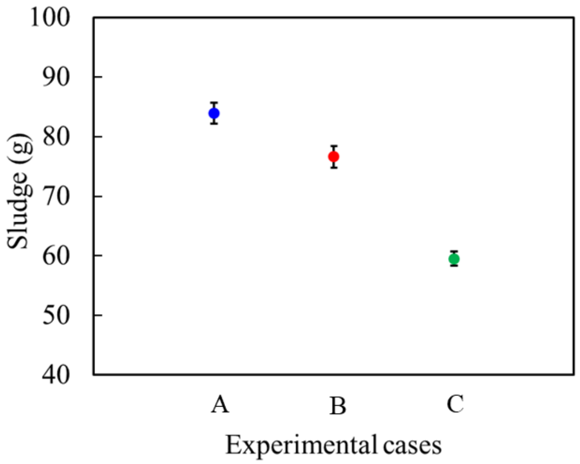

Figure 5-6. Sludge generation in three different experimental cases (A – C) (per 1-L raw leachate) at DOD 0.5 (Case A – Standalone Fenton's oxidation; Case B – FO + Fenton's oxidation; Case C – FO + HA recovery + Fenton's oxidation).

Perspectives

Despite the advantages and benefits demonstrated by the results, we must also note that the proposed system has two major challenges to address, water recovery from diluted draw solution from FO and applications of recovered HA. The concentrate from FO is further treated by HA recovery and Fenton's oxidation. The recovered water (diluted draw solution), on the other hand, will also need a post-treatment to separate draw solute and the recovered water to obtain reusable water. A typical separation method is to use reverse osmosis (RO), which can generate a high-quality water for either reuse or direct discharge. Although RO could be energy intensive, the diluted draw solution is a much simpler liquid than leachate, and thus it is expected to have less membrane fouling and energy consumption when treating the diluted draw solution. As discussed by Shaffer et al. 2015, the incorporation of RO as a post-treatment after FO can be more energy efficient for high strength wastewater (e.g., leachate) than an standalone RO unit. This is because of the lower susceptibility and higher reversibility of FO membrane fouling than RO.

The recovered HA may be used as fertilizer or soil amendments; though further purification would be needed. For agricultural applications, the composition may need adjustment as demonstrated by a previous study that amended an ultrafiltration recovered liquid HA with extra nutrients (N, P, and K) to meet the guideline of liquid fertilizers (Xu et al. 2017). The adjustment of the nutrients content can be accomplished by simple addition of external nutrients; however, the toxicity of the HA towards plants and soil microbial population should be determined. As discussed previously, the leachate recovered HA have a higher carbon content than the commercial counterpart. This is highly desirable for application as a soil stabilizer in regions where soil erosion is dominant. However, the toxicity to soil microbiota still needs careful investigation.

Conclusions

This study has presented a successful integration of FO and HA recovery with Fenton's oxidation to treat landfill leachate with notable benefits of reduced chemical reagents and decreased sludge production. Some specific conclusions are as follows:

- FO treatment has decreased the volume of leachate and also reduced its alkalinity attributed to the concentration gradient driven movement of the alkalinity causing species, resulting in the decreased H_2SO_4 requirement from 4.87 mL g^{-1} to 2.61 mL g^{-1} during the subsequent HA recovery at pH 2.
- HA recovery increased from 1.86 to 2.45 g L^{-1} at pH 2 after FO treatment of raw leachate, likely because of the replacement of O in the weak acidity zones of HA by other elements (i.e., Cl, Na, K) with higher molecular weight.
- The incorporation of HA recovery prior to Fenton's oxidation has improved the removal of COD, TOC, UV absorbance, and NH_3-N, benefited from the removal of humic substances during HA recovery.
- With both FO and HA recovery, the overall reagents requirement by Fenton's oxidation has decreased by 25.2% for H_2SO_4, 34.6% for NaOH, 35.1% for $FeSO_4$ $7H_2O$ and H_2O_2 at DOD 0.5.

- Sludge volume decreased significantly by 29.1%, mainly because of the lower reagent dose for lower organics concentrations. A smaller sludge generation will lower the requirement for handling of ferric based sludge.

Supporting Information

Table S5- 1. Different chemical properties of the leachate.

Parameters	**Values**
pH	8.46 ± 0.01
Alkalinity, meq L^{-1}	260±3
Conductivity, mS cm^{-1}	30.63 ± 0.19
UV absorbance, cm^{-1}	64.93 ± 0.22
COD, mg L^{-1}	10750 ± 520
BOD_5/COD	0.08
TOC, mg L^{-1}	3360 ± 180
HA, mg L^{-1}	765 ± 80
FA, mg L^{-1}	740 ± 85
HPI, mg L^{-1}	1860 ± 65
NH_3-N, mg L^{-1}	2900 ± 115
Na^+, mg L^{-1}	5691 ± 8
Cl^-, mg L^{-1}	4940 ± 16
K^+, mg L^{-1}	1586 ± 51
Mg^{2+}, mg L^{-1}	123 ± 4
Ca^{2+}, mg L^{-1}	57 ± 11

Table S5-2. Forward osmosis operation and performance.

FO operating conditions	Values
Draw volume (mL)	200
Draw type	5-M NaCl
Feed volume (mL)	500
Recirculation flow rate (mL min^{-1})	40
Operation time (h)	10
TOC in draw (mg L^{-1})	437 ± 5
HA in draw (mg L^{-1})	119 ± 2
FA in draw (mg L^{-1})	166 ± 7
HPI in draw (mg L^{-1})	152 ± 5
NH_3-N in draw (mg L^{-1})	1370 ± 90
RSF (gMH)	10.35 ± 0.50

Table S5-3. Acidity values of the leachate organic fractions.

Sample	Acidity (meq L^{-1})			Absolute acidity (meq)		
	Carboxylic acidity	Phenolic acidity	Total acidity	Carboxylic acidity	Phenolic acidity	Total acidity
HA (Raw leachate)	6.3±0.3	7.0±0.6	13.3±0.7	6.3±0.3	7.0±0.6	13.3±0.7
HA (FO concentrate)	26.3±0.3	12.3±0.3	38.7±0.3	8.3±0.1	3.9±0.1	12.2±0.1
FA+HPI (Raw Leachate)	29.7±0.3	189.3±0.7	219±0.6	29.7±0.3	189.3±0.7	219±0.6
FA+HPI (FO concentrate)	63.3±0.7	220.0±4.2	283.3±3.5	20.6±0.2	69.2±1.3	89.1±1.1

Table S5-4. Alkalinity values of the raw leachate and FO concentrate.

Sample	Alkalinity (meq L^{-1})			Absolute alkalinity (meq)		
	Carbonate alkalinity	Bicarbonate alkalinity	Total alkalinity	Carbonate alkalinity	Bicarbonate alkalinity	Total alkalinity
Raw Leachate	13.3±0.7	252.7±8.9	266.0±9.2	13.3±0.7	252.7±8.9	266.0±9.2
FO concentrate	28.0±7.2	536.7±12.0	564.7±13.8	8.8±2.3	168.8±3.8	177.6±4.3
Draw solution	0.3±0.1	94.3±1.2	94.7±1.3	0.2±0.1	51.3±0.7	51.5±0.7

Table S5-5. UV absorbance (cm^{-1}) at different experimental cases after Fenton oxidation.

Experimental cases	DOD	Leachate	UV absorbance, cm^{-1}		% Removal
			Before Fenton	After Fenton	
A	0.25	Raw	64.93 ± 0.22	17.07 ± 0.48	73.7
	0.5	Raw	64.93 ± 0.22	9.21 ± 0.53	85.8
	1	Raw	64.93 ± 0.22	6.95 ± 0.18	89.3
B	0.25	FO Concentrate	190.50 ± 2.11	33.30 ± 1.31	82.5
	0.5	FO Concentrate	190.50 ± 2.11	30.37 ± 1.09	84.1
	1	FO Concentrate	190.50 ± 2.11	21.77 ± 0.76	88.6
C	0.25	FO Concentrate (FA+HPI)	190.50 ± 2.11	22.44 ± 1.26	88.2
	0.5	FO Concentrate (FA+HPI)	190.50 ± 2.11	14.87 ± 0.53	92.2
	1	FO Concentrate (FA+HPI)	190.50 ± 2.11	12.91 ± 1.11	93.2

Table S5-6. Specific UV absorbance (L mg^{-1} m^{-1}) at different experimental cases after Fenton oxidation.

Experimental cases	DOD	Leachate	SUVA, Lmg^{-1} m^{-1} Before Fenton	SUVA, Lmg^{-1} m^{-1} After Fenton	% Change
A	0.25	Raw	1.94 ± 0.11	1.82 ± 0.01	- 6.2
	0.5	Raw	1.94 ± 0.11	1.18 ± 0.09	- 39.2
	1	Raw	1.94 ± 0.11	1.03 ± 0.03	- 46.9
B	0.25	FO Concentrate	2.34 ± 0.03	1.14 ± 0.11	- 51.3
	0.5	FO Concentrate	2.34 ± 0.03	1.04 ± 0.04	- 55.6
	1	FO Concentrate	2.34 ± 0.03	0.93 ± 0.07	- 60.3
C	0.25	FO Concentrate (FA+HPI)	2.34 ± 0.03	0.98 ± 0.09	- 58.1
	0.5	FO Concentrate (FA+HPI)	2.34 ± 0.03	0.98 ± 0.08	- 58.1
	1	FO Concentrate (FA+HPI)	2.34 ± 0.03	0.89 ± 0.18	- 62.0

Table S5-7. Ammonia nitrogen (NH_3-N) concentration (mg L^{-1}) at different experimental cases after Fenton oxidation.

Experimental cases	DOD	Leachate	NH_3-N, mg L^{-1}		% Removal
			Before Fenton	After Fenton	
A	0.25	Raw	2900 ± 115	2582 ± 184	11.0
	0.5	Raw	2900 ± 115	2322 ± 191	19.9
	1	Raw	2900 ± 115	2476 ± 138	14.6
B	0.25	FO Concentrate	3800 ± 115	2730 ± 200	28.2
	0.5	FO Concentrate	3800 ± 115	2650 ± 300	30.3
	1	FO Concentrate	3800 ± 115	2600 ± 250	31.6
C	0.25	FO Concentrate (FA+HPI)	3800 ± 115	1690 ± 120	55.5
	0.5	FO Concentrate (FA+HPI)	3800 ± 115	1833 ± 88	51.8
	1	FO Concentrate (FA+HPI)	3800 ± 115	2000 ± 150	47.4

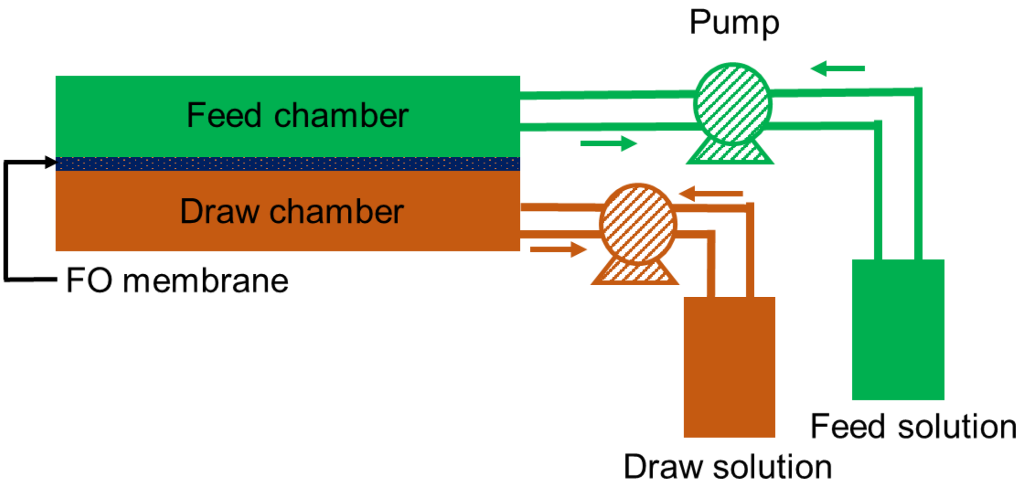

Figure S5- 1. Forward osmosis set up used in the study.

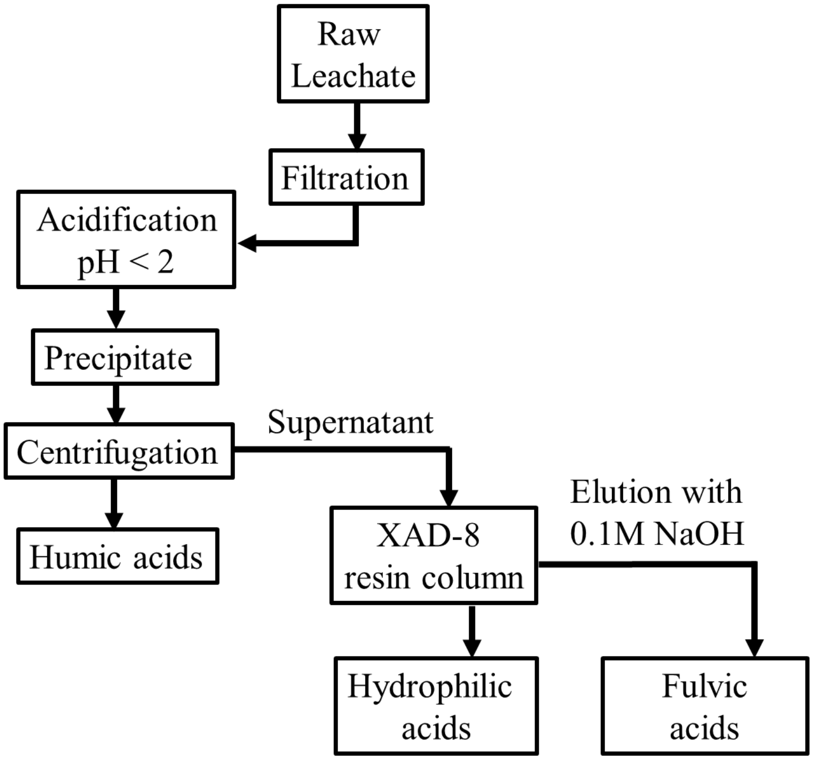

Figure S5-2. Fractionation process for separating leachate organics into humic, fulvic and hydrophilic acids.

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CHAPTER 6

Fenton’s oxidation of chloride-rich landfill leachate leads to disinfection byproducts formation

Abstract

Fenton’s oxidation is the most effective for landfill leachate treatment. Although effective, Fenton’s oxidation of landfill leachate can lead to the formation of disinfection byproducts (DBPs). We investigated five classes of these unwanted byproducts: Trihalomethanes, Haloacetic acids, Haloacetonitriles, Haloketones, and Halonitromethanes. As the H_2O_2: Cl^- molar ratio increased, DBP concentration increased due to the increased concentration of chlorine and bromine species. The highest DBP concentration was 4860 µg L^{-1} at an H_2O_2: Cl^- molar ratio of 4.0, the lowest DBP concentration was 84 µg L^{-1} at an H_2O_2: Cl^- molar ratio of 0.25. The reaction system generated chlorine and bromine species during the first five minutes of the reaction, leading to the instantaneous formation of DBPs. Moreover, DBPs were recalcitrant to hydroxyl radicals at higher organics concentrations. Due to this, the total DBP concentration remained stable at various reaction times. Trihalomethanes dominated the DBP concentration in most cases, while Haloactonitriles dominated total toxicity. The results indicate a tradeoff between COD removal and DBP concentration during Fenton’s oxidation of leachate, which requires further investigation.

Introduction

About half of the municipal solid waste in the US ends up in landfills. In a landfill, the combination of precipitation and solid waste degradation produce leachate, a complex wastewater (Kjeldsen et al. 2002, Renou et al. 2008). Leachate contains recalcitrant organics (i.e., humic and fulvic acids), inorganics (i.e., NH_4^+, Cl^-, Na^+), xenobiotics (i.e., aromatic compounds), and heavy metals (Kang et al. 2002, Kjeldsen et al. 2002). Among the various leachate treatments, biological co-treatment with sewage is the most common (Iskander et al. 2018). However, recalcitrant leachate organics, which is 10 to 1000 times stronger than sewage, can escape biological treatment and interfere with the final disinfection steps in wastewater treatment plants (Bolyard 2016, Li and Deng 2012, Zhao et al. 2013). Thus, other treatment approaches are receiving attention. Among them, Fenton's oxidation is the most effective for leachate treatment (Deng and Englehardt 2006). Fenton's is the reaction of ferrous salt and hydrogen peroxide that produces hydroxyl radical, a strong oxidizing agent, which can effectively degrade leachate organics (Hermosilla et al. 2009, Iskander et al. 2019, Walling 1975). It was reported that Fenton's oxidation can remove up to 90% of COD, 80% of TOC, and significantly increase the bioavailability (Deng and Englehardt 2006, Jung et al. 2017). The removal of the contaminants depends upon many factors including the molar ratio of H_2O_2 to Fe^{2+}, reaction time, initial pH, and temperature (Deng and Englehardt 2006, Gupta et al. 2014a).

Besides these factors, the presence of different anions in leachate can create unwanted consequences to Fenton's oxidation by reacting with H_2O_2 and oxidant radicals. Chlorides, which is one of the most abundant (150 – 4500 mg L^{-1}) inorganic ions in leachate, react with hydroxyl radical and goes through chain reactions that can yield free chlorine species (i.e., HOCl and Cl_2) (Gaca et al. 2005, J Whebi et al. 2010, Kjeldsen et al. 2002). The instantaneously produced free chlorine again reacts with abundantly present ammonia (typical concentration: 50 – 5000 mgL^{-1}) to produce combined chlorine (i.e., mono-, di-, and trichloramine) (Li and Deng 2012, Renou et al. 2008). In addition, Br^- and I^- can be oxidized to Br_2 and I_2 from reactions with H_2O_2 (J Whebi et al. 2010). Produced $HOCl/OCl^-$ can also oxidize bromide (Br^-) and iodide (I^-) into $HOBr/OBr^-$ and HOI/OI^- (Parker et al. 2014). These unwanted reactions along with leachate organics can generate disinfection byproducts. The presence of a large fraction (> 50%) of hydrophobic leachate organics (humic and fulvic acids) can accelerate the DBP formation (Gupta et al. 2014b, Iskander et al. 2018). A previous study demonstrated 110 times higher THMs formation potential during chlorination of landfill leachate compared to a WWTP effluent (Li and Deng 2012). These DBPs are carcinogens and mutagens (Li and Mitch 2018, Parker et al. 2014, Szczuka et al. 2017). Brominated and iodinated DBPs are more toxic than chlorinated counterpart (Li and Mitch 2018, Szczuka et al. 2017). The discharge of leachate after Fenton's oxidation treatment can cause the exposure of DBPs to human and aquatic animals and the environment.

It is evident that the molar ratio of H_2O_2 to Cl^- during Fenton's oxidation dictates the formation of free and combined chlorine. In Fenton's oxidation system, the ratio of H_2O_2 to Fe^{2+} may also dictate the formation of free chlorine; the less the fraction of Fe^{2+}, the higher the probability of the reaction of Cl^- and H_2O_2. Of more than 600 identified DBPs (Li and Mitch 2018), this study investigated four trihalomethanes (THMs), three haloacetonitriles (HANs), nine haloacetic acids (HAAs), two halo ketones (HKs), and one halonitromethanes (HNMs) (Table S6-1). Even if DBPs are produced in a Fenton's oxidation of leachate system, the simultaneous production of hydroxyl radical can destroy most of the DBPs. Thus, the objectives of this study are to: 1. investigate the effect of H_2O_2: Cl^- molar ratio on DBP formation; 2. investigate the effect of H_2O_2: Fe^{2+} molar ratio on DBP formation; 3. investigate the effect of reaction time on DBPs formation during Fenton's oxidation of landfill leachate, 4. investigate the effect of leachate type and organics on DBP formation.

Materials and methods

Landfill leachates

Landfill leachates were collected from two different cells of a landfill in Virginia, USA. The dark brown leachates, after collection, were immediately transferred to the lab and stored at 4°C for further use. The Leachate A had 6.14 pH, 37.1 mS cm^{-1} conductivity, 53800 mg L^{-1} COD, 2500 mg L^{-1} NH_3-N and the Leachate B had 7.80 pH, 23.2 mS cm^{-1} conductivity, 9800 mg L^{-1} COD, 2000 mg L^{-1} NH_3-N. The chemical properties of the leachates are given in Table S-2. The initial DBP concentration in the leachates are listed in the Table S6-3. Details of leachate characterization can be found in the SI (Text S6-1).

Experimental conditions

The first set of experiments were performed to investigate the effect of H_2O_2: Cl^- molar ratio on DBP formation during Fenton's oxidation of Leachate A. In this, H_2O_2 concentration was varied to create H_2O_2: Cl^- molar ratio of 0.25, 0.33. 0.5, 1.0, 2.0, 4.0. The H_2O_2: Fe^{2+} concentration was kept constant at 1.5 by adjusting the Fe^{2+} concentration with the changing H_2O_2 concentration. This ratio of H_2O_2: Fe^{2+} = 1.5 was chosen because it is the optimum for batch Fenton's oxidation of leachate (Hermosilla et al. 2009, Zhang et al. 2005). The total reaction time was fixed at 2 hours. In the second set of experiments, the effect of H_2O_2: Fe^{2+} molar ratio on DBP formation was investigated. In this, the initial H_2O_2 concentration was kept constant at 0.35 M (corresponding to H_2O_2: Cl^- = 2.0), while the concentration of Fe^{2+} was decreased to create H_2O_2: Fe^{2+} molar ratios of 1.0, 1.5, 2.0, 2.5, 3.0, and 3.5. The reaction time was same as the first set. In the third set of experiments, the effect of reaction time on DBP formation was investigated. For this, the H_2O_2: Cl^- molar ratio of 2.0 and H_2O_2: Fe^{2+} molar ratio of 1.5 was investigated. Eleven different reaction times (1 min., 2 min., 3 min., 4 min., 5 min., 30 min.,1 hr., 1.5 hr., 2.0 hr., 2.5 hr., and 3.0 hr.) were investigated to understand the evolution of DBPs during Fenton's oxidation of landfill leachate. To understand the effect of leachate type on DBP formation, in the fourth set of experiments, a new leachate (Leachate B; the first three sets of experiments were conducted with Leachate A) was investigated for DBP formation at H_2O_2: Cl^- molar ratio of 2.0 and H_2O_2: Fe^{2+} molar ration of 1.5 during a 2 hours reaction time. The Leachate B was also amended with NaCl (Fisher Scientific, Hampton, NH) and NaBr (Fisher Scientific, Hampton, NH) to make the concentration of Cl^- and Br^- same as Leachate A (Table 6S-2). Fenton's oxidation was also performed for the amended Leachate B at H_2O_2: Cl^- = 2.0, H_2O_2: Fe^{2+} = 1.5 and 2-hours reaction time.

Fenton's oxidation

Fenton's oxidation was performed in triplicates in 220 mL snap cap plastic bottles (Weber Scientific, Hamilton, NJ). Prior to oxidation, the pH of the raw leachates was adjusted to 3 by adding 0.25-M H_2SO_4 (Fisher Scientific, Hampton, NH). 150 mL pH adjusted leachate was used in each plastic reactor. After that, $FeSO_4.7H_2O$ (Fisher Scientific, Hampton, NH) was added in the reactor and mixed for five minutes at 1000 rpm using an IKA RO 10 multi-position magnetic stirrer (Wilmington, NC, USA) followed by the addition of a specific volume of 30% (wt.%) H_2O_2 solution (Fisher Scientific, Hampton, NH). The reaction typically continued for 2 hours at ~800 rpm mixing unless otherwise stated. Once the reaction was over, 31 mg L^{-1} L-ascorbic acid

(Fisher Scientific, Hampton, NH) was added to quench the residual chlorine in the system (Zeng and Mitch 2015, 2016). Finally, 10-M NaOH (Fisher Scientific, Hampton, NH) solution was added to the reactant to adjust the pH to 6.5 to complete the coagulation. The sample was then centrifuged for 10 minutes at 5000 rpm (Beckman Coulter, Brea, CA) and filtered through 1.5 µm filter for DBP extraction.

Extraction and analysis

For THMs, HANs, HKs, and HNMs, 50 mL 1.5 µm filtered sample was collected and extracted using EPA method 551.1. For HAA analysis, 40 mL 1.5 µm filtered sample was collected and extracted using EPA method 552.3. The detail of the extraction and analysis can be found in the Text S6-2. Minitab® 18 was used for performing statistical analysis (two sample t-test and one-way ANOVA) using a confidence interval of 95%. Bromine incorporation factor (BIF) for the THMs was calculated using the following equation according to a previous literature (Zeng et al. 2016).

BIF = $\frac{[BDCM]+2[DBCM]+3[TBM]}{[TCM]+[BDCM]+[DBCM]+[TBM]}$; Here the concentration of each species is in molar basis.

Because, DBP toxicity differs from species to species, it is important that both concentration and toxicity of DBPs be considered to conclude about their overall impact. The DBP toxicity was calculated by dividing their concentration with the harmful concentration determined in toxicological assays that can cause adverse health effects (Zeng et al. 2016). DBP toxicities are considered additive (Stork et al. 2007, Tang et al. 2013, Yeatts et al. 2010). For all the DBP classes investigated, the DBP concentration that caused a 50% reduction of Chinese hamster ovary (CHO) cell counts compared to the untreated controls were used as the adverse concentration (Zeng et al. 2016). The CHO LC_{50} values for THMs (Plewa et al. 2002), HAAs (Plewa et al. 2010), HANs (Muellner et al. 2007), and HNMs (Plewa et al. 2004) are listed in Table S6-4. This is not a conservative estimate since the LC_{50} value corresponds to the concentration that kills 50% of the treated cells; extrapolation for human exposure can be a difficult task (Zeng et al. 2016). Two haloketones 1,1-Dichloro-2-Propanone and 1,1,1-Trichloropropanone were not included in the toxicity calculation, because neither the CHO cell LC_{50} values or the 10^{-6} lifetime cancer risk data were available (Zeng et al. 2016).

Results and discussions

Effect of H_2O_2 to Cl^- molar ratio on DBP formation

The total DBP concentration decreased significantly with the decrease of H_2O_2: Cl^- molar ratios, which could be because of the production of lesser concentration chlorine and bromine species as the H_2O_2: Cl^- molar ratio decreased (Fig. 6-1A; Fig. S6-1). In most of the cases, chlorine and bromine species were generated and available for the first five minutes of the reactions. It was found that the maximum free chlorine concentration in H_2O_2: Cl^- = 2.0 (H_2O_2: Fe^{2+} = 1.5) was 2.7 times higher (26.7 vs 10 mg L^{-1}) than that of H_2O_2: Cl^- = 0.25 (H_2O_2: Fe^{2+} = 1.5) (Fig. S6-1). The maximum total chlorine and total bromine for H_2O_2: Cl^- = 2 (H_2O_2: Fe^{2+} = 1.5) were 9.0 (240.0 vs 26.7 mg L^{-1}) and 12.5 (456.7 vs 36.7 mg L^{-1}) times higher than that of H_2O_2: Cl^- = 0.25 (H_2O_2: Fe^{2+} = 1.5) (Fig. S6-1). Of the investigated DBP classes, THMs, HANs, HKs showed significant decrease ($p<0.5$) with the decrease of the H_2O_2: Cl^- molar ratios. Decrease of HAAs were not as responsive as these DBP classes with the change of H_2O_2: Cl^- molar ratios. HNMs did not show any trend with the change of H_2O_2: Cl^- molar ratios. HNMs concentration in all the cases was similar to the initial concentration found in the raw leachate (Fig.6-1A; Table S6-3). This could be because trichloronitromethane is probably resistant to hydroxyl radicals at higher organics concentration; this is less likely that TCNM was formed and degraded simultaneously in the reaction system that kept its concentration constant. Of the DBP classes, THMs constituted about ~80% of the total DBP concentration at H_2O_2: Cl^- molar ratios of 4.0, 2.0, and 1. This ranged from 32 to 59% for the H_2O_2: Cl^- molar ratios of 0.5, 0.33 and 0.25 (Fig. 6-1B). This is probably because the concentration decrese of other DBP classes were not as dominant as THMs. The contribution of HANs remained in the range of 12.9 to 19.3 % for all the H_2O_2: Cl^- molar ratios. However, the relative percentage of HAAs and HNMs increased as the H_2O_2: Cl^- molar ratio decreased (Fig. 6-1B). This was mainly because other DBP classes concentration decreased significantly with the decrease of the H_2O_2: Cl^- molar ratio, while insignificant or no change of concentration for HAAs and HNMs were observed.

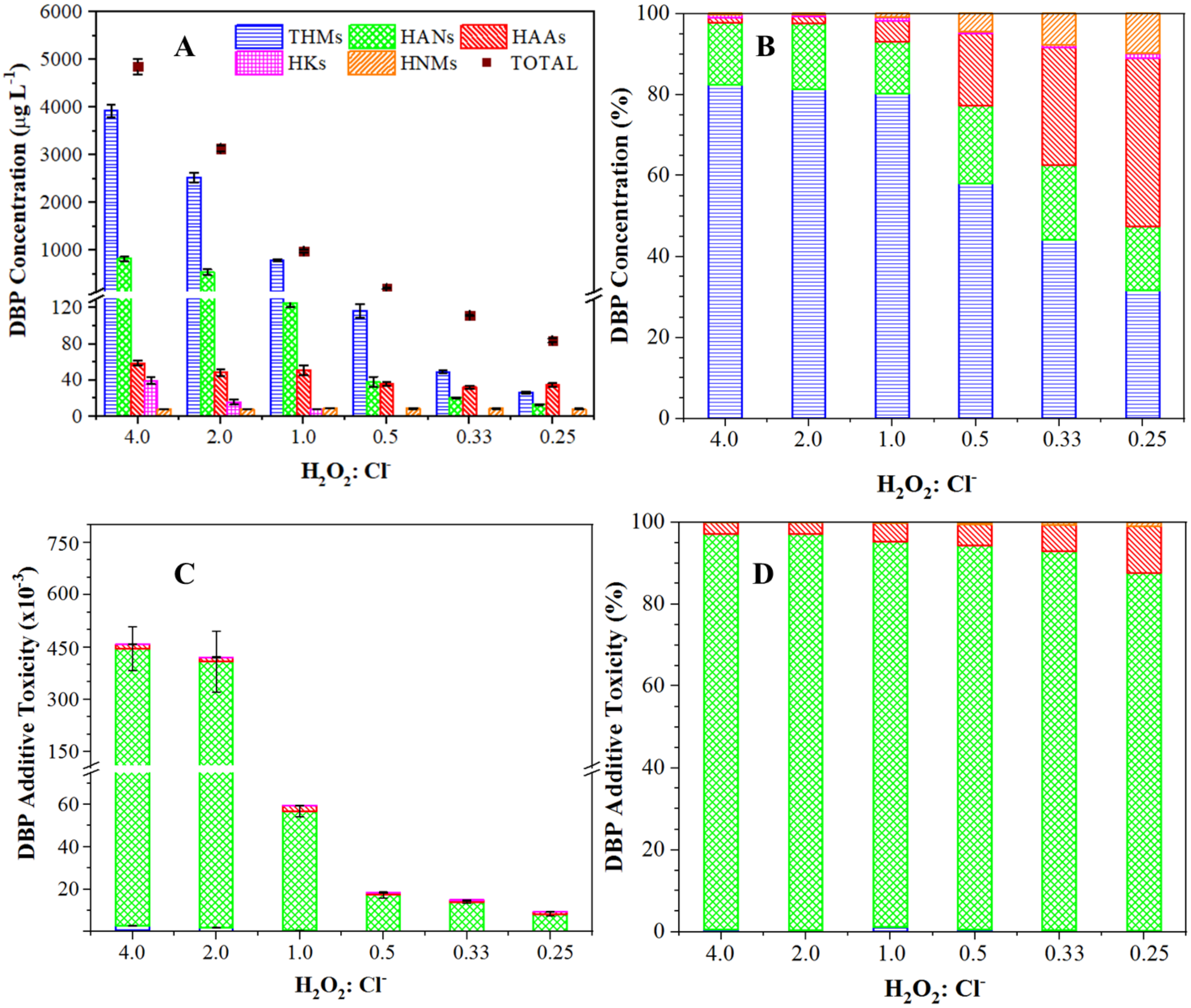

Figure 6-1. A. DBP concentration at different H_2O_2: Cl^- molar ratios (Cl^- concentration was constant; H_2O_2: Fe^{2+} = 1.5); B. Relative contribution of the DBP classes to the total concentration of DBPs; C. DBP additive toxicity for different classes of DBPs at different H_2O_2: Cl^- molar ratios (Cl^- concentration was constant; H_2O_2: Fe^{2+} = 1.5); and D. Relative contribution of the DBP classes to the DBP additive toxicity.

The produced DBPs during Fenton's oxidation of leachate can have significant environmental implications. The treated leachate may end up in the natural water bodies through treatment in wastewater treatment plants. Eventually it may end up in potable water reuse systems or hamper the aquatic life and human through different exposure routes. The lowest concentration of THM_4 was 26.5±1.4 µg L^{-1} for H_2O_2: Cl^- molar ratio of 0.25, while the highest (3928.6±133.2 µg L^{-1}) was for H_2O_2: Cl^- molar ratio of 4.0. The concentration for THM_4 was within the regulated drinking water standard of 80 µg L^{-1} (Li and Mitch 2018) for H_2O_2: Cl^- molar ratio of 0.33 and 0.25, while the concentration was 1.5 to 49.1 times higher than the regulated standard for H_2O_2: Cl^- molar ratio of 0.5 to 4.0. The concentration of HAA_9 was in the range of 32.4 to 58.8 µg L^{-1}. Considering only the regulated HAA_5 (MCAA, MBAA, DBAA, DCAA, TCAA), this concentration was in the range of 0.37 to 17.3 µg L^{-1}, which is within the range of the regulated drinking water standard of 60 µg L^{-1} for HAA_5 (Li and Mitch 2018). Although there is no regulated limit for HANs, HKs, and HNMs, the concentration of these exceeded the commonly reported values in treated wastewater. Thus, it is evident that Fenton's oxidation of landfill leachate can produce a significant amount of DBPs in the finished effluent. Fenton's is considered the best treatment for landfill leachate, while the DBP formation issue was unknown. Thus, it is of concern to figure out an optimum dose of the reagents based on the chemical properties of leachates and treatment performance. It is evident that Fenton's oxidation of landfill leachate should be conducted at lower H_2O_2: Cl^- molar ratio to reduce the formation of DBPs. However, there is a tradeoff between COD removal and DBP formation. With the increase of H_2O_2: Cl^- molar ratios, the COD removal increased (Fig. S6-2), likely because of the production of more hydroxyl radicals that degrades organics. Thus, a reasonable COD removal should be targeted while keeping the DBP concentration within the regulated limit.

In terms of toxicity of the DBP classes, the associated additive toxicities decreased with the decrease of H_2O_2 to Cl^- molar ratio, which ranged from 9.4 x 10^{-3} to 460 x 10^{-3} (Fig. 6-1C). The lowest toxicity was at H_2O_2: Cl^- = 0.25, while the highest for H_2O_2: Cl^- = 4.0. This is because of the reduction of the DBP concentration with the decrease of H_2O_2: Cl^- molar ratio. The additive toxicity values are more than 10 to 1000 times than the values reported in previous literatures. Among different DBP classes, HAN contributed more than 90% of the toxicity at all the H_2O_2: Cl^- molar ratios except 87.4% for 0.25 (Fig. 6-1D). This is because of the higher toxicity of the HANs than other DBPs (Table S4). Of the HANs, DCAN and DBAN were detected in the reaction system and DBAN was the major contributor to the toxicity of HAN. This can be explained by the 20-fold lower CHO LC_{50} value of DBAN than DCAN (Table S6-4). Of the other DBPs, HAAs contributed 2.9 to 11.4% of the total additive toxicity, and the proportion increased as the H_2O_2: Cl^- ratio decreased (Fig. 6-1D). This is because of the percentage contribution of the HAAs to the DBP concentration increased as the H_2O_2: Cl^- ratio decreased (Fig. 6-1 B). Additionally, the concentration and toxicity of HANs decreased with the decrease of H_2O_2: Cl^- molar ratios. The additive toxicity contributed by HAAs ranged from 0.95 x10^{-3} to 13.2 x 10^{-3}, which is higher than previous literature. The other two classes of DBPs, THMs and HNMs, contributed 0.26 – 1.1% and 0.02 – 0.99% of the total additive toxicity. Although THMs dominated the total DBP concentration (32.0 to 81.4 %), the higher CHO LC_{50} values compared to other DBP classes contributed to their lower additive toxicity (Table S6-4). The lower concentration and associated lower toxicity were responsible for the lower toxicity contribution from HNMs.

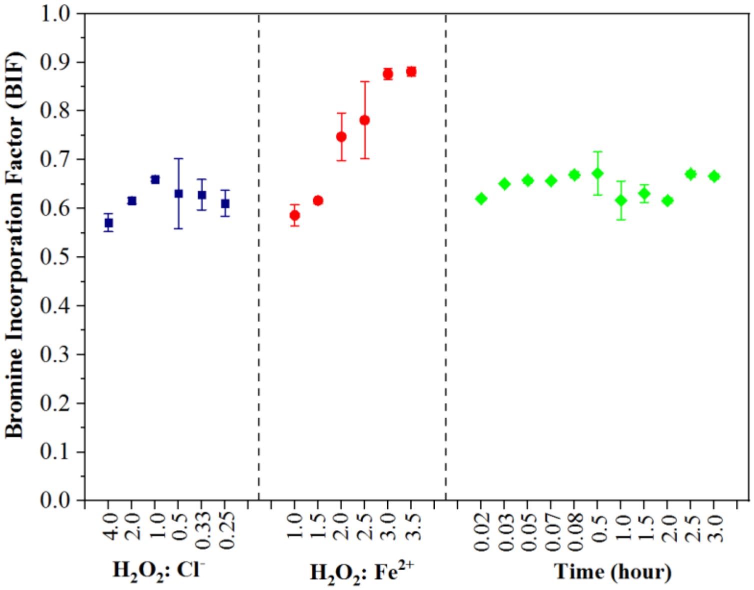

Figure 6-2. Bromine incorporation factor (BIF) at different H_2O_2: Cl^- molar ratios, H_2O_2: Fe^{2+} molar ratios, and reaction times.

The bromine incorporation factor for THMs remained in the range of 0.57 – 0.66 for different H_2O_2: Cl^- molar ratios (Fig. 6-2). This indicates that the increase of THMs with the increase of H_2O_2: Cl^- ratio was because of the increase of the DBP concentration, not because of the bromine incorporation in different THM species (Zeng et al. 2016). The bromine incorporation increased with the H_2O_2: Fe^{2+} increase. This is also depicted by the 2.6 times increase of the bromoform concentration from H_2O_2: Fe^{2+} = 1 to 3.5. The BIF values for at different time points ranged from 0.62 – 0.67. This short range is indicative of the similar initial reagent concentrations and indicate that the reaction time doesn’t impact bromine incorporation in THMs.

Effect of H_2O_2 to Fe^{2+}molar ratio on DBP formation

The DBP concentration increased with the increase of the H_2O_2: Fe^{2+} molar ratios. Overall, the total DBP concentration was lower for H_2O_2: Fe^{2+} molar ratios of 1 and 1.5 compared to others (2.0 to 3.5) (Fig. 6-3A). There was no significant difference among the DBP concentrations for H_2O_2: Fe^{2+} molar ratios from 2 to 3.5. THMs and HANs were the major contributor to the DBP concentration in all the cases. For THMs, the percent contribution ranged from 64.7 to 84.9% and this decreased as the molar ratio increased (Fig. 6-3B). This could be because of the higher increase of the HAN concentration compared to THM concentration and due to this, the percent contribution for HAN (12.9 to 33.5%) increased with the increase of the H_2O_2: Fe^{2+} molar ratios. HAAs and HNMs contributed slightly to the total DBP concentrations in all the cases. DBP additive toxicity ranged from ($180x10^{-3}$) to ($1317x10^{-3}$) and it was lower (180 to 420 $x10^{-3}$) for H_2O_2: Fe^{2+} = 1 and 1.5 molar ratios than higher ratios (Fig. 6-3C). The higher additive toxicity at higher molar ratios was mainly because of the higher concentration of HANs with increased molar ratios. Thus, this can be an interesting outcome for Fenton’s oxidation of leachate. The H_2O_2: Fe^{2+} molar ratios to some extents dictates the DBP toxicity in landfill leachate during Fenton’s oxidation. In terms of the relative contribution of the DBP classes to the total additive toxicity, HAN contributed more than 95% of the total toxicity (Fig. 6-3D).

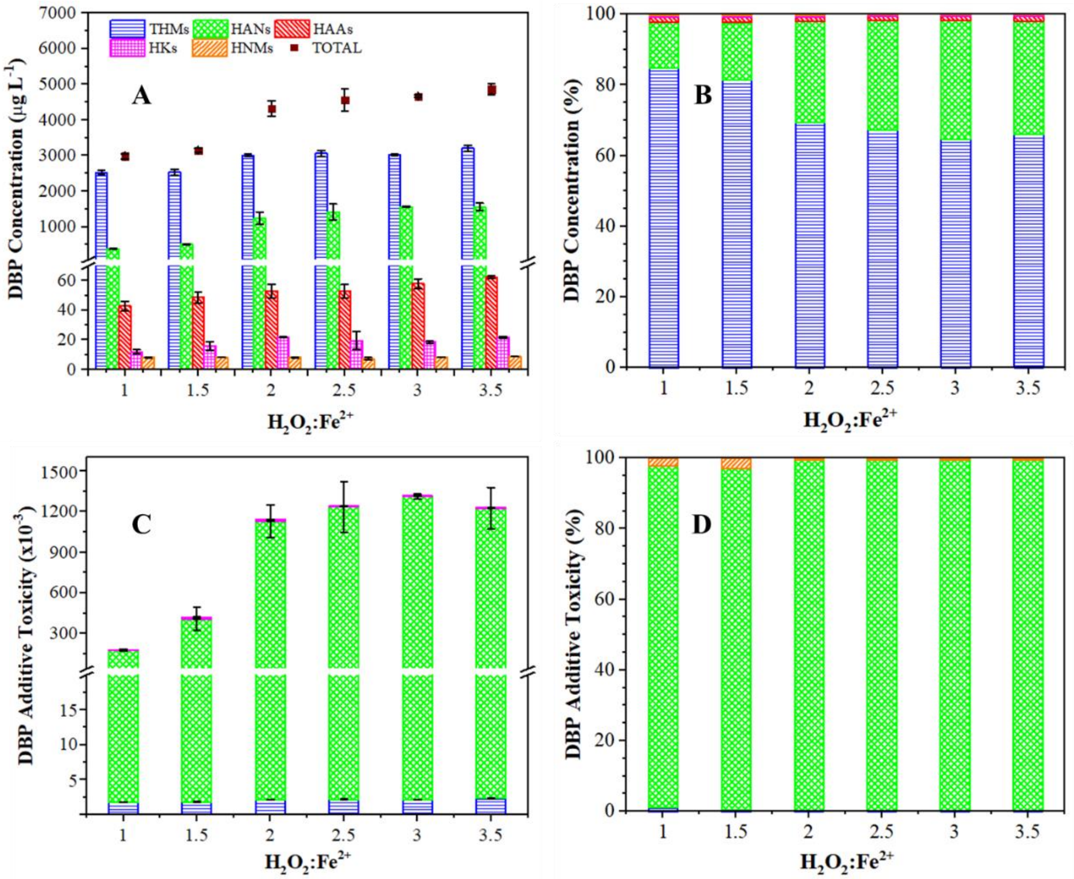

Figure 6-3. A. DBP concentration at different H_2O_2: Fe^{2+} molar ratios (H_2O_2: Cl^- = 2, Reaction time = 2 hours); B. Relative contribution of the DBP classes to the total concentration of DBPs; C. DBP additive toxicity for different classes of DBPs at different H_2O_2: Fe^{2+} molar ratios; and D. Relative contribution of the DBP classes to the DBP additive toxicity.

Effect of reaction time on DBP formation

The DBP concentration stayed consistent for all the DBP classes with the increase of the reaction time (Fig. 6-4). It is surprising that most of the DBPs were formed during the first minute of the reaction and stayed consistent over the reaction period up to 3 hours. There can be two reasons behind this: 1. the DBPs are probably unreactive to hydroxyl radicals at higher organics concentration, or 2. the DBPs were probably formed and destroyed at the same rate which kept the concentration of the total and individual DBPs almost constant over time. Nevertheless, this is difficult to measure. However, from the evolution of the chlorine and bromine species (Fig. S6-1), it is evident that the DBPs were formed during the first five minutes of the reaction and stayed stable for the rest of the reaction. The total DBP concentration evolution followed the trend of THMs, which is because THMs contributed 70 – 81% of the total DBPs at all time points (Fig. S6-3A). The other contributors to the total DBP concentration was HANs (16 to 27%) followed by HAAs (~2%), HKs (~0.5%), and HNMs (~0.3%) (Fig. S6-3A). The additive toxicity values ranged from 317 to 501 (x10^{-3}) (Fig. S6-3B). Because of the higher toxicity of the HANs compared to other DBP classes, expectedly, over 95% of the DBP toxicity was contributed by the HANs (Fig. S6-3C). The COD removal performance improved with time and became stable after 0.5 hour (Fig. S6-2C). Thus, in terms of reaction time, no strong tradeoffs exist between DBPs concentration and organics removal.

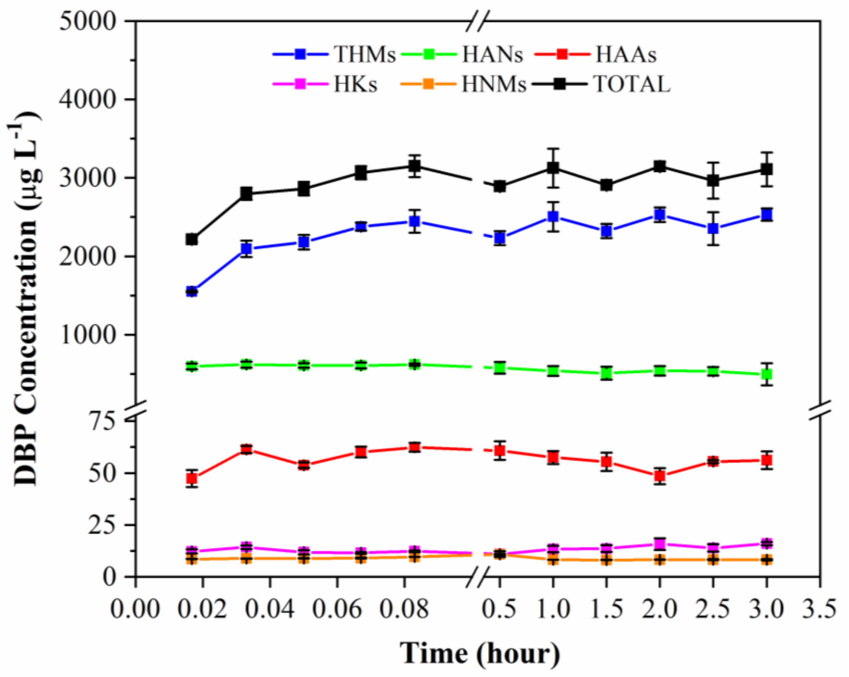

Figure 6-4. DBP concentration at different reaction times (H_2O_2: Cl^- = 2 and H_2O_2: Fe^{2+} = 1.5).

Effects of leachate type on DBP formation

The initial concentration of chloride and bromide dictated the DBP formation during Fenton's oxidation, while the organics concentration and types demonstrated no or insignificant effect. Comparing Leachate B and Leachate A show significant difference in

DBP concentration (534 vs 3135 µg L^{-1}) (Fig. 6-5A). The possible reason was the higher initial concentration of chloride and bromide (Table S6-2) in Leachate A than in Leachate B, which yielded higher concentration of chlorine and bromine species during Fenton's oxidation. When Leachate B was amended with chloride and bromide to make the concentration same as the Leachate A, the system produced similar concentration of total DBPs (3232 vs 3135 µg L^{-1}) (Fig. 6-5A). Thus, it is evident that the initial concentration of the organics had minimal effect on the DBP concentration during Fenton's oxidation of landfill leachate. Rather, the concentration of chloride and bromide played the major role. In terms of DBP classes, lower HANs concentration was observed for Amended Leachate B than Leachate A (375 vs 540 µg L^{-1}), while for THMs, HAAs, and HKs it was vice versa (Fig. 6-5; S6-4A). Due to the higher concentration of HANs for Leachate A, the additive toxicity was higher than Amended Leachate B (Fig. 6-5B) and around 95% was contributed by the HAN only (Fig. S6-4B). For Amended Leachate B, ~80% toxicity was contributed by HANs, while the other ~20% by HAAs (Fig. S6-4B). The leachate organics types and dissolved organic nitrogen (Table S6-2) could have played a role in these variations of DBP species concentration between the two leachates.

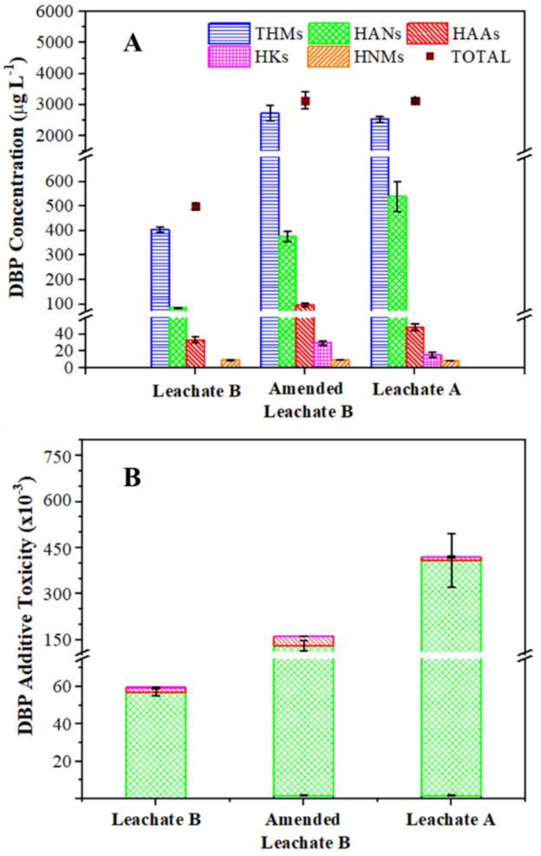

Figure 6-5. Comparison of DBP concentration and DBP additive toxicity between Leachate A and Leachate B (H_2O_2: Cl^- = 2.0; H_2O_2: Fe^{2+} = 1.5, reaction time = 2hr.); Amended Leachate B contains the same concentration of Cl^- and Br^- as Leachate A.

This study did not look for iodinated DBPs because of the presence of the undetectable concentration of iodide. Iodinated DBPs are more cytotoxic and genotoxic than its chlorinated and brominated counterparts (Richardson et al. 2008). Considering the high ammonia concentration in leachate, chloramination would be more dominant than chlorination. Both NH_2Cl and HOCl can oxidize iodide (I^-) to HOI, but the oxidation pathway of HOCl and I^- generates less harmful iodate (IO_3^-), which reduces the iodinated DBP formation potential (Bichsel and von Gunten 2000, Jones et al. 2011, Szczuka et al. 2017). Although reduced, studies have proved the formation of I-THMs during chlorination of iodide containing water (Parker et al. 2014). Thus, iodinated DBPs should get consideration for leachate with higher concentration of iodide.

Conclusions

This study has proved the formation of DBPs during Fenton's oxidation of landfill leachate. To date, Fenton's has been considered the best for leachate treatment, while the issue of DBP formation was unknown. This study is the first to report this. This study can be an eye opener as this DBP formation during advanced oxidation can also happen for chloride rich industrial wastewater. Thus, more study is required to figure out a clear-cut relationship with Fenton's oxidation and DBP formation. Because of the wide variability of leachate types and organics, this is evident that more studies are required to see the effect of organic types of leachate on DBP formation.

Supporting Information

Text S1. *Characterization of landfill leachates*

pH and conductivity of the leachates were measured using a benchtop pH meter (OAKTON Instruments, Vernon Hills, IL USA) and a benchtop conductivity meter (Mettler-Toledo, Columbus, OH, USA). NH_3-N and COD were measured with a spectrophotometer according to the manufacturer's instructions (DR 890, HACH, Loveland, CO). Total dissolved nitrogen was measured using HACH persulfate digestion method. BOD_5 was measured following a standard procedure (APHA et al. 2005). Iodometric titration (Schumb et al. 1955) was used to measure H_2O_2 concentration and no detectable H_2O_2 was present at the end of the reactions. UV_{254} absorbance (cm^{-1}) was measured using a spectrophotometer (Beckman Coulter, Brea, CA). The leachate was fractionated into humic, fulvic, and hydrophilic acid fractions according to previous studies (Christensen et al. 1998, Iskander et al. 2017a). At first leachate was filtered through 0.45-µm filter (Fisher Scientific, Hampton, NH) to remove suspended particles. After that, the pH of the filtered leachate was reduced to 2 by adding 0.25-M H_2SO_4 to precipitate the humic acid fraction. The solution was further centrifuged ((Beckman Coulter, Brea, CA) at 8000 rpm for 30 min to separate all the humic acid from solution. The supernatant was filtered through 1.5-µm filter (LabFilterz, P. City, CA) and passed at 1 mL min^{-1} through an ion exchange resin column (Amberlite® XAD-8 ion-exchange resin, Sigma Aldrich, St. Louis, MO). The hydrophilic fraction was the passed through fraction and the fulvic acid was sorbed on the resin. The sorbed fulvic acid was back eluted at 1 mL min^{-1} using 0.1 M NaOH solution. The precipitated humic acid was also dissolved in 0.1 M NaOH solution for quantification. Each fraction was quantified by TOC measurement with a TOC-VCSN (Shimadzu, Japan). Specific UV absorbance (SUVA) was calculated by dividing the UV absorbance with TOC concentration (Iskander et al. 2017b). Concentration of different ions (anions and cations) were measured using ion chromatography (Dionex LC20 ion chromatograph, Sunnnyvale, USA) in combination with an ED_{40} electrochemical detector. The free and total chlorine, and total bromine concentrations were measured using *N,N-diethyl-p-phenylenediamine* (DPD) colorimetric method (HACH, Loveland, CO).

Text S2. ***Extraction and analysis***

For THMs, HANs, HKs, and HNMs 50 mL 1.5 µm filtered sample was collected and extracted using EPA method 551.1. Calibration standard was purchased from Chem Service Inc. (West Chester, PA) and decafluorobiphenyl solution (Chem Service Inc, West Chester, PA) was used as the surrogate. The detail of the extraction is in Text S1. At first, 50 mL sample was collected in a 60 mL glass vial. In each vial 1 g of phosphate buffer reagent was added and gently mixed. This buffer was added to bring the pH of the sample in the range of 4.8 to 5.5 to stop the base catalyzed hydrolysis of haloacetonitriles. The buffer was prepared by mixing the granular form of 1% sodium phosphate dibasic (Na_2HPO_4, Fisher Scientific, Hampton, NH) and 99% potassium phosphate monobasic (KH_2PO_4, (Fisher Scientific, Hampton, NH) by weight. In each vial, 6 mg of dechlorinating agent (NH_4Cl, Fisher Scientific, Hampton, NH) was added. This addition was simplified by making a homogeneous mixture of 1.2 g of NH_4Cl and 200 g of phosphate buffer. After that 30 µL of 50 mg L^{-1} surrogate was added in each sample and gently mixed. This followed by the addition of 10 g NaCl (Fisher Scientific, Hampton, NH; baked for 30 min at 400°C) in each vial. After that, 3 mL of MTBE (Fisher Scientific, Hampton, NH) was added in each vial, recapped, and shaked vigorously for at least four minutes. The vial was kept at rest to allow the separation of the MTBE and sample. After five minutes, 1 mL of MTBE was separated using a Pasteur pipette in an autosampler vial.

For HAA analysis, 40 mL 1.5 µm filtered sample was collected and extracted using EPA method 552.3. HAA standards (Sigma Aldrich, St. Louis, MO) were used to generate the calibration curve and 2,3 – dibromopropionic acid (Sigma Aldrich, St. Louis, MO) was used as the internal standard. The Was used to generate calibration curve. Initially, 40 mL sample was separated in a 40 mL vail followed by the addition of 10 µL of 100 mg L^{-1} internal standard. The vail was capped and mixed once after the addition of the internal standard. After that 2 mL concentrated H_2SO_4 was added, capped and shaked to ensured that pH of the sample is less than 1. pH was checked with a pH paper. This step followed by a quick addition of 16 g Na_2SO_4 (Fisher Scientific, Hampton, NH; baked in a muffle furnace at 300°C for 60 minutes) in the vial. Hand mixing was done for five minutes to dissolve most of the solids. After that, 4 mL of MTBE was added and vigorously shaked for 2 minutes. The vial cap was loosened to vent several times and recapped during this mixing. The vail was kept undisturbed for 5 minutes to separate the upper MTBE layer. Approximately 3 mL of the upper MTBE layer was separated using a Pasteur pipette to a 15 mL test tube. This was followed by an addition of 1 mL 10% sulfuric acid in methanol in the test tube. After gentle mixing, the test tube was kept in a 50ºC heating block for 2 hours. Once the heated sample came at room temperature, 4 mL saturated sodium bicarbonate was added in 1 mL increments. The mixture was capped and mixed for 2 minutes. During this period, the test tube was vented several times. After the test tube was kept for 5 minutes undisturbed, 1 mL upper MTBE layer was transferred to an autosampler vial using a Pasteur pipette. The extracted samples were analyzed immediately or kept in ≤ -10ºC and analyzed within 7 days.

The extracted samples were analyzed using a HP Agilent 6890 GC Series Gas Chromatograph (Agilent, Santa Clara, CA) coupled with an electron capture detector. The column used for THMs, HANs, HKs, and HNMs was a Rxi-624Sil MS fused silica (Restek, Bellefonte, PA) and for HAA Supelco SPB 1701fused silica (Sigma Aldrich, St. Louis, Missouri).

HP Agilent 6890 GC Series Gas Chromatograph

THMs, HANs, HKs, HNMs

GC Column: Restek 13868
Restek Rxi-624Sil MS: 30 meters (length) X 0.25 mm (ID) X 1.4 µm (film thickness)
Column flow: 1 ml min^{-1}

Injector setting (front injector):
Temperature: 200ºC
Carrier: Helium gas
Injection mode: Split less

Temperature mode:
Temperature hold at 40ºC for 10 minutes
Increase of temperature at a rate of 10ºC $minute^{-1}$ to 145ºC and hold for 2 minutes
Increase temperature at a rate of 20ºC $minute^{-1}$ to 225ºC and hold for 3 minutes
Total runtime is 30 minutes

ECD (Electron Capture Detector) settings (back detector):
Temperature: 275ºC
Makeup flow (Nitrogen): 59 mL min^{-1}
Total makeup (makeup + column flow): 60 mL min^{-1}

HAAs
GC column: Supelco 24113
SPB 1701: 30 meters (length) X 0.25 mm (ID) X 0.25 µm (film thickness)
Column flow: 1 mL min^{-1}
Injector settings (Front injector):
Temperature: 210C
Carrier: He
Injection mode: Splitless

Temperature program:
Temperature hold at 40ºC for 10 minutes
Increase temperature at a rate of 2.5ºC $minute^{-1}$ to 65ºC and hold for 0 minutes.
Increase temperature at a rate of 10ºC $minute^{-1}$ to 85ºC and hold for 0 minutes.
Increase temperature at a rate of 20ºC $minute^{-1}$ to 200ºC and hold for 0 minutes.
Total runtime is 27.75 minutes.

ECD (Electron Capture Detector) settings (back detector):
Temperature: 275ºC
Makeup flow (Nitrogen): 59 mL $minute^{-1}$
Total makeup (makeup + column flow): 60 mL $minute^{-1}$

Table S6- 1. The DBPs investigated in the study.

Disinfection byproducts (DBPs) classes
Trihalomethanes (THMs)
Chloroform (TCM)
Dichlorobromomethane (DCBM)
Dibromochloromethane (DBCM)
Bromoform (TBM)
Haloactonitriles (HANs)
Trichloroacetonitrile (TCAN)
Dichloroacetonitrile (DCAN)
Dibromoacetonitrile (DBAN)
Haloacetic acids (HAAs)
Methyl chloroacetic acid (MCAA)
Methyl bromoacetic acid (MBAA)
Dichloroacetic acid (DCAA)
Trichloroacetic acid (TCAA)
Bromochloroacetic acid (BCAA)
Bromodichloroacetic acid (BDCAA)
Dibromoacetic acid (DBAA)
Chlorodibromoacetic acid (CDBAA)
Tribromoacetic acid (TBAA)
Haloketones (HKs)
1,1-Dichloro-2-Propanone (1,1-DCP)
1,1,1-Trichloropropanone (1,1,1-TCP)
Halonitromethanes (HNMs)
Trichloronitromethane (TCNM)

Table S6- 2. Chemical properties of the leachates used in this study.

Parameters	**Leachate A**	**Leachate B**
pH	6.14±0.01	7.8±00.01
Conductivity (mS cm^{-1})	37.1±0.01	23.2±0.01
COD (mg L^{-1})	53800±1850	9800±213
TOC (mg L^{-1})	17900±300	4425±145
Humic acid (mg L^{-1})	1992±65	27±1.5
Fulvic acid (mg L^{-1})	2773±66	1485±25
Hydrophilic acid (mg L-1)	13790±149	3084±60
Cl^- (mg L^{-1})	6400±115	2163±13
Br^- (mg L^{-1})	93.7±1.5	6.0±0.58
NH_3 (mg N L^{-1})	2500±150	2000±100
NO_3 (mg N L^{-1})	0.00±0.00	0.00±0.00
NO_2 (mg N L^{-1})	0.00±0.00	0.00±0.00
TDN (mg N L^{-1})	2840±80	2240±60
UV_{254} (cm^{-1})	137.83±0.15	15.27±0.23
$SUVA_{254}$ (L $mg^{-1}m^{-1}$)	0.77±0.01	0.35±0.02

Table S6- 3. Initial disinfection byproducts (DBPs) concentration in the raw leachates.

Disinfection byproducts	**DBP concentration (µg L-1)**	
	Leachate A	Leachate B
Trihalomethanes (THMs)	**3.09±0.07**	**1.68±0.11**
Chloroform (TCM)	2.48±0.05	1.68±0.11
Dichlorobromomethane (DCBM)	0.62±0.02	0.00±0.00
Dibromochloromethane (DBCM)	0.00±0.00	0.00±0.00
Bromoform (TBM)	0.00±0.00	0.00±0.00
Haloactonitriles (HANs)	**4.33±1.47**	**0.00±0.00**
Trichloroacetonitrile (TCAN)	0.00±0.00	0.00±0.00
Dichloroacetonitrile (DCAN)	0.33±0.01	0.00±0.00
Dibromoacetonitrile (DBAN)	4.00±1.48	0.00±0.00
Haloacetic acids (HAAs)	**0.18±0.01**	**0.05±0.03**
Methyl chloroacetic acid (MCAA)	0.00±0.00	0.00±0.00
Methyl bromoacetic acid (MBAA)	0.00±0.00	0.00±0.00
Dichloroacetic acid (DCAA)	0.00±0.00	0.00±0.00
Trichloroacetic acid (TCAA)	0.00±0.00	0.00±0.00
Bromochloroacetic acid (BCAA)	0.09±0.01	0.05±0.03
Bromodichloroacetic acid (BDCAA)	0.00±0.00	0.00±0.00
Dibromoacetic acid (DBAA)	0.00±0.00	0.00±0.00
Chlorodibromoacetic acid (CDBAA)	0.04±0.01	0.00±0.00
Tribromoacetic acid (TBAA)	0.06±0.01	0.00±0.00
Haloketones (HKs)	**0.00±0.00**	**0.00±0.00**
1,1-Dichloro-2-Propanone (1,1-DCP)	0.00±0.00	0.00±0.00
1,1,1-Trichloropropanone (1,1,1-TCP)	0.00±0.00	0.00±0.00
Halonitromethanes (HNMs)	**10.18±0.20**	**8.69±1.36**
Trichloronitromethane (TCNM)	10.18±0.20	8.69±1.36

Table S6- 4. Molecular weight and LC_{50} values of different DBP classes investigated in this study.

DBP classes	MW (g mol^{-1})	LC_{50} (M)	Reference
Trihalomethanes (THMs)			
Chloroform (TCM)	119.38	9.17E-03	(Plewa et al. 2002)
Bromodichloromethane (BDCM)	163.80	1.15E-02	
Dibromochloromethane (DBCM)	208.28	5.36E-03	
Bromoform (TBM)	252.73	3.96E-03	
Haloacetonitriles (HANs)			
Dichloroacetonitrile (DCAN)	109.94	5.73E-05	(Muellner et al. 2007)
Bromochloroacetonitrile (BCAN)	154.39	8.46E-06	
Dibromoacetonitrile (DBAN)	198.85	2.85E-06	
Trichloroacetonitrile (TCAN)	144.38	1.60E-04	
Halonitromethanes (HNMs)			
Trichloronitromethane (TCNM)	164.38	5.36E-04	(Plewa et al. 2004)
Haloacetic acids (HAAs)			
Methyl chloroacetic acid (MCAA)	94.49	8.48E-04	(Plewa et al. 2010)
Methyl bromoacetic acid (MBAA)	138.95	9.60E-06	
Dichloroacetic acid (DCAA)	128.94	7.30E-03	
Trichloroacetic acid (TCAA)	163.38	2.40E-03	
Bromochloroacetic acid (BCAA)	173.39	7.78E-04	
Bromodichloro acetic acid (BDCAA)	207.83	6.85E-04	
Dibromoacetic acid (DBAA)	217.84	5.21E-04	
Chlorodibromoacetic acid (CDBAA)	252.34	2.00E-04	
Tribromoacetic acid (TBAA)	296.74	8.50E-05	
Haloketones (HKs)			
1,1-Dichloro-2-Propanone (1,1-DCP)	126.96	NA	NA
1,1,1-Trichloropropanone (1,1,1-TCP)	147.42	NA	

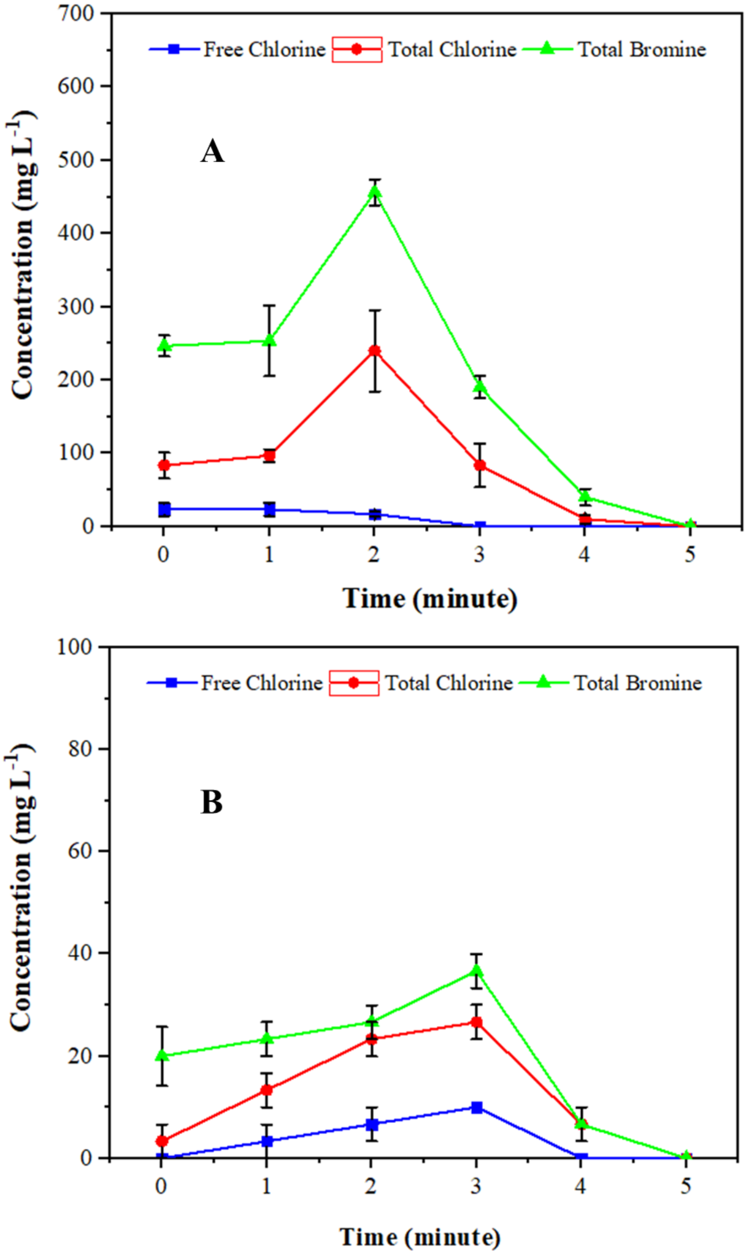

Figure S6- 1. Chlorine and Bromine species generated in the reaction systems: A. H_2O_2: Cl^- = 2, H_2O_2: Fe^{2+} = 1.5, Reaction time = 2 hours; B. H_2O_2: Cl^- = 0.25, H_2O_2: Fe^{2+} = 1.5, Reaction time = 2 hours.

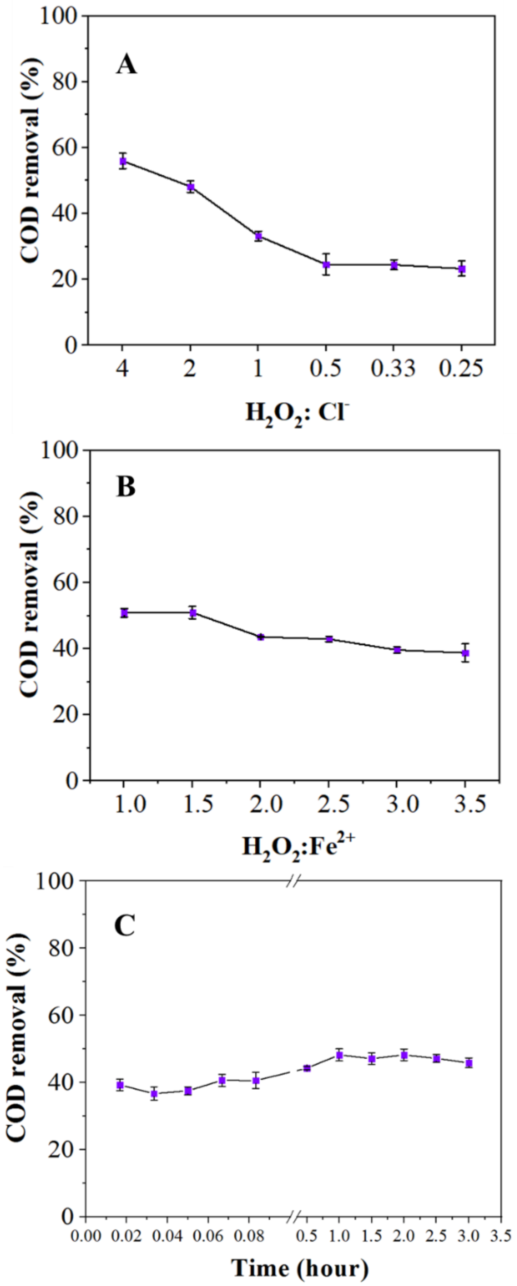

Figure S6- 2. Chemical oxygen demand (COD) removal performance at different experimental conditions: A. at different H_2O_2: Cl^- molar ratios (H_2O_2: Fe^{2+} = 1.5, Reaction time = 2 hours); B. at different H_2O_2: Fe^{2+} molar ratios (H_2O_2: Cl^- = 2.0, Reaction time = 2 hours); and C. at different reaction times (H_2O_2: Cl^- = 2.0 and H_2O_2: Fe^{2+} = 1.5).

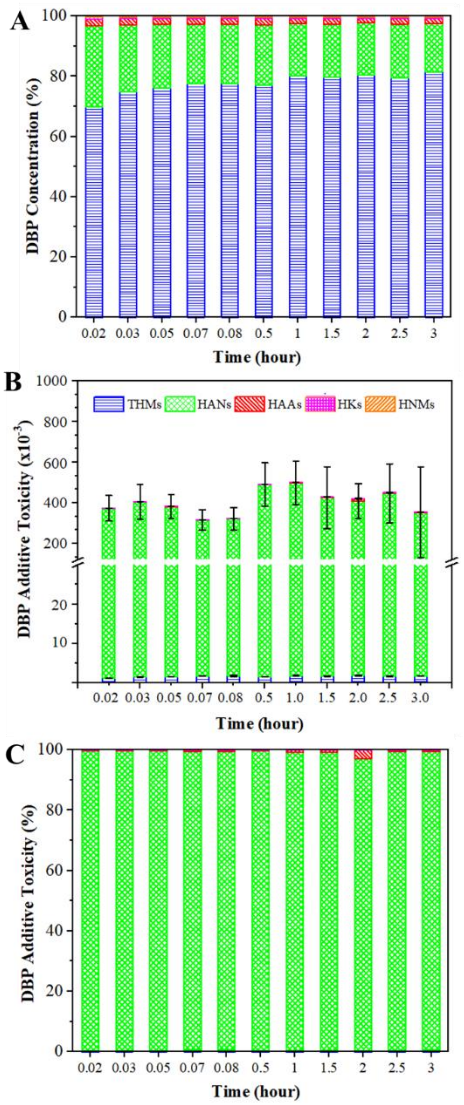

Figure S6- 3. A. The relative contribution of the DBP classes to the total concentration of DBPs at different reaction times (H_2O_2: Cl^- = 2 and H_2O_2: Fe^{2+} = 1.5); B. DBP additive toxicity for different classes of the DBPs at different reaction times (H_2O_2: Cl^- = 2 and H_2O_2: Fe^{2+} = 1.5); and C. The relative contribution of the DBP classes to the DBP additive toxicity at different reaction times (H_2O_2: Cl^- = 2 and H_2O_2: Fe^{2+} = 1.5).

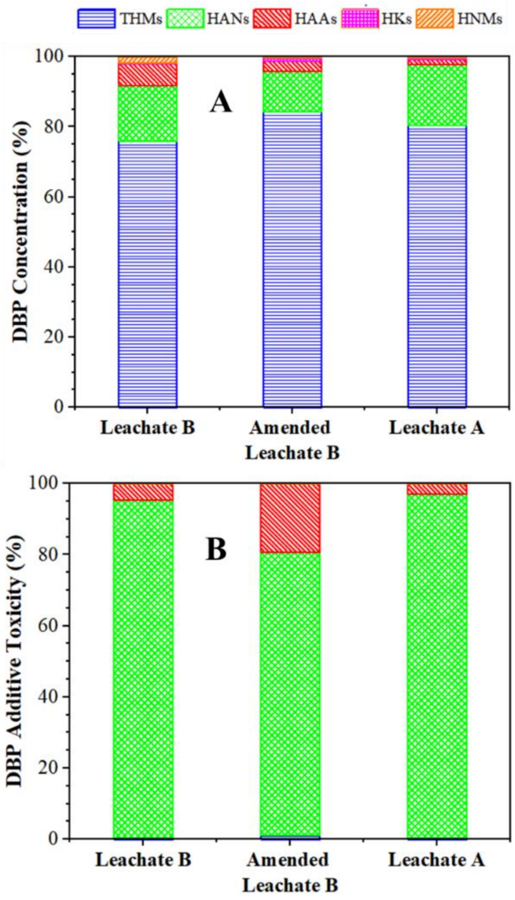

Figure S6- 4. A. The relative contribution of the DBP classes to the total concentration of DBPs (H_2O_2: Cl^- = 2, H_2O_2: Fe^{2+} = 1.5, Reaction time = 2 hours) for different leachates; B. The relative contribution of the DBP classes to the DBP additive toxicity for different leachates.

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CHAPTER 7

Simultaneous Energy Generation and UV Quenchers Removal from Landfill Leachate Using a Microbial Fuel Cell

Abstract

The presence of UV quenching compounds in landfill leachate can negatively affect UV disinfection in a wastewater treatment plant when leachate is co-treated. Herein, a microbial fuel cell (MFC) was investigated to remove UV quenchers from a landfill leachate with simultaneous bioelectricity generation. The key operating parameters including hydraulic retention time (HRT), anolyte recirculation rate, and external resistance were systematically studied to maximize energy recovery and UV absorbance reduction. It was found that nearly 50% UV absorbance was reduced under a condition of HRT 40 days, continuous anolyte recirculation, and 10 Ω external resistance. Further analysis showed a total reduction of organics by 75.3%, including the reduction of humic acids (95.2%), fulvic acids (77.2%), and hydrophilic fraction concentration as TOC (67.5%). The MFC consumed 0.056 kWh m^{-3} by its pump system for recirculation and oxygen supply. A reduced HRT of 20 days with periodical anode recirculation (1 hour in every 24 hours) and 39 Ω external resistance (equal to the internal resistance of the MFC) resulted in the highest net energy of 0.123 kWh m^{-3}. Granular activated carbon (GAC) acted as an effective post-treatment step and could achieve 89.1% UV absorbance reduction with 40 g L^{-1}. The combined MFC and GAC treatment could reduce 92.9% of UV absorbance and remove 89.7% of UV quenchers. This study encourages further exploration of using MFCs as an energy-efficient method for removing UV quenchers from landfill leachate.

Introduction

Landfill leachate is a complex wastewater that is produced from the degradation of decomposable waste within landfills and water precipitation (Ghosh et al. 2015). Among myriad contaminants, leachate contains a substantial amount of organics, which can be divided into humic acids, fulvic acids, and a hydrophilic fraction (Renou et al. 2008). Both humic and fulvic acids can constitute 70 – 80% of mature leachate's organics (Christensen et al. 1998; Zhang et al. 2009). In a young leachate, the hydrophilic fraction can be the dominating organic fraction (Christensen et al. 1998). These hydrophobic (humic and fulvic acids) and hydrophilic organics are called ultraviolet (UV) quenchers and can hinder UV application in wastewater treatment plants by negatively affecting disinfection (Dahlen et al. 1996; Gupta et al. 2014; Imai et al. 2002). Due to their recalcitrance to conventional biological treatment, there has been a considerable amount of research on UV quenchers of landfill leachate and there is an urgent need to find an effective way to reduce the concentrations of UV quenchers in landfill leachate before its discharge to conventional municipal wastewater treatment plants.

Most of the studies for removing UV quenchers from landfill leachate involved advanced oxidation. For example, Fenton oxidation is effective in removing UV quenchers from landfill leachate. A previous study showed a removal of 85% humic acids from landfill leachate by coagulation assisted Fenton reactions (Wu et al. 2010). Fenton was able to reduce 97% of UV absorbance of humic acids and 92% of UV absorbance from hydrophilics (Gupta et al. 2014). Ozonation was able to reduce 58% of UV absorbance by partial degradation of fulvic and hydrophilics and complete degradation of humic acids from reverse osmosis – nanofiltration treated concentrated leachate brine (Wang et al. 2016). Electrocoagulation was reported to remove humic like substances from wastewater by using iron as sacrificial anode electrode (Kliaugaite et al. 2013). However, these proven techniques have issues with cost and intricacy in applications. For example, Fenton requires an optimum pH of 2-4 and produces a substantial volume of sludge (Xu et al. 2017; Zhang et al. 2005). Biological treatment is usually low cost and can remove biodegradable portion of UV quenchers from landfill leachate. A study showed 16% removal of organics from landfill leachate using a sequential batch reactor (SBR), with a minimal or no removal of the hydrophilic fraction (Cui et al. 2016). Using powdered activated carbon (PAC) as a posttreatment step of a SBR system could significantly improve the removal of both total organic carbon and UV absorbance (Zhao et al. 2012).

Landfill leachate contains chemical energy that may be recovered to offset the treatment consumption. In addition to biogas production by a conventional anaerobic digester (Xia et al. 2016), bioelectricity can also be generated from landfill leachate by bioelectrochemical systems (BES) (Damiano et al. 2014; Iskander et al. 2016). BES use microorganisms as biocatalysts to realize organic oxidation and electron transfer to a solid electron acceptor; as a result, bioelectricity is generated (Kim et al. 2015). Commonly studied BES include microbial fuel cells (MFCs), microbial electrolysis cells (MECs), and microbial desalination cells (MDCs) (Rozendal et al. 2008). The removal of organics in a BES ranged from 40% to over 80%, which was largely dependent on bioavailability of leachates (Ozkaya et al. 2013; Zhang et al. 2015). Fermentation pretreatment was able to improve the performance of an MEC in terms of organics removal and electricity generation (Mahmoud et al. 2014). Nutrient removal is also a key interest to BES treatment of leachate, because of a large amount of ammonia in landfill leachate. BES could achieve ammonia removal ranging from 0% to 90%, affected by retention time, electricity generation, and presence of effective microbes (GaneshandJambeck 2013; Zhang et al. 2015). The power production from leachate could be as high as 12.8 W m^{-3} (current density 41 A m^{-3}) (Zhang et al. 2008). Despite the importance of energy performance (He 2017), only one study has reported energy production of 0.00190 kWh per kg of COD from landfill leachate in an MFC (ZhangandHe 2013).

The feasibility of organics removal and electricity generation from landfill leachate by BES encourage further exploration of other key issues such as UV absorbance and UV quenchers' fate after BES treatment. In addition, the missing parameters such as energy consumption and production during leachate treatment by BES require more investigation. In this study, an MFC was employed to treat a landfill leachate with a focus on removing UV quenchers. Energy performance was also investigated in detail. The specific objectives of this study were to: (1) investigate the effects of MFC operating conditions on energy generation; (2) examine the reduction of UV absorbance and removal of UV quenchers from landfill leachate; and (3) employ granular activated carbon (GAC) as post-treatment to enhance the removal of both organics and UV quenchers.

Materials and Methods

MFC setup

A tubular MFC was used in this study, consisting of an anode chamber (800 mL) and a cathode chamber (1000 mL) (Fig. 7-1). The separator between the anode and cathode chamber was a piece of cation exchange membrane (CEM, Membrane International Inc., Ringwood, NJ, USA) that was folded in a tubular shape to create the anode chamber. A 32-cm long carbon brush was used as an anode electrode (Gordon Brush Mfg. Co. Inc., Commerce, CA, USA). Before use, the carbon brush was soaked in acetone for 24 hours and heat treated in a muffle furnace (Model 550 Isotemp Series, Fisher Scientific, Pittsburgh, PA, USA) for 30 mins at 450 °C. The cathode electrode was made of carbon cloth with an active area of 450 cm^2. The carbon cloth was coated with 5 mg cm^{-2} activated carbon powder (Thermo Fisher Scientific, Bridgewater, NJ, USA) by using a binder agent (15% polytetrafluoroethylene (PTFE) solution) and subsequent heat treatment at 370 °C for 30 mins. The anode was inoculated with anaerobic sludge from a local wastewater treatment plant (Christiansburg, VA, USA). The aeration to the cathode chamber was provided by a peristaltic pump.

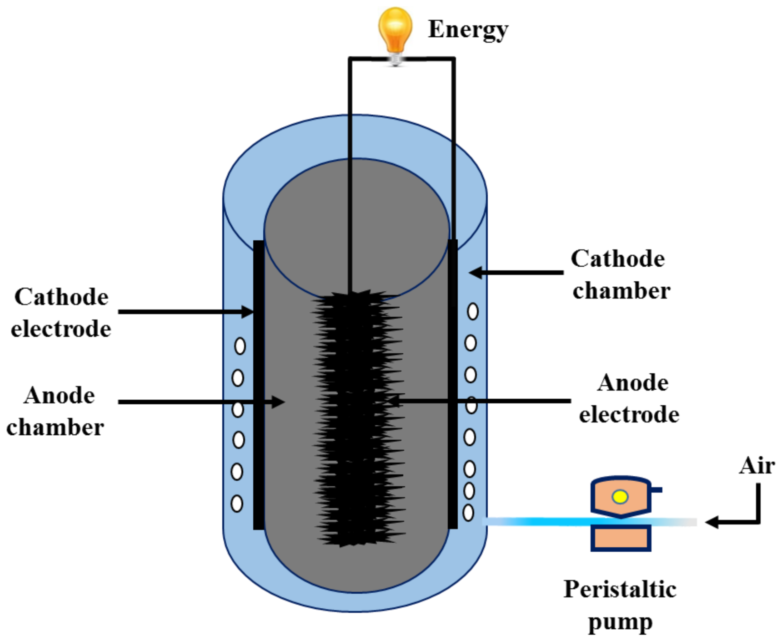

Figure 7-1. The configuration of the tubular microbial fuel cell used in this study.

MFC Experiments

Leachate was collected from a landfill in Virginia, USA, and stored at 4 °C before use. It was dark brown in color, and its basic characteristics are shown in Table 7-1. Five different operating conditions (C1-5, Table 7-2) were examined for the effects of hydraulic residence time (HRT), external resistance, and anolyte recirculation on UV quencher removal and energy production. Two HRTs, 40 days (C1) and 20 days (C2), were investigated. For the 40 days HRT, 60 mL of anolyte (leachate) was replaced with fresh leachate every 3 days, while for the 20 days HRT, 120 mL of anolyte was replaced every 3 days. Two different external resistances were studied – 39 Ω (equal to the internal resistance of the MFC reactor for high power output, C3) and 10 Ω (for high current generation, C2). The MFC internal resistance was determined by a polarization curve using a potentiostat (Reference 600; Gamry Instruments, Warminster, PA). Because a significant part of the energy is consumed by the anolyte recirculation (Zhang et al. 2010), an intermittent recirculation mode (C4) was examined and compared to continuous recirculation (C3). The open circuit mode (C5) acted as a control that had no current generation.

Table 7-1. Chemical properties of the landfill leachate.

Properties	Values
pH	7.81
Conductivity, mS cm^{-1}	27.1
COD, mg L^{-1}	4737
BOD_5, mg L^{-1}	892
UV absorbance, cm^{-1}	15.80
TOC, mg L^{-1}	1771
Humic acids, mg L^{-1}	289
Fulvic acids, mg L^{-1}	604
Hydrophilics, mg L^{-1}	878
NH_3-N, mg L^{-1}	1897

Table 7-2. Different operating conditions used in this study.

Operating conditions	HRT (days)	Resistance (Ω)	Anode recirculation (30 mL min^{-1})
C1	40	10	Continuous
C2	20	10	Continuous
C3	20	39	Continuous
C4	20	39	1 hour in every 3 days
C5	20	Open circuit	Continuous

GAC posttreatment

Granular activated carbon (GAC) (CENTAUR® 12x40, Calgon Carbon, Pittsburgh, PA) was used as a post-treatment step after the MFC treatment. The GAC experiments were performed in triplicate. Four GAC loadings, 40, 60, 80, and 100 g L^{-1} were investigated. The effluent from the MFC (C4) was used for GAC treatment for a period of 12 hours with samples collected at 2, 4, 6, and 12 hours. The reaction vials were stirred continuously by a magnetic stirrer to ensure complete mixing of the MFC effluent with GAC. At each time point, samples were collected and filtered through a 1.5 µm filter before analyzing different parameters (e.g. COD, NH_3-N, TOC, and UV absorbance).

Measurement and analysis

The MFC voltage across the external resistor was measured using a digital multimeter (2700, Keithley Instruments Inc., Cleveland, OH, USA). The solution conductivity was measured by using a benchtop conductivity meter (Mettler-Toledo, Columbus, OH, USA). The pH of the solution was measured using a benchtop pH meter (OAKTON Instruments, Vernon Hills, IL USA). The concentrations of chemical oxygen demand (COD) and NH_3-N were measured using a spectrophotometer according to the manufacturer's instructions (DR 890, HACH Company, USA). Total organic carbon (TOC) was measured with TOC- Vcsn (Shimadzu, Japan). Five-day biochemical oxygen demand (BOD_5) was measured following a standard procedure (APHA 2005). Ultraviolet absorbance (cm^{-1}) was measured at 254 nm wavelength by using a spectrophotometer (Beckman Coulter, Brea, CA). Coulombic efficiency (CE) was calculated following a previous study (Qin et al. 2015). Leachate organics were divided into humic, fulvic, and hydrophilic fractions according to a previous study (Christensen et al. 1998). To measure humic acids, suspended particles were first removed by filtering through a 1.5 µm filter and then humic acids were precipitated by reducing the pH of the filtrate to 1.5 by adding concentrated hydrochloric acid. The precipitated humic acids were separated by centrifuging at 8000 rpm for 30 min, and the supernatant was then passed through an ion exchange resin column (Amberlite® XAD-8 ion-exchange resin, Sigma Aldrich, St. Louis, MO) at a flow rate of 1 mL min^{-1}. The fluvic acids fraction was sorbed into the resin and the hydrophilics were collected directly. The sorbed fulvic acids were captured by running 0.1 M NaOH solution through the resin column at a flow rate of 1 mL min^{-1}. The quantification of the concentrations was performed by measuring the TOC of the respective fractions (Leenheer 1981; Thurman and Malcolm 1981). Specific ultraviolet absorbance ($SUVA_{254}$, L mg^{-1} m^{-1}) was calculated according to Eqn. 7-1. SUVA value less than 2 L mg^{-1} m^{-1} indicates the presence of aliphatic groups as the dominant fraction of the total organic carbon (Wang et al. 2016).

$$\mathrm{SUVA}\ (\mathrm{L\ mg^{-1}\ m^{-1}}) = \frac{\text{UV absorbance at 254 nm } (\mathrm{cm^{-1}}) \times 100}{\text{Total organic carbon } (\mathrm{mgL^{-1}})} \qquad (7\text{-}1)$$

The produced energy from the MFC was calculated according to Equation 7-2.

$$E_{cell} = \frac{P_{cell} * T}{V} \qquad (7\text{-}2)$$

Where, E_{cell} ($\mathrm{kWhm^{-3}}$) is the generated energy, P_{cell} (kW) is the produced power, T (h) is the operating time, and V ($\mathrm{m^3}$) is the volume of the treated leachate.

P_{cell} (W) was calculated according to the following equation (Logan et al. 2006):

$$P_{cell} = \frac{E_{cell}^2}{R_{ext}} \qquad (7\text{-}3)$$

Where, E_{cell} (V) is the voltage across the external resistance R_{ext} (Ω).

Energy consumption ($E_{MFC,}$ kWh $\mathrm{m^{-3}}$) of the MFC was mainly from anolyte recirculation and cathode aeration, and was calculated according to the following equation (Ge et al. 2014). Cathode aeration was conducted with a peristaltic pump by pumping air in the cathode chamber.

$$E_{MFC} = \frac{P_{system} * T}{V} \approx \frac{P_{pump} * T}{V} \qquad (7\text{-}4)$$

P_{pump} (W) was calculated according to Eqn. 7-5 (Zou and He 2016).

$$P_{pump} = \frac{Q_{pump} \times (H_{Hydraulic} + H_{Dynamic})}{\eta} = \frac{\frac{v\pi d^2}{4} \times \left(\rho g h + \frac{\rho v^2}{2}\right)}{\eta} \qquad (7\text{-}5)$$

where Q_{pump} ($\mathrm{m^3\ s^{-1}}$) is the recirculation rate, $H_{hydraulic}$ (Pa) and $H_{dynamic}$ (Pa) are the hydraulic and dynamic head of the pump, respectively, η (%) is the efficiency of this pump, h (m) is the head loss (water height difference before and after the pump head), d (m) is the diameter of the tubing, v ($\mathrm{m\ s^{-1}}$) is the water velocity through the tube, and ρ($\mathrm{kg\ m^{-3}}$) is the density of water. Net energy was calculated according to the following equation.

$$\text{Net Energy} = E_{cell} - E_{MFC} \qquad (7\text{-}6)$$

Results and discussions

Energy performance

Electricity generation from the leachate in the present MFC was first examined by monitoring current generation. Fig. 7-2 shows typical batch profiles of current generation and the highest peak current density of 9.76 A m^{-3} (current normalized by the anode liquid volume) was obtained from the C2, which was operated in a continuous anolyte recirculation mode with a 20-day HRT and 10-Ω external resistance. Integrating current with time gives the total coulombs (TC) of each batch, and the highest TC of 808 ± 24 C was also obtained from the C2 (inset, Fig. 7-2). Because of a lower HRT for the C2 compared to that of the C1, the organic loading rate in the C2 would be higher, leading to its higher coulomb production than the C1 (672 ± 19 C). With the same organic loading rate and anolyte recirculation mode, the TC of the C2 was higher than that of the C3 (589 ± 54 C), because a lower external resistance of 10 Ω in the C2 was expected to generate more current than that of 39 Ω in the C3. There was no significant difference in the TC between the C3 and C4, indicating that the anolyte recirculation had a minor effect on current generation; it was also likely that this effect was not obvious under the condition of high power output (39 Ω), and a lower external resistance for higher current generation would create more demand for substrate supply/mass transfer, which is expected to be affected by the electrolyte mixing.

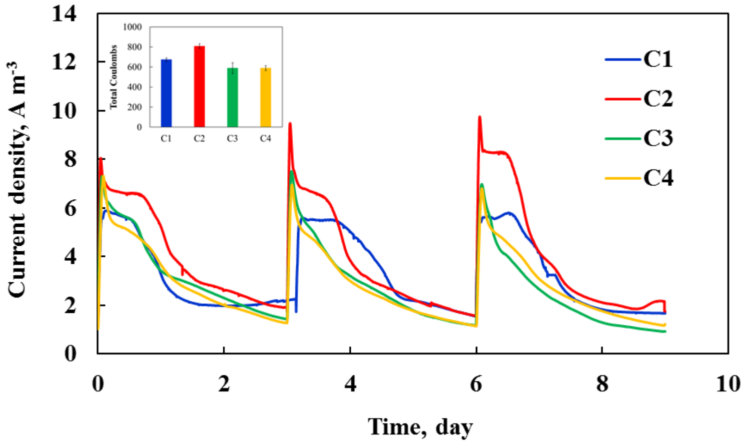

Figure 7-2. Batch profile of current generation by the MFC under different operating conditions. The inset shows total coulomb production.

Next, energy performance of the present MFC treating leachate was evaluated by examining its energy production and consumption (Fig. 7-3). Energy production could be estimated based on the information in Fig. 7-2. In the C5 (open circuit mode), there was no electricity generation and thus the net energy was negative (- 0.056 kWh m^{-3}), which was attributed to the pump energy requirement (for both anolyte recirculation and cathode aeration). Another negative net energy was obtained from the C1, because its energy production (0.099 kWh m^{-3}) was lower than the energy consumption (0.113 kWhm^{-3}). The C2-4 had positive net energy, and both C3 and C4 exhibited much higher net energy than the C2 (five times higher), because of a high-power output mode resulting in more energy production than a high current mode. The highest net energy was 0.123 kWh m^{-3} obtained in the C4, benefited from its lower energy demand (0.029 kWh m^{-3}, much lower than 0.056 kWh m^{-3} for the C3) due to intermittent anolyte recirculation.

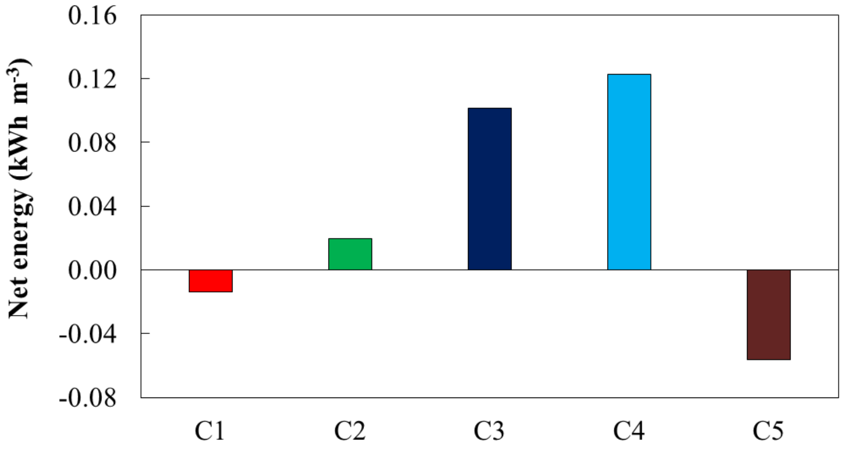

Figure 7-3. Net energy production from the MFC under different operating conditions.

Removal of UV quenchers by MFC treatment

After the MFC treatment, the UV absorbance decreased by 49.5, 41.9, 37.1, 34.9, and 25.4% for the C1, 2, 3, 4, and 5 respectively (Fig. 7-4A). The highest reduction of UV absorbance was from the C1, likely because of its higher HRT (40 days) that resulted in a lower loading rate and allowed more treatment time. The decrease of UV absorbance of all the organic fractions contributed to the overall UV absorbance decrease (Fig. 7-4A).

The C1 exhibited the highest UV absorbance decrease with reduction of humic acids (48.2 %), fulvic acids (45.6%), and hydrophilics (52.6 %), while the C5 showed the lowest reduction of UV absorbance with humic acids (31.1%), fluvic acids (19.9%), and hydrophilics (28.5%). This indicates that current generation might have stimulated the decrease of UV absorbance to a certain extent. Both the C3 and 4 showed a high UV absorbance decrease for humic acids (71.7 and 69.2%); however, their UV absorbance decreases of fulvic and hydrophilics were lower than those of the C1 and 2 (higher current mode). The CEM acted as a functional barrier to prevent leachate organics from entering the catholyte (no detectable organics and UV absorbance ~ 0 cm^{-1} in the catholtye).

Specific UV absorbance (SUVA, L mg^{-1} m^{-1}) increased in the effluents under all the operating conditions with the highest increase in the C5 (from 0.89 to 2.31 L mg^{-1} m^{-1}) (Fig. 7-4B). Such an increase could be related to the recalcitrance of aromatic rings during the MFC treatment, which increased SUVA or degree of aromaticity in the effluents. The highest SUVA increase in the C5 indicated that only the aliphatic fractions of the organics were consumed while aromatics were left behind in the open circuit mode. The lower SUVA of the C1 and 2's effluents than that of the C3 and 4's effluents suggested that a higher current generation might have helped with reducing recalcitrant fractions of organics. Humic acids SUVA values in the effluent of C1 and 2 were 4.99 and 3.55 L mg^{-1} m^{-1}, respectively (Fig. 7-4B), which increased by 9.8 and 6.7 times from the initial SUVA of the influent humic acids (0.46 L mg^{-1} m^{-1}), indicating the production of the recalcitrant humic acids (metabolic products) after the MFC treatment. Because SUVA is the ratio between UV absorbance and TOC as shown in Eqn. 1, the relative change in UV absorbance and TOC can change SUVA. For example, in the C1, the increase in SUVA of humic acids from 0.46 to 4.99 L mg^{-1} m^{-1} was because of the relatively lower decrease of UV absorbance (48.2%) than its concentration (95.2%) (Fig. 7-4, Table S7-1). Although there has not been any study on the fate of UV quenchers of landfill leachate after BES treatment, there have been studies mainly based on chemical oxidation for removing UV quenchers and UV absorbance from landfill leachate. Study showed a removal of 97 % UV absorbance of humic substances from landfill leachate after Fenton's oxidation (Gupta et al. 2014). While, 58 % reduction of UV absorbance was reported after ozone treatment (Wang et al. 2016). The superiority of Fenton's over ozone in removing UV quenchers has been reported by a previous study (Jung et al. 2017). The maximum removal of UV absorbance (49.5%) in this study after MFC treatment is less than what have been reported for oxidation removal. The increase in SUVA value after MFC treatment for all the operating conditions was in accord with a previous study that reported an increase of SUVA value from 2.1 to 3.4 L mg^{-1} m^{-1} after sequential batch reactor treatment (Zhao et al. 2012).

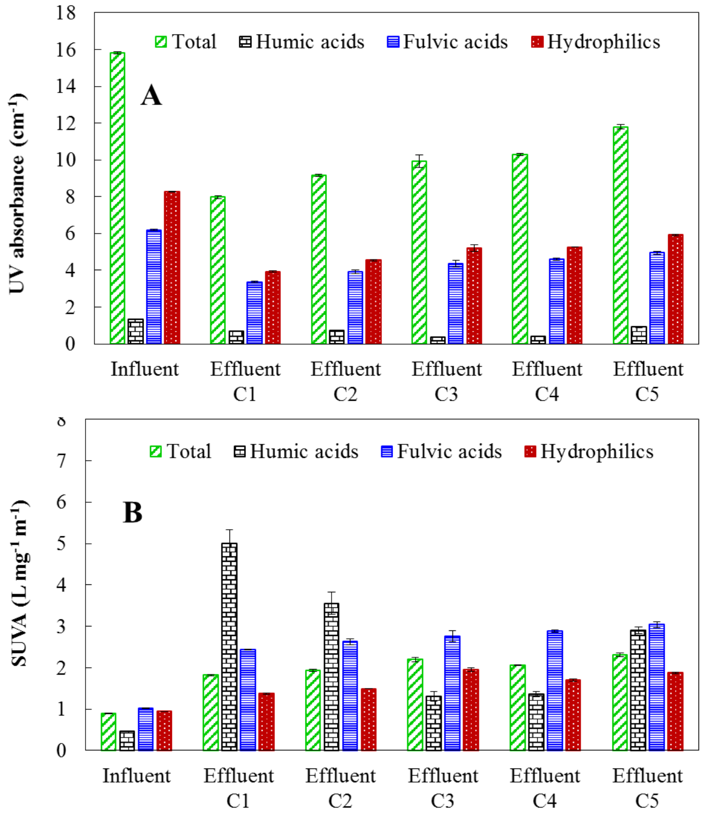

Figure 7-4. Contributions of different organic fractions to UV absorbance decrease under different operating conditions: (A) UV absorbance decrease; and (B) specific UV absorbance.

The concentrations of both COD and ammonia nitrogen in the MFC influent and effluents are shown in Fig. 7-5. The C1 had the lowest concentrations of both, leading to removal efficiency of 64.4 % (COD) and 74.5 % (NH_3-N). This COD removal was within the range of COD removal by BES (40-80%), likely affected by leachate composition and BES operation (Ozkaya et al. 2013; Zhang et al. 2015). COD removal is via complex biological processes including anaerobic degradation, aerobic degradation (with the oxygen diffused through membrane), and electricity generation. Ammonia removal is due to ammonia transport from the anode chamber into the cathode chamber driven by a concentration gradient and current flow. Ammonia removal from the current study is comparable with previous BES studies treating leachates that have reported a removal range of 0 to 99% (GaneshandJambeck 2013; Zhang et al. 2015). Electricity generation would play a role in both removals, but not significantly. This is reflected by a low coulombic efficiency (CE) under all the conditions, which ranged from 2.1 to 2.8%. Most of the previous studies on landfill leachate treatment by MFCs reported CE values of less than 10% (GaneshandJambeck 2013; Puig et al. 2011). The poor CE value despite considerable COD reduction indicates that most of the organics were consumed in non-electricity generation processes such as methane production, sulfate reduction, and denitrification (Ozkaya et al. 2013; You et al. 2006). Additionally, the toxicity of leachate may hinder the electron producing bacteria in the MFC (Iskander et al. 2016).

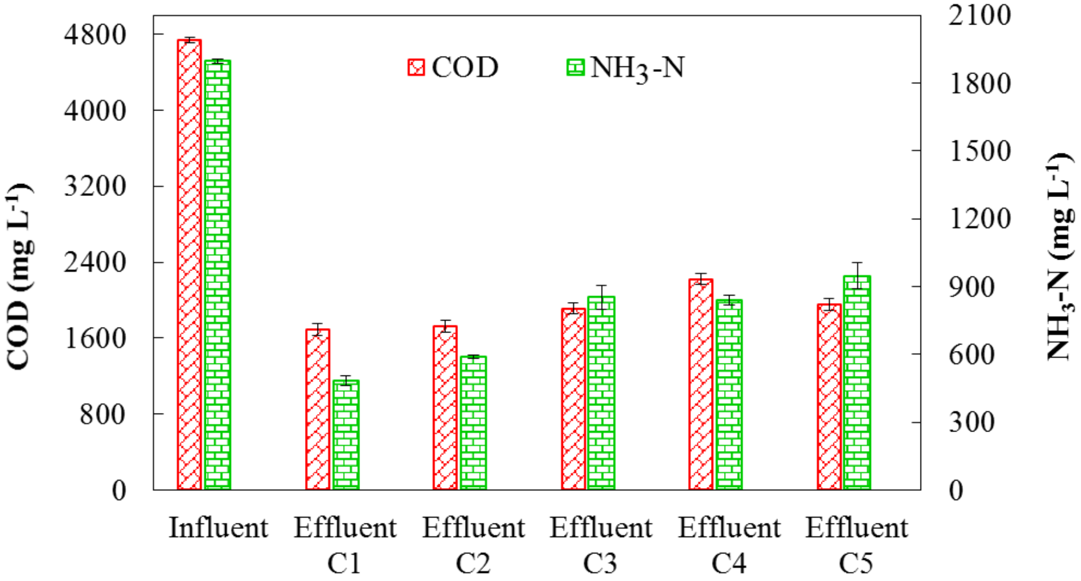

Figure 7-5. The concentrations of chemical oxygen demand (COD) and ammonia nitrogen in the MFC effluent under different operation conditions.

GAC posttreatment

The leachate UV absorbance decreased by 34.9 % (from 15.80 cm^{-1} to 10.29 cm^{-1}) after the MFC treatment in the C4. To enhance the UV absorbance reduction, its effluent was subjected to granular activated carbon (GAC) treatment under four different GAC concentrations – 40, 60, 80, and 100 g L^{-1}. The GAC posttreatment has significantly decreased UV absorbance and within six hours, the highest decrease was 94.7% (100 g L^{-1}) and the lowest was 89.1% 40 g L^{-1}) (Fig. 7-6). A higher GAC concentration would create more sorption sites for organics removal (FooandHameed 2009). Extending the adsorption period to 12 hours increased the removal of UV absorbance to a limited extent, for example from 89.1% to 94.7% with 40 g L^{-1} GAC. After GAC treatment for 12 hours, COD removal was around 70%, resulting in an average COD concentration in the GAC effluent of 658 ± 24 mg L^{-1} (Fig. S7-1). However, the ammonia nitrogen removal was very low after GAC treatment. The highest removal was only 3.2% for 100 g L^{-1} GAC treatment for 12 hours. This low removal of ammonia after GAC treatment confirms that sorption-based techniques are not as effective as biological and physicochemical treatments (e.g. air stripping, chemical precipitation) in removing ammonia from leachate (Gao et al. 2015; Renou et al. 2008). A previous study on biological treatment combined with powdered activated carbon could remove 54.3 % UV quenchers and 54.3 % UV absorbance from a landfill leachate (Zhao et al. 2012). The current study removed 92.9 % UV absorbance and 89.7 % UV quenchers in a combined MFC and GAC posttreatment with a 0.123 kWhm^{-3} net energy production.

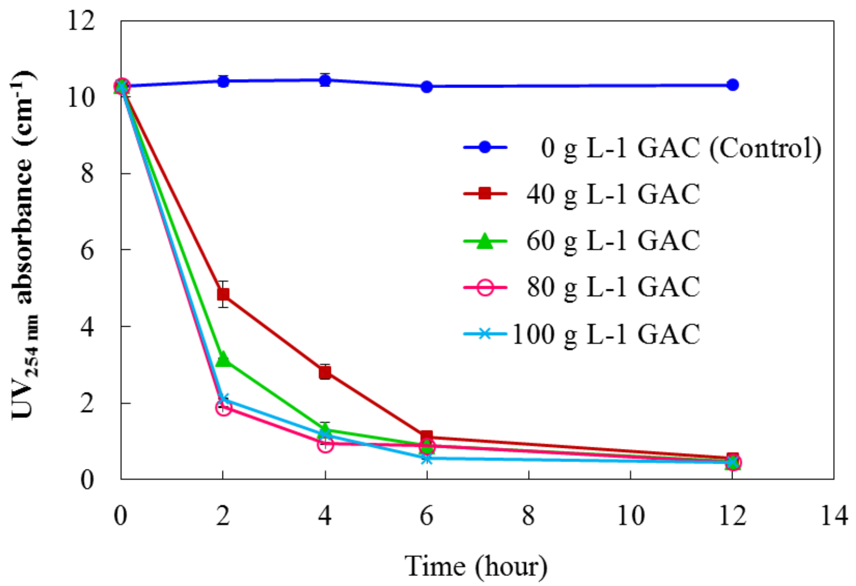

Figure 7-6. UV absorbance profile during granular activated carbon (GAC) treatment of the MFC effluent (from the C4).

To understand the change of different organic fractions during the GAC treatment, samples were analyzed for organic fractions after 6 hours with 40 g L^{-1} GAC treatment. The results showed that the total UV absorbance decreased by 89.1 % (10. 29 cm^{-1} to 1.12 cm^{-1}), and this decrease was mainly because of the decrease of the UV absorbance of fulvic acids (94.0 % decrease) and the hydrophilic fraction (89.6 % decrease) (Fig. 7.7A). The UV absorbance of the humic acids decreased by only 19.5 %. The specific UV absorbance decreased significantly after the GAC treatment, attributed to the SUVA decrease of humic acids, fulvic acids, and hydrophilic fraction (Fig. 7.7B). This decrease in SUVA value for all organic fractions was because of the higher decrease of UV absorbance compared to the decrease of organic concentrations. For example, after 40 g L^{-1} GAC treatment for 6 hours, UV absorbance for humic, fluvic, and hydrophilics decreased by 19.5, 94.0 and 89.6 %, respectively; while the organics concentration decrease was 7.0, 45.8 and 81.3 %, respectively, for humic acids, fluvic acids and hydrophilics (Fig. 7-7, Table S7-2). In total, the UV absorbance decrease was 88.8 %, and the organics decrease was 65.5 %. The decrease of SUVA after GAC treatment confirms that GAC can sorb the biorefractory UV quenchers of landfill leachate (Zhao et al. 2012).

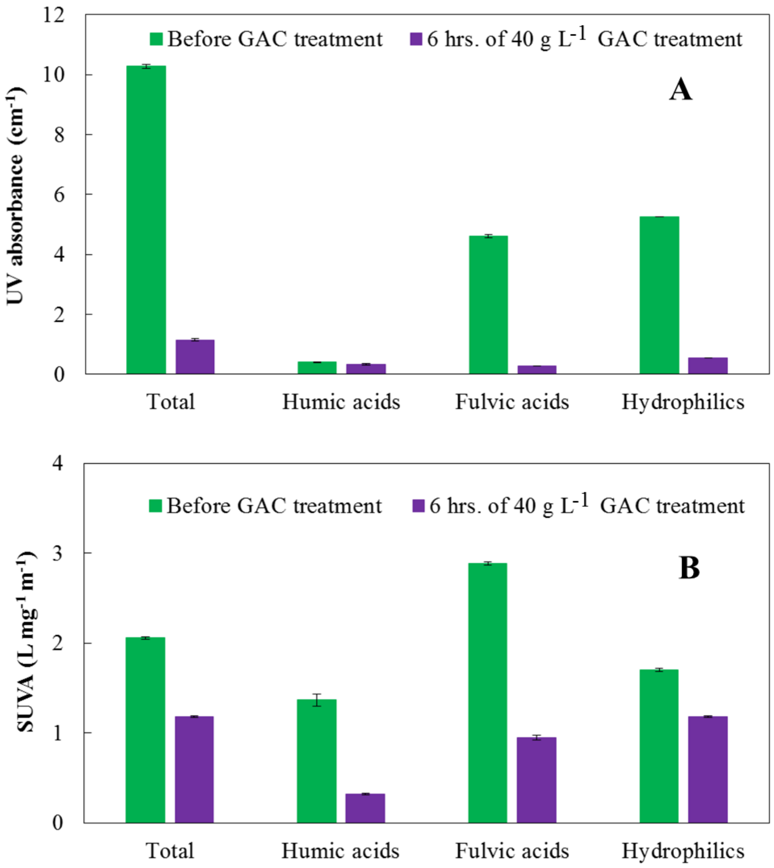

Figure 7-7. Different organic fractions after GAC treatment: (A) UV absorbance; and (B) SUVA.

Perspectives

This study has demonstrated that MFCs can be an effective approach to remove UV quenchers in landfill leachate; however, the removal is affected by recalcitrant components in leachate and thus post-treatment such as GAC will be necessary to achieve a high removal. The results imply some key benefits of this MFC+GAC method: (1) direct electricity generation can be accomplished in the MFC and the additional harvested energy may be used to offset energy consumption by other treatment steps; (2) in addition to energy production, the MFC can reduce the concentration of major organic compounds to a certain extent, which will benefit the downstream GAC treatment (e.g., reducing the burden of GAC treatment and thus extend the GAC lifetime); and (3) GAC treatment can greatly reduce UV quenchers to a very low level. Despite those benefits, this study also has limitations that warrant further investigation. For example, the low CE in the MFC can be further improved via optimizing the MFC configuration and design; organic degradation may be accelerated in the MFC by applying an external voltage and in that way, hydrogen gas may be produced in its cathode; regeneration of GAC after the treatment was not studied here and should be investigated further; and the effects of various organic portions on electricity generation needs to be further understood.

Conclusions

This study focused on the removal of UV quenchers from landfill leachate by using an MFC followed by GAC posttreatment. A higher HRT and higher current generation mode resulted in more removal of organics and reduction of UV absorbance, while a lower HRT and high-power generation mode led to higher energy output. GAC posttreatment was found effective in removing the recalcitrant portion of the organics that were left behind after the MFC treatment. Although the standalone MFC could not treat the leachate to an acceptable level, the generated energy from the MFC would potentially reduce the treatment cost. As an early attempt to understand the UV quenchers’ fate in an MFC, this study will encourage further investigation towards the development of an effective and cost-efficient treatment option for landfill leachate’s UV quenchers.

Supporting Information

Table S7-1. Change in organic concentrations after MFC treatment of leachate for different operating conditions.

Organics mg L^{-1}	Influent	Effluent					% Reduction				
		C1	C2	C3	C4	C5	C1	C2	C3	C4	C5
Humic acids	288.97	13.90	20.74	28.96	30.08	31.55	95.2	92.8	90.0	89.6	89.1
Fulvic acids	603.53	137.60	148.43	157.76	159.85	162.91	77.2	75.4	73.9	73.5	73.0
Hydrophilics	878.07	285.77	304.26	265.75	309.39	315.40	67.5	65.3	69.7	64.8	64.1
Total	1770.57	437.27	473.43	452.46	499.32	509.87	75.3	73.3	74.4	71.8	71.2

Table S7-2. Change in organic concentrations after 40 gL^{-1} GAC treatment of the effluent of C4.

Organics, mg L^{-1}	Effluent TOC of C4	Effluent TOC After 40 gL^{-1} GAC	% Decrease
Humic acids	30.08	27.98	7.0
Fulvic acids	159.85	86.58	45.8
Hydrophilics	309.39	57.74	81.3
Total	499.32	172.29	65.5

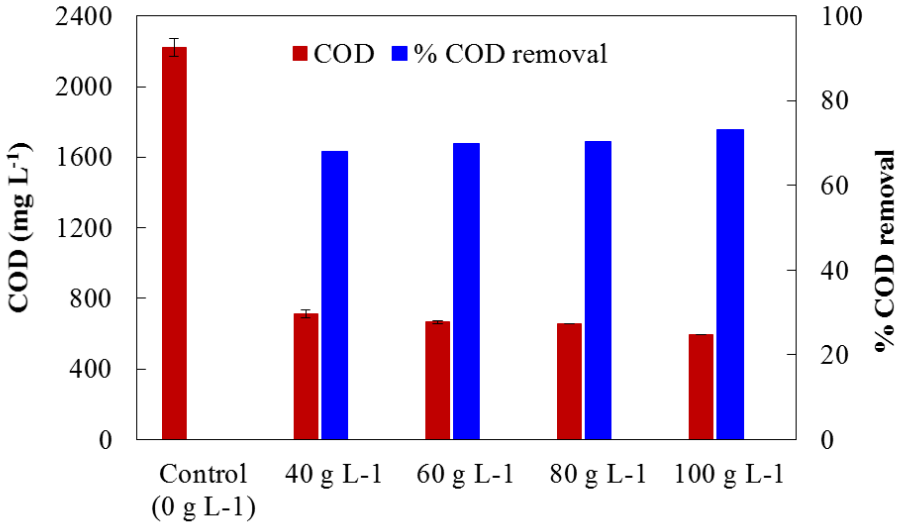

Figure S7-1. Chemical oxygen demand (COD, mg L^{-1}) removal after 12 hours of GAC treatment of the MFC treated leachate (Effluent from C4).

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CHAPTER 8

Percarbonate Oxidation of Landfill Leachate towards Removal of Ultraviolet Quenchers

Abstract

Landfill leachate can introduce compounds that absorb ultraviolet (UV) light and thus affect UV disinfection efficiency at municipal wastewater treatment plants when leachate is co-treated. Thus, UV quenchers should be removed or reduced before leachate is sent to a municipal wastewater treatment plant. Herein, a chemical oxidant, sodium percarbonate (SPC, Na_2CO_3 1.5 H_2O_2), was investigated to oxidize two types of landfill leachates with a focus on UV quenching reduction. The oxidation with 0.2 M SPC for 24 hours reduced Leachate A's organics concentration by 15.6 % and UV_{254nm} absorbance by 43.4 %; it was 15.1 % and 7.9 %, respectively, for Leachate B. Both the specific ultraviolet absorbance ($SUVA_{254nm}$) and e_{280nm} absorption coefficient decreased in Leachate A after 0.2 M SPC oxidation, but increased in Leachate B. The organics with size < 1 kDa were the major contributor to UV absorbance in both raw leachates, but exhibited different behaviors after SPC oxidation with significantly different contributions to UV absorbance reduction. The maximum chemical oxygen demand (COD) reduction was 5.3 kg m^{-3} (with 0.05 M SPC) in Leachate A, resulting in a treatment cost of $0.8 per kg of COD removed. SPC oxidation greatly reduced the turbidity of Leachate A (>99%), and increased its bioavailability. The results of this study can be used to develop a cost-effective method for removing UV quenchers from landfill leachate.

Introduction

Landfill leachate is a complex wastewater that is generated from the degradation of solid wastes within landfills. It contains a wide range of contaminants including a substantial amount of organics (Renou et al., 2008). In mature landfill leachates, humic acids (HA) and fulvic acids (FA) (i.e. humic substances) constitute around 70-80% of the organics (Christensen et al., 1998; Zhang et al., 2009). However, in young leachate, hydrophilic fractions (HPI) (i.e. carboxylic acid as the main functional group) can be the dominating fractions (Christensen et al., 1998). Both hydrophobic (i.e. humic substances) and hydrophilic fractions are strong ultraviolet (UV) absorbers (Gupta et al., 2015; Gupta et al., 2014). In addition, these refractory fractions of leachate organics are immune to conventional biological treatment. When leachate is discharged to sewerage systems and then treated in municipal wastewater plants, the UV quenching compounds contained in the leachate can decrease the efficiency of UV treatment (Dahlen et al., 1996; Imai et al., 2002; Kieber et al., 1990). Therefore, reduction of UV quenching compounds from leachate would be critically important to ensure healthy treatment in the subsequent processes.

Prior efforts have attempted to remove UV quenching compounds from landfill leachate by using advanced oxidation. Effective removal of humic substances (humic and fulvic acids) by ozonation from reverse osmosis (RO) - nanofiltration (NF) treated concentrated leachate was reported, and complete degradation of humic acids and partial degradation of fulvic acids and hydrophilics were accomplished by ozonation, resulting in 58% removal of the UV_{254nm} absorbance (Wang et al., 2016). A significant portion of this degradation was reported as primary degradation. Primary degradation is the change in structural pattern of organics, while conversion of organics into inorganics (i.e. CO_2) is considered as ultimate degradation. The use of Fenton reagent has improved the removal of UV_{254nm} absorbance from biologically pretreated leachate, compared to ozonation (Jung et al., 2017). Fenton’s oxidation achieved 97% removal of UV absorbance of humic substances and 92% UV absorbance removal for hydrophilic fractions (Gupta et al., 2014). Electrocoagulation is a method to remove humic-like substances from wastewater using iron coagulant produced from a sacrificial anode electrode (Kliaugaite et al., 2013). With the assistance of coagulation, Fenton’s oxidation achieved over 85% removal of humic acids from a landfill leachate (Wu et al., 2010). Despite great promise of Fenton’s treatment, it also has drawbacks such as complexity in application (pH 2 - 4), sludge production, etc. (Hermosilla et al., 2009; Zhang et al., 2005). Therefore, there is a need to explore alternative chemical oxidation methods for removing UV quenchers from landfill leachate.

Chemical oxidations have been well investigated for leachate treatment. Of them, permanganate, persulfate, H_2O_2, UV + H_2O_2, ozone, ozone + H_2O_2, Fenton's are most commonly studied (Renou et al., 2008). These treatments mainly focused on COD, color, turbidity, and ammonia removal (Hilles et al., 2016; Renou et al., 2008). Sodium percarbonate (Na_2CO_3 1.5 H_2O_2, SPC), an adduct of sodium carbonate and hydrogen peroxide, is a powerful and easy to use chemical oxidant with a relatively low cost (McKillop & Sanderson, 2000). SPC is soluble in water at high concentrations at 20 ˚C, and the pH of a 1% aqueous solution is around 10.5 (Wada & Koga, 2013). The alkaline pH of SPC in an aqueous solution initiates the decomposition of H_2O_2 into hydroperoxide anion ($H_2O_2 = HO_2^- + H^+$, pKa = 11.6) (McKillop & Sanderson, 1995). The decomposition of SPC in the aqueous solution can, however, follow another pathway — into peroxymonocarbonate anion (HCO_4^-) (Lin & Liu, 2009). In this pathway, homolysis of the O-O bond in HCO_4^- starts a series of reactions to produce hydroxyl radicals (OH•), carbonate radicals ($CO_3 \bullet^-$) (Eqn. 8-1), perhydroxyl radicals ($HO_2 \bullet$) (Eqn. 8-2), and superoxide radical anions ($O_2 \bullet^-$) (Eqn. 8-3) (Ahmed, 2012; Lin & Liu, 2009; Watts, 2016). The hydroxyl radical is a strong oxidant, superoxide is a weak reductant and nucleophile, perhydroxyl radical is a weak oxidant, and hydroperoxide anion is a strong nucleophile with diverse reactivity (Watts & Teel, 2005).

$$HCO_4^- \longrightarrow CO_3^{\bullet -} + OH^\bullet \qquad (8\text{-}1)$$

$$CO_3^{\bullet -} + H_2O_2 \longrightarrow HCO_3^- + HO_2^\bullet \qquad (8\text{-}2)$$

$$HO_2^\bullet \longrightarrow O_2^{\bullet -} + H^+ \qquad (8\text{-}3)$$

Because of these features, SPC has recently been studied as an oxidant for some organics (i.e. benzene, toluene, aniline) (McKillop & Sanderson, 1995; McKillop & Sanderson, 2000). It has also been used in remediation of organics (de la Calle et al., 2012), and thus is expected to be able to mineralize organics in landfill leachate. SPC in combination with other oxidizing agents was limitedly investigated mainly for industrial wastewater treatment that yielded very effective performance in decoloration, but ineffective COD removal (Babaei & Ghanbari, 2016; Barbusinski, 2008; Pieczykolan et al., 2016). SPC is nontoxic to microbes, making it suitable in combination with biological treatment and superior to the Fenton's process, which produces substantial amount of iron precipitates that can be toxic to microbes (Winterbourn, 1995; Zhang et al., 2005). In this study, the feasibility of using SPC to treat landfill leachate in removing UV quenchers was examined. The specific objectives of this study were to: (1) investigate the effects of SPC doses on UV absorption removal; (2) determine the effects of the SPC oxidation treatment on UV quenchers' transformation; and (3) understand the effects of SPC oxidation on different molecular size fractions of organics and their interchange.

Materials and Methods

Landfill leachate

Two types of leachate, named "Leachate A" and "Leachate B", were collected from different cells of a landfill in Virginia, USA, and stored at 4 °C before use. Leachate A was yellowish to light brown in color, while Leachate B was dark brown in color. The basic characteristics of both leachates are shown in Table 8-1. Leachate A (46570 mg L^{-1} COD) can be considered as a strong leachate and Leachate B (4740 mg L^{-1} COD) a weak leachate.

Table 8-1. Properties of Leachate A and Leachate B.

Parameters	**Leachate A**	**Leachate B**
pH	6.08	7.81
Conductivity, mS cm^{-1}	19.9	27.1
COD, mg L^{-1}	46566	4737
BOD_5, mg L^{-1}	10303	892
TOC, mg L^{-1}	13486	1771
UV absorbance, cm^{-1}	16.11	15.79
NH_3-N, mg L^{-1}	1510	1897
Na^+, mg L^{-1}	1739	3837
Cl^-, mg L^{-1}	1890	5273
F^-, mg L^{-1}	476	57
K^+, mg L^{-1}	961	993

Mg^{2+}, mg L^{-1}	377	219
Ca^{2+}, mg L^{-1}	2041	59

Experimental process

The sodium percarbonate (MW = 157.01 g mol^{-1}, Sigma Aldrich, St. Louis, MO) oxidation study was performed in 20 mL borosilicate vials lined with PTFE septa. Four different concentrations of SPC (0.01, 0.05, 0.1, 0.2 M) were examined for oxidation. Each oxidation test was conducted for 24 hours. Samples were collected at six different time points: 0, 2, 4, 6, 12, and 24 hours. At each time point, triplicate reaction vials were sacrificed. In the experiment of separation of leachate into different organics and molecular size fractions, 150 mL raw or oxidized leachate was oxidized in triplicate with 0.01 M or 0.2 M SPC for 24 hours.

Measurement and analysis

The concentrations of chemical oxygen demand (COD) and NH_3-N were measured using a spectrophotometer according to the manufacturer instructions (DR 890, HACH Company, USA). Conductivity was measured by using a benchtop conductivity meter (Mettler-Toledo, Columbus, OH, USA). The solution pH was measured using a benchtop pH meter (OAKTON Instruments, Vernon Hills, IL USA). Total organic carbon (TOC) was measured with TOC- Vcsn (Shimadzu, Japan). Hydrogen peroxide (H_2O_2) concentration was measured with HACH kit (Model HYP-1) according to manufacturer's instructions. Turbidity of unfiltered sample was measured using a Micro TPW Turbidimeter (HF Scientific, FT. Myers, FL) in NTU unit. Five day biochemical oxygen demand (BOD_5) was measured following a standard procedure (APHA et al., 2005). Ultraviolet absorbance (cm^{-1}) was measured at 254 and 280 nm wavelength by using a spectrophotometer (Beckman Coulter, Brea, CA).

Humic, Fulvic, and Hydrophilics fractions of leachate organics were divided according to previous studies (Christensen et al., 1998; Leenheer, 1981; Thurman & Malcolm, 1981). Leachate was filtered through a 1.5 µm (DSC - Grade TSS Borosilicate Glass Fiber Filter, LabFilterz, P. City, CA) to remove the suspended particles. Then, the leachate pH was decreased to 1.5 by adding hydrochloric acid to precipitate all the humic acids. After that, leachate was centrifuged for 30 min at 8000 rpm to remove the precipitated humic acids. The supernatant was passed through an ion exchange resin column (Amberlite® XAD-8 ion-exchange resin, Sigma Aldrich, St. Louis, MO) at 1 mL min^{-1} to separate the fulvic acids by sorption on the resin. The portion of the supernatant passed through the column contained the hydrophilic fraction only. The absorbed fulvic acids were separated from the ion exchange resin by passing 0.1 M NaOH solution (at a rate of 1 mL min^{-1}) through the column. Humic, fulvic, and hydrophilic fractions were quantified by measuring TOC of the respective fractions. Before measuring the TOC of the oxidized leachate, it was stripped of at pH 3.5 for 2 hours at 50 ± 5 mL min^{-1} by pure nitrogen gas to remove the inorganic carbons that were contributed by the added SPC. Specific ultraviolet absorbance (SUVA_{254}, L mg^{-1} m^{-1}) and e_{280} (L mg^{-1} m^{-1}) absorption coefficient were calculated according to Equation 8-4 and 8-5 respectively.

$$\text{SUVA (L mg}^{-1}\text{ m}^{-1}) = \frac{\text{UV absorbance at 254 nm } \left(\text{cm}^{-1}\right) \text{ x } 100}{\text{Dissolved organic carbon } \left(\text{mg L}^{-1}\right)} \tag{8-4}$$

$$e_{280\text{nm}} \text{ (L mg}^{-1}\text{ m}^{-1}) = \frac{\text{UV absorbance at 280 nm } \left(\text{cm}^{-1}\right) \text{ x } 100}{\text{Dissolved organic carbon } \left(\text{mg L}^{-1}\right)} \tag{8-5}$$

Both raw and oxidized leachates were examined for different molecular size fractions using ultrafiltration before and after separation into different organics fractions, according to the process described previously (Zhao et al., 2012)**.** Three sizes of ultrafiltration membranes (1 kDa, 3 kDa, and 100 kDa, EMD Millipore Corporation, Billerica, MA, USA) were used to divide the leachate or different organics fractions into four size fractions: < 1 kDa, 1 – 3 kDa, 3 – 100 kDa, and 100 kDa – 1.5 µm.

Results and discussion

Leachate characterization

The leachate samples were characterized for their organic compositions as shown in Fig. 8-1. The organic portion of Leachate A was comprised of 5 % humic acids, 13 % fulvic acids, and 82 % hydrophilics, among which 84 % humic acids, 97 % fulvic acids, and 94

% hydrophilics were < 1 kDa size. In Leachate B, the organic fraction contained 16% humic acids (76.9 % < 1 kDa size), 34 % fulvic acids (78.8 % < 1 kDa size), and 50% hydrophilics fraction (90.0 % < 1 kDa) (Fig. 8-1). Humic substances constituted 18% of Leachate A's organics (39.2 % of the total UV absorbance) and 50 % of Leachate B's organics (47.5% of the total UV absorbance), indicating a higher degree of humification of Leachate B compared to Leachate A. This is also evident from the higher biodegradability index (BOD_5 / COD) of Leachate A at 0.22 compared to Leachate B (0.19). The UV_{254nm} absorbance of Leachate A was 16.11 ± 0.05 cm^{-1}, and it was 15.78 ± 0.02 cm^{-1} for Leachate B.

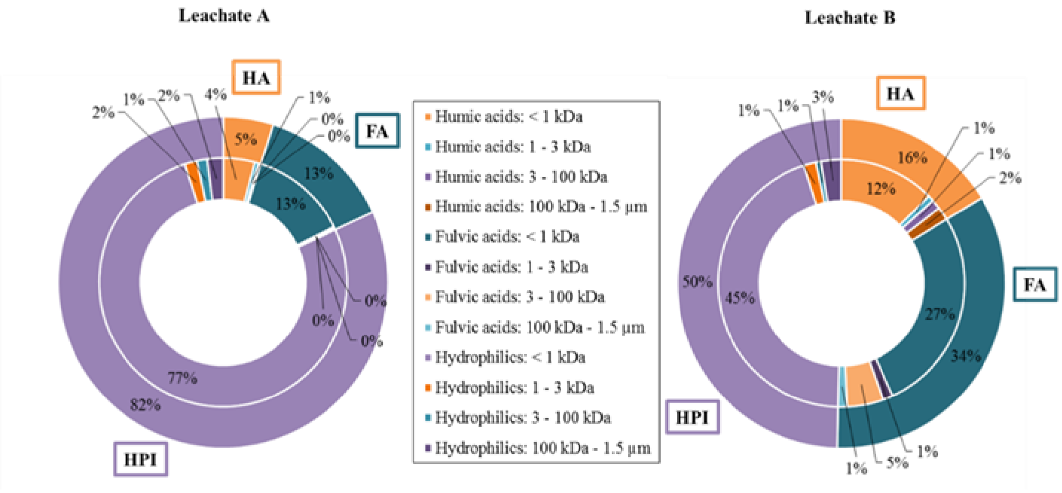

Figure 8-1. Molecular size fractions of the organic fractions in: (A) Leachate A; and (B) Leachate B. HA: Humic acids; FA: Fulvic acids; HPI: Hydrophilics.

Effects of SPC oxidation on UV absorbance

The effects of SPC oxidation on UV absorbance of Leachate A and B were studied at four different concentrations (0.01 M, 0.05 M, 0.1 M, and 0.2 M) of SPC dosage and no SPC addition as a control. In the absence of SPC (control), UV_{254nm} absorbance did not significantly change over the testing period in both leachates (Fig. 8-2). With addition of SPC, UV absorbance in Leachate A clearly decreased with the highest removal of UV absorbance of 43.4% (from 16.12 cm^{-1} to 9.13 cm^{-1}) in 24 h with 0.2 M SPC (Fig. 8-2 and Table S8-1). The removal efficiency decreased to 34.7 %, 35.1 %, and 36.5 % with

0.01 M, 0.05 M, and 0.1 M SPC, respectively (Fig. 8-2A). Most of the removal occurred in the initial 6 h, likely because of an initially high concentration of hydrogen peroxide that was generated as SPC dissolved in the aqueous phase. After 24 h there was no measurable H_2O_2 except for the case of 0.2 M SPC that showed a minimum presence of 1 mg L^{-1} H_2O_2 in the system. The effect of SPC oxidation on removing UV absorbance in Leachate B was not as significant as that in Leachate A. UV absorbance removal in Leachate B ranged from 5.9 % to 7.9 % in 24 h, with the SPC concentrations varied from 0.01 M to 0.2 M (Fig. 8-2B, Table S8-1). As discussed, the maximum decrease of UV absorbance (UVA) after 0.2 M SPC oxidation for Leachate A and B yielded an UV absorbance of 9.13 cm^{-1} and 14.54 cm^{-1}. In a wastewater treatment plant the acceptable UV transmittance should be at least 65 % and UV absorbance should be $\leq$ 0.187 cm^{-1} (NWRI, 2012), which calls for dilution and proper posttreatment of SPC oxidized leachates.

$$UVT = 10^{-UVA} \times 100 \qquad (8\text{-}6)$$

The decrease in UV absorbance may be explained by the oxidation of organics from leachate. As shown in Table S8-2, Leachate A's total organics removal was 13.0% or 15.6% for 0.01 M or 0.2 M SPC oxidation, and this number was 7.6 % or 15.1 % in Leachate B. This removal was due to a decrease in TOC, so it is considered to be ultimate degradation – conversion of organic carbon to CO_2 (Wang et al., 2016). Despite similar organic removal of ~ 15% with 0.2 M SPC oxidation in both Leachate A and B, their UV absorbance removal was significantly different (43.4 % vs. 7.9 %), which could be related to their different initial organic concentrations (i.e. 13500 mg L^{-1} in Leachate A and 1770 mg L^{-1} in Leachate B). To understand the TOC concentration difference on SPC oxidation, diluted Leachate A (TOC concentration equal to Leachate B) was oxidized with 0.2 M SPC for 24 hours. After oxidation, UV absorbance and organic concentration decreased by 19.7 % and 16.9 % respectively. This decrease was greater than the Leachate B's decrease after 0.2 M SPC oxidation (7.9 % and 15.1 % for UV absorbance and organics). However, for raw Leachate A, the UV absorbance decrease was much higher (43.4 % compared to 19.7 %). This could be explained by the short lifetime and diffusion limited reactivity of hydroxyl radicals in aqueous solution (Walling, 1975). When the organic concentration is higher, hydroxyl radicals can react instantly with organics. In reaction system with low organics, this reaction may not be that effective. And these effective reactions in the organic dense medium can lead to a higher removal of UV absorbance through primary and ultimate degradation of organics. In addition, the higher removal of UV absorbance in Leachate A than that in Leachate B was likely because of the complex interchange and interaction of different organic fractions of leachates, and different degree of humification of leachates.

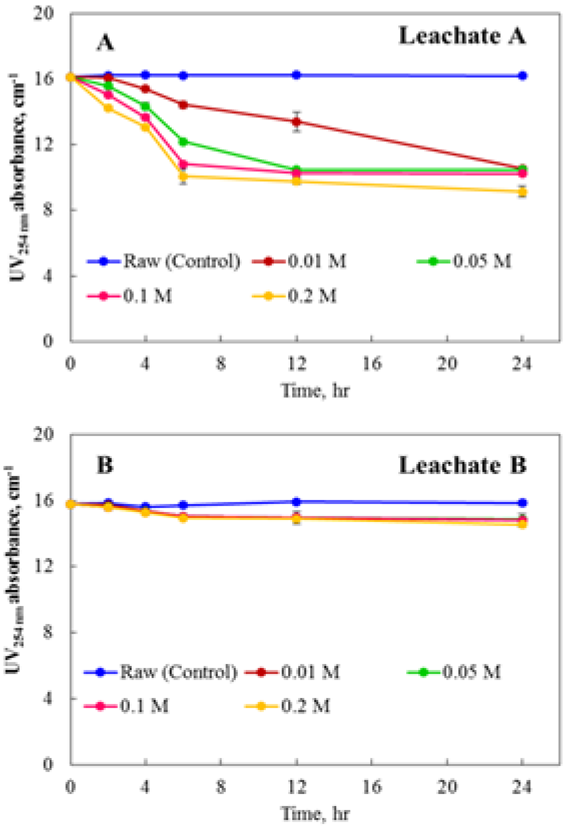

Figure 8-2. Trends in UV$_{254nm}$ absorbance (cm^{-1}) change during sodium percarbonate oxidation of: (A) Leachate A; and (B) and Leachate B. Each point in the graph represents the mean of triplicate data, while the error bar represents the standard error of the mean.

In Leachate A, the contributions to the decrease in UV absorbance after 0.2 M SPC oxidation came from humic acids (56.9%), hydrophilics (34.8%), and fulvic acids (8.3%) (Table S8-1). Clearly, humic acids had the most contribution, although they represented only 4.9% of organics and 25.5% of UV absorbance in the original Leachate A. Hydrophilics were the dominant compounds in the original Leachate A (82.0% of organics and 60.8% of UV absorbance) and exhibited the second most contribution to the reduction of UV absorbance. The concentration of fulvic acids increased by 1.8%, but its UV absorbance decreased by 26.2%, which was 8.3% of the total decrease. This could be related to the primary degradation of the organics structures (i.e. structural alterations) after oxidation (Zhang et al., 2005). For example, humic acids or other organics can be converted into fulvic acids, and this has been shown in a previous study (Wu et al., 2010). While in Leachate B, the small net decrease in UV absorbance (8.0%) was mostly attributed to humic acids and fulvic acids: humic acids UV absorbance decreased by 29.3 % and fulvic acids UV absorbance decreased by 16.1 % after 0.2 M SPC oxidation (Table S8-1). In the original Leachate B, hydrophilics were still the dominant compounds (49.6% of organics and 52.4% of UV absorbance). However, after oxidation with 0.2 M SPC, hydrophilics increased by 3% in TOC and 1.5% in UV absorbance (Table S8-1 and S8.2). This could be because of the recalcitrance of the Leachate B's hydrophilic fraction to SPC oxidation and also the primary conversion of other organic fractions into hydrophilics which resulted in the increase of the UV absorbance from the hydrophilic fractions. The COD: SPC dosage (mass basis) for Leachate A varied from 1: 0.03 to 1: 0.67 with the SPC concentration from 0.01 M to 0.2 M. Because Leachate B's COD concentration was much less than that of Leachate A (Table 8-1), the normalized SPC dosage for Leachate B was ten times larger than Leachate A (1: 0.33 to 1: 6.63). However, at this high dosage, Leachate B was still recalcitrant, which resulted in a low UV absorbance reduction.

The oxidation removal of organics in both leachates was performed by the reactive radicals that were generated in the aqueous SPC. The hydroxyl radical is a strong oxidant and can attack the carbon in the organics to achieve ultimate degradation or primary oxidation that will change the organic structures of the available organics. The reactions of hydroxyl radicals are very rapid (rate constant: 10^{-8} to 10^{-10} $M^{-1}S^{-1}$) and can unselectively react with aquatic compounds (Deng & Englehardt, 2006; Jung et al., 2017). The reaction of hydroxyl radical with organics can follow four different pathways such as radical addition, radical combination electron transfer, and hydrogen abstraction. During the reaction of organics and hydroxyl radicals, generated carbon cantered radicals react further with aqueous oxygen and hydroxyl radicals to do the ultimate degradation of organics into CO_2 and H_2O (Deng et al., 2013). Beside hydroxyl radicals, superoxide radicals may play a significant role in the removal of leachate organics after SPC oxidation as superoxide is another major product of the aqueous dissociation of SPC (Ahmed, 2012).

Because leachate also contains many inorganics, it is very difficult to selectively attack the organics during oxidation. Both leachates had a high concentration of chloride (Cl^-), which is a known hydroxyl radical scavenger (Liao et al., 2001). The 99.8 % decrease of Cl^- for Leachate A (1929.1 to 3.9 mg L^{-1}) and 99.9 % decrease for Leachate B (5221.2 to 7.8 mg L^{-1}) after 0.2 M SPC oxidation for 24 hours indicate that Cl^- was oxidized to other forms (i.e. ClO_2^-, ClO_2, Cl•, etc.) after SPC oxidation (Liao et al., 2001; Moore et al., 2004). As Leachate A had lower concentration of Cl^- than Leachate B, to understand its effect, Leachate A was spiked with Cl^- to make the Cl^- concentration equal to that of Leachate B. After 0.2 M SPC oxidation of Leachate A with same Cl^- concentration as Leachate B, the organic removal was 11.1 % and UV absorbance removal was 30.1 %. This removal was lower than the removal for oxidized Leachate A with same concentration of SPC (15.6 % and 43.4 % for organics and UV absorbance respectively). This indicated the quenching effect of Cl^- ions on the SPC oxidation. This limitation could reduce the effectiveness of SPC oxidation of landfill leachate organics. Although it was reported that the reaction efficiency with hydrogen peroxide improves with increased concentrations of organics (Zhang et al., 2005), the recalcitrance of the organics would also greatly affect the reaction efficiency. The low UV absorbance reduction in Leachate B was likely due to its high fraction of recalcitrant compounds.

Changes in molecular size fractions

To better understand the UV absorbance of different molecular size fractions of leachate and their dynamics before and after oxidation, ultrafiltration was performed on both raw leachates and oxidized leachates. Of the four size fractions (< 1 kDa, 1 – 3 kDa, 3 – 100 kDa, and 100 kDa – 1.5 µm), the fraction < 1 kDa contributed the most to the UV absorbance in both original Leachate A (75 %) and Leachate B (68 %) (Fig. 8-3). This is related to their higher concentrations compared to the other fractions: 94 % of Leachate A's organics were < 1 kDa, while for Leachate B it was 84 %. The 34.7 % and 43.3 % reduction of UV absorbance of Leachate A after 24 hours oxidation with 0.01 M and 0.2 M SPC was mainly because of the reduction of UV absorbance of the fraction < 1kDa (48.5 % and 52.4 % of the total decrease for 0.01M and 0.2 M SPC oxidation respectively). Although the 100 kDa – 1.5 µm fraction constituted only 2.5 % of the Leachate A's organics, it was responsible for 16.6 % of the UV absorbance in the raw leachate, which decreased by 86.2 % and 88.8 % after 0.01 M and 0.2 M SPC oxidation. This decrease was 41.3 % and 34 % of the total decrease, respectively (Fig. 8-3). In Leachate B, the UV absorbance of <1 kDa fraction increased slightly after oxidation and the total UV absorbance decrease was attributed by the slight decrease in the other three size fractions' UV absorbance (Fig. 8-3). Different behaviors of the molecular size fraction interchange between Leachate A and Leachate B demonstrate the different treatment responses of leachate organics, which is unique to each leachate. A previous study demonstrated the different response of different organic size fractions in two leachates after biological treatment in terms of UV absorbance reduction: one leachate showed UV_{254} absorbance reduction for all the organic size fractions, while the other showed a mixed response (Zhao et al., 2012). The increase of the smaller size fractions could be explained by the degradation of the larger size fractions and the increase of the larger size fractions could be because of the bio-coagulation of the smaller fractions into larger fractions, which is specific to the chemistry of different leachates.

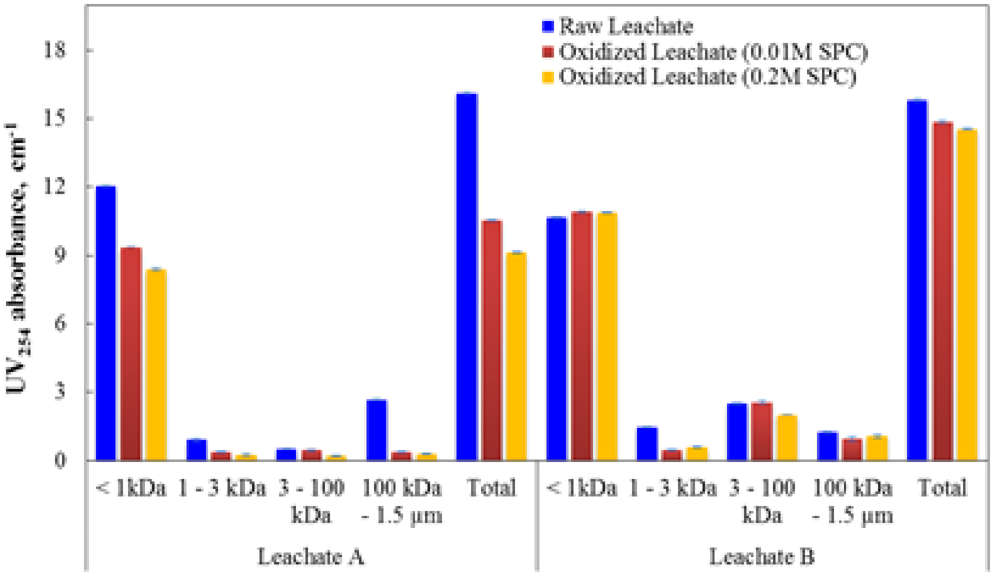

Figure 8-3. UV$_{254nm}$ absorbance (cm^{-1}) of different molecular size fractions of Leachate A and B before and after oxidation with 0.01 M and 0.2 M sodium percarbonate for 24 hours. Each point in the graph represents the mean of triplicate data, while the error bar represents the standard error of the mean.

Specific UV absorbance

The relative UV absorbance of aromatic dissolved organic carbons can be higher than that of the aliphatic carbons, likely because of the presence of aromatic rings (Weishaar et al., 2003). To understand the aromaticity, specific UV absorbance (SUVA) and e$_{280nm}$ absorption coefficients were calculated (Chin et al., 1994; Wang et al., 2016). According to the data, no leachate has a high degree of aromaticity (SUVA > 2 L mg^{-1} m^{-1}), which means that organics are mainly aliphatic (Wang et al., 2016). Leachate A's SUVA value is lower than that Leachate B (0.12 vs. 0.90), indicating a lower degree of aromaticity in Leachate A. The e$_{280nm}$ absorption coefficients show complete agreement with SUVA. Because SUVA and e$_{280}$ are the ratio of UV absorbance and total organic carbon (TOC), the variation of these could be explained by the change in both UV absorbance and organics concentration. If UV absorbance decreases more than TOC, the SUVA will decrease. This is true for e$_{280nm}$ coefficient as well. For example, Leachate A's SUVA and

e_{280nm} decreased after oxidation, mainly because of a greater decrease in UV absorbance compared to that of the organics concentration (Fig. 8-4A and 8-4B, Table S811, S8-2). However, in Leachate B, both SUVA and the e_{280nm} coefficient increased after oxidation (Fig. 8-4C and 8-4D). The UV absorbance decrease was less than the organics decrease, resulting in increased SUVA and the e_{280nm} coefficient (Table S8-1, S8-2). The increase in SUVA and the e_{280nm} coefficient suggests that organics are consuming more UV light after oxidation. In other words, SPC oxidation failed to decrease the aromatics in Leachate B, and as a result, the relative concentration of aromatics increased after oxidation. This is an indication of the refractory properties of UV quenchers in Leachate B as explained by a previous study that found an increase in the SUVA value of a leachate from 2.1 to 3.4 after sequential batch reactor treatment (Zhao et al., 2012). To understand how different organic fractions are contributing to the SUVA and the e_{280nm} absorption coefficients, both were calculated for HA, FA, and HPI. In Leachate A, humic acids had the highest SUVA and e_{280nm}, which is typical (Fig. 8-4A, 8-4B) (Zhao et al., 2013). After SPC oxidation, the total decrease of SUVA and the e_{280nm} in Leachate A was contributed by all the organics fractions. However, for Leachate B, the increase in these coefficients (SUVA and e_{280nm}) after SPC oxidation was because of the increase of the SUVA and the e_{280nm} for almost all the organics fractions. The only exception was a slight decrease in the fulvic acids' SUVA and e_{280nm} value after oxidation with 0.01 M SPC (Fig. 8-4C, 8-4D).

At the level of the molecular size fractions, the 100 kDa – 1.5 µm fraction had the highest SUVA for both humic and fulvic acids in Leachate A (Fig. 8-5A). This is true for humic acids in Leachate B as well. It is evident that for humic and fulvic acids of both Leachate A and B, the size fractions < 1 kDa had the lowest SUVA. For Leachate A's hydrophilic fractions, all the molecular size fractions had the similar SUVA values. While in Leachate B, the size fraction 1 – 3 kDa exhibited the highest SUVA for hydrophilic fraction (Fig. 8-5B). The decrease in SUVA for different organics fractions of Leachate A was because of the decrease of the SUVA values for all the molecular size fractions corresponding to the organic fractions (Fig. 8-5A). However, for Leachate B, the increase in the SUVA for different organics fractions was a combined effect of both increase and decrease of different molecular size fraction's SUVA value as shown in Figure 8.5B.

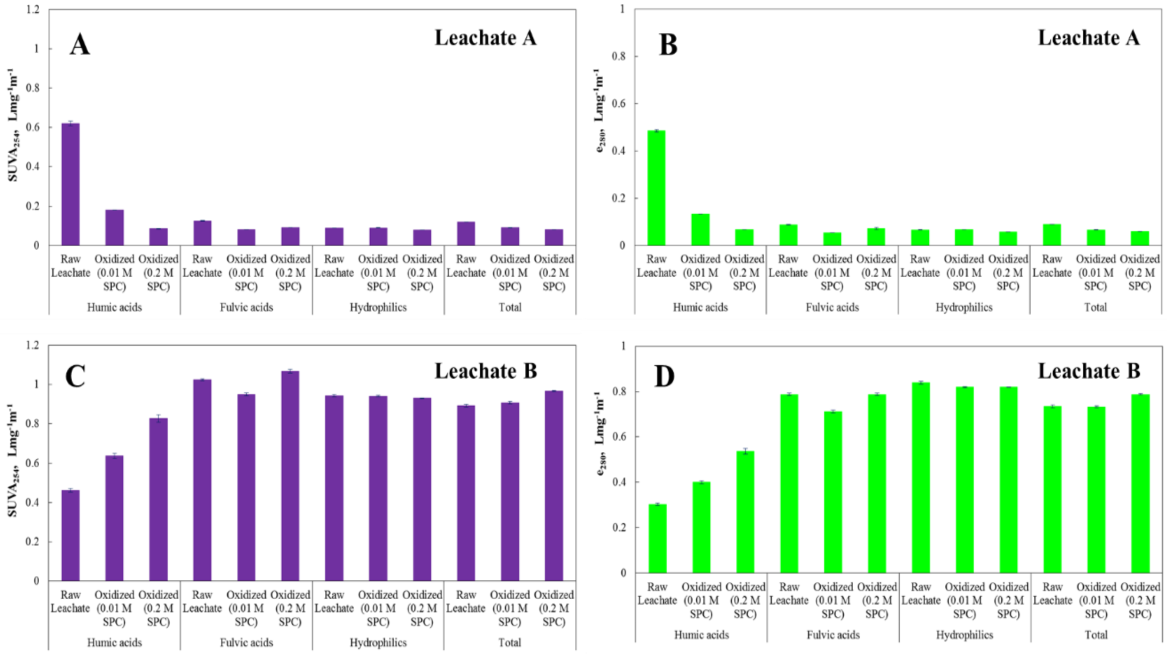

Figure 8-4. Specific Ultraviolet Absorbance (SUVA, L mg^{-1} m^{-1}) and e$_{280nm}$ absorption coefficient (L mg^{-1} m^{-1}) for different organic fractions of Leachate A (A and B) and Leachate B (C and D) before and after oxidation with 0.01 M and 0.2 M sodium percarbonate for 24 hours. Each point in the graph represents the mean of triplicate data, while the error bar represents the standard error of the mean.

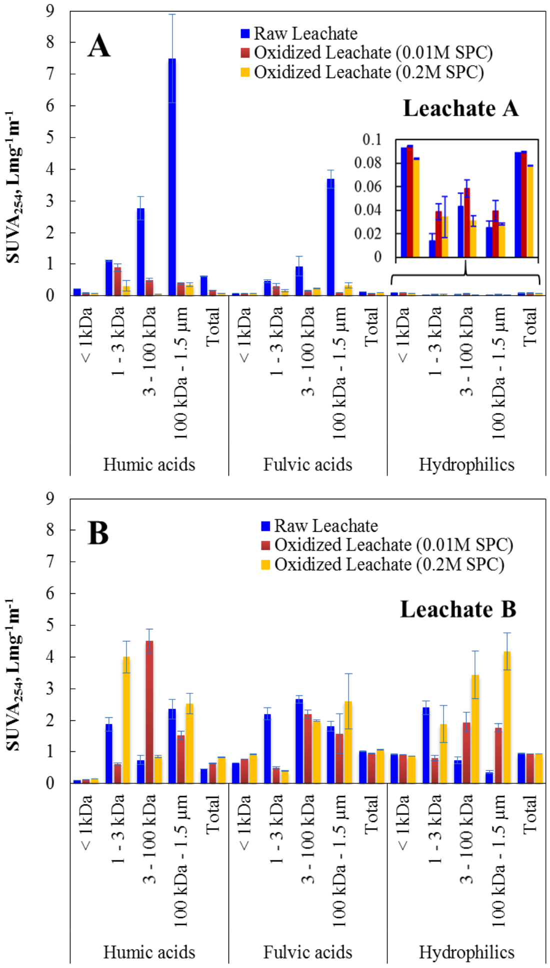

Figure 8-5. Specific Ultraviolet Absorbance (SUVA, L mg^{-1} m^{-1}) of different molecular size fractions of leachates' organic fractions - Leachate A (A) and Leachate B (B) before and after oxidation with 0.01 M and 0.2 M sodium percarbonate for 24 hours. Each point in the graph represents the mean of triplicate data, while the error bar represents the standard error of the mean.

Change of other parameters of leachate after oxidation

The SPC oxidation also changed other parameters such as turbidity and BOD_5. According to the initial values of turbidity of the two leachates (4155 and 131 NTU), it is evident that Leachate A was particularly high in suspended solids. The turbidity decrease in Leachate A after SPC oxidation ranged from 36.4 % (0.01 M SPC) to 99.7 % (0.2 M SPC); while, the maximum decrease in turbidity for Leachate B was only 12.7 % with

0.05 M SPC (Fig. 8-6A). The high removal of suspended solids (i.e. turbidity) from Leachate A demonstrated that SPC oxidation improved the settling capacity of organics possibly by coagulation and flocculation, and this settling capacity increased with the increase of SPC concentration (Amokrane et al., 1997; Tatsi et al., 2003). The greater concentration of Fe (68.9 mg L^{-1}) and S (1146.1 mg L^{-1}) might have played a role in the possible coagulation and flocculation of Leachate A organics. The 94.2 % removal of Fe and 99.9 % removal of S after 0.2 M SPC oxidation of Leachate A suggest this possible pathway of coagulation and greater turbidity removal for Leachate A than B. Leachate B had a relatively low concentration of Fe (7.0 mg L^{-1}) and S (177.3 mg L^{-1}) and the removal of 10.9 % Fe and 99.9 % S were observed after 0.2 M SPC oxidation, which along with lower suspended solid (i.e. low turbidity) yielded lower turbidity removal. A higher SPC concentration might also have increased the charged sites in the organic structures, which may have facilitated greater coagulation and flocculation. Such a high turbidity reduction is comparable to those with membrane treatment of leachate (> 99% removal of turbidity after membrane treatment, i.e. ultrafiltration, nanofiltration, and reverse osmosis) and ozone treatment (e.g., ~ 80% removal by ozone oxidation) (Renou et al., 2008).

The bioavailability index as indicated by the BOD_5/COD ratio increased from 0.22 to 0.25 after 0.2 M SPC oxidation of Leachate A (Fig. 8-6B). Previous studies found an increase in biodegradability (BOD_5/COD) after oxidation, mainly because of the removal of recalcitrant organics (Renou et al., 2008). As Leachate B's organics were more resistant to degradation, the BOD_5/COD ratio decreased from 0.19 to 0.12 after 0.2 M SPC oxidation (Fig. 8-6B). The increase of bioavailability could be beneficial for the subsequent biological treatment of Leachate A. The initial concentration of ammonia nitrogen in Leachate A and B was 1510 and 1897 mgL^{-1}, respectively (Table 8-1). No change in ammonia nitrogen was observed for both Leachate A and Leachate B after oxidation. The effective pathway of ammonia removal from leachate is biological treatment or stripping at a high pH (Bae et al., 1997; Cheung et al., 1997). It was reported that oxidation that produces hydroxyl radicals (i.e. Fenton) is unresponsive to ammonia (Deng & Englehardt, 2006). The pH increases in both leachates (to 9.84 in Leachate A, and to 9.64 in Leachate B) after addition of 0.2 M SPC was mainly contributed by the carbonates in the SPC. Even at this high pH, no ammonia was lost because of minimal disturbance of the reaction vials during oxidation treatment.

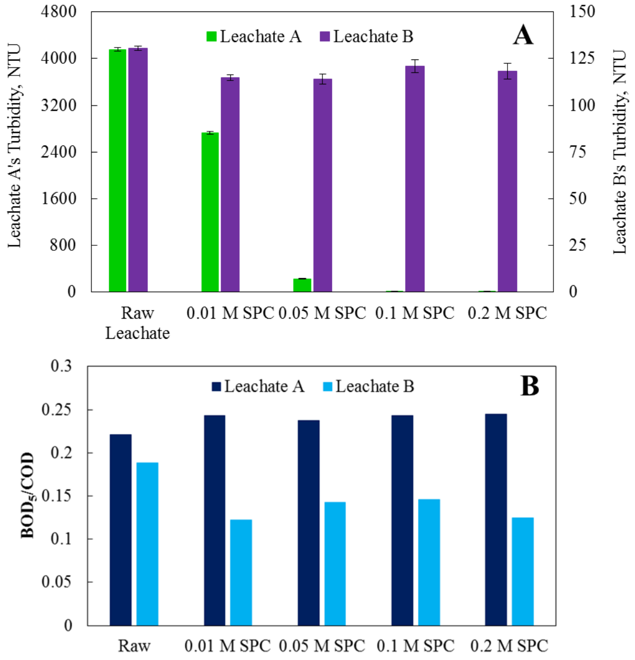

Figure 8-6. Additional effects of SPC oxidation: (A) change in Turbidity (NTU) of Leachate A and B; (B) BOD_5/COD ratio of Leachate A and B.

Cost analysis

As a new oxidation reagent for leachate treatment, the cost of the treatment is very important to potential applications. The oxidant sodium percarbonate has a low cost ($0.5 per kg) compared to other conventional oxidants (i.e. $14 per kg of potassium permanganate, $0.8 per kg sodium persulfate) (Abdullah et al., 2014; Hilles et al., 2016). The normalized cost with 0.01 – 0.2 M SPC treatment is $0.3 - $4.6 per kg of COD removed for Leachate A. While for Leachate B, this varied from $1.8 to $61.9 per kg of COD removed. In Leachate A, the maximum COD removal was 5.3 kg m^{-3} of leachate treated (with 0.05 M SPC), which yielded a treatment cost of $0.8 per kg of COD removed. In Leachate B, this was 0.6 kg m^{-3} of leachate treated (with 0.05 M SPC) and the cost was $6.7 per kg of COD removed. Previous studies have reported significantly higher cost of chemical oxidation treatment of leachate, for example $450 per kg of COD removed by potassium permanganate oxidation and $121 per kg of COD by H_2O_2

oxidation (Abdullah et al., 2014). A recent study showed $11.3 per kg of COD removal by sodium persulfate + H_2O_2 oxidation of leachate (Hilles et al., 2016). Therefore, the present SPC oxidation could be cost competitive. Because leachates are highly variable, the actual cost of treating a specific leachate will need studies to determine the optimum SPC concentration and the limitations of mass of COD removed per m^3 leachate treated.

Perspectives

Removal of UV quenchers is important if landfill leachates are to be treated in municipal wastewater treatment plants with minimal effects on the treatment process. This study has demonstrated a potentially cost-effective chemical oxidation method for reducing UV quenchers in two different types of leachates. Despite some success, we must also realize the challenges that need to be addressed with further research. First, the mechanism of SPC oxidation reducing UV quenchers needs to be better understood. Although this study has provided initial evidence and data support (e.g., the role of different organics or molecular size in UV absorbance reduction), the detailed reasons remain unclear. For example, revealing the composition of different size fractions would help us to better understand why Leachate A and B exhibited different response to SPC oxidation. Second, the removal efficiency by SPC oxidation needs to be further enhanced. This may be accomplished by examining the operating factors such as mixing, temperature, and pH. Third, synergistically linking the SPC oxidation to other treatment methods may help accomplish leachate treatment. For example, SPC oxidation increased BOD in Leachate A, which could benefit biological treatment. Physical treatment such as granular activated carbon can also be used to polish the SPC treated leachate. Fourth, the additional benefits of SPC oxidation such as decreasing turbidity via chemical oxidation enhanced coagulation are worth further exploration. The third and fourth challenges described here indicate the possible use of SPC oxidation as a pre-treatment for landfill leachate. The increase of bioavailability and the reduction of turbidity (>99%) of certain type of leachate after SPC oxidation will help post treatment like biological treatment (increased BOD_5/COD ratio) and sorption treatments (e.g. GAC). The sorption treatment could be highly benefitted from the SPC pre-treatment of leachate as it removes the suspended solids, which will increase the lifetime of GAC and frequency of regeneration (Foo & Hameed, 2009). However, this needs further investigation.

Conclusions

Sodium percarbonate is a cost-effective and easy to use oxidant for reducing UV quenchers in landfill leachate. The results of the present study can be important to understand the effectiveness of SPC oxidation of leachate in removing contaminants, especially UV quenchers. SPC could effectively reduce the UV absorbance and organics from certain types of leachate. Additional benefits such as great reduction of turbidity (>99%) and increasing BOD_5 have also been demonstrated. Further investigations are warranted to better understand the mechanism of SPC oxidation for reducing UV absorbance, enhance oxidation efficiency, and explore the integration of SPC oxidation with other methods for improving leachate treatment.

Supporting Information

Table S8-1. Change in the UV_{254nm} absorbance (cm^{-1}) of different organic fractions of Leachate A and B after oxidation with 0.01 M and 0.2 M SPC for 24 hours.

Organics	Leachate A (UV_{254} absorbance, cm^{-1})			% Change		Leachate B (UV_{254} absorbance, cm^{-1})			% Change	
	Raw	0.01 M SPC	0.2 M SPC	0.01 M SPC	0.2 M SPC	Raw	0.01 M SPC	0.2 M SPC	0.01 M SPC	0.2 M SPC
Humic acids	4.10	0.40	0.12	-90.3	-97.0	1.33	1.24	0.94	-6.5	-29.3
Fulvic acids	2.21	1.46	1.63	-33.8	-26.2	6.18	5.25	5.18	-15.1	-16.1
Hydrophilics	9.80	8.67	7.37	-11.5	-24.8	8.28	8.35	8.41	0.8	1.5
Total	16.12	10.53	9.13	-34.7	-43.4	15.80	14.84	14.54	-6.1	-8.0

Table S8-2. Change in the concentration (mgL^{-1}) of different organic fractions of Leachate A and B after oxidation with 0.01 M and 0.2 M SPC for 24 hours.

Organics	Leachate A (Organics concentration, mgL^{-1})			% Change		Leachate B (Organics concentration, mgL^{-1})			% Change	
	Raw	0.01 M SPC	0.2 M SPC	0.01 M SPC	0.2 M SPC	Raw	0.01 M SPC	0.2 M SPC	0.01 M SPC	0.2 M SPC
Humic acids	661	221	147	-66.6	-77.8	289	196	114	-32.3	-60.6
Fulvic acids	1769	1792	1802	1.3	1.8	604	553	485	-8.4	-19.6
Hydrophilics	11056	9717	9440	-12.1	-14.6	878	887	904	1.0	3.0
Total	13486	11731	11388	-13.0	-15.6	1771	1636	1504	-7.6	-15.1

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Appendices

List of Related Publications

1. Iskander, S., Novak, J. and He, Z. (2018). Reduction of reagent requirements and sludge generation in Fenton oxidation of landfill leachate by synergistically incorporating forward osmosis and humic acid recovery. Water Research, 151, 310-317.
2. Iskander, S.M., Zhao, R., Pathak, A., Gupta, A., Pruden, A., Novak, J.T., He, Z. 2018. A review of landfill leachate induced ultraviolet quenching substances: Sources, characteristics, and treatment. Water Research, 145, 297-311.
3. Iskander, S.M., Novak, J.T. and He, Z. 2018. Enhancing forward osmosis water recovery from landfill leachate by desalinating brine and recovering ammonia in a microbial desalination cell. Bioresource Technology, 255, 276-282.
4. Iskander, S.M., Novak, J.T., Brazil, B., He, Z., 2017a. Percarbonate oxidation of landfill leachates towards removal of ultraviolet quenchers. Environmental Science: Water Research & Technology, 3(6), 1162-1170.
5. Iskander, S.M., Novak, J.T., Brazil, B., He, Z., 2017b. Simultaneous energy generation and UV quencher removal from landfill leachate using a microbial fuel cell. Environmental Science and Pollution Research, 24 (33), 26040–26048.
6. Iskander, S.M., Zou, S., Brazil, B., Novak, J.T., He, Z., 2017c. Energy consumption by forward osmosis treatment of landfill leachate for water recovery. Waste Management, 63, 284-291.
7. Iskander, S.M., Brazil, B., Novak, J.T., He, Z., 2016. Resource recovery from landfill leachate using bioelectrochemical systems: Opportunities, challenges, and perspectives. Bioresource Technology, 201, 347-354.

Conferences presentations

Oral presentations

- Reduction of reagent requirements and sludge generation in Fenton’s oxidation of landfill leachate by synergistically incorporating forward osmosis and humic acid recovery. Association of Environmental Engineering and Science Professors (AEESP) conference, Tempe, AZ, May 2019.
- An Integrated forward osmosis - microbial desalination cell technique for enhanced water recovery from landfill leachate. Annual Alpha Epsilon Honor Society research symposium, Agricultural, Food, and Biological Engineering Department, Virginia Tech, VA, March 2019

- Reduction in required reagents and sludge generation in Fenton’s oxidation of landfill leachate through forward osmosis and humic acid recovery. 35th Graduate Student Assembly (GSA) symposium, Virginia Tech, VA, March 2019.
- Simultaneous energy generation and ultraviolet quenchers removal from landfill leachate using a microbial fuel cell. Global Waste Management Symposium, Palm Springs, CA, February 2018.
- An Integrated forward osmosis – microbial desalination cell technique for enhanced water recovery from landfill leachate. EREF WasteExpo, New Orleans, LA, May 2017.
- Integrating microbial desalination with forward osmosis to complement water recovery from landfill leachate. 33rd Graduate Student Assembly (GSA) symposium, Virginia Tech, VA, March 2017.
- Pretreatment of landfill leachate for enhanced electricity generation in a microbial fuel cell. 32nd Graduate Student Assembly (GSA) symposium, Virginia Tech, VA, March 2016.

Poster presentations

- Enhancing the recovery of humic acids from landfill leachate using forward osmosis and its application in the Fenton's oxidation of Benzene. 34th Graduate Student Assembly (GSA) symposium, Virginia Tech, VA, March 2018.
- Peroxygen oxidation towards understanding the ultraviolet quenchers transformation in landfill leachate. Borchardt conference, Ann Arbor, MI, February 2017.
- Recovery of organics and water from landfill leachate. WaterJam conference, Virginia Beach, VA, September 2016.
- Oxidation pretreatment of landfill leachate for enhanced electricity generation in a microbial fuel cell. Air and Waste Management Association (A&WMA) Conference, New Orleans, LA, June 2016.
- An Integrated forward osmosis – microbial desalination cell technique for enhanced water recovery from landfill leachate. Association of Environmental Engineering and Science Professors (AEESP) conference, Ann Arbor, MI, June 2017; Eighth annual CEE research day, Virginia Tech, VA, April 2018.
- Resource recovery from landfill leachate using bioelectrochemical systems. Sixth annual CEE research day, Virginia Tech, VA, April 2016.