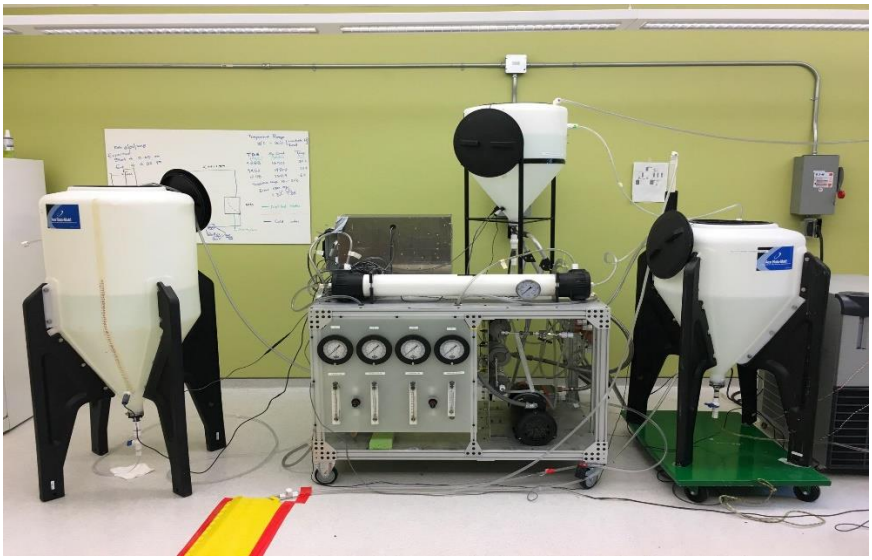
Simultaneous concentration and treatment of landfill leachate by hybrid osmotically driven membrane processes

Andrea Achilli and Tenzin Phakdon
University of Arizona
achilli@email.arizona.edu

KEYWORDS: water reuse, forward osmosis, membrane distillation, waste heat recovery



FINAL REPORT

Prepared for the
Environmental Research and Education Foundation

EREF

2020

Executive Summary

Landfill leachate is the liquid that percolates through the solid wastes in the landfill and leaches or draws chemicals or constituents from the waste. It contains high concentrations of organics, inorganics, ammonia-nitrogen, heavy metals and xenobiotic organic compounds (Kjeldsen et al., 2002). The chemical composition of landfill leachate depends on waste composition, climatic conditions, degradation rate of solid waste and the age of the landfill (Stefanakis, Tsihrintzis, & Constructed, 2014). Landfill leachate poses serious threat to surface and ground water. Common leachate treatment technologies include leachate recirculation, treatment in municipal wastewater plant, biological, and physico-chemical processes. Due to regulations continuously becoming stricter on discharge limits and standards and the ageing of landfill sites with more and stabilized leachates, conventional treatments are not sufficient to reach the level of treatment needed. In addition, operational challenges pose serious threat due to variable loads and flows during drought and seasonal precipitation, elevated temperatures (75- 115 °F) and presence of numerous inhibitory compounds poses serious threat to the performance of conventional treatment processes. In recent years, more effective treatments based on pressure-driven membrane technology, such as nanofiltration (NF) and reverse osmosis (RO), have emerged as a viable treatment alternative. RO has been most widely used due to its ability to retain both organic and inorganic contaminants dissolved in the leachates with high efficiency. Despite this high efficiency, membrane fouling and disposal of large volumes of concentrate streams generated from pressure-driven membrane processes are regarded as the two main draw backs of treating landfill leachate using membrane-based processes. Membrane fouling results in short membrane lifetime, decreases process productivity, and requires extensive membrane pretreatment or chemical cleaning, while generation of large volume of concentrate requires further treatment or costly disposal of the leachate.

The objective of this research was to investigate alternative technologies for landfill leachate management. Municipal landfill leachate discharge poses significant threat to landfill operators as leachate characteristics vary dramatically over time. Surplus leachate is frequently discharged to municipal wastewater treatment facilities because of cost and complexity of onsite treatment. Due to high nutrient loading, interference with UV disinfection or capacity challenges, municipal wastewater treatment plants have stopped accepting leachate. Therefore, more effective treatment method (i.e., membrane-based technologies) were investigated for better management practices. This study systematically investigated integrated membrane systems that utilizes a forward osmosis (FO) process and a membrane distillation (MD) process compared to a more conventional RO reconcentration process. FO operates on a gradient of osmotic pressure. This osmotic pressure gradient drives fresh water to diffuse across a selectively permeable membrane from a feed solution of relatively low ionic concentration (landfill leachate) into a solution with a higher concentration of ions. Because of the absence of pressure, in FO, membrane fouling is usually much lower than in pressure driven systems such microfiltration or RO. MD is a thermally driven water treatment process. A hot feed solution is separated from a cold distillate solution by a hydrophobic microporous membrane and, in the case of air gap MD (AGMD), a stagnant air gap is maintained between the membrane and the condenser channel by using a condenser foil which functions as a thermal insulation layer. A vapor pressure gradient exists across this membrane, the hot solution having a higher vapor pressure than the cold solution. This vapor pressure gradient drives transfer of water vapor across the hydrophobic membrane

into the cold distillate solution. As this process is driven by thermal gradient, it is especially suited when low grade “waste” heat is available. In this study, the operating conditions were optimized for treatment of landfill leachate. Rejection performances of organic carbon (TOC), specific conductivity (µS/cm), ammonium nitrogen and volatile organics were investigated in the integrated systems.

Key findings include the following:

- FO reduces the fouling limitations inherent in pressure driven membrane process.
- Water flux results showed that the FO-RO system produced higher and more stable permeate in comparison to the FO-AGMD system.
- AGMD can operate at draw solution salinity of up to 200 g/L in comparison to RO that can operate up to 70 g/L which shows the limitations of RO system for high saline draw solutions.
- The performance of the FO-RO hybrid system was better than the FO-AGMD system to reject contaminants.
- RO permeate had a lower concentration of organic carbon (TOC) and ammonia in comparison to the AGMD distillate.
- AGMD system had higher concentration of TOC and ammonia as volatile compounds are bypassed by the AGMD system.
- AGMD is suitable to treat high saline feed water with proper pretreatment or post treatment to trap volatile organic compounds and ammonia from the distillate water.
- The vapor pressure plays an important role in distillate flux production in AGMD as distillate flux declines when feed salinity is increased.
- The thermal energy consumption of AGMD increased when the feed salinity increased.
- It is feasible to extract high-quality water from leachate through FO to accomplish water reuse or direct discharge.

Leachates from hazardous waste landfills which require chemical treatment requires a large number of chemical agents and produce sewage with additional metal elements (such as coagulation-flocculation) (Zhou, Huang, Deng, & Cai, 2017). Hybrid FO/RO system can concentrate hazardous landfill leachate to 10-20 % of the feed volume and can be further concentrated economically using a thermal crystallizer. When treating stabilized (less biodegradable) leachate, the integrated FO/RO or FO/AGMD system can be used to remove organic refractory substances.

Landfill gas (LFG) is a natural byproduct of the decomposition of organic material in landfills. It is composed of around 50 percent methane, 50 percent carbon dioxide, and a minuscule portion comprises of non-methane organic compounds. The third largest source of human-related methane emission in the united states is from municipal solid waste (MSW) landfills. Methane emissions from the landfills can be used as an energy source for integrated FO/AGMD system.

Table of Contents

Executive Summary i
Table of Contents iii
List of Figures iv
List of Tables vi
Introduction and Background 1
Results and Discussions 3
Conclusions 19
Materials and Methods 20
Acknowledgements 26
References 27
Appendices 28

List of Figures

Figure 1: Reverse osmosis described graphically. The left channel represents the incoming impaired water containing a high amount of dissolved ions. P equals the pressure applied to the feed side. The right channel represents the produced permeate which contains fewer dissolved ions. The center line represents a RO membrane……8
Figure 2: Forward osmosis described graphically. The left side channel represents the incoming impaired feed water. The right side represents the highly saline draw solution. J_w is the water flux across the FO membrane. J_s is the reverse solute flux crossing from the draw solution.……9
Figure 3: Air gap membrane distillation described graphically. The red feed solution shown on the left side of the membrane is heated causing this side of the process to have a higher vapor pressure than the colder permeate side shown on the right side.……10
Figure 4: Flow path schematic of the FO-RO process. Notice the recirculating loops exiting the RO process. The orange pathways represent saline brine and the blue pathways represent RO permeate water ……11
Figure 5: Flow path schematic of the FO-AGMD process. The orange pathways represent saline brine and the blue pathways represent AGMD distillate water……12
Figure 6: Water flux and salt flux in FO membrane. Operating conditions 1 M NaCl draw solution concentration, deionized water feed, 3lpm feed and draw solution flow velocities and feed and draw solution temperature varied from 25 °C to 33 °C……13
Figure 7: Water flux and specific conductance of leachate feed in FO membrane experiment ……14
Figure 8: Water flux and salt flux in FO membrane. Operating conditions 1 M NaCl draw solution concentration, deionized water feed, 3lpm feed and draw solution flow velocities……14
Figure 9: Distillate production rate and STEC as a function of coolant inlet temperature in pilot AGMD of tap water. Other operating conditions: T_e=70 °C, F_{feed}=4……15
Figure 10: Influence of feed salinity on the distillate production rate……15
Figure 11: Influence of feed salinity at three different feed salinity……16
Figure 12: Distillate production rate and specific conductance of distillate as a function of experiment time in FO diluted draw solution ……16
Figure 13: Total organic carbon content of the FO-RO experiment solutions before and after the treatment ……17
Figure 14: Total organic carbon content of the FO-AGMD experiment solutions before and after the treatment ……18
Figure 15: Ammonia content of the FO-RO experiment solutions before and after the treatment ……18
Figure 16: Ammonia content of the FO-AGMD experiment solutions before and after the treatment ……19
Figure 17: Excitation-Emission Matrix of FO-RO permeate ……20
Figure 18: Excitation-Emission Matrix of AGMD distillate ……20
Figure 19: UV absorbance of FO-RO permeate and FO-AGMD distillate ……21
Figure 20: Three RO elements arranged in series as mounted on the lower level of the FO-RO cart. Notice the needle valve in the foreground of the image. This valve is used to control the operating pressure of the RO process……22
Figure 21: Air Gap Membrane Distillation……23

Figure 22: A two-horsepower, three phase pump motor selected to operate the high-pressure feed loop to the RO process ……24
Figure 23: A high-pressure Hydra-Cell® diaphragm pump used to circulate high salinity brine at high pressure while operating in FO-RO mode, or at low pressure and low flow during FO-AGMD mode ……24
Figure 24: A one-half horsepower AC pump motor manufactured by Marathon® pumps ……24
Figure 25: A Procon® vane pump capable of delivering low pressure, low flow circulation for the Draw solution and Feed solution loops of the FO process ……24
Figure 26: A The FO-RO system with three necessary tanks. Shown left to right they are Leachate/Feed, Diluted Draw/RO Feed, and Draw Solution. Note that the Draw solution tank is elevated to allow any overflow to drain to the Diluted Draw tank to conserve draw solution salt during long experiments……25

LIST OF TABLES

Table 1. Composition of Los Reales Landfill Leachate (Values in mg/L unless otherwise stated) 11

Table 2. FTS 4040-85 elements specification 19

Table 3. Operating parameters of DOW Filmtec™ RO membranes. Adapted from (DOW n.d.) 20

1. Introduction and Background

Landfilling is the most common disposal method for municipal solid waste (MSW), alternative methods i.e. recycling, composting and incineration are adopted in the recent years. In 2015, 262.5 million tons of municipal solid waste were generated of which 52.5 percentage were delivered to landfills and recycling (25.8%), composting (8.9%), respectively (US EPA 2018).

Landfill leachate is the liquid that drains from waste layers due to excess rainwater and it comprises of dissolved organic macro components, inorganic macro components, heavy metals and xenobiotic organic compounds (Kjeldsen et al., 2010). As populations increase and consumer economies grow globally, the amount of MSW and industrial solid waste generated in total as well as per capita increases(Renou, Givaudan, Poulain, Dirassouyan, & Moulin, 2008). Throughout the lifetime of a landfill, rainwater percolation, biochemical processes, and the accumulation of the original water content of solid waste produce a highly toxic wastewater effluent called landfill leachate(Renou et al., 2008).

The objective of this research is to find alternative technologies for landfill leachate management, which poses major environmental threat. Municipal landfill leachate discharge poses significant threat to landfill operators as leachate characteristics vary dramatically over time. Surplus leachate is frequently discharged to municipal wastewater treatment facilities because of cost and complexity of onsite treatment. Due to high nutrient loading, interference with UV disinfection or capacity challenges, municipal wastewater treatment plants have stopped accepting leachate. Therefore, more effective treatment method i.e. membrane-based technologies were investigated for better management practices. As such, to achieve the research objective, we examined emerging membrane-based technologies with the potential to improve treatment efficiency and minimize concentrate disposal issues. A novel integrated membrane system that utilizes a forward osmosis (FO) process and an air gap membrane distillation (AGMD) process in a reconcentration process will be investigated in comparison to a more established FO process and Reverse osmosis (RO) process.

Prior to describing the integrated systems, the basic RO, FO and MD processes will be outlined. RO is a water purification or demineralization process that utilizes applied pressure greater than the osmotic pressure existing between two solutions of differing ionic concentration. These two solutions are separated by a selectively permeable membrane, with the pressure being applied to the solution with the higher ionic concentration (Kucera 2015). The RO process can be seen graphically in Fig 1.

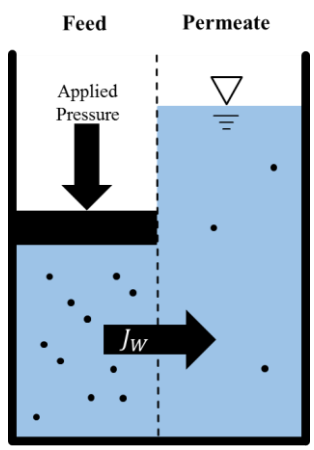


Fig 1. Reverse osmosis described graphically. The left channel represents the incoming impaired water containing a high number of dissolved ions. P equals the pressure applied to the feed side. The right

channel represents the produced permeate which contains fewer dissolved ions. The center line represents a RO membrane.

Rather than utilizing applied pressure to force a solution with high ionic concentration across a selectively permeable membrane such as in the RO process, FO operates on a gradient of osmotic pressure. This osmotic pressure gradient drives fresh water to diffuse across a selectively permeable membrane from a feed solution of relatively low ionic concentration into a solution with a higher concentration of ions. This highly saline solution is referred to as the draw solution (Cath et al. 2006). A schematic of the FO process can be seen in Fig 2.

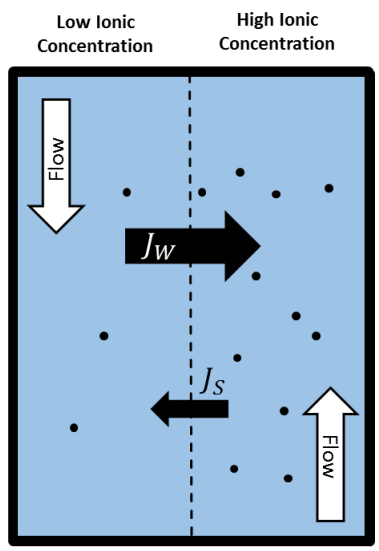


Fig 2. Forward osmosis described graphically. The left side channel represents the incoming impaired feed water. The right side represents the highly saline draw solution. J_w is the water flux across the FO membrane. J_s is the reverse solute flux crossing from the draw solution into the feed solution.

AGMD is a thermally driven water treatment process. A hot feed solution is separated from a cold distillate solution by a hydrophobic microporous membrane and a stagnant air gap is maintained between the membrane and the condenser channel by using a condenser foil which functions as a thermal insulation layer. A vapor pressure gradient exists across this membrane, the hot solution having a higher vapor pressure than the cold solution. This vapor pressure gradient drives transfer of water vapor across the hydrophobic membrane into the cold distillate solution (Hilal et al. 2012). A graphical representation of AGMD can be seen in Fig 3.

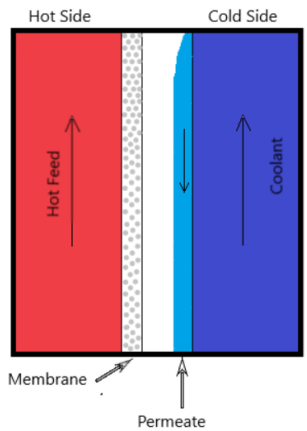


Fig 3. Air gap membrane distillation described graphically. The red feed solution shown on the left side of the membrane is heated causing this side of the process to have a higher vapor pressure than the colder permeate side shown on the right side.

Design of the two lab-scale hybrid membrane systems requires selection and sizing of major system components. These system components include necessary membranes and their pressure vessels or modules, pumps, power supplies, plumbing, valves, heating elements, proportional integral derivative (PID) temperature controllers, electronic probes and transducers, data acquisition hardware and software, and structural material for portable carts.

2. Results and Discussions

2.1 Reverse salt flux of FO membrane

The reverse NaCl flux J_S, was determined using the following protocol. An FTS CTA membrane was placed in a custom-built crossflow cell. After loading the membrane, the feed tank was filled with DI water and draw tank was filled with 1 M NaCl prepared in DI water. The membrane was exposed to the feed and draw solutions, and data recording was initiated. The volume of the feed solution was monitored as a function of time to determine the water flux and the NaCl concentration of the feed solution was monitored by using calibrated conductivity meter at 15 minutes time intervals. The data collected after the water flux had stabilized was used to calculate the experimental reverse draw solute flux.

2.2.1 FO-RO Configuration

An FO/RO system was utilized to perform continuous pilot scale experiments. This system made it possible to operate the FO process with the DS at a constant concentration. The continuous FO/RO system was an integration of two systems: the pilot scale FO membrane and three pilot scale RO modules connected in series.

Experiments with feed solution were conducted with leachate filtered with 1-micron cartridge filters and concentrated NaCl as the DS (30 ± 2 g/L NaCl). The flow rates of both the feed and draw solution were 3 L/min. Experiments were run for 3 hours and data were collected as previously mentioned. At the termination of each cycle, the feed solution was drained from the system and the membrane was osmotically washed for half an hour.

To determine at which points and in which solutions organics accumulate, results needed to operate the FO-RO and FO-AGMD systems for extended periods of time. For this purpose, the water that is treated by each hybrid process is recycled back into the draw solution loop and only wasted in the case that the draw solution tank or diluted draw solution tank overflow. Fig 4 describes the flow paths for the FO-RO configuration that allow for extended experiments.

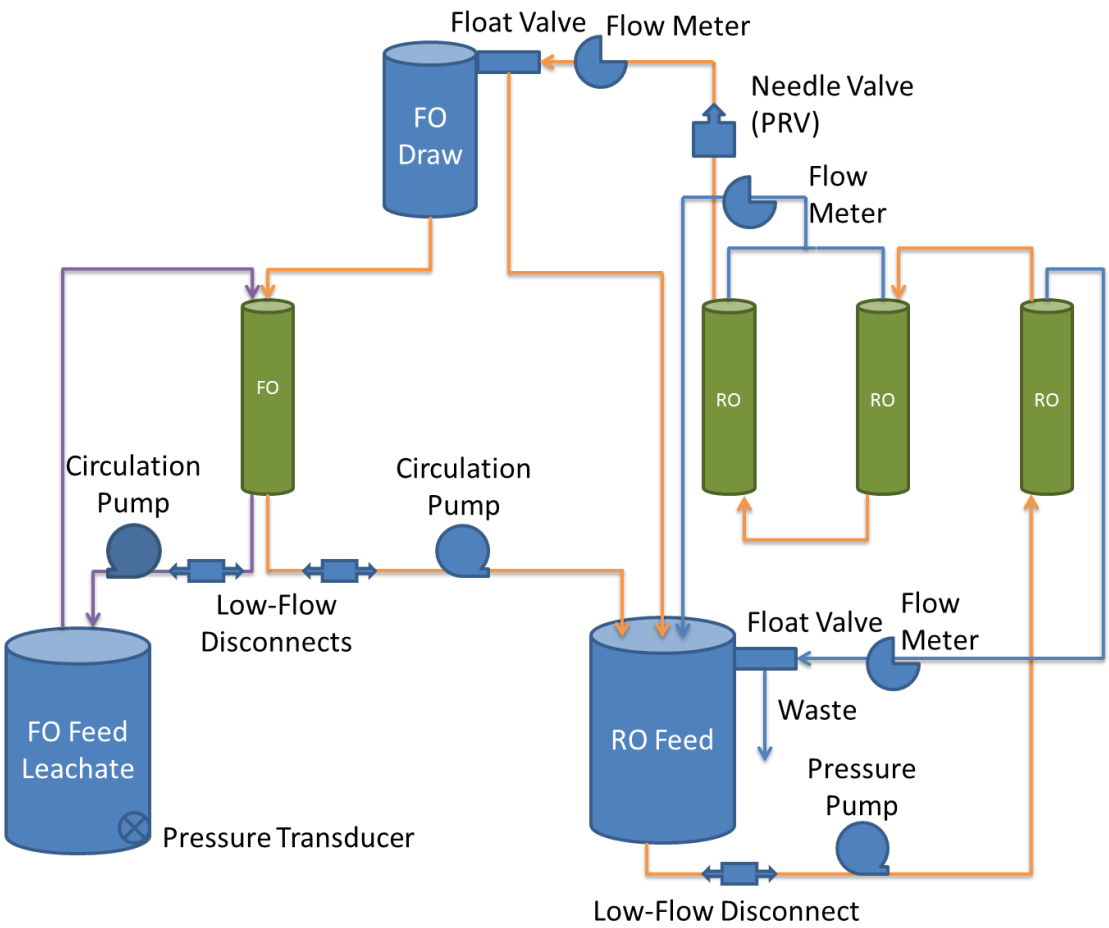


Fig 4. Flow path schematic of the FO-RO process. Notice the recirculating loops exiting the RO process. The orange pathways represent saline brine and the blue pathways represent RO permeate water.

2.2.3 FO-AGMD configuration

The FO membrane subsystem was assembled as previous experiment and coupled with a spiral wound AGMD module to reconcentrate the diluted draw solution (Fig 5). In the AGMD module, the saline solution from the feed (draw solution) tank first entered the condenser channels of the membrane module to primarily function as a coolant. When the coolant was flowing along the condenser channels, it facilitated the condensation of the water vapor across the evaporation channel and as a result was also preheated. The preheated saline solution leaving the condenser channels was further heated using an inline heat exchanger. The heated saline solution was then fed into the evaporator channels, where water vapor was formed and diffused across the membranes to the distillate channels. The warm concentrate (i.e. brine) leaving the evaporator channels were returned to the FO draw tank. A cooler was employed to maintain a constant temperature of the saline solution in the feed tank.

Temperatures of the process streams at the inlet and the outlet of the condenser and evaporator channels were measured using four temperature sensors. The hydraulic pressure along the spiral wound AGMD membrane module was measured using two pressure gauges. The temperature sensors were connected to the supervisory control and data acquisition system of the pilot system for continuous measurement and data recording. Conductivity of the feed and the distillate was

measured using a conductivity meter probe and the distillate production rate was measured using a weighing scale.

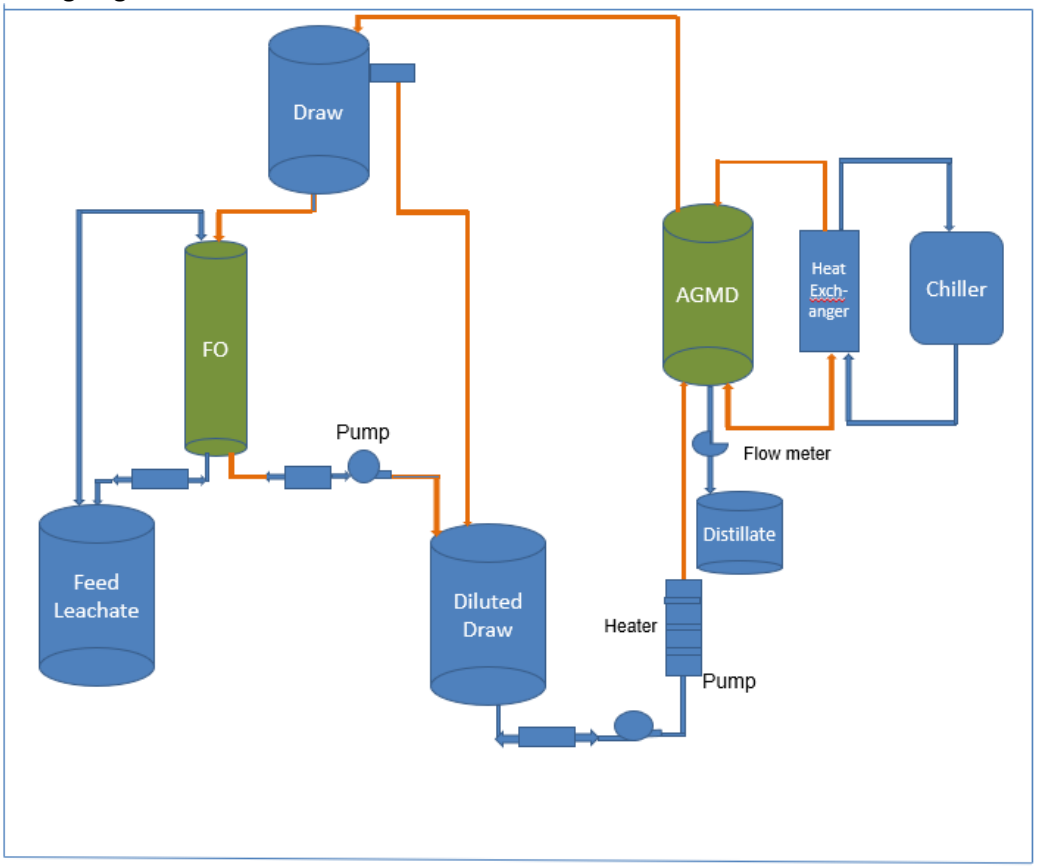


Fig 5. Flow path schematic of the FO-AGMD process. The orange pathways represent saline brine and the blue pathways represent AGMD distillate water.

2.3 FO - RO configuration.

For FO testing, a 1 M NaCl draw solution and deionized feed water were selected. This draw solution concentration and the concentration difference across the membrane produce a reasonable water flux in the FO membrane. Performance test was conducted for two hours of experiment time due to system constraint as it required a large volume of draw solution. Water flux was calculated by the rate of change of feed volume and then dividing by the area of the membrane, expressed in units of $Lm^{-2}h^{-1}$. Reverse salt flux was calculated by multiplying the rate of change of feed solution and then dividing by the area of the membrane, expressed in units of $gm^{-2}h^{-1}$. Specific salt flux is the ratio of the salt flux to water flux for a given FO membrane. Water flux, specific salt flux and Reverse salt flux as a function of membranes used and operating mode are presented in fig 4 for the FO membrane. The average salt flux of the FO membrane was $4 \pm 0.05\ gm^{-2}h^{-1}$. The results indicate that the water flux of DI water was much higher than that in leachate feed mode with the same draw solution concentration. The average salt flux of the FO membrane was 3 $\pm$ 0.5 (g/m^2hr), which is consistent with the results of previous publication(Cath, Mccutcheon, Mcginnis, & Achilli, 2013).

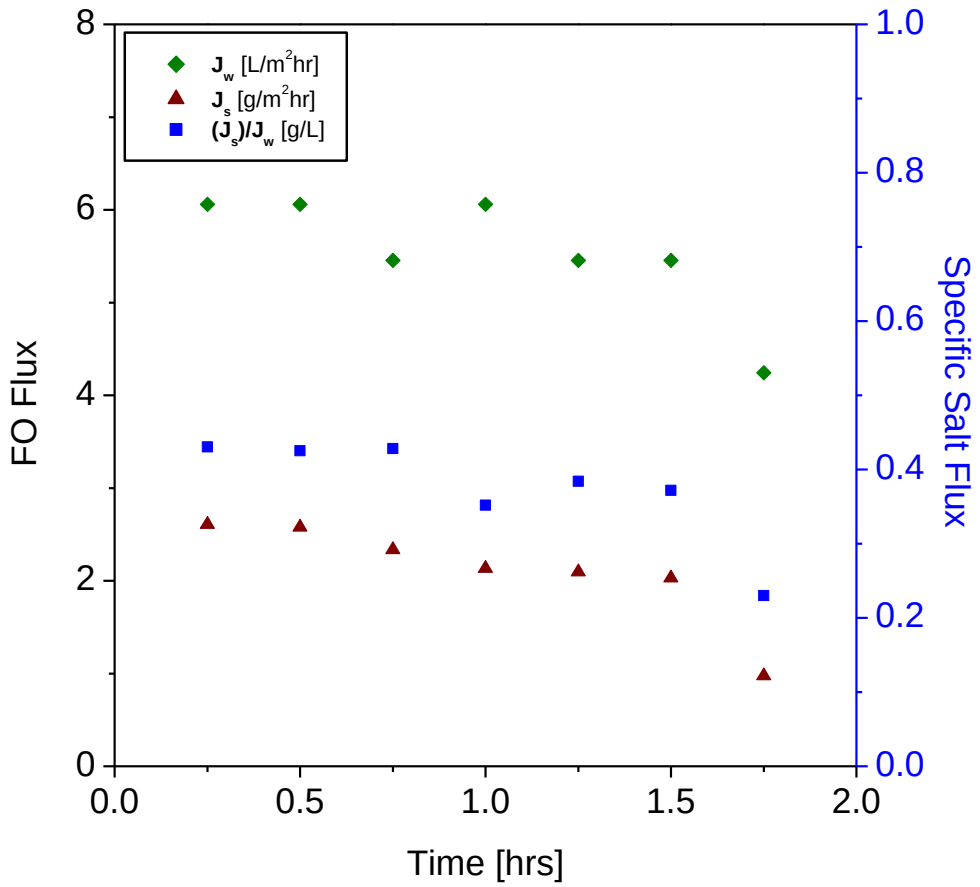


Fig 6. Water flux and salt flux in FO membrane. Operating conditions 1 M NaCl draw solution concentration, deionized water feed, 3lpm feed and draw solution flow velocities and feed and draw solution temperature varied from 25 °C to 33 °C.

Leachate from the Los Reales landfill (Tucson, AZ) was used as feed solution and draw solution concentration of 40 g/L synthetic NaCl solution was used. A three-hour course of experiment was conducted with leachate feed and synthetic NaCl solution which was recharged using RO membrane module. The initial water flux at the beginning of the experiment was 9 L/m^2hr which later dropped to 5 L/m^2hr for the FO membrane and the specific conductance of the leachate feed increased from 4069 $\mu S/cm$ to 11161 $\mu S/cm$ as presented in fig 7. Such distinct flux decline during each run can be observed, indicating that the increase in the feed conductance decreases the flux and the FO performance(Achilli, Cath, Marchand, & Childress, 2009).

Table 1. Composition of Los Reales Landfill Leachate (Values in mg/L unless otherwise stated.)

Parameter	Range
pH	7~8

Spec. Cond (µS/cm)	10,000
Total Organic Carbon	100
Ammonia	70~80

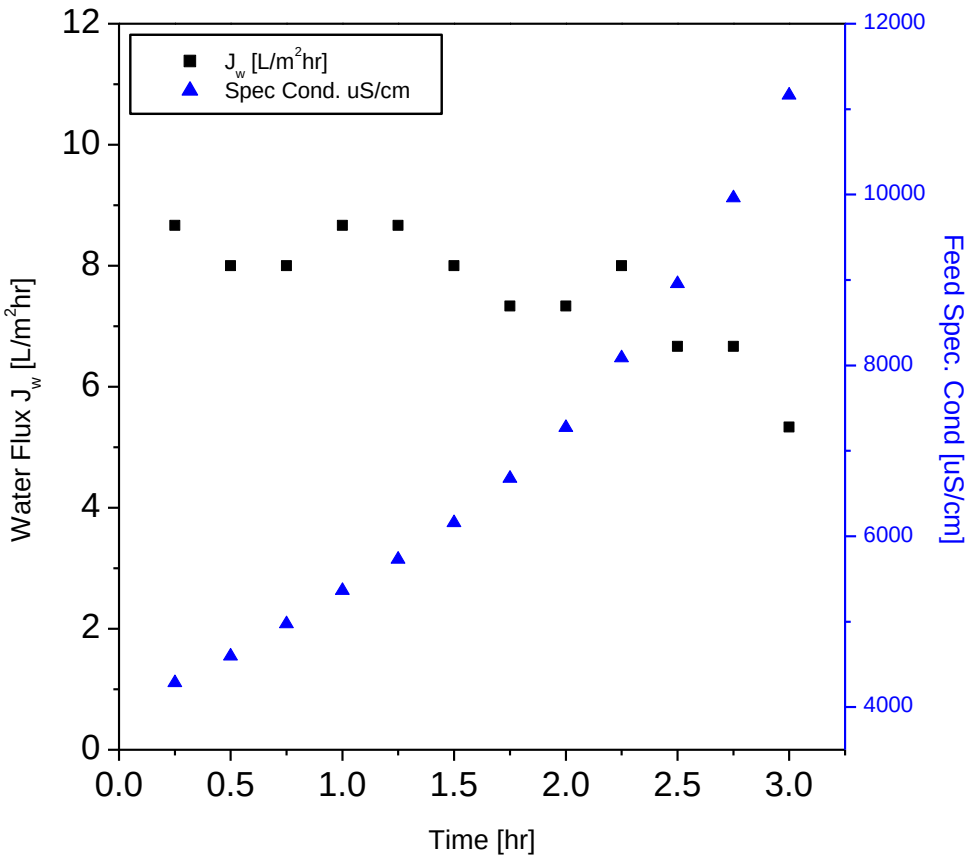


Fig 7. Water flux and specific conductance of leachate feed in FO membrane experiment.

The permeate production and salt concentration of the diluted draw, draw and permeate were measured during FO-RO testing and are presented in fig 8. Results show that the salt rejection ranged between 99.8 and 99.9 % and the permeate production rate varied from 8 to 9.4 L/hr. The permeate water quality was very good as indicated by very low salt concentration. The draw and diluted draw solution salt concentration gradually decreased from 30 and 35 g/L NaCl to 24 and 22 g/L NaCl due to dilution as the experiment progressed over a period of three hours. These salt rejection results were very similar to the rejection reported by the membrane manufacturers data.

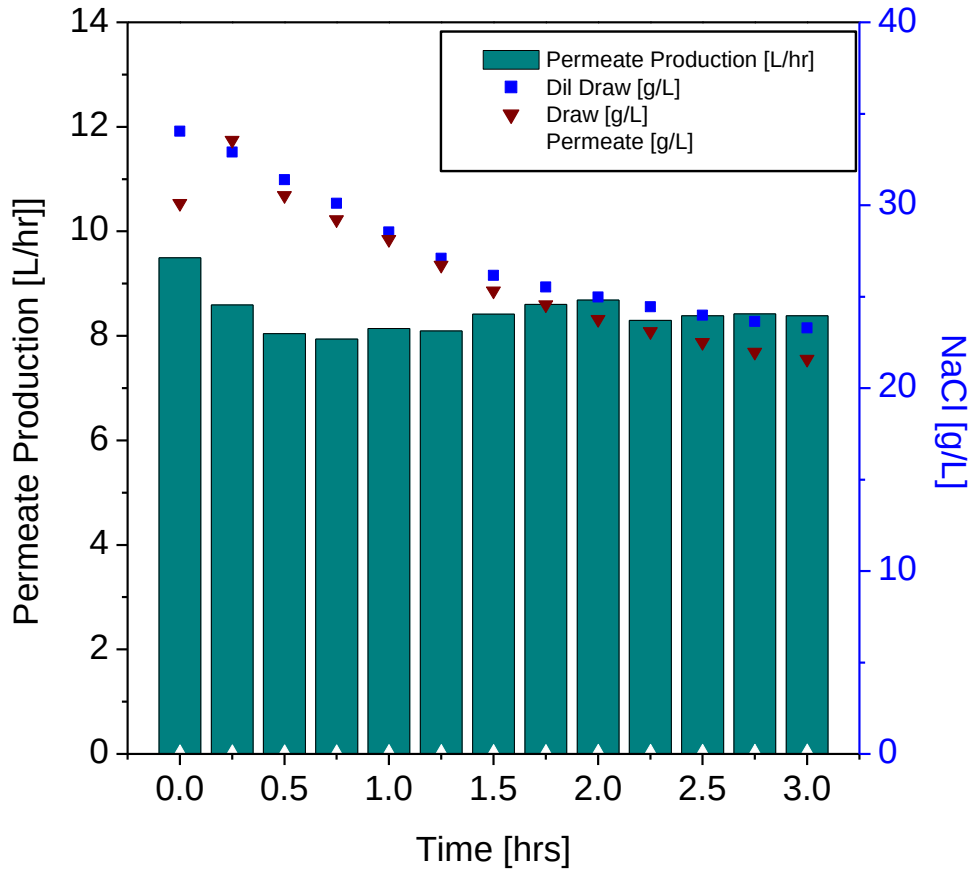


Fig 8. Water flux and salt flux in FO membrane. Operating conditions 1 M NaCl draw solution concentration, deionized water feed, 3lpm feed and draw solution flow velocities.

2.2 AGMD

Preliminary experiments with distilled water and NaCl solutions were conducted to characterize the performance of the pilot system and it was run in batch mode. In these experiments, the optimum evaporator inlet temperature and water circulation rates were determined using experiments with synthetic NaCl solutions which was used to evaluate AGMD performance.

To examine the effect of change in coolant inlet temperature on the process, experiments with coolant inlet temperatures varied from 25°C to 35°C which increased the distillate production rate from 8.4 to 10 L/h. This observed increase in the distillate production rate can be attributed to increase in the thermal efficiency of the AGMD process. The system specific thermal energy consumption (STEC) decreased from 258.5 to 206.8 kWh/m^3 for coolant inlet temperatures of 25°C and 35°C respectively as presented in fig 9. The benefit of operating the process at a high coolant temperature is to lower energy consumption for external cooling.

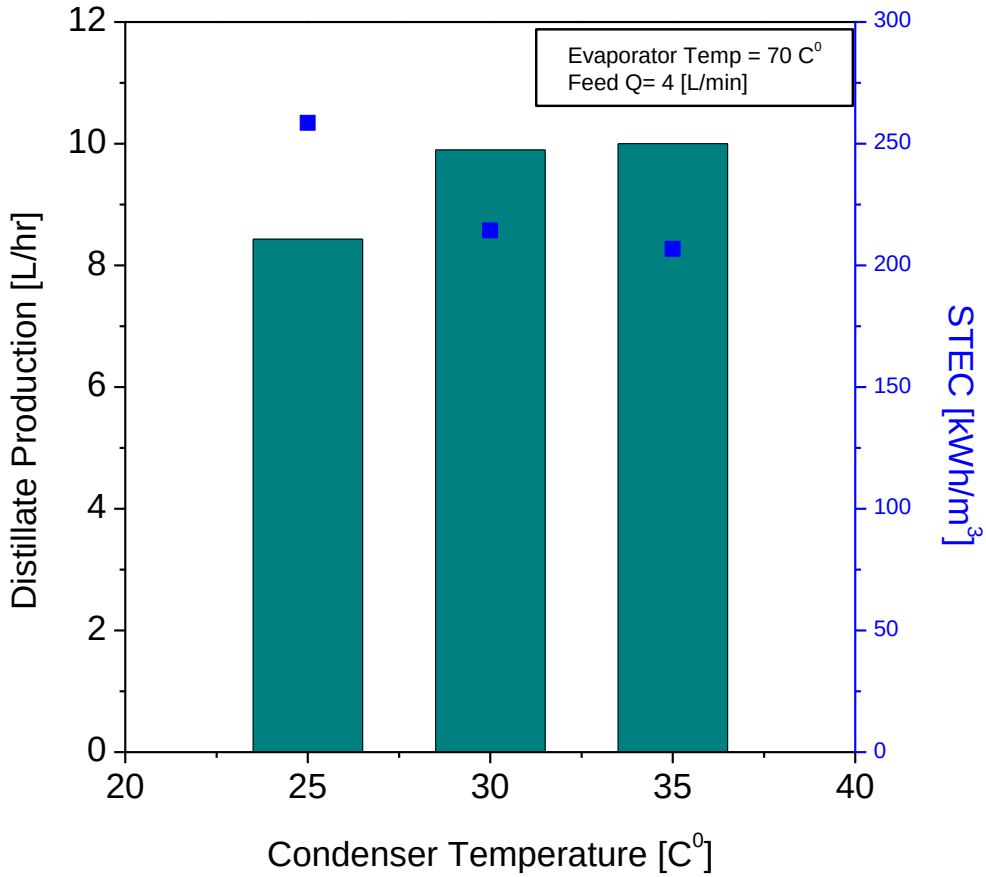


Fig 9. Distillate production rate and STEC as a function of coolant inlet temperature in pilot AGMD of tap water. Other operating conditions: T_e=70 °C, F_{feed}=4.

The presence of NaCl in the feed solution significantly reduced the distillate production rate of the pilot AGMD compared to the reference experiment using DI water feed. Dissolved NaCl in the feed solution decreases water activity, which is the actual driving force of the MD process(Winter, Koschikowski, & Wieghaus, 2011). In addition to water activity, concentration polarization effect might also cause a reduction in the distillate production rate when using a saline feed. Thus, the decline in the distillate production rate in relation to higher feed salinity is presented in fig 10.

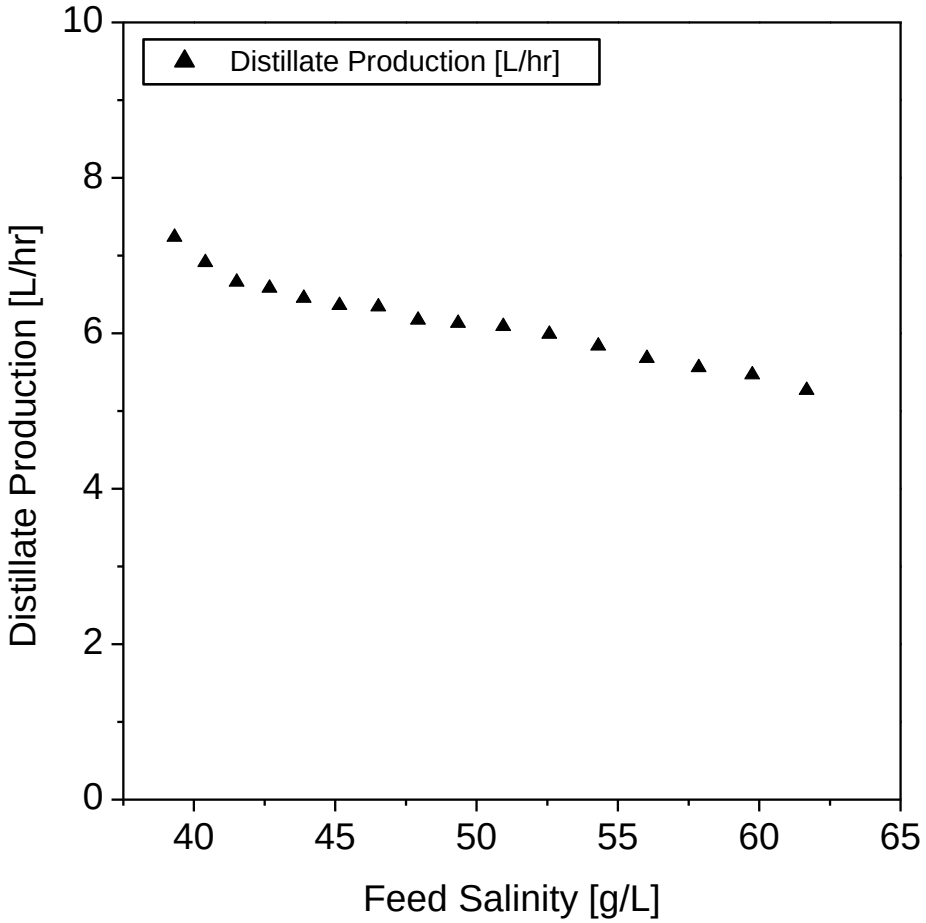


Fig 10. Influence of feed salinity on the distillate production rate.

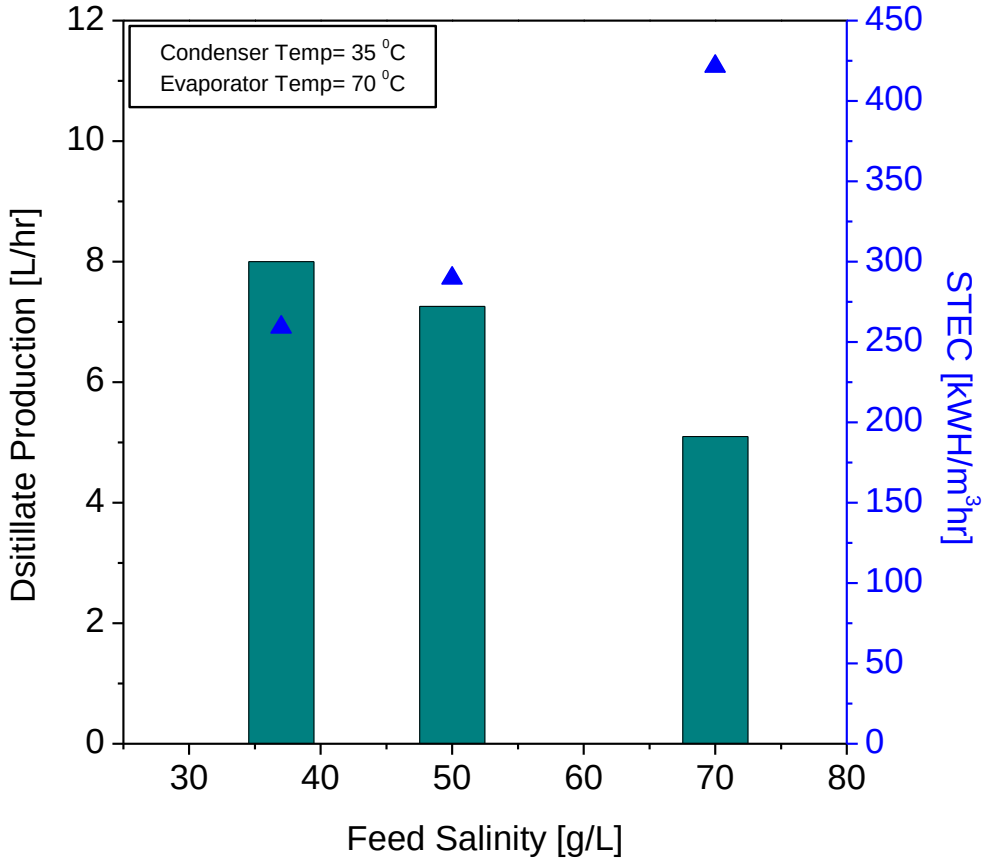


Fig 11. Influence of feed salinity at three different feed salinity.

The diluted draw solution collected from FO-RO system were used as feed stream in batch experiments for the pilot scale AGMD system. The distillate production rate decreased from 8.3 to 7.5 L/h and the specific conductance of the distillate increased from 80 to 140 µS/cm as presented in fig 12. Such distinct decline in production rate can be attributed to the increase in feed salinity due to continuous re-concentration. The increase in distillate specific conductivity could be attributed to accumulation of volatile organics and inorganics from the feed stream.

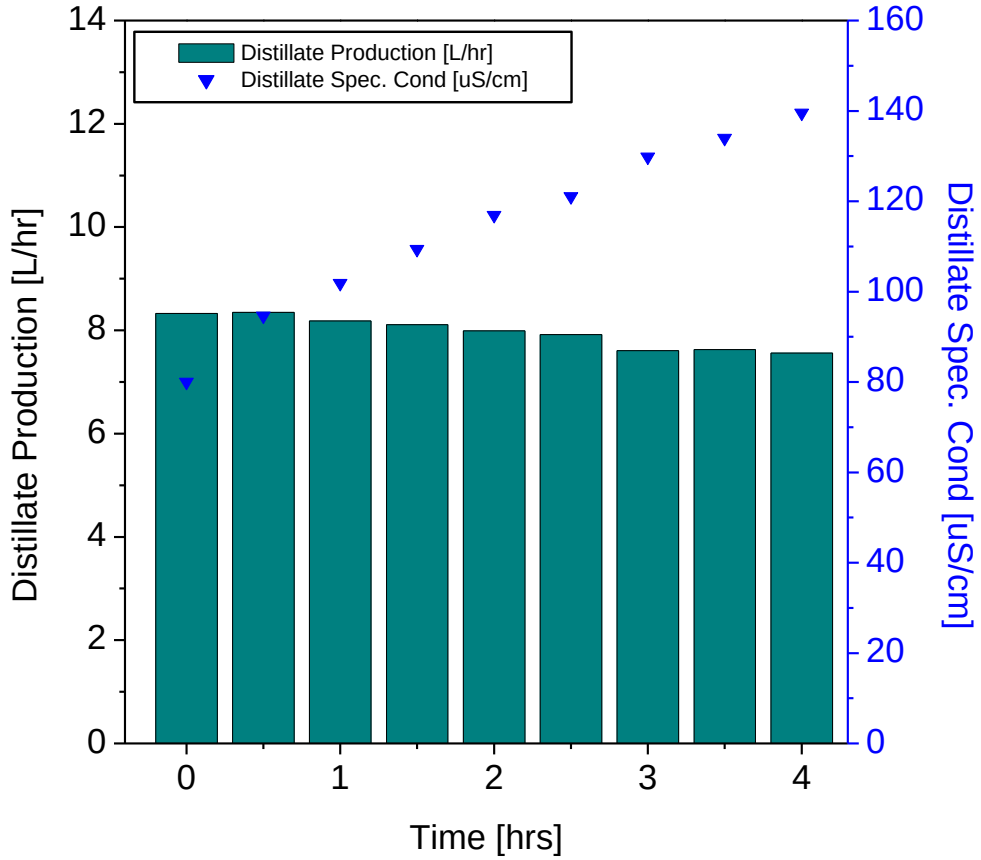


Fig 12. Distillate production rate and specific conductance of distillate as a function of experiment time in FO diluted draw solution

2.3 Solution Chemical Analysis

2.3.1 Total Organic Carbon Analysis

TOC concentrations were determined using Shimazu Autosampler TOC Analyzer. Appropriate dilutions were performed on all samples to allow measurements within the calibration range.

The FO-RO configuration experiments were run for a duration of 4 hours. Each of the leachate feed, diluted draw, draw and permeate samples were stored at the beginning of the experiment recorded as time at zero hour and the final samples at the end of the experiment recorded at time equal to 4 hours. All samples were acidified to pH equal to 2 and analyzed in the Shimazu Autosampler TOC Analyzer.

In FO-RO configuration, 6.9 ppm TOC in diluted draw solution, 6.2 ppm TOC in draw solution and 0.3 ppm TOC were accumulated in the RO permeate which initially had no traceable amount of ammonia or TOC as presented in fig 13. The leachate feed solution was concentrated from an initial TOC concentration of 40 ppm to 497.5 ppm TOC in the final feed residue. This shows that FO greatly reduces TOC concentration as shown by a very minute TOC concentration in the diluted

draw solution and RO process further reduces the TOC concentration as RO permeate TOC concentration is very low.

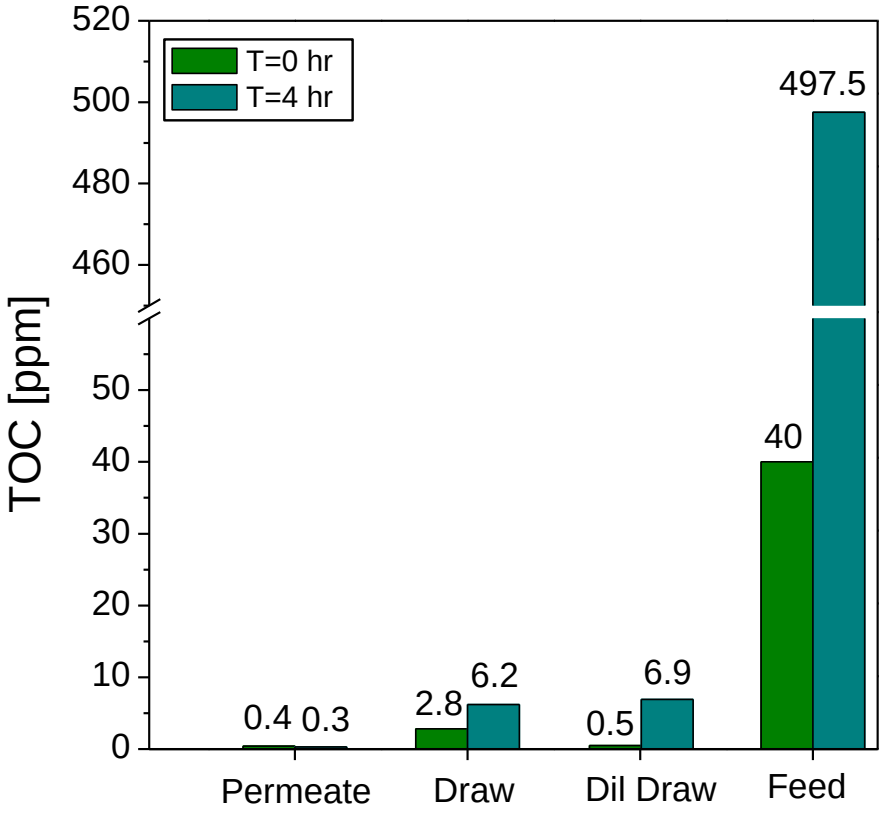


Fig 13. Total organic carbon content of the FO-RO experiment solutions before and after the treatment.

The FO-AGMD configuration experiments were run in batch mode, hence the diluted draw solution collected from FO experiment were used as feed solution for the batch experiments with AGMD membrane process for a duration of 3 hours. Each of the leachate feed, diluted draw, draw and permeate samples were stored at the commencement of the experiment recorded as time at zero hour and the final samples at the end of the experiment recorded at time equal to 3 hours. All samples were acidified to pH equal to 2 and analyzed in the Shimazu Autosampler TOC Analyzer.

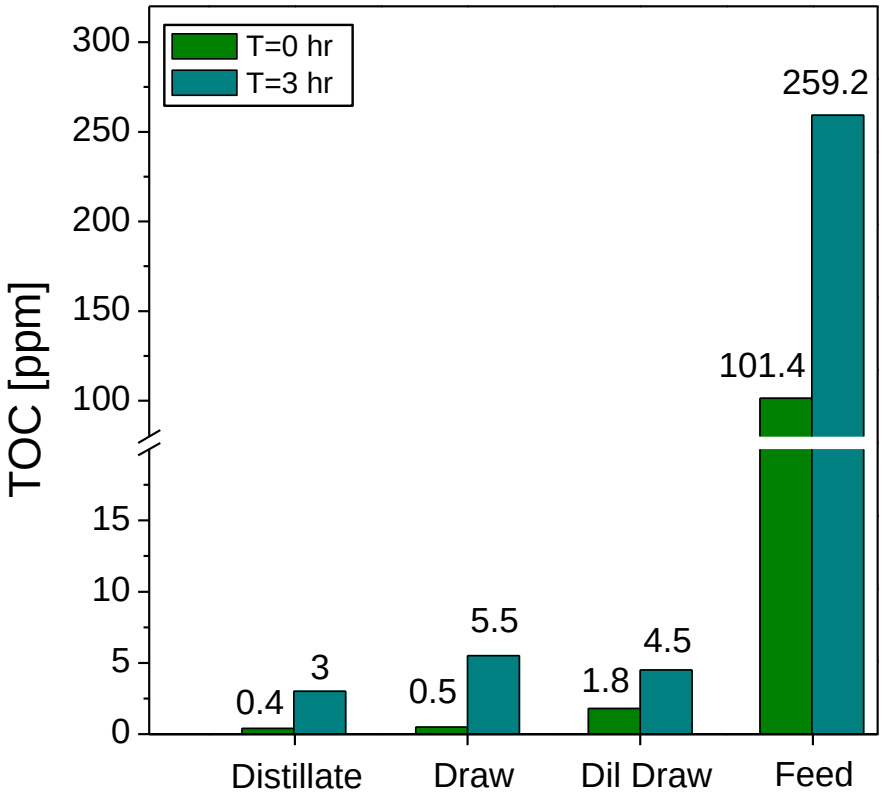


Fig 14. Total organic carbon content of the FO-AGMD experiment solutions before and after the treatment.

In FO-AGMD configuration, 5.5 ppm TOC in diluted draw solution, 4.5 ppm TOC in draw solution and 2.993 ppm TOC were accumulated in the RO permeate which initially had no traceable amount of TOC as presented in fig 14. This shows that FO greatly reduces TOC concentration as shown by minute TOC concentration in the diluted draw solution and AGMD process further reduces the TOC concentration as AGMD distillate TOC concentration of 2.993 ppm is low, but it is comparatively higher than RO permeate TOC concentration of 0.278 ppm. Hence, RO process has a better removal proficiency.

2.3.2 Ammonia Analysis

Ammonia concentrations were determined using a Hach spectrophotometer (DR/2400, Hach) and Hach method 10031.

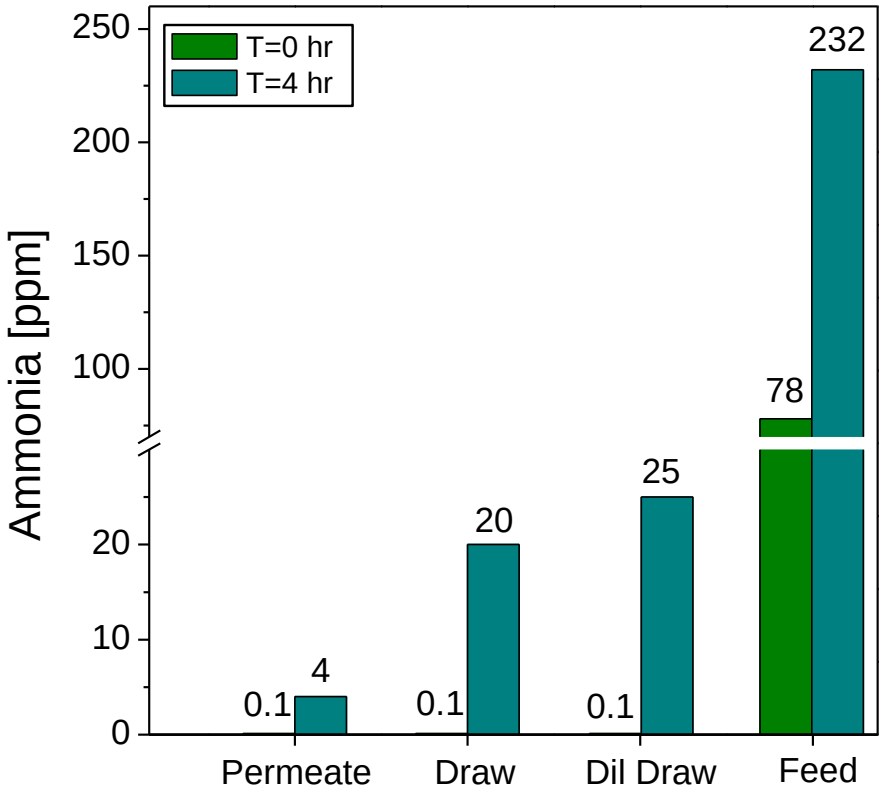


Fig 15. Ammonia content of the FO-RO experiment solutions before and after the treatment.

In FO-RO configuration, 20 mg/L ammonia in diluted draw solution, 25 mg/L ammonia in draw solution and 4 mg/L ammonia were accumulated in the RO permeate which initially had no traceable amount of ammonia in fig 15. The leachate feed solution was concentrated from an initial ammonia concentration of 78 mg/L to 232 mg/L in the final feed residue. This shows that FO greatly reduces ammonia concentration as shown by a very minute ammonia concentration in the diluted draw solution and RO process further reduces the TOC concentration as RO permeate ammonia concentration is very low.

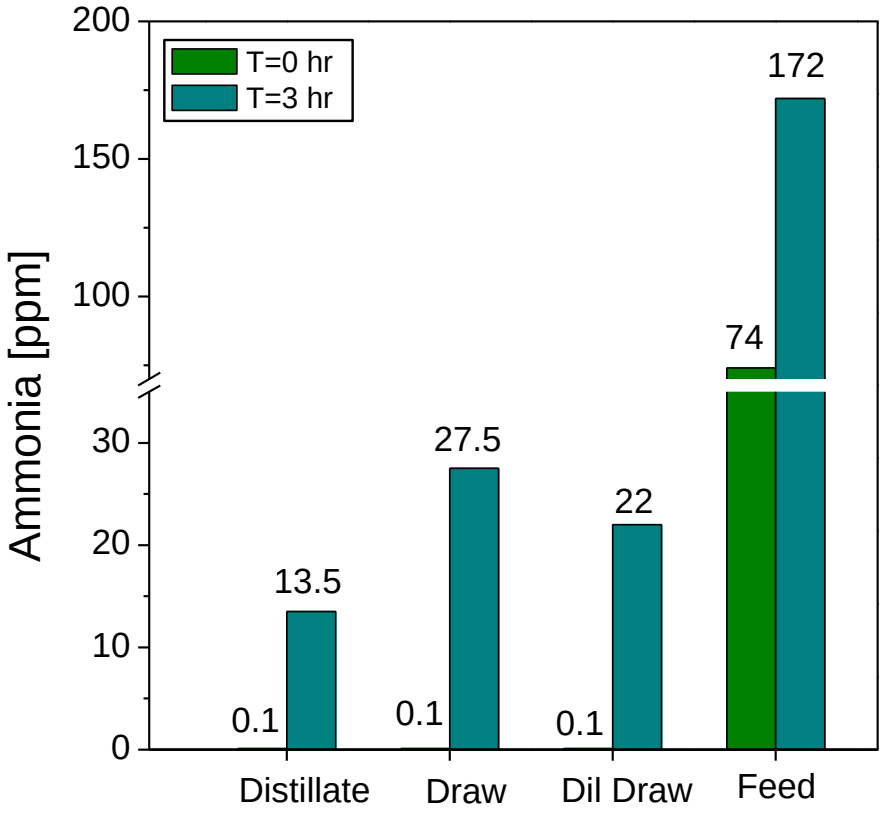


Fig 16. Ammonia content of the FO-AGMD experiment solutions before and after the treatment

In FO-AGMD configuration, 27.5 mg/L ammonia in diluted draw solution, 22 mg/L ammonia in draw solution and 13.5 mg/L ammonia were accumulated in the AGMD distillate which initially had no traceable amount of ammonia in fig 16. This shows that FO greatly reduces ammonia concentration as shown by a very minute ammonia concentration in the diluted draw solution and RO process further reduces the TOC concentration as AGMD distillate ammonia concentration of 13.5 mg/L is low, but it is comparatively higher than RO permeate ammonia concentration of 4 mg/L. Hence, RO process has a better ammonia removal proficiency in comparison to AGMD.

2.3.3 Florescence spectrum

Florescence EEM measurements were conducted using Aqualog Fluorometer Analysis. Excitation emission matrix (EEM) fluorescence spectroscopy has been widely used to characterize dissolved organic matter (DOM) in water and soil. EEMs were delineated into five excitation-emission regions based on fluorescence of model compounds, DOM fractions, and marine waters or freshwaters. Using consistent operationally defined excitation emission boundaries were divided into five regions as region I for aromatic proteins, region II for aromatic proteins type II i.e. BOD's,

region III for fulvic acid organics, region IV for soluble microbial like byproducts and region V for humic acid like organics.

The permeate of FO-RO configuration, no fluorescence emitting organic substances were present in permeate as presented in fig 17. In AGMD, location of EEM peaks in region I and region IV based on literature reports indicates the presence of Aromatic protein and soluble microbial byproducts in the distillate water as presented in fig 18.

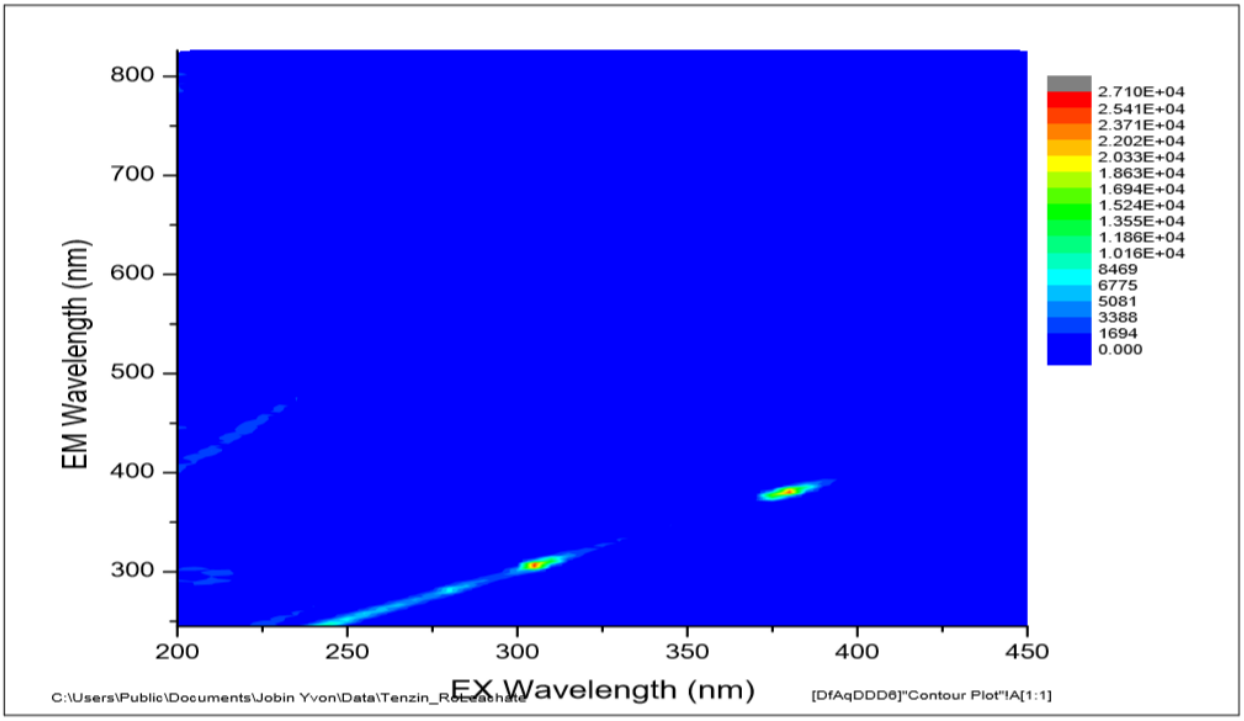


Fig 17. Excitation-Emission Matrix of FO-RO permeate.

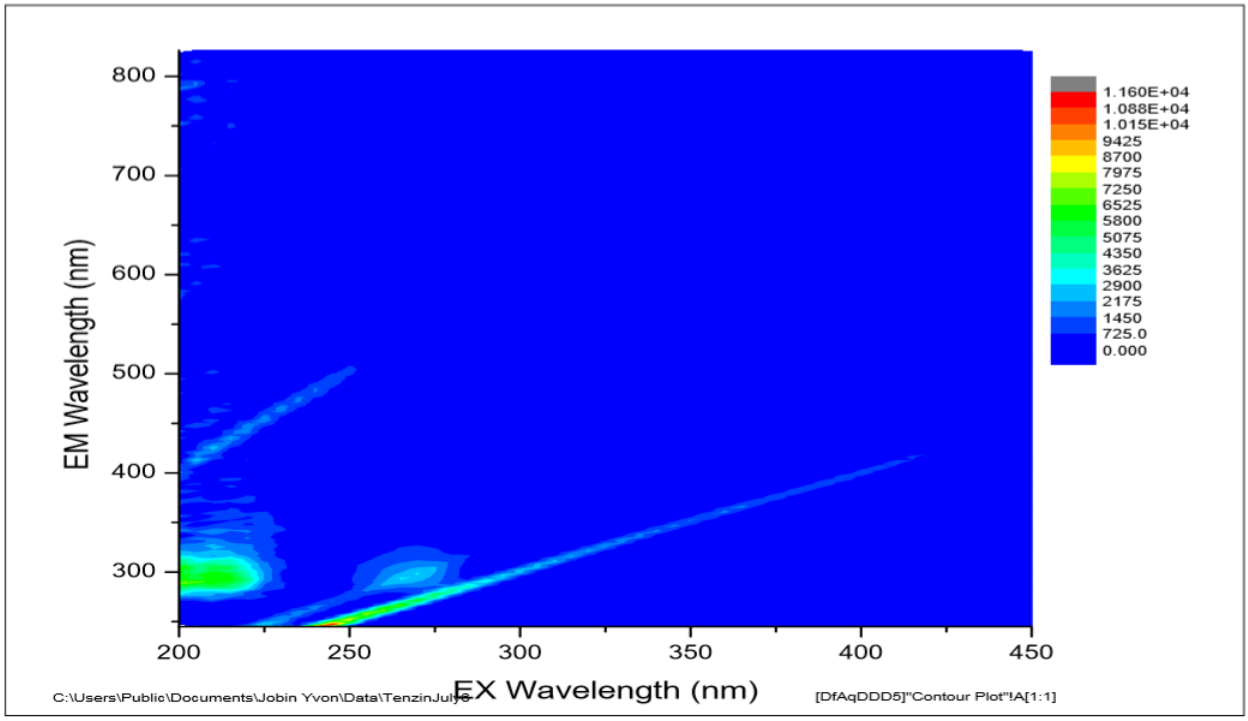


Fig 18 Excitation-Emission Matrix of AGMD distillate.

2.3.4 UV Absorbance

The UV absorbance for FO-AGMD indicates presence of contaminants in UV-254 range. The FO-AGMD distillate had a small absorption peak around 250 nm, which indicates the presence of contaminants.

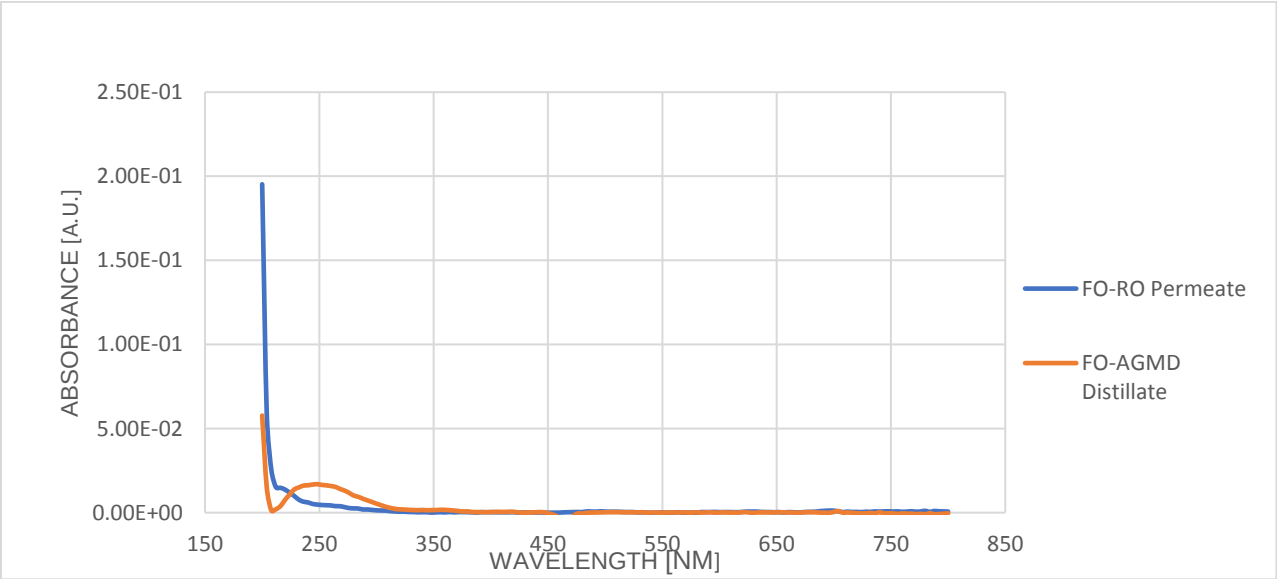


Fig 19 UV absorbance of FO-RO permeate and FO-AGMD distillate

3. Conclusion

Air gap membrane distillation is a promising energy efficient process as a very high recovery of evaporation heat is possible. The major findings can be summarized as follows:

- FO reduces the fouling limitations inherent in pressure driven membrane process.
- Water flux results showed that FO-RO system produced higher and more stable permeate production in comparison to FO-AGMD system.
- AGMD operates at draw salinity of up to 200 g/L in comparison RO system can operate up to 70 g/L which shows the limitations of RO system for high saline draw solutions.
- The performance of FO-RO hybrid system was better than FO-AGMD system to reject contaminants.
- RO permeate had a better rejection performance of organic carbon (TOC), ammonia and Dissolved organic matter (DOM) in comparison to AGMD distillate.
- AGMD system had lower rejection rate as volatile organic compounds and ammonia bypassed the AGMD system.
- AGMD is suitable to treat high saline feed water with proper pretreatment or post treatment to trap volatile organic compounds and ammonia from the distillate water.
- The vapor pressure plays an important role in distillate flux production in AGMD as distillate flux declines when feed salinity is increased.
- The thermal energy consumption increased when the feed salinity increased. This can be explained by the fact that the higher the concentration, the higher the boiling point.
- It is feasible to extract high-quality water from leachate to accomplish water reuse or direct discharge.

4. Materials and Methods

4.1 Forward Osmosis

A Fluid technology Solutions (FTS) 4040-85 FO-CS double-leaf spiral wound element was used in the hybrid system.

Table 2. FTS 4040-85 elements specification.

Membrane Requirements	Membrane must always be kept moist (do not allow to freeze)
Membrane Type	Cellulose Acetate
Max. Operating Temp.	120°F (50°C)
Max. Side-Port Pressure	75 psi (0.5 MPa)
Minimum Transmembrane Pressure	5 psi (35 kPa)
pH Operating Range	3 to 7
Maximum Chlorine	2 ppm
Maximum Silt Density Index	Less than 5
Maximum NTU	Less than 1

Performance literature indicates that FTS's 4040-85 FO-CS element flux rates are 8 ± 2 LMH (5 ± 1 GFD) with feed and draw solutions of 45°C. Given a usable membrane area of 3.3 m^2, flowrates between 9 and 15 L/h are predicted for the operating temperatures and draw solution. These flowrates easily allow the system design flowrate of 6 L/h to be achieved.

4.2 Reverse Osmosis

Three DOW Filmtec™ RO membranes were selected for use in the FO-RO hybrid system. These RO membranes are arranged in series, allowing for specific permeate flow paths to be recycled during long experiments. Recycling higher concentration permeate flows to the draw solution loop before the FO process and lower concentration permeate flows to the draw solution loop after the FO process maintains the effective draw solution concentration [g/L NaCl]. Table 2 describes the operating parameters of the selected RO membranes.

Table 3. Operating parameters of DOW Filmtec™ RO membranes. Adapted from (DOW n.d.).

DOW Membrane	Applied Pressure (psig)	Permeate Flow Rate (gpd)	Stabilized Salt Rejection (%)
SW30-2521	800	300	99.4

Pressure vessels were selected to fit the dimensions of the DOW RO membranes and allow for operating pressures needed to desalinate the draw solution in the FO-RO process. Hydrocomponents and Technologies, Inc. PV-2500SW Series pressure vessels were used, as they have proper dimensions for the DOW RO membranes and have a working pressure of 1000 psi. Feed inlet port and permeate port allow for removable stainless-steel pressure fittings. The housings are fiberglass, which allows for the use of highly saline draw solutions without corrosion. Fig 20 shows the RO elements and pressure vessels assembled in series on the FO-RO cart.

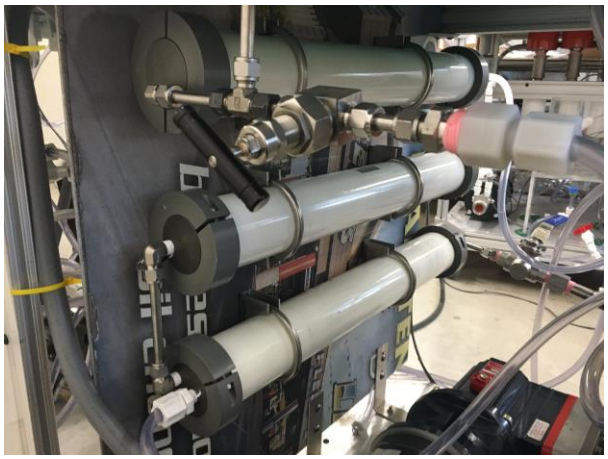


Fig 20. Three RO elements arranged in series as mounted on the lower level of the FO-RO cart. Notice the needle valve in the foreground of the image. This valve is used to control the operating pressure of the RO process.

4.3 Air Gap Membrane Distillation

A pilot-scale AGMD system was used (Fig 21). The system consisted of a spiral-wound AGMD membrane module (Aquastill, Sittard, The Netherlands), a feed tank, a water-circulating pump, temperature and pressure sensors, and a magnetic flow meter.

The spiral wound membrane module had 6 evaporator channels, 6 condenser channels, and 12 distillate channels. Each evaporator channel was formed with microporous low-density polyethylene (LPDE) membranes with normal pore size of 0.3 μm, thickness of 76 μm, and porosity of 85%. Aluminum foils were used as condenser channels and 1 mm mesh spacers were used in between evaporator channels and condenser channels to create the distillate channels, 2 mm mesh spacers were used in evaporator channels and condenser channels to reduce temperature and concentration polarization effects.

Fig 21. Air gap membrane distillation.

4.4 Pumps

The three processes discussed in Sections 2.1 to 2.3 require pumps for circulation. The FO process requires low pressure and low flow for both the leachate and draw solution loops. The RO process requires a low flow, high pressure pump to desalinate the draw solution at a pressure between

500 and 800 psi. The AGMD processes require low transmembrane pressure as such a low-pressure and low-flow pump is picked.

4.4.1 High pressure Reverse Osmosis Pump

A two-horsepower, three phase motor and a diaphragm pump were selected to drive the high-pressure loop of the RO process. The pump head is a Hydra-Cell® diaphragm pump capable of operating at a pressure of 1200 psi and a flow rate of 3.1 gpm (Hydra-Cell® 2016). The pump had a three-way ball valve added to the exit port of the pump to allow flow to be routed at high pressure through the three RO elements discussed in Section 2.1.2, or at low pressure to the feed side of the AGMD process. This eliminated the need for an extra pump to operate in the FO-AGMD mode. The pump motor is shown in Fig 22 and the Pump head is shown in Fig 23.

Fig 22. A two-horsepower, three phase pump motor selected to operate the high-pressure feed loop to the RO process

Fig 23. A high-pressure Hydra-Cell® diaphragm pump used to circulate high salinity brine at high pressure while operating in FO-RO mode, or at low pressure and low flow during FO-AGMD mode

Since pressure is the driving force of the RO process, precise control over the flow rate and operating pressure are necessary. An Automation Direct variable frequency drive (VFD) was selected to control the flow of the RO pump motor and head configuration described above. This piece of electric hardware allows the manual adjustment of power frequency delivered to the pump motor. A rotameter flow meter is positioned at the exit port of the pump so a user can adjust the VFD settings while monitoring flow rate.

4.4.2 Forward Osmosis Feed and Draw Solution Circulation Pumps

FO membranes are constructed by laminating an extremely thin active layer to a relatively thicker porous support material. This configuration facilitates the transport characteristics that drive the FO process, but result in sensitive operating constraints. These constraints are described in Section 2.1.1. The method of meeting these transmembrane pressure constraints is by matching the flow rates of the feed and draw solution loops. One half horsepower pump motor and Procon® vane pump heads were selected to achieve the necessary range of flow rates needed for the FO process. Each loop has an identical pairing of motor and pump head. The selected pump motor and head can be seen in Figs 24 and 25 respectively.

Fig 24. A one-half horsepower AC pump motor manufactured by Marathon® pumps.

Fig 25. A Procon® vane pump capable of delivering low pressure, low flow circulation for the Draw solution and Feed solution loops of the FO process.

The feed and draw solution flow rates delivered to the FO element are controlled using flow reducing loops in which the exit flow of the pump is split and partially returned to the input of the pump. This loop is assembled with a needle valve that enables variable amounts of flow to be recirculated or sent to the FO process.

4.4.3 Air Gap Membrane Distillation Feed Pump

AGMD has a constraint that the applied transmembrane hydrostatic pressure must be lower than the membrane liquid entry pressure of 0.5 bar. Thus, a good selection of pump system, which meets the operational requirement of the AGMD system for a full-scale implementation, would reduce system failure. A three-way ball valve is located at the exit port of the high pressure, low flow diaphragm pump used for the RO process. When operating in the FO-AGMD mode, this valve is positioned such that flow is routed at low pressure to the feed port of the AGMD module stack. Again, this flow is controlled using a VFD, which allows for precise adjustments. An additional pump was selected to circulate the cold distillate side of the AGMD process. This loop requires low pressure low flow, so a one third horsepower Marathon® pump motor was selected to be paired with a low flow, low pressure Procon® pump head.

4.5 Tanks

Various tanks are necessary to contain three solutions involved in the FO-RO process. These are Leachate/Feed, Draw Solution, and Diluted Draw/RO Feed. Fig 26 shows FO-RO cart and necessary tanks.

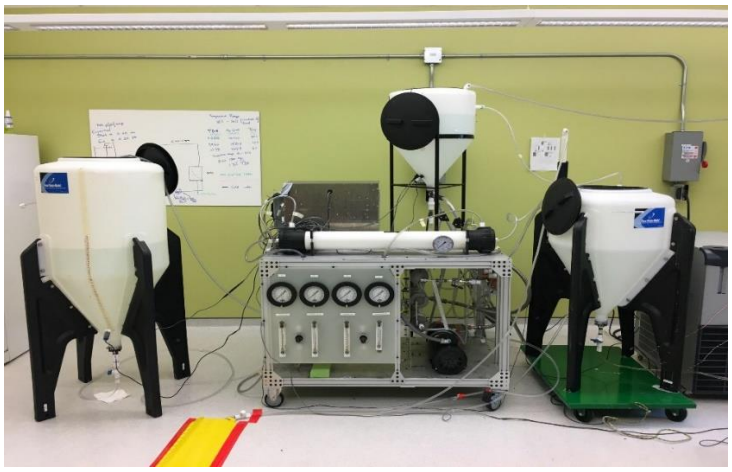


Fig 26. The FO-RO system with three necessary tanks. Shown left to right they are Leachate/Feed, Diluted Draw/RO Feed, and Draw Solution. Note that the Draw solution tank is elevated to allow any overflow to drain to the Diluted Draw tank to conserve draw solution salt during long experiments.

These tanks are made of high-density polyethylene plastic and are NSF International and American National Standards Institute (ANSI) certified for drinking water. The draw solution is split into a concentrated (middle tank of Fig 26) and diluted draw (right tank of Fig 26) to aid in mitigating any imbalances in FO and RO flow rates as well as re-concentrate the draw solution after it is diluted by the water flux through the FO membrane.

Polyethylene plastic tanks of the same construction and manufacturer of the FO-RO system were selected for the FO-AGMD system. An additional custom-made acrylic tank was machined to hold the distillate solution and is placed in the lower level of the AGMD cart.

4.6 Immersion Heaters

The system was designed to precisely control the temperature of the solutions in the system for energy calculations to further understand the energy demand. Membrane distillation can operate at temperatures as low as 60 ℃ and produce distillate. Three immersion heaters are arranged in parallel to heat the draw solution/AGMD feed. Since the temperature and in turn vapor pressure gradient that exists across the AGMD membrane is the driving force of the AGMD water flux, it is necessary to be able to precisely control and read the temperature of the heated draw solution/AGMD feed for energy calculation. This is accomplished in two approaches and equipment configurations. The first configuration is to set the temperature of the draw solution as it exits the three immersion heaters. This is done using a PID controller that delivers varying amounts of power to the heaters in response to a temperature reading at their exit ports. If the temperature of the solution is too cold, the PID sends a signal to a solid-state relay (SSR) that closes the power supply circuit to the immersion heaters. Previous experiments involving hybrid FO-MD systems conducted in the Achilli Research and Teaching lab found that setting regulatory temperatures of the AGMD process caused highly fluctuating water fluxes from the FO and AGMD processes. To study the energy demand to heat the system, a more consistent heat was supplied for research purposes. Though AGMD can operate at temperatures as low as 60℃ and produce distillate. To mitigate this instability, a “percent on” approach is also made available within the heating equipment configuration. The PID controller can be disconnected from the heater SSR and replaced with an Arduino microcontroller. This Arduino is loaded with a simple program that provides a constantly pulsing voltage to the SSR, this powering the immersion heaters. This approach represents a more consistent source of heat that is a more realistic approach when considering a scaled-up system for industrial application.

4.7 Heat Exchanger and Chiller

As mentioned in the previous section, the hot and cold temperatures need to be precisely controlled to regulate water flux of the AGMD process. To control the temperature of the cold feed, loop a chiller was selected. This chiller is placed in series with a DUDA brazed plate heat exchanger.

4.8 Data Acquisition

Secondly data is collected for the purpose of recording water fluxes, temperatures, solution concentrations, and pressures at points of interest throughout the FO-RO and FO-AGMD systems. This data acquisition is accomplished using National Instruments™ hardware and LabVIEW visual programming language. The FO-RO system also relies on analog flow and pressure gages that will be recorded during startup procedures and lower resolution intervals during experiments.

4.8.1 Probes and Meters

Various electronic and analog probes and meters are necessary to record conductivity, temperature, pressure, and flow during experiments. This equipment is described in the following sections.

4.8.2 Conductivity

In both the FO-RO and FO-AGMD systems, conductivity is used as a proxy to determine solution concentrations. Conductivity probes are placed in the leachate feed, draw solution, diluted draw solution, and distillate tanks. These signals are then converted to g/L of NaCl using developed calibration curves. Signals are initially sent to EUTECH Instruments alpha COND500 conductivity measurement boxes. These boxes are set to an appropriate range and calibrated to read solution temperature and conductivity. These boxes display conductivity in real time in S/cm, mS/cm, or µS/cm depending on the salinity range required. The boxes then send a 4-20 mA signal to National Instruments data acquisition hardware which is routed by USB cable to a computer and LabVIEW program. The LabVIEW program uses a developed calibration curve to convert the 4-20 mA signal to g/L of NaCl. These NaCl concentrations are saved as secondly data in the comma separated value (CSV) data file exported by the LabVIEW program.

4.8.3 Temperature Probes

Several PT-100 style resistance temperature detectors (RTD) are placed at points of interest in the FO-RO and FO-AGMD systems. As discussed above the PID controllers governing the heated and cooled loops of the AGMD process are sent temperature signals. RTDs are also used in the data acquisition configuration. Temperatures are recorded at the inlet and outlet of each level of the AGMD stack to monitor the condition of the set temperature couple. These RTDs are connected to the National Instruments data acquisition hardware, then processed through a calibration curve within a LabVIEW program where the resistance signal is converted to °C. Temperatures are then exported on a secondly basis to a CSV.

4.8.4 Pressure Probes

Pressure data are recorded for two purposes within the hybrid membrane systems. The transmembrane pressure of the AGMD membranes is determined by pressure transducers placed at the inlet ports of each level of the AGMD module stack. These values are displayed in real time in the front panel of the developed LabVIEW program to allow users to adjust the heated and cooled loop flow rates to values that exist within the operating pressure constraints. Pressure transducers are also embedded in the bottom of each fluid tank to calculate tank volume by fluid pressure head. For each of these purposes, Dwyer® pressure transducers are used. These pressure transducers produce a 4-20 mA signal that is routed to National Instruments data acquisition hardware. Calibration curves were developed for to obtain psi in the AGMD stack and L within each tank. These values are exported on a secondly basis to a CSV file.

ACKNOWLEDGEMENTS

We would like to acknowledge the Environmental Research and Education Foundation (EREF) for funding this project. We acknowledge Professor Kerri Hickenbottom, for research guidance and the undergraduate research assistants Gavin Zirkel, Paulo Lopez Molina, and Emily Ramirez for assistance on this project. Los Reales Landfill is greatly appreciated for providing leachate sample for this project.

References:

1. Achilli, A., Cath, T. Y., Marchand, E. A., & Childress, A. E. (2009). The forward osmosis membrane bioreactor : A low fouling alternative to MBR processes. *DES*, *239*(1–3), 10–21.
2. Cath, T. Y., Mccutcheon, J. R., Mcginnis, R. L., & Achilli, A. (2013). *Standard methodology for evaluating membrane performance in osmotically driven membrane processes*. *312*, 31–38.
3. Kjeldsen, P., Barlaz, M. A., Rooker, A. P., Baun, A., Ledin, A., & Christensen, T. H. (2002). Present and long-term composition of MSW landfill leachate: A review. *Critical Reviews in Environmental Science and Technology*, *32*(4), 297–336.
4. Kjeldsen, P., Barlaz, M. A., Rooker, A. P., Baun, A., Ledin, A., Christensen, T. H., … Christensen, T. H. (2010). *Technology Present and Long-Term Composition of MSW Landfill Leachate : A Review Present and Long-Term Composition of MSW Landfill Leachate : A Review*. *3389*.
5. Renou, S., Givaudan, J. G., Poulain, S., Dirassouyan, F., & Moulin, P. (2008). Landfill leachate treatment: Review and opportunity. *Journal of Hazardous Materials*, *150*(3), 468–493.
6. Stefanakis, A., Tsihrintzis, V. A., & Constructed, F. (2014). *Landfill Leachate Learn more about Landfill Leachate Treatment of Special Wastewaters in VFCWs*.
7. Winter, D., Koschikowski, J., & Wieghaus, M. (2011). *Desalination using membrane distillation : Experimental studies on full scale spiral wound modules*. *375*, 104–112.
8. Zhou, Y., Huang, M., Deng, Q., & Cai, T. (2017). Combination and performance of forward osmosis and membrane distillation (FO-MD) for treatment of high salinity land fi ll leachate. *Desalination*, *420*(February), 99–105.

Appendices

Poster presentations

- Treatment of landfill leachate by hybrid osmotically driven membrane processes. 27th North American Membrane Society, Lexington Conference, KY, May 2018.
- Treatment of landfill leachate using hybrid osmotically driven membrane processes. Arizona Student Energy Conference, Tucson, AZ, Oct 2018.

Supporting Information

Table S.1. Ammonia of FO-RO

Solution	Initial (ppm)	Final (ppm)
Dil Draw	0.1	4
Draw	0.1	20
Distillate	0.1	25
Feed	78	232

Table S.2. TOC of FO-RO

Time (hr)	Initial(ppm)	Final(ppm)
Permeate	0.4	0.3
Dil Draw	0.5	6.9
Draw	2.8	6.2
Feed	40	497.5

Table S.3. Ammonia of FO-AGMD

Solution	Initial (ppm)	Final (ppm)
Dil Draw	0.1	13.5
Draw	0.1	27.5
Distillate	0.1	22
Feed	74	172

Table S.4. TOC of FO-AGMD

Time (hr)	Initial(ppm)	Final(ppm)

Permeate	0.4	3
Dil Draw	0.5	5.5
Draw	1.8	4.5
Feed	101.4	259.2