

**Membrane Distillation for Leachate Treatment with
Fenton's Oxidation as a Pre-treatment Process**

Kyungsun Jessie Chung

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in partial fulfillment of the requirements for the degree of

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Zhen (Jason) He, Chair
Andrea M. Dietrich
Zhiwu (Drew) Wang

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ACADEMIC ABSTRACT

Landfill leachate is considered as a complex wastewater with various organic and inorganic species which must meet strict discharge standards before its release. Due to such high concentration of diverse pollutants, leachate is low in biodegradation; therefore, a proper usage of physicochemical treatments is required. In this study, membrane distillation (MD) has been used along with Fenton treatment process for pre-coagulation to achieve an effective removal of contaminants. MD is a technology derived with vapor pressure difference across the hydrophobic membrane which traps the feed-wastewater vapor at the entrance of the hydrophobic side before permeation. In order to modify and assist in membrane technology's common drawback, which is dealing with foulants, Fenton oxidation is coupled in the leachate treatment process. Fenton is reserved to be the most effective for leachate treatment and is widely used due to its simple operation and low costs. Fenton oxidation was able to lessen the chemical oxygen demand (COD) concentration of leachate up to 55% while increasing the conductivity and reducing the concentration of $\text{NH}_4\text{-N}$. The membrane flux and volume had a significant increase with a use of lower COD leachate after Fenton treatment coupled with MD.

Membrane Distillation for Leachate Treatment with Fenton Pre-Coagulation Treatment Process

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GENERAL AUDIENCE ABSTRACT

Landfilling has been recognized as a principal disposal process of municipal solid wastes globally over the past decades, and this disposal method has been one of the leading concerns for a continuous production of landfill leachate. Leachate is considered as a complex wastewater with a variety of organic and inorganic species which must meet strict discharge standards before its release. Due to such high concentration of diverse pollutants, leachate is low in biodegradation; therefore, a proper usage of physicochemical treatments is required. In this study, membrane distillation (MD) has been used along with Fenton treatment process for pre-coagulation to achieve an effective removal of contaminants.

MD is a technology derived with vapor pressure difference across the hydrophobic membrane which traps the feed-wastewater vapor at the entrance of the hydrophobic side before permeation. MD has several advantages which include reduced operating temperature compared to conventional distillation processes, fewer requirements of membrane cleaning, and lower operating hydraulic pressure than other conventional pressure-driven membrane processes such as reverse osmosis (RO). This technology has a common drawback along with other membrane-required technologies which is dealing with foulants. For a reduction in membrane fouling, Fenton oxidation is coupled in the leachate treatment process. Fenton is reserved to be the most effective for leachate treatment and is widely used due to its simple operation and low costs.

Dedicated to my parents, Sung Ho Chung and Hyun Suk Leem.

You are my constant motivation and inspiration for my success.

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1. Literature Review

1.1. Background

Landfilling has been recognized as a dominant disposal process of municipal solid wastes globally over the past decades (Jung et al. 2017; Tchobanoglous and Kreith 2002). From landfilling, one of the leading concerns is a continuous production of landfill leachate. Leachate is considered as a complex wastewater with a variety of organic and inorganic species which must meet strict discharge standards before its release (Zhao et al. 2013; Torrens 2013). The amount and type of involved treatments differ depending on the leachate characteristics. The characteristics and quantity of landfill leachate are affected by properties of solid waste, site hydrology, waste compact operation, landfill age, and rainfall frequency (Di Iaconi, Ramadori, and Lopez 2006; Hermosilla, Cortijo, and Huang 2009).

Organic pollutants and level of environmental threat are often measured using total oxygen-use equivalence methods, such as chemical oxygen demand (COD), biological oxygen demand (BOD) and/or measured total organic carbon (TOC) concentrations before releasing the landfill leachates to meet the acceptable effluent goal during and after their treatments (Shabiimam and Dikshit 2012). Amongst the major influencing parameters, the “age” of a landfill is widely studied due to a large difference in COD and BOD levels between young and mature leachate. Young leachate can be categorized to be aged 0-5 years, intermediate/mid-aged are between 5-15 years and stabilized/mature leachates are aged over 15 years. Young landfill leachates can produce high COD levels over 10,000 mg/L, mid-aged landfills commonly produce between 6,000 to 10,000 mg/L and old leachates contain lower COD levels, approximately 3,000 mg/L at 20 years. However, regardless of the oxygen demand concentration, older age provides difficulty

in the decomposition process (Renou et al. 2008). Due to the leachate's complexity, a wide-ranging selection of treatment involving biological, chemical, physical, and electrochemical treatments are selected also depending on the composition and flow rate of the leachates (Baiju et al. 2018). Young leachate is more acceptable in a variety of treatment methods including biological techniques that are broadly practiced. With the mature leachate, the intensity of high molecular weight resistant organics brings better treatment utilizing physicochemical techniques.

With leachate's complexity, cases of off-site and on-site treatment projects have been accomplished to remove common leachate contaminants including heavy metals, ammonia, dissolved organic matter, toxic gases (Zhao et al. 2013). As regulations intensify, leachate management is gathering a larger part of attention in solid waste management due to high capital, operations, and maintenance costs (Walker 2013; Torrens 2013). Amongst the selection, biological treatments are well-known and most widely practiced due to its simplicity, cost, and high efficiency in biodegradable matter removal; however, it is limited in treating leachates with high refractory contaminants (Umar, Aziz, and Yusoff 2010; Kurniawan, Lo, and Chan 2006). Therefore, numerous physicochemical techniques have been applied either as a pre-treatment or full treatment of landfill leachate over the years (Shi et al. 2019; Gao et al. 2015).

Current physical treatment methods publicized for handling leachate concentrates include adsorption and air stripping. The adsorption of pollutants is effective in COD level reduction, but the need for frequent replacement of powdered activated carbon (PAC) is counted as the main drawback (Rodríguez et al. 2004). Air stripping is today's most commonly applied technology to eliminate a high concentration of NH_4^+ -N from wastewater and remove the toxicity originated

from high levels of ammonium nitrogen. But the major concern comes from releasing NH_3 into the atmosphere and leading air pollution when failed to be absorbed with H_2SO_4 or HCl (Renou et al. 2008).

For further advanced treatments, membrane technologies are expanding as well. Current membrane treatment methods for treating leachate include micro/ultrafiltration, nanofiltration, reverse osmosis, forward osmosis and membrane distillation. Micro/ultrafiltration are often used to eliminate colloids and suspended matters, but they are both either too low in retention rate or too high in membrane recovery cost; as a result, they cannot be used alone (Ince et al. 2010). There are several studies operated with nanofiltration for leachate treatment where nearly 60-85% COD was removed; however, a wide spectrum of constituents was found to affect this membrane process with fouling (Chaudhari and Murthy 2010). Reverse osmosis (RO) is considered to be the most promising and it, in fact, has been applied across the European countries such as Germany, the Netherlands, etc. in a form of disc-tube-module (DT-module) (Cingolani et al. 2018). However, it has issues such as a high-pressure requirement, generation of large volume of concentrate and high cost. Forward osmosis is another emerging technology successfully used in leachate, seawater, and other wastewater treatment that require low to no pressure for a water extraction (Zhou et al. 2017). Some drawbacks come from a continuous recirculation requirement which exhaust a significant amount of energy (Zou et al. 2016) and also the FO performance is negatively affected by a continuous dilution of draw solution during the running process (Zhou et al. 2017).

1.2. Membrane Distillation

MD is a technology derived with vapor pressure difference across the hydrophobic membrane which traps the feed-wastewater vapor at the entrance of the hydrophobic side before permeation (Curcio et al. 2010). The advancement in the ultrafiltration membrane in recent years enabled further development of membrane distillation from membrane functionality to process design and application in more complex systems since the late 1960s (Li et al. 2016). Since MD employs a heat and mass transfer simultaneously, temperature gradient between the feed and permeate sides performs an important role in determining the amount of pure water molecules transport through the membrane. As the temperature gradient increases, the flux and flow rate may increase depending on the concentration of the contaminants.

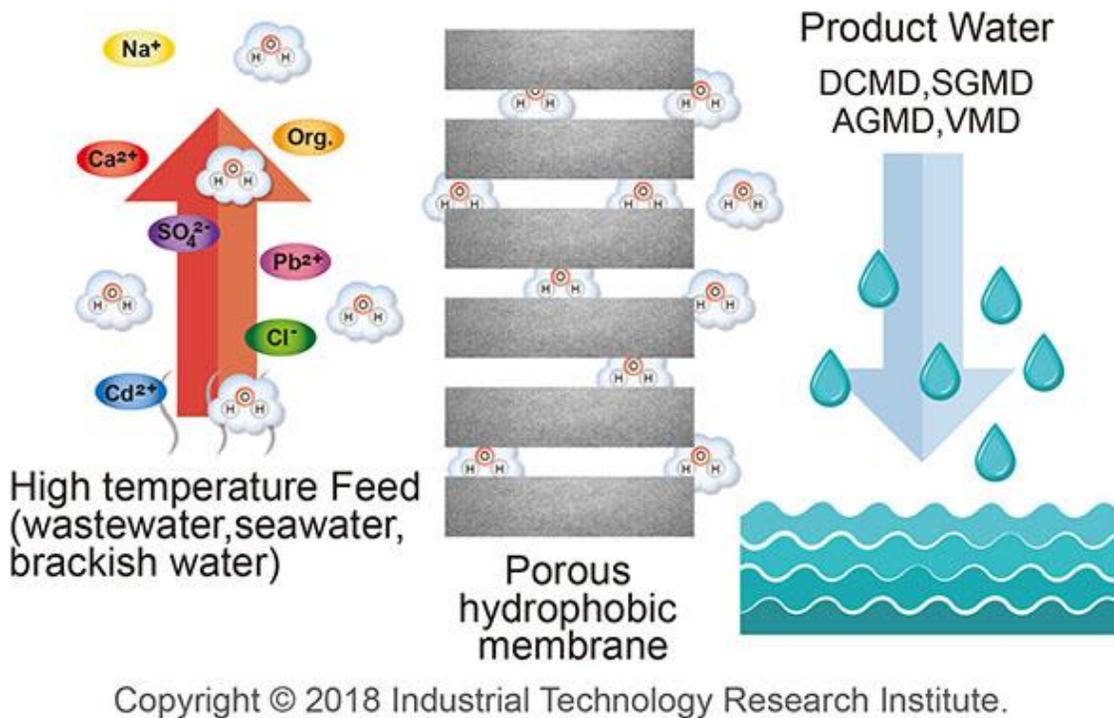


Figure 1.1. Schematic diagram of membrane distillation obtained from a previous study with permission (Ho 2018)

MD has several advantages which include reduced operating temperature compared to conventional distillation processes, fewer requirements of membrane cleaning, and lower operating hydraulic pressure than other conventional pressure-driven membrane processes such as reverse osmosis (RO) (Razmjou et al. 2012; Yang et al. 2011). Additionally, MD's attraction has increased compared to RO or other membrane technology with a possibility of utilizing low-grade waste heat and other natural sources such as solar or geothermal energy to conserve in constant energy cost (Wang and Chung 2015). As a result, there are many different applications of MD for organic wastewater treatment including biologically treated coking wastewater, anaerobically digested livestock wastewater, reverse osmosis concentrate wastewater, and other organic wastewater (Kim, Lee, and Cho 2016; Liu et al. 2016). These studies have successfully demonstrated the MD's ability in trapping almost all the organic pollutants from the feed solution which indicates that MD will be an effective method for the further treatment of leachate along with an assist in membrane fouling prevention method.

In MD process, the membrane unit is reported to correlate 20-25% of the total capital cost of a desalination plant; therefore, it is significant to understand anything that result in fouling membrane performance and membrane condition (Voutchkov 2018; Dydo et al. 2004). The important characteristics of MD membrane parallel to performance include hydrophobicity, porosity, uniformity in pore size and pore distribution, membrane position, and thin thickness (Tijing et al. 2015). Like all other membrane processes, fouling is considered as a major inefficiency causing a reduction in the permeability due to the accumulation of substances inside the membrane pores and on the surface. As MD's applications widen, numerous studies have been investigating an overall MD process design for a reduction in fouling utilizing different

types of membranes such as flat-sheet and hollow fibers (Khayet 2011; Tijing et al. 2014). However, for MD, the issue on fouling and scaling is still not well presented compared to other pressure driven membrane technologies such as RO, NF, and UF (El-Bourawi et al. 2006). Investigation in fouling phenomenon is continuously growing for MD as well; however, it is a time-dependent process which cannot be easily predicted in a short-term. Several other methods reported for foulant reduction include pre and post treatment and this paper will review the MD process applied with Fenton oxidation which is one of the most well-known pre-treatments for resistant elements.

In addition to fouling, membrane wetting is another challenge within MD during a long-term operation. Wetting phenomenon is associated to the organic fouling which causes a reduction of hydrophobicity of membrane from a formation of attractive forces between hydrophobic materials within an aqueous system (Rezaei et al. 2018). Notably, MD membranes are prone to wetting by organic compounds, they have been shown to experience less flux decline than reverse osmosis or forward osmosis membranes undergoing biofouling (Jang et al. 2016).

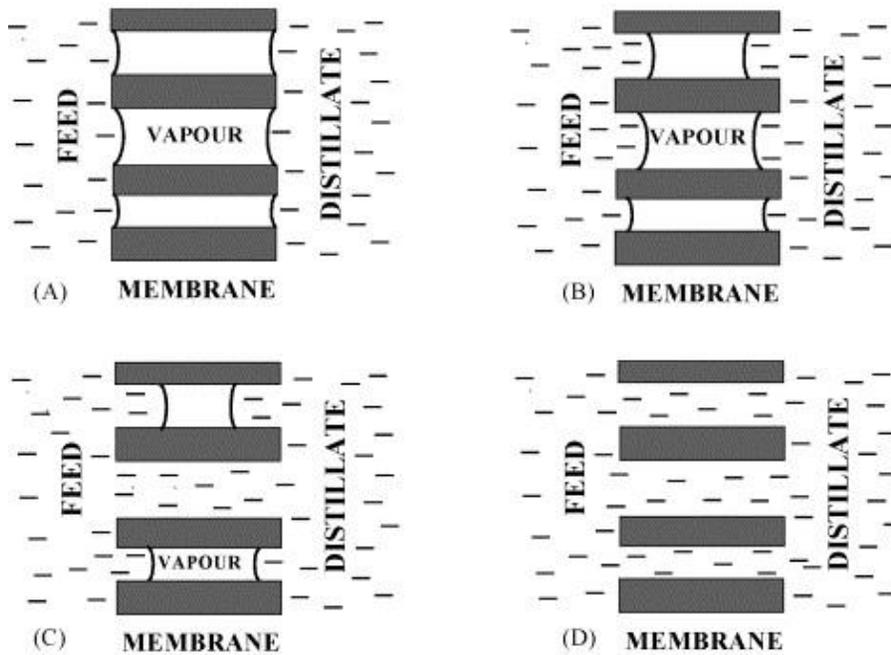


Figure 1.2. Presentation of four forms of membrane wetting phenomenon in MD process: (A) non-wetted; (B) surface-wetted; (C) partial-wetted; (D) fully-wetted obtained from a previous study with permission (Gryta 2007).

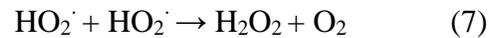
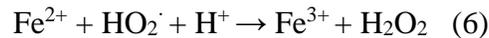
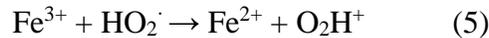
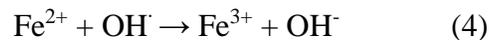
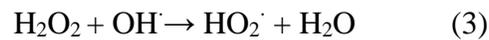
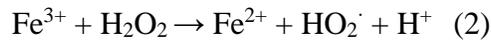
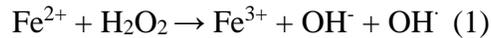
Typically, there are four forms of wettability of a membrane: non-wetted, surface wetted, partial-wetted and fully-wetted membrane. Non-wetted is the ideal condition of the membrane. Surface wetting happens due to fouling on the surface, but the pores remain open for the vapor to pass through. Partial-wetting is similar to the surface-wetting but some of the pores of the membrane are also clogged along with the surface. Fully-wetted leads to a critical error in MD performance results because the feed water just flows pass through the membrane and creates permeate with low quality presentation. This wetting can be prevented by coating the hydrophilic layer on a hydrophobic membrane (Rezaei et al. 2018) and by choosing membrane with small maximum pore size and good postsynaptic density (Tijing et al. 2015).

pH, conductivity, COD, and NH₃-N are the main chemical components investigated for this study. The pH of leachate is highly related to the components of the landfill and influenced by the amount of ammonium ions, carbonic ions, and dissolved materials and gases where the ease of hydrogen cations and bicarbonate anions productions are determined (Naveen et al. 2017). The concentration of dissolved matters such as carbonic, humic, fulvic and other organic acids increase the acidity level in leachate (Mahapatra, Chanakya, and Ramachandra 2011) while leachate above pH 7 carries greater and more mature load of dissolved substances (Jorstad, Jankowski, and Acworth 2004). Through removing organic and inorganic substance through MD, the pH level may be balanced to match the regulation. Several studies reported that fewer occurrences of humic acid fouling was observed with MD compared to other membrane processes (Srisurichan, Jiratananon, and Fane 2005) since the operating pressure of the process is lower and the decomposition of humic acid aggregates on the membrane surface is less compact reducing the transport resistance (Khayet 2011). The conductivity is a parameter used for identifying the concentration of ionized chemicals in water. Usually, an increase in conductivity is presented when dissolved salts and other inorganic chemicals conduct electrical current and a decrease shows a presence of organic compounds since they do not conduct electrical current very well when in water (Hem and Minear 2012). Several studies investigated the relationship between high salt concentration and the permeate flux of MD and concluded that the concentration attributed to the reduction in the permeate flux and an overall treatment activity due to a creation of fouling layer on the membrane surface and inside the pores (Alkudhiri, Darwish, and Hilal 2012; Martínez 2004). As mentioned previously, organic pollutants and level of environmental threat are often measured using total oxygen-use equivalence methods such as COD and many studies saw results presenting a decrease in COD concentration using variety of

feed wastewater solutions. Ammonia (NH₃-N) is another common pollutant in wastewaters produced from a depletion of oxygen due to nitrification. Qu et al. investigated that the ammonia removal efficiency was independent on the ammonia concentration from a feed source and the removal rate was constant (Qu et al. 2013). Since other ammonia removing technologies required specific range of feed ammonia concentrations, MD is an effective choice of technology for ammonia removal.

1.3. Fenton Oxidation

Fenton oxidation and advanced oxidation processes (AOP) are well known chemical treatments that have been implemented as a pre-treatment for leachate. Both treatments utilize the reaction between a strong oxidant and the organics which result in improving leachates' biodegradability and treatability (Renou et al. 2008).



(Eq. (1)) Hydrogen peroxide molecules are decomposed from an oxidation conducted from ferrous ions to ferric iron; (Eq. (2)) Several studies reported how the reduction occurs from ferric

to ferrous iron using hydrogen peroxide (Chen et al. 2011); (Eq. (3)) In the absence of other oxidizable substance, the net reaction produce oxygen and water molecules in the iron-catalyzed conversion of hydrogen peroxide (Hermosilla, Cortijo, and Huang 2009). In the Fenton process, ferric iron becomes a predominant species when the molar ratio of hydrogen peroxide to total iron is high, and highly reactive hydroxyl radicals initiate the oxidative destruction of organic substances (Lopez et al. 2004).

AOPs are attractive methods to remove color and treat effluents with high refractory compounds in leachates since they can be adapted to old or well-stabilized leachates. But AOPs bring a high cost and energy demand while using ozonizers, UV lamps, and ultrasounds. Also, complete degradation can only be accomplished with high oxidants doses (Lopez et al. 2004). Fenton is a catalyst-steered oxidation process including ferric iron (Fe (II)) and hydrogen peroxide (H_2O_2) that produces hydroxyl radical ($\bullet OH$) to oxidize organics (Aftab, Shin, and Hur 2018; Bu et al. 2010). Compared to AOP, Fenton oxidation is reserved to be the most effective for leachate treatment and is widely used due to its simple operation and low costs, and also reports have been informing its possibility in attaining high COD and TOC removal, decolorization, and a significant increase in biodegradability (Jung et al. 2017).

The performance of Fenton oxidation is highly affected by operation parameters such as reaction time, pH, mole ratio of H_2O_2 to Fe (II), H_2O_2 dosage, and Fe (II) dosage (Zhang, Choi, and Huang 2005; Mohajeri et al. 2011). First, the efficiency of Fenton performance is depended on pH level. Several studies have confirmed that the oxidation reaction is favored in acidic pH since the oxidation potential of hydroxyl radicals ($\bullet OH$) decreases with an increase in pH. In a Fenton

process, pH level is controlled with a use of sulfuric acid solution (H_2SO_4) to lower pH and sodium hydroxide solution (NaOH) to raise pH. The optimum pH level ranges from 2 to 4 which is very narrow in terms of flexibility because this range is the most effective with H_2O_2 regeneration and a reaction rate escalation. According to studies by Sedlak and Andren (1991) and Zhao et al (2013), Fenton oxidation coped in treating landfill leachate was effective at a pH range between 2 and 4 (Sedlak and Andren 1991; Zhao et al. 2013). H_2O_2 decomposes in an ineffective way with no contribution to oxidation reactions when pH is above 4 and the treatment performance was deteriorated at pH above 6. Additionally, Hermosilla et al. (2009) observed insignificant difference in COD removal within the pH range between 2 to 4; therefore, the optimum pH was set.

The dosing ratio between ferric iron and hydrogen peroxide also plays an important role during the Fenton process. An increase in reagent concentrations tend to increase the removal of organic contaminants; however, there is a threshold level that balances out the maximum concentration requirement until it becomes insignificant (Deng and Englehardt 2006). Too much of iron dosage may result in a substantial increase in total dissolved solids (TDS) and conductivity which will require further treatment of the effluent before its discharge (Gogate and Pandit 2004).

Additionally, excessive concentration of hydrogen peroxide will generate gas bubbles resulting in sludge sedimentation impedance and it will disadvantage biological treatment process (Deng and Englehardt 2006). The optimum reagents concentration ratio $[\text{H}_2\text{O}_2]/[\text{Fe(II)}]$ range is currently found to equal 1.5 to 2 with 1.5 being the best operation condition (Zhang, Choi, and Huang 2005). The range was determined by comparing COD removal rate and at the ratio=1.5, COD removal increased rapidly to 60% removal (Hermosilla, Cortijo, and Huang 2009). COD

removal is a crucial factor for a leachate treatment and is a suitable indicator for foulant reduction.

Chemical component removal through Fenton's oxidation depends on the initial pH, conductivity, COD and NH₃-N concentrations. As mentioned previously, leachate characteristics are highly differed by the components of the landfill. According to many studies, the optimal initial pH is ranged between 2 to 4. However, the ability to conduct initial pH adjustment and neutralization varies with different concentration of dissolved matters such as carbonic, humic, fulvic and other organic acids (Mahapatra, Chanakya, and Ramachandra 2011) as well as salts which create stronger buffering capacity and weaken the pH adjustment of strong acids or bases during processes. Higher concentrations in leachate also relates to stronger ionic strength which lowers the activity of the acids and bases and causes much more difficulties in pH changes (Mohajeri et al. 2011; Naveen et al. 2017). The conductivity will increase after the Fenton's oxidation process due to the chemical reagent introduction. When the leachate holds greater amount of organic, the increase will be less because the presence of organic compounds decreases the electrical current conductivity (Hem and Minear 2012). Fenton's oxidation is generally the most common chemical process for treatment of refractory wastewater and there were variety of cases using different operational conditions all reporting a success in removing COD from studied wastewater as well as leachate (Bianco, De Michelis, and Vegliò 2011; Singh and Tang 2013). Zhang et al. (2005) reported that higher initial COD of leachate triggers higher COD removal rates for the equal amount of Fe (II) and H₂O₂ usage and this was agreed by Amiri and Sabour in 2014 using different landfill leachate sample (Amiri and Sabour 2014). Regardless of such high COD removal, the ammonia removal is not as sufficient the Fenton process requires

higher concentration of H_2O_2 to lead a degradation of ammonium and for more than 90% removal, ratio between $[\text{H}_2\text{O}_2]/[\text{Fe}^{2+}]$ is recommended to be more than 10 (Goi and Trapido 2002).

Even though Fenton oxidation provides such high COD removal rate, there are several drawbacks needed to be addressed. There are four stages in Fenton treatment: pH adjustment to the optimum pH range, oxidation reaction, neutralization of pH to an acceptable effluent condition, and filtration. During the first stage, inorganic acid such as H_2SO_4 or HCl is added depending on the initial leachate pH level to reach the optimum pH range of 2 to 4. Afterward, addition of reagent $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ as $\text{Fe}(\text{II})$ and H_2O_2 contribute in a material cost and the ratio and the concentration are highly depended on the type of leachate as well. Moreover, when H_2O_2 and $\text{Fe}(\text{II})$ react with leachate, foaming may occur because of CO_2 production triggered from conversion of HCO_3^- and CO_3^{2-} at such acidic condition (Deng and Englehardt 2006), and this result in requiring a larger volume for a reaction. The third stage is neutralization, and this is usually performed with a high base solution such as NaOH and Lime. Use of highly basic solution will cause a formation of Fe^{3+} resulting in the production of ferric based sludge because Fe^{3+} precipitate to iron oxyhydroxides in an increased pH (Lin, Wu, and Zhang 2013). The sludge is required to be handled and disposed in a proper manner which contributes in large portion of disposal cost (Umar, Aziz, and Yusoff 2010). Overall, cost is one of the biggest factors considered in enhancing the Fenton oxidation technology for leachate treatment, and in recent studies, Fenton oxidation has been modified by combining electricity such as UV-light to fasten the oxidation process with a less use of reagents (Umar, Aziz, and Yusoff 2010).

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2. Effects of Membrane Distillation on Landfill Leachate Treatment Coupled with Fenton Oxidation as a Pre-Treatment

2.1. Abstract

Landfill leachate is considered as a complex wastewater with various organic and inorganic species which must be properly treated to reduce its impact on human health and environment. Due to such high concentrations of diverse pollutants, leachate is low in biodegradation and thus a proper usage of physicochemical treatment is required. In this study, membrane distillation (MD) has been used along with Fenton's oxidation as a pre-treatment to achieve an effective removal of contaminants and reduction of leachate volume with water recovery. Fenton's oxidation alone was effective in removing up to 55% of COD concentration and 37% of NH₃-N concentration. Combining Fenton with MD process could deliver $20 \pm 5\%$ higher permeate water flux, compared to a standalone MD without any pretreatment. The total water decline in permeate flux with the Fenton treatment was only at 7% (93% water recovery) while without the pretreatment, it decreased by 27% (73% water recovery) in the course of 50 hours. In terms of longevity, the membrane wetting phenomenon was eliminated using the combined process with a stability and longevity in the treatment performance when tested for 168 hours. The chemical quality of permeates using Fenton pretreatment displayed a high stability with less than 10% increase in COD and NH₃-N concentrations and conductivity in 144 hours. On the contrary, the permeate extracted without Fenton experienced a membrane wetting which increased by around 200% in all three parameters. These results have demonstrated that MD coupled with Fenton's oxidation pre-treatment could be a promising solution for enhanced hazardous landfill leachate treatment.

2.2. Introduction

Landfilling has been recognized as a dominant disposal process for municipal solid wastes globally over the past decades (Jung et al. 2017; Tchobanoglous and Kreith 2002) but one of the leading concerns is the production of landfill leachate. Leachate is a complex wastewater containing various organic and inorganic compounds along with heavy metals and toxic gases (Zhao et al. 2013). Leachate is often treated offsite by being transferred to a municipal wastewater treatment plant (WWTP) for co-treatment with domestic sewage (Comstock et al. 2010). This co-treatment can affect the WWTP treatment process because of leachate's high refractory organic contaminants with low biodegradability and heavy metals with toxic effects (Ferraz et al. 2014). Therefore, leachate should be properly treated to minimize its effects on co-treatment in WWTP. The complexity of leachate has allowed a wide selection of treatment involving biological, physical, chemical, and electrochemical treatments (Baiju et al. 2018). Onsite leachate treatment should not only decrease the contaminant concentration, but also reduce the volume of leachate.

An effective treatment method for reducing leachate volume is based on membrane technologies. Current membrane treatment methods for treating leachate include micro/ultrafiltration, nanofiltration, reverse osmosis, forward osmosis and membrane distillation. Micro/ultrafiltration are often used to eliminate colloids and suspended matters, but they are either too low in retention rate or too high in membrane recovery cost; as a result, they cannot be used alone (Ince et al. 2010). There previous studies about nanofiltration for leachate treatment reported the removal of nearly 60-85% COD; however, a wide spectrum of constituents was found to affect this membrane process with fouling and high operating pressures (Chaudhari and Murthy 2010).

Reverse osmosis (RO) is considered to be the most promising and it, in fact, has been applied to treat landfill leachate across the European countries such as Germany, the Netherlands, etc. in a form of disc-tube-module (DT-module) (Cingolani et al. 2018). However, it has issues such as a high-pressure requirement, generation of large volume of concentrate and high cost. Forward osmosis (FO) is another emerging technology successfully used in leachate, seawater, and other wastewater treatment that require low to no pressure for a water extraction (Zhou et al. 2017). Some drawbacks come from a continuous recirculation requirement which exhausts a significant amount of energy (Zou et al. 2016) and also the FO performance is negatively affected by a continuous dilution of draw solution during the operation process (Zhou et al. 2017).

Membrane distillation (MD) is an emerging method applied for wastewater treatment and has demonstrated high efficiency in separating contaminants from water (Wang and Chung 2015). MD uses vapor pressure difference across the hydrophobic membrane which acts as a barrier to extract water (vapor) from wastewater (Curcio et al. 2010). MD has several advantages such as 100% nonvolatile source rejection, lower operating temperature compared to conventional distillation processes, fewer requirements of membrane cleaning, and lower operating hydraulic pressure than other conventional pressure-driven membrane processes such as RO (Liu et al. 2016; Razmjou et al. 2012). As a result, there are many different applications of MD for treating various wastewaters such as digested livestock wastewater, biologically treated coking wastewater, reverse osmosis concentrate wastewater, and other organic wastewaters (Kim, Lee, and Cho 2016; Li et al. 2016). However, utilizing MD as a main leachate treatment has not been well studied before.

Treating a complex wastewater like landfill leachate in MD will undoubtedly cause membrane fouling, which can subsequently affect MD separation performance. Thus, proper pre-treatment that can reduce contaminant concentrations will be beneficial to MD operation. The goal of this study is to examine the performance of MD treating actual landfill leachate with Fenton's oxidation as a pre-treatment step. Fenton's oxidation is a catalyst-steered oxidation process including Fe (II) and H₂O₂ that produces hydroxyl radical (\bullet OH) to oxidize organics. This advanced oxidation process is effective in attaining up to 90% COD removal, 82% TOC removal, 92% decolorization, and a significant increase in biodegradability (BOD₅/COD) (Deng and Englehardt 2006). The specific objectives of this study were to (1) demonstrate the effect of Fenton pre-treatment on leachates; (2) examine water recovery through MD; and (3) investigate changes in the key characteristics of the leachate affected by Fenton pretreatment.

2.3. Materials and Methods

2.3.1. Landfill Leachate Sample

Two leachate samples were studied, Leachate A and Leachate B. Leachate A was the original, unmodified leachate from a municipal solid waste landfill located near Virginia Beach in VA, USA. Leachate B was a dilution of Leachate A with distilled water. The leachates were stored at 4°C until use. The water quality of the leachates was given in Table 2.1.

Table 2.1. Characteristics of the two leachates. Leachate B was a dilution of Leachate A.

Parameters	Leachate A	Leachate B
pH	6.38 ± 0.02	6.60 ± 0.05
Conductivity, mS cm ⁻¹	42.8 ± 0.55	6.37 ± 0.09
COD, mg L ⁻¹	251,000 ± 1700	44,000 ± 833
NH ₃ -N, mg L ⁻¹	28,000 ± 300	5,900 ± 193

2.3.2. Fenton Oxidation

Fenton oxidation was performed at an optimal molar ratio of [H₂O₂]/ [Fe²⁺] = 1.5 reported for Fenton's oxidation operation of leachate (Hermosilla, Cortijo, and Huang 2009). All the reactions were conducted in triplicates. For the Fenton reaction reagents, ferrous sulfate heptahydrate (FeSO₄ 7H₂O, Fisher Scientific, Hampton, NH) and 30% (wt%) hydrogen peroxide (H₂O₂, Fisher Scientific, Hampton, NH) were used. The leachate was adjusted to pH of 3 with sulfuric acid, H₂SO₄. Then, FeSO₄ 7 H₂O was added and mixed at 300 rpm for 5 min for complete dissolve followed by an addition of H₂O₂. The solution was further mixed at 500 rpm for 2 hours, and its final pH was adjusted to 6.5 with the addition of 10-M sodium hydroxide (Acros Organics, Czech Republic) and gentle mixing of 30 min was conducted. A settling period of 5 hours was allowed and then the supernatant was filtered through a 1.5 μm microfiber filter (DSC, Van Nuys, CA).

2.3.3. Membrane Distillation

Membrane distillation was set up as shown in Fig 2.1 by using a 0.45 micrometer pore sized hydrophobic membrane (GE Healthcare Amersham Hybond, Buckinghamshire, United

Kingdom) with a 70 cm² active surface area facing the feed side. MD test was conducted with a feed leachate volume of 300 mL along with 200 mL distilled water as an initial permeate cooling solution in a batch mode of 12 hours. The recirculation rate was applied at 20 mL min⁻¹ (3.5 cm s⁻¹) to both feed and permeate chambers to reduce the concentration polarization effect while enhancing the heat transfer (Alkudhiri, Darwish, and Hilal 2012). The temperature gradient was established by applying 40°C difference between the permeate and feed solutions: the feed solution was heated up to 60°C and the permeate solution was stabilized at 20°C. The temperature difference was chosen regarding the most effective for the MD process while considering the energy usage.

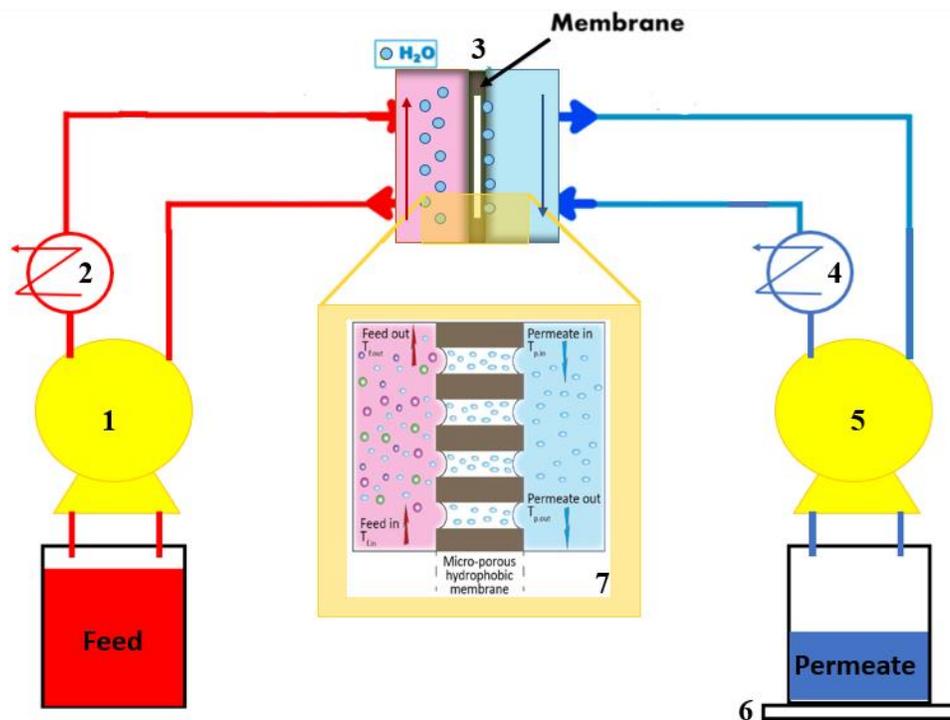


Figure 2.1. Schematic of the MD system; (1) feed pump, (2) water heater, (3) membrane module, (4) water temperature stabilizer, (5) permeate pump, (6) electronic scale (7) zoomed membrane module design was taken from a previous study with permission (Duong et al. 2015).

2.3.4. Chemical Cleaning of MD Membrane

To ensure the maximum water recovery in MD, the membrane was cleaned via chemical cleaning with H₂SO₄ (Fisher Scientific, Hampton, NH) and NaOH solutions after every 48-hour experiments. During the chemical cleaning process, the recirculation flow rate was increased to 40 mL min⁻¹ (7 cm s⁻¹). First, the feed side of MD membrane was rinsed with a diluted H₂SO₄ solution that has a pH 3 for 30 minutes, and 500 mL of distilled water was used to rinse the permeate side. After the acid rinse, the entire system was rinsed with 500 mL of distilled water in both feed and permeate for the equal amount of time. Then, a NaOH mixture solution with its pH adjusted to 12 was employed as the feed source to clean the MD membrane for 30 minutes, followed by a rinse of the whole system with distilled water.

2.3.5. Measurement and Analysis

The key parameters that were measured include pH, Conductivity, COD (chemical oxygen demand) and NH₃-N. The solution pH was measured with an Oakton pH 700m device (OAKTON Instruments, Vernon Hills, IL). The solution conductivity was recorded with a benchtop conductivity meter that sensors the temperature as well (Mettler-Toledo, Columbus, OH). The COD concentration and NH₃-N concentration were measured with a colorimeter under the manufacturer's instruction (DR 890, HACH Company, USA). Water flux was measured by recording the change of mass of the permeate solution every 0.5 min on an electric balance (Scort Pro, Ohous, Columbia, MD). The water flux J_w in Lm⁻²h⁻¹ (LMH) was calculated according to the following Eqn. 1 (Zhou et al., 2017).

$$J_w = \frac{\Delta V}{S_m \cdot \Delta t} \quad (\text{Eqn. 1})$$

where ΔV is the change of water permeate volume at an operating time which is symbolized Δt . and S_m is the membrane surface area measured in m^2 . Then the water flux was normalized by the maximum water flux using Eqn. 2 for an easier quantification during a comparison between different leachate feed sources.

$$\text{Normalized Water Flux} = \frac{J_{w,m}}{J_{w,o}} \quad (\text{Eqn. 2})$$

where $J_{w,m}$ is the measured water flux and $J_{w,o}$ is the maximum water flux which was recorded to be the initial water flux for all experiments.

2.4. Experimental Results and Discussions

2.4.1. Fenton Pre-treatment

Although both Leachate A and Leachate B had the similar initial pH of 6.50 ± 0.05 shown in Fig. 2.2A for Leachate A and Fig. 2.2B for Leachate B, their requirement of reagents for the pH adjustment and subsequent neutralization after the Fenton's oxidation differed significantly. Leachate A had a much higher requirement for acid (H_2SO_4) and base (NaOH) solution usages, which were 88% more and 70% more than those of Leachate B, respectively. This result was likely due to the different concentrations of dissolved matters such as carbonic, humic, fulvic and other organic acids (Mahapatra, Chanakya, and Ramachandra 2011) as well as salts which may create a stronger buffering capacity and thus weaken the pH adjustment by acids or bases. The higher concentrations of salinity and total dissolved solids in Leachate A also related to a stronger ionic strength which lowers the activity of the acids and bases and causes much more difficulties in pH changes (Mohajeri et al. 2011; Naveen et al. 2017). However, with the Fenton's oxidation reaction, the COD removal was more significant in Leachate A even with an equal amount of oxidation reagent uses to that of Leachate B, indicting a higher reagent

efficiency with Leachate A. The initial COD concentration of Leachate A was $251,000 \pm 1700$ mg L^{-1} displayed in Fig. 2.2A, which was reduced to $100,000 \pm 1365$ mg L^{-1} , approximate of 60% reduction. For comparison, Leachate B only had a 41% decrease in COD concentration dropping from $44,000 \pm 833$ mg L^{-1} to $26,000 \pm 464$ mg L^{-1} presented on Fig. 2.2B. This relation was agreed and presented by a previous study in which the authors reported a higher initial COD triggers higher COD removal rates for the equal amount of Fe (II) and H_2O_2 usage (Amiri and Sabour 2014). Landfill leachate typically presents high concentrations of nitrogenous pollutants which are harmful to the environment. The removal of $\text{NH}_3\text{-N}$ was not as sufficient as COD removal; however, the average of 32% removal was presented from both leachates, resulting in a decrease of ammonia concentration from $28,000 \pm 300$ mg L^{-1} to $20,300 \pm 333$ mg L^{-1} in Leachate A and from $5,900 \pm 913$ mg L^{-1} to $3,600 \pm 101$ mg L^{-1} in Leachate B. According to a previous study, ammonia removal may be further increased by using higher concentration of H_2O_2 , for example a ratio between $[\text{H}_2\text{O}_2]/[\text{Fe}^{2+}]$ to be more than 10 could lead to more than 90% removal of ammonia (Goi and Trapido 2002). The solution conductivity is a parameter used for identifying the concentrations of ionized chemicals in water. The conductivity of both Leachate A and Leachate B increased due to an addition of chemical reagents; however, the increase in Leachate B was more significant from 6.37 ± 0.09 mS cm^{-1} to 19.47 ± 0.77 mS cm^{-1} indicated in Fig. 2.2B compared to Leachate A which had about a 28% increase from 42.83 ± 0.55 mS cm^{-1} to 59.10 ± 0.18 mS cm^{-1} demonstrated in Fig. 2.2A.

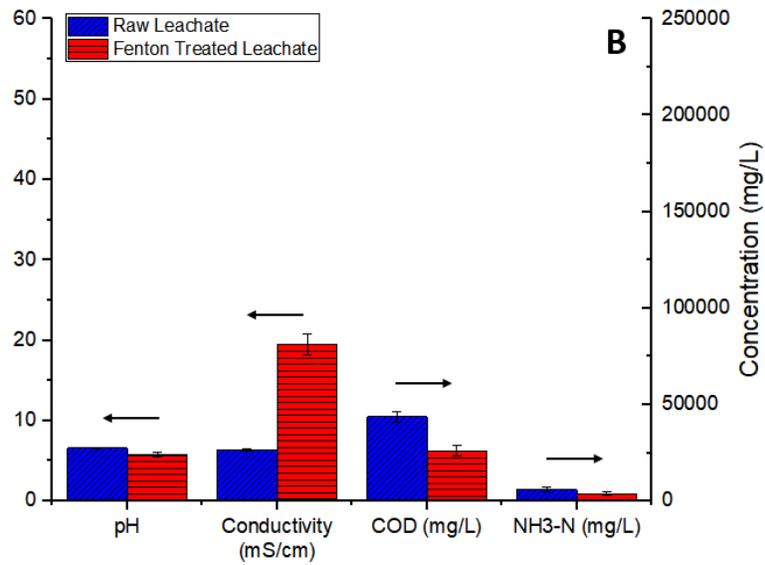
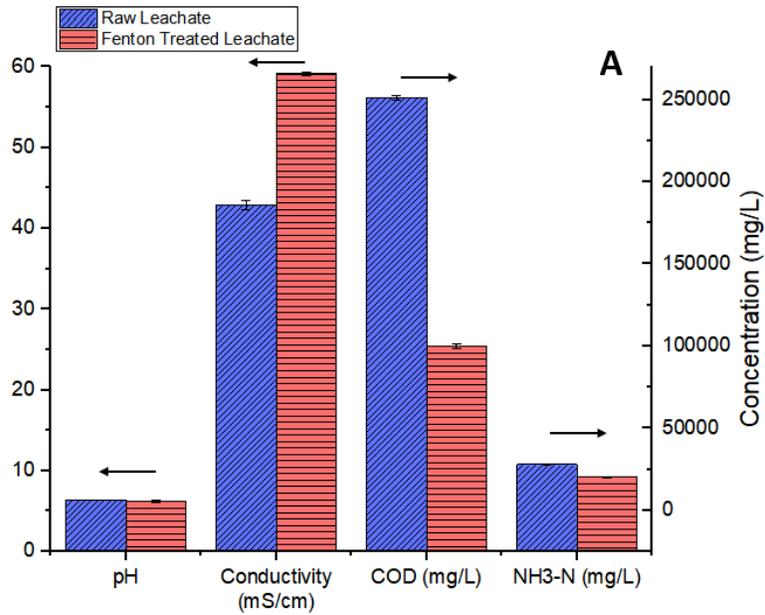


Figure 2.2. Chemical parameters of leachates post Fenton’s oxidation pre-treatment; (A) Leachate A chemical quality results, (B) Leachate B chemical quality results.

2.4.2. Water Recovery by Membrane Distillation

MD treatment experiment was continued for 175 hours (6.5 days) for both Leachate A and Leachate B, with and without Fenton's pre-treatment. Water flux is used as an indicator for membrane fouling since flux decline is highly influenced by membrane foulants (Li et al. 2016).

A severe fouling was developed when Leachate A was used as a feed source (see Fig. 2.3A) regardless of the pre-treatment when observed over 50 hours of time period. The initial flux drop from pristine membranes to the beginning of leachate treatments were 0.46 and 0.72 for without and with Fenton treatment of Leachate A, respectively. The flux decline was more gradual until after 24 hours of experiment when Fenton treated Leachate A was compared to raw Leachate A; however, both feed sources ended up declining to around the average of 0.57 water flux at 24th hour. After that, the trend of decrease in flux continued to be the same. On the contrary, Leachate B had much stabilized decrease in flux over the course of 50 hours according to Fig. 2.3B. The initial drop of Fenton treated Leachate B was 0.79 and without Fenton treatment, the decrease was 0.7. The flux stayed in the similar range for the entire 50 hours. From 24th hour to 36th hour, the flux went from 0.94 to 0.89 with Fenton treatment which was only a 4% drop, and from 36th to 48th hour, the decline was made from 0.89 to 0.87 which made a 2% drop. Without the Fenton treatment to Leachate B, the flux went from 0.70 to 0.65 from 24th to 36th hour which was approximately a 7% decrease in flux, and 0.65 to 0.62 was the transition from 36th to 48th hour which made a 5% drop. Through a study with Leachate B in Fig. 2.3B, it was clearly displayed that the decline in flux between hours were less and general water flux rate stayed approximately 30% higher with the Fenton pre-treatment.

Comparing Fig. 2.3A and 2.3B, the water flux of Leachate B had a more stabilized performance with or without the pre-treatment where 13% and 38% reductions from the pristine membrane were made after 50 hours respectively. For both cases, a more gradual water flux reduction rate was observed in both Leachate A and B results when Fenton's oxidation was coupled with MD. However, after 50 hours of MD treatment, Leachate A did not produce desirable water flux quantities compared to Leachate B since the reductions were more than 73% for both with and without the pre-treatment after 50 hours of operation; therefore, further data related to Leachate A's water flux recovery will not be presented for a comparison. This result concluded that the MD's performance is effective with leachate with lower concentration of organics or COD level. Leachate B can be recovered from an appropriate cleaning such as physical cleaning and/or chemical cleaning; however, the Leachate A had such a serious fouling issue due to the fact that even with the Fenton's oxidation, the COD concentration of Leachate A was $100,000 \pm 1365 \text{ mg L}^{-1}$ which was about 74% higher than post Fenton sample of Leachate B.

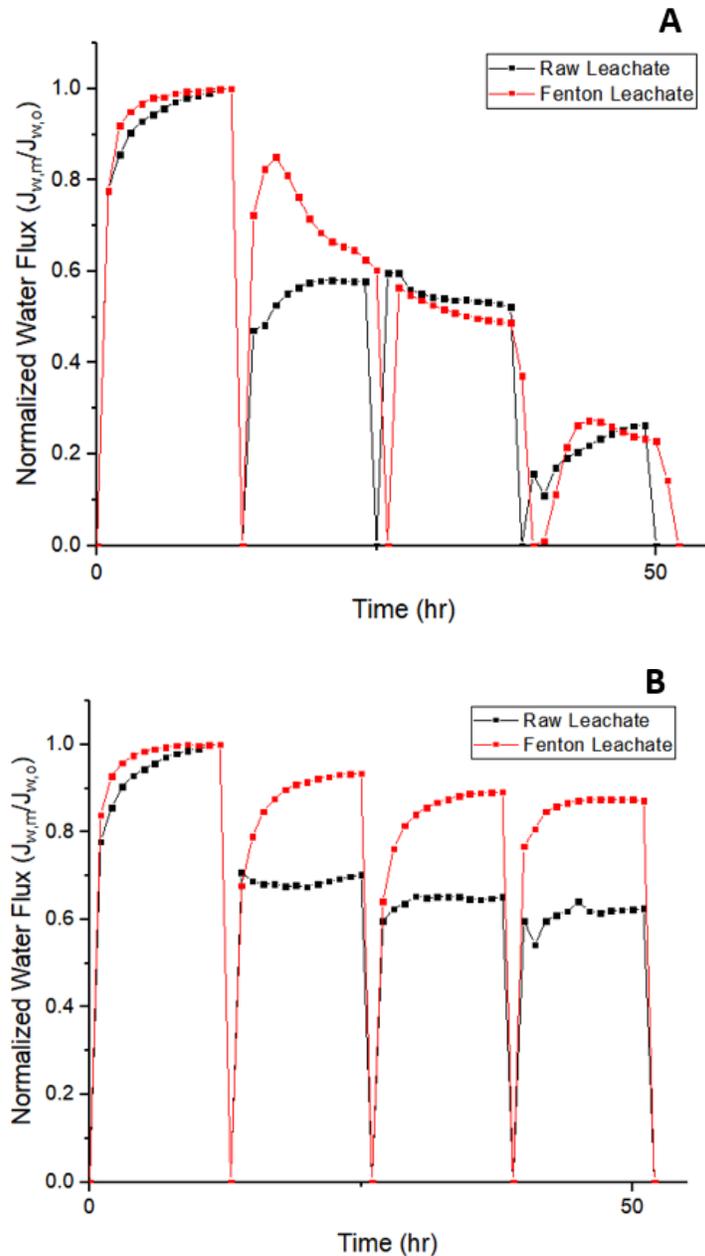


Figure 2.3. MD performance under various initial feed leachate samples; (A) normalized water flux of Leachate A, (B) normalized water flux of Leachate B.

Effects of membrane fouling with and without Fenton pre-treatment was investigated with an extended treatment of Leachate B and chemical cleaning. As shown in Fig. 2.4, the overall performance in the water recovery with Fenton's oxidation was better in terms of both water flux

and recovered performance after chemical cleaning. At the 50th hour, the reduction in normalized water flux of raw leachate was 38% whereas Fenton treated leachate had 13% decrease in its water flux. At the 100th and at the 150th hour, the normalized water flux reduction was 43% and 49% in the raw leachate while 25% and 35% were reduced using Fenton treated leachate as a feed, respectively. Those results have demonstrated that the Fenton pre-treatment could greatly reduce degree of the membrane fouling and maintained 15% to 25% higher water flux compared to that of raw leachate, likely due to the reduction of foulants by Fenton's oxidation.

However, fouling still occurred and proper cleaning would be required. In every 48 hours, chemical cleaning was performed to reduce the fouling. After each chemical cleaning at 48th and 96th hours (Fig. 2.4), we performed a MD test with DI water for 12 hours to examine the recovery of the fouled MD membrane comparing to the pristine membrane (the 1st cycle indicated by the yellow arrow on Fig. 2.4). After the first chemical cleaning, the membrane recovery was up to 89% with the Fenton treated leachate; however, the recovery was only at 67% without a pre-treatment compared to its pristine membrane. A slight improvement in the permeate flux from the raw leachate feed was obtained after the second chemical cleaning which rose to approximately 71% recovery rate. This marginal improvement indicated that the membrane surface and in the pores were affected by foulants and created a partial-wetting. More appropriate cleaning method should be recommended for the future studies to reduce the presence of irreversible fouling. The entire chemical cleaning process of this study ran for two hours: the membrane was initially flushed with H₂SO₄ solution for 30 mins followed by 30 minutes of DI water rinse, and then the system was cleaned with NaOH solution for another 30

minutes and rinsed for 30 minutes again. Some previous studies have recommended that the chemical cleaning should be conducted for more than two hours, for example approximately for six hours only using a base solution and DI water (Guillen-Burrieza et al. 2014; Srisurichan, Jiraratananon, and Fane 2005). Additionally, drying membrane after cleaning could be a vital process in MD to reduce wetting according to a study (Gryta 2007). Therefore, the chemical cleaning should be further optimized to better restore the MD membrane performance.

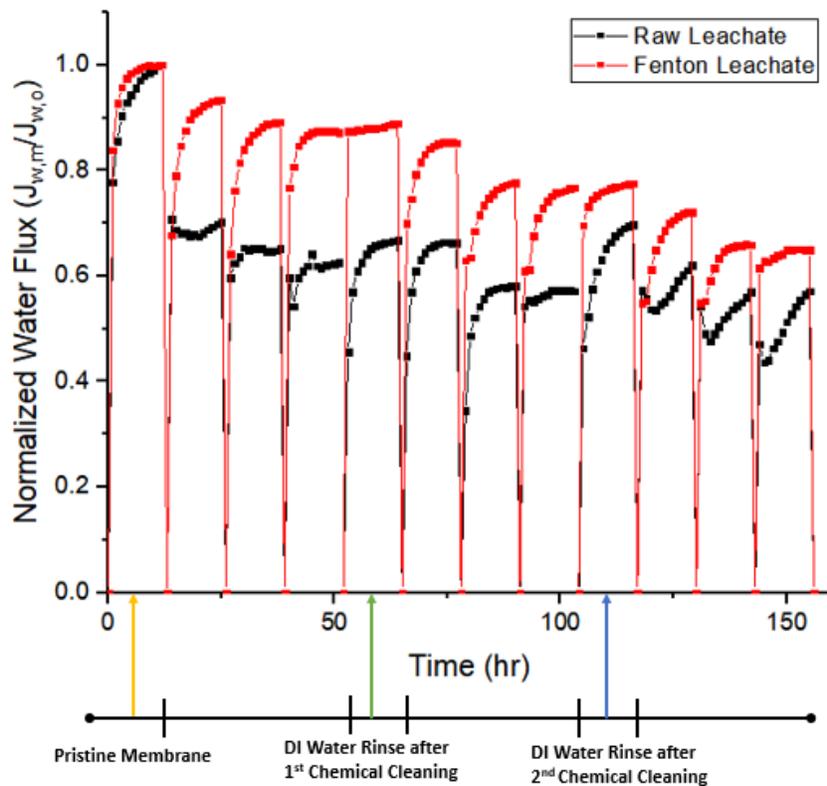


Figure 2.4. Extended full MD permeate flux performance result using Leachate B to observe the longevity and stability.

2.4.3. Chemical Compositions of the MD Permeate

Although MD can effectively recover water from leachate and reduce the volume of the treated leachate, the quality of permeate (recovered water) is important to the next-step application, such

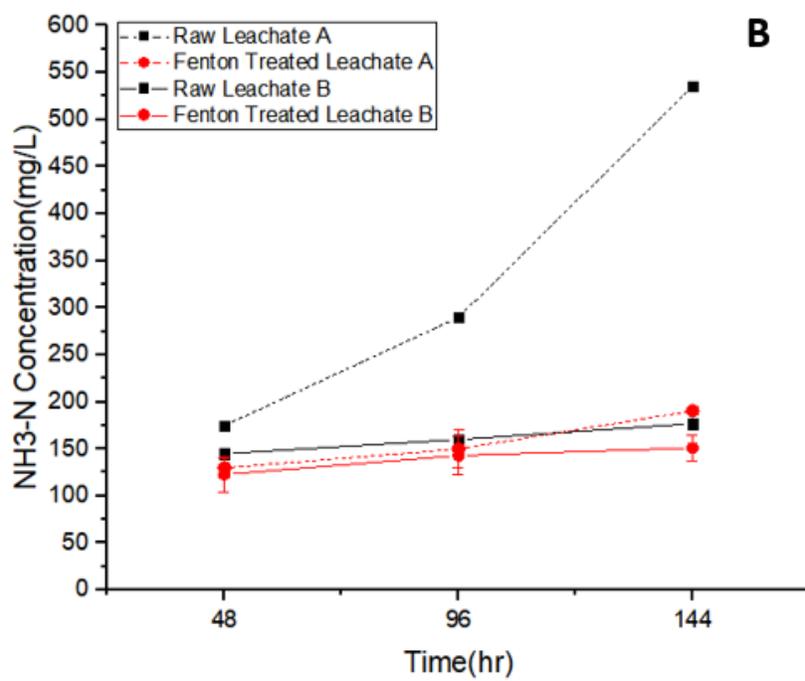
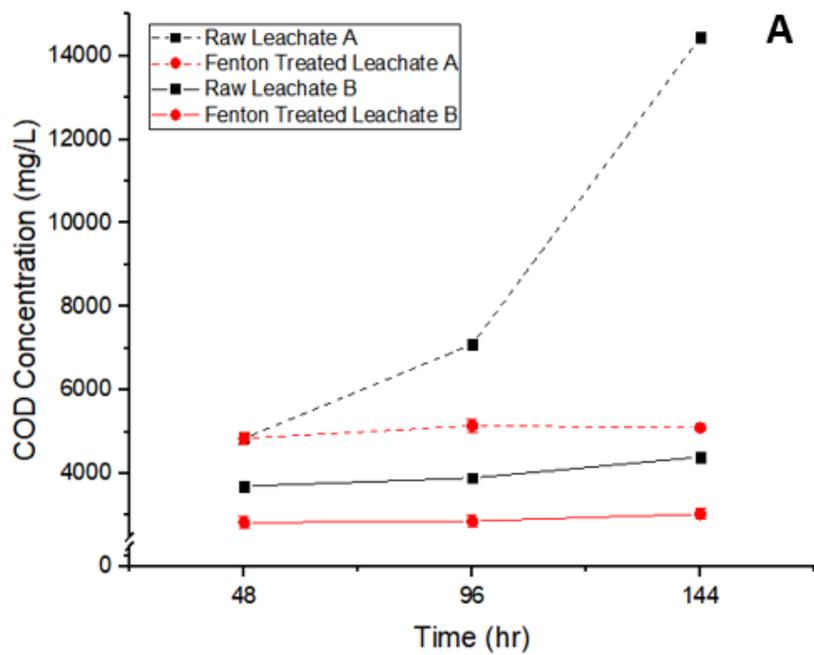
as direct discharge or reuse for non-potable purposes. Herein, several key parameters of the permeate quality including COD, $\text{NH}_3\text{-N}$ and conductivity were investigated and the comparison was made between that with and without Fenton's oxidation.

The COD concentration in the permeate was relatively stable when MD was combined with Fenton's oxidation for both Leachate A and Leachate B, with an average of $5,033 \pm 150 \text{ mg L}^{-1}$ and $2,910 \pm 140 \text{ mg L}^{-1}$, respectively (see Fig. 2.5A). Such COD likely resulted from volatile organic compounds in the leachate that could move across MD membrane. In the absence of Fenton pretreatment (raw leachate treatment), a partially-wetting to fully-wetting phenomenon was introduced after 96th hour in Leachate A, resulting in an increase of COD concentration by 103% from 96th hour ($7,100 \text{ mg L}^{-1}$) to 144th hour ($14,450 \text{ mg L}^{-1}$). However, Leachate B without Fenton pretreatment exhibited minor increase by 700 mg L^{-1} (19%). Those results suggest that MD would not be an effective method to treat high-strength leachate, despite the use of Fenton pretreatment.

Similar trend was observed with $\text{NH}_3\text{-N}$ concentration (Fig. 2.5B). In general, the ammonia concentration was much lower than COD concentration, likely because of the relatively low pH of the leachate that is not suitable for ammonium conversion to its volatile form (ammonia). With Fenton pretreatment, both Leachate A and B had ammonia in their permeates at 123 to 191 mg L^{-1} . When there was no pretreatment, Leachate B could still have a low ammonia concentration of 150 mg L^{-1} in its permeate, but Leachate A exhibited a dramatic increase in its permeate ammonia concentration by 210% from 175 mg L^{-1} to 535 mg L^{-1} . Like the COD results, the ammonia variation in the permeate also suggests that MD cannot well handle high-

strength leachate even with Fenton pretreatment and the permeate would need further treatment/disposal due to high concentrations of both COD and ammonia.

In addition to fouling, membrane wetting is another challenge within MD during a long-term operation. Wetting phenomenon is associated to the organic fouling which causes a reduction of hydrophobicity of membrane from a formation of attractive forces between hydrophobic materials within an aqueous system (Rezaei et al. 2018). With the conductivity results (Fig. 2.5C), surface wetting to full wetting could be observed with Leachate A. In Leachate A, the conductivity increased from $337 \mu\text{S cm}^{-1}$ to $983 \mu\text{S cm}^{-1}$ with the Fenton pretreatment or $794 \mu\text{S cm}^{-1}$ to $2370 \mu\text{S cm}^{-1}$ in the absence of a pretreatment. On the other hand, the conductivity was much more stabilized in Leachate B for both with and without the pretreatment, varied from $122 \mu\text{S cm}^{-1}$ to $125 \mu\text{S cm}^{-1}$ (no pretreatment) or from $99 \mu\text{S cm}^{-1}$ to $126 \mu\text{S cm}^{-1}$ (Fenton pretreatment) Higher increase in values using Leachate A could be related to the intense organic fouling that caused reduction of hydrophobicity of membrane via formation of attractive forces between hydrophobic materials within an aqueous system. The waterlogging of some pores origin an occurrence of membrane wetting phenomenon (Rezaei et al. 2018). Notably, MD membranes are prone to wetting by organic compounds, and they have been shown to experience less flux decline than reverse osmosis or forward osmosis membranes undergoing biofouling (Jang et al. 2016). This wetting can be prevented by coating the hydrophilic layer on a hydrophobic membrane (Rezaei et al. 2018).



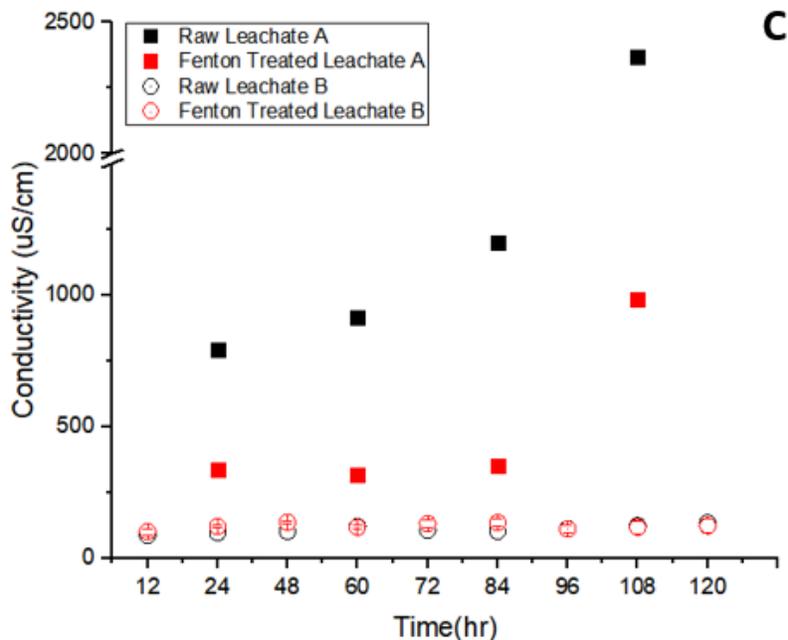


Figure 2.5. COD, NH₃-N concentrations and conductivity of permeates extracted from various feed leachate samples through MD process; (A) comparison in COD concentration removal rate, (B) NH₃-N concentration removal rate over time, (C) change in conductivity with an evidence of membrane wetting phenomenon in Leachate A results.

2.5. Conclusions

In this study, an MD coupled with Fenton’s oxidation pre-treatment for landfill leachate treatment was proposed and investigated. While the Fenton-MD system displayed a relative stability in permeate extraction performance from leachate feeds, fouling condition was still observed during an extended period of experiment leading to a reduction in the water recovery rate. Periodical and effective MD membrane cleaning against foulants should be preferred for a better water flux recovery, organic composition removal, and enhanced stability. Quantification of COD, NH₃-N concentrations, and conductivity showed that the quality of the recovered water was acceptable for both permeates with and without Fenton’s oxidation when the initial

leachate's contaminants were low. However, the performance was improved when the pretreatment was coupled with MD while avoiding the membrane wetting phenomenon. These results have exhibited the effective arrangement between Fenton's oxidation and MD could deliver a potential solution for enhanced treatment of a landfill leachate with low-moderate contaminant concentrations.

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