Drawing a Solution:
Forward Osmosis Water Desalination

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Abstract

Water infiltration and tsunamis cause aquifer salinization, which threatens our main supply of freshwater. Current research suggests that forward osmosis is a novel, low-energy, and thus low cost method of desalination, and developing practical draw solutions can improve the efficiency of this process. To study this on a small scale, an osmometer was built of 1.5" (3.81 cm) PVC piping; low pressure, flat sheet reverse osmosis membranes were used as selectively permeable membranes to separate a sodium-chloride (NaCl) feed solution from sucrose ($C_{12}H_{22}O_{11}$) draw solutions at various concentrations. The average water flow from the feed to draw solution was calculated based on the change in the salinity of the feed solution over time. Statistical tests were performed to analyze the effect of initial concentration of the $C_{12}H_{22}O_{11}$ solution on average water flux and to compare the performance of forward osmosis across two different membranes. Increasing membrane surface area should increase water flow. Water desalination for domestic use is important to mitigate the inconvenience of groundwater salinization and well contamination.

Introduction

Water scarcity is a major global problem physically and economically. The demand for clean water has increased twice as rapidly as the global population due to the spread of technology and an increase in energy production ("UN-Energy Statistics," 2013); meanwhile the supply of clean water has decreased due to pathological contamination, human pollution, excessive overuse, and climate change. The United Nations (UN) has estimated that within the next decade, approximately two-thirds of the global population will live in areas of water stress, where there is less than 1,700 cubic meters of water per person per year, and 1.8 billion of those people will live in areas of absolute water scarcity, where there is less than 500 cubic meters of water per person per year ("UN-Water Statistics," 2013). Thus, the need to control water usage and strengthen water supplies is obvious.

Although arid or agricultural regions permanently or seasonally lack natural water resources, other areas have an abundance of clean water. Because of this imbalance, some advocates support government-enforced water conservation to improve water distribution, while others support a long-distance bulk water transport industry. However, water control and water transport proposals have faced political and public opposition, and water transport is particularly expensive. Alternatively, developing more water-efficient agricultural techniques or power production methods could alleviate water needs.

Many humanitarian and governmental organizations, such as the Water Project and the UN, encourage water planning, recycling, and conservation by spreading awareness about water pollution and water scarcity. In 2010, the Millennium Development Goals prioritized [improving] access to clean water and reduce the number of people without clean water by 50% before 2015 as second most important goal of the decade. Other charities aim to provide water filters or filtered water to developing areas that lack economic resources to access potable water. Yet, efficient, small-scale water desalination could help improve water supplies.

Literature Review

Aquifer Salinization

Studies have shown how topographical conditions, groundwater overpumping, and extreme weather can cause accumulation of salt in the soil and groundwater. Aquifers provide approximately 97% of freshwater available for human use ("UN-Water Statistics," 2013). In particular, many residents of developing countries rely on wells to pump groundwater for domestic or agricultural purposes. However, consumption of salty water causes potentially fatal dehydration, and few crops tolerate salty water. Thus, aquifer salinization exacerbates water scarcity.

In certain regions, topographical features increase the salinity of the ground water. For example, in the Nurra region of northwestern Sardinia, Italy. Mongelli, Monni, Boggiano, Paternoster, and Sinisi (2013) conducted a dual-isotope analysis of dissolved SO_4 levels and considered the ratios between Cl^- and other ions in the water. Although they found Thad mixing from rainfall and saltwater intrusion contributed to high levels of salinity in the groundwater, they concluded that the main cause of salinization in the Nurra region is dissolution of surrounding halite that dates back to the Paleozoic and the Quaternary periods. This rock reacts with the surrounding water, releasing salt ions dissolve into the water.

In many coastal cities, overburdened aquifers experience saltwater intrusion. When large volumes of freshwater are pumped from the soil, saltwater from the ocean seeps through the soil to replenish the depleted freshwater with salt water. Coastal aquifers are particularly sensitive to water infiltration because coastal soils are characterized by fine-grained sands, which have a greater permeability (Illangasekare et al., 2006), and moreover, cities maintain high water demands. Forced convection via pumping intensifies the process of saltwater intrusion.

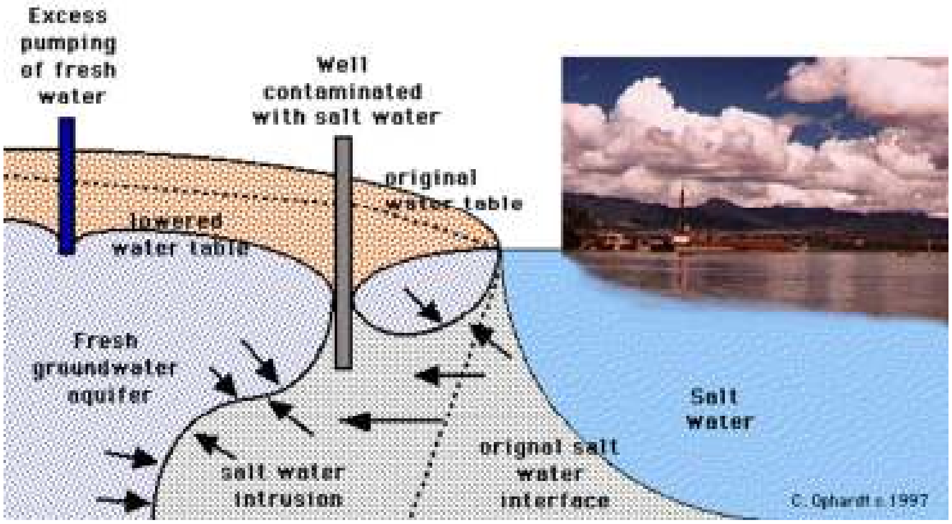

Figure 1: Salt Water Intrusion in Coastal Areas. Overpumping of ground water in coastal areas causescan cause salwater intrusion, through which the well can be contaminated by saltwater. (*Salt Water Intrusion*, n.d.)

Furthermore, seawater displaced by coastal storms can contaminate surface water and groundwater. For example, on December 26, 2004, a tsunami compromised drinking supplies and coastal aquifers across southern Asia. Many residential wells were filled with seawater, including approximately 40,000 hand-dug wells merely throughout Sri Lanka (Illangasekare et al. 2006). After the tsunami, aquifer contamination left a lasting impact. Seawater contaminated the groundwater from the surface via open wells or direct infiltration through the soil, and saltwater intrusions also extended vertically to merge with the aquifers. Although extensive well pumping effectively removed the saltwater in some areas, over-pumping exacerbated saltwater intrusion and increased groundwater salinity. Illangasekare et al. (2006) predict that a significant amount of groundwater in Sri Lanka will experience decreased salinity after several monsoons recharge the sandy coastal aquifers, however access to potable water will remain a difficulty due to the high demand and limited resources. Coastal areas experience several obstacles, including insufficient groundwater supplies, saltwater infiltration, and seawater contamination due to extreme weather events.

Water desalination

Most major seawater desalination plants such as Modern Oasys use reverse osmosis because recent developments have enabled it to be the most efficient large scale method. In this process, pre-treated seawater is pumped through a semi-permeable membrane, which prevents the salts from passing through, thus separating the water from the saline solution. Unfortunately, the membranes require high maintenance and frequent cleaning because contaminants are more likely to get caught in the membrane when the seawater is pumped at such a high pressure. These cleanings are costly and they hinder water production ("Manipulated Osmosis Factsheet," 2013). Additionally, reverse osmosis requires much energy to pump the water through the membrane. Finally, there is concern about the effect of the withdrawal of seawater and the concentration of brine on marine organisms (Elimelech & Phillip, 2011).

Water-Energy Nexus

A major concern in the development of water desalination methods is the energy requirement. Methods that require large amounts of energy are undesirable because a large energy requirement is inherently more expensive, and furthermore, energy production itself may use large amounts of water and increase the demand for water.

Table 1. UEC values for various desalination processes (Martínez, et al., 2010).

Method	UEC
MSF	21.4
MED	8.3
ED	8.0
RO	5.5

Martínez, Ucher, Rubio, and Carrasquer (2010) evaluated the energy efficiency and cost of current water-related methods of transportation, purification, and desalination by calculating the unit exergy cost (UEC), the ratio of the amount of fuel necessary to produce a fuel to the exergy of the product. The specific desalination methods that were analyzed were elecrodialysis, reverse osmosis, multiple effect distillation, and multi-stage flash distillation, and these methods had UEC values of 8.0, 5.5, 8.3, and 21.4 respectively. With a UEC value of 21.4, commercial multi-stage flash distillation had the greatest UEC, showing how thermodynamically energy inefficient chemical-based water treatment methods are (Martinez et al., 2010).

Furthermore, Martínez et al. (2010) computes the total exergy replacement cost (ERC), which measures how much energy is necessary to restore any degraded water resource, based on the UEC values. This method of cost analysis is more useful than standard economic indices because it considers the thermodynamic efficiency and can be applied to multi-stage systems more accurately. ERC is an important cost that the European Water Framework Directive believes water users should compensate. It can also be applied to approximating the environmental costs of physic-chemical degradation of water bodies.

Forward Osmosis

Forward osmosis (FO), also known as manipulated desalination, is the process in which water travels through a selectively permeable membrane from an area of high water concentration to low water concentration to filter impure water. Studies has shown that FO is a more cost-effective desalination process than current methods, and the increasing energy crisis has renewed interest in this “new hot topic” of low-energy water desalination (M. Balaban, personal communication, December 17, 2013). Forward osmosis operates based on the change in the intrinsic osmotic pressure between the two solutions, so the system does not require additional energy to increase the pressure. Modern Water’s forward osmosis plant in Al Khaluf, Oman uses 42% less energy than its reverse osmosis plant, both of which process the same feed water ("Manipulated Osmosis Factsheet," 2013). The implications of this minimal energy-requirement are that the energy costs are low and the risk of membrane fouling is greatly reduced. Therefore, forward osmosis membranes require lower maintenance, less frequent cleaning, and fewer replacements; for example, since the formation in 2010 of Modern Water's Oman forward osmosis plant has not required cleaning, while its existing Oman reverse osmosis plant has required multiple cleanings ("Manipulated Osmosis Factsheet," 2013).

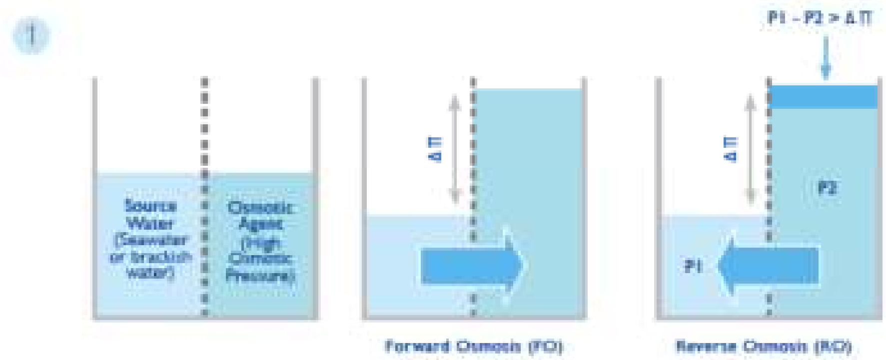

Figure 2: Water pressures in forward osmosis and reverse osmosis. Reverse osmosis requires an applied pressure greater than the pressure of the water, while forward osmosis functions on the water pressure of the source water ("Manipulated Osmosis Factsheet," 2013).

The water flux of a specific forward osmosis unit is affected by the type of membrane used and the type of draw solute used. The components include membrane development, draw solute selection, and post-treatment methods, during which recovery or re-application of the draw solution occurs.

Semi-permeable Membranes

FO membranes are mechanically supported by an embedded polyester mesh, in contrast to reverse osmosis membranes, which are supported by a thick membrane layer. The membranes are designed to be dense, non-porous, and selectively permeable. A hydrophilic skin layer is also desirable to increase the durability of the membrane, thus reducing maintenance. Additionally, the FO desalination process requires two cross-flow channels at both sides of the membrane (Qin et al,. 2012).

There are four membrane configurations: flat sheet, tubular, hollow fiber, and spiral wound. Recent research has shown that hollow fiber configuration simplifies this process of simultaneous flow on both sides of the membrane. Moreover, hollow fiber membranes have more self-support and a more compact shape than flat sheet membranes, which are currently the most widely used FO membrane, Qin et al. (2012) conclude that hollow fiber membranes are more suitable for FO desalination than the current flat sheet model and that future research should focus on developing high performance FO hollow fiber membranes.

Significantly more studies have been conducted on membranes than draw solutes, especially before the recent increase of scientific interest in the FO process. Yet, much current research is focused on improving membrane performance (M. Balaban, personal communication, December 17, 2013); specifically, developments should be made to increase the water flux, lower the reverse solute flux, and increase the durability of the membrane (Qin et al., 2012). This may be accomplished by developing thinner membranes that are still durable.

Draw solutes

A major obstacle in the development of efficient forward osmosis is separating and removing the draw solute (DS) with little energy. The main general DS characteristics that affect FO performance are osmotic pressure and water solubility, but other general DS characteristics include viscosity/diffusivity, molecular weight, concentration, and temperature. An ideal draw solution would have a high osmotic pressure, high solubility, low viscosity but high diffusivity, low molecular weight, high concentration, and high temperature. However, it is important to note that larger DS molecules have a desirably lower reverse draw solute flux, that median concentrations are not significantly less effective than extremely high concentrations because water flux and DS concentration form a non-linear relationship, and that low temperature reduces the need for membrane maintenance (Chekli et al., 2012).

A specific DS may be more or less appropriate depending on the application of the FO process. For example, NaCl or seawater is an effective DS for water purification, but not desalination. Fertilizers may be useful as a DS because the diluted fertilizer can then be applied directly to irrigation and fertigation. Additionally, special characteristics of unique DS may affect performance. Thermolytic solutions, including ammonia carbonates have shown good potential for desalination, but low-grade heat is required for DS recovery. Magnetic nanoparticles (MNPs) can be easily recovered, which is important for desalination, but have a uniquely problematic tendency to aggregate. Other particular DS characteristics include particle size, and ability to cause scaling or membrane fouling (Chekli et al., 2012).

Research Plan

Research Question:

How does increasing the initial concentration of a $C_{12}H_{22}O_{11}$ solution affect the average water flux due to forward osmosis for 1.5 hours across a semipermeable membrane from a 150mL 0.67% NaCl solution to the 150mL $C_{12}H_{22}O_{11}$ solution?

Hypothesis:

If the concentration of the $C_{12}H_{22}O_{11}$ solution increases, the average water flux due to forward osmosis for 1.5 hours across a semipermeable membrane from a 150mL 0.67% NaCl solution to the 150mL $C_{12}H_{22}O_{11}$ sucrose solution will increase.

Procedure:

A small water filter will be made out polyvinyl (PVC) piping, a PVC union, and PVC joints, which will be connected and sealed with PVC glue. Circular flat sheet semipermeable membrane samples will be secured in the PVC union. The NaCl feed solution and the sucrose draw solution will be pre-mixed at 20°C.

The feed and the draw solutions will be poured in the piping on opposite sides of the membrane. After 90 minutes, the solutions will be poured into separate containers. The salinity of the draw and feed solutions will be measured before and after filtration, and the salinity of the feed solution will be tracked throughout the 90 minutes using a TDS Water Purity meter. The measurements will be recorded and used to calculate the average water flux. Goggles and latex gloves will be used as safety precautions.

Methodology

All preparation and experimentation occurred inside at a room temperature of 20°C. Safety goggles and synthetic latex gloves were worn as safety precautions throughout construction and experimentation.

Initial Prototype:

An initial prototype was constructed of ½" polyvinyl chloride (PVC) pipe (standard schedule 40, 1.27 cm inner diameter, purchased from Home Depot), two ½" 90 degree PVC elbow joints (standard schedule 40, 1.27 cm inner diameter, slip fitting, purchased from Home Depot), and a ½" PVC union (standard schedule 80, 1.27 cm inner diameter, purchased from Home Depot). Two 30.48 cm pieces of pipe and two 6.67 cm pieces of pipe were cut using a hand saw (Stanley Miter Box and Hand Saw). The parts were connected as shown below and sealed with PVC glue (Oatey® Clear PVC cement, purchased at Home Depot).

Figure 3: The first prototype was constructed by connecting a long pipe, a slip elbow, a short piece, a union, a short piece, a slip elbow and a long piece of ½" inner diameter PVC piping.

Final Prototype:

A second prototype was constructed of a 1 ½" PVC Slip Union (standard 3.81 cm inner diameter, Schedule 80, purchased at Home Depot), two 1 ½" 90 degree PVC street elbows (standard 3.81 cm inner diameter, Schedule 40, purchased at Home Depot). To hold the union and elbows in place, the connection between the male fitting of each elbow with a fitting union was sealed with PVC glue (Oatey® Clear PVC cement, purchased at Home Depot).

A piece of thick cardboard was marked as shown below:

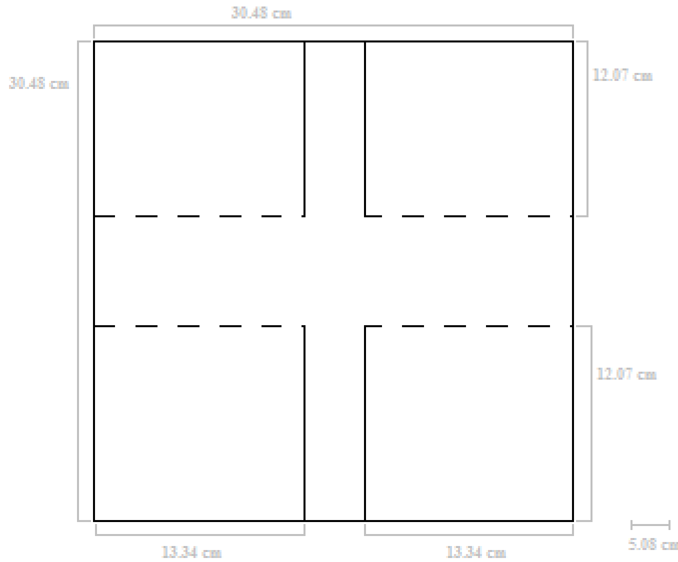

Figure 4: Thick cardboard was scored and cut along the dotted and solid lines, and masking tape secured the cardboard to create a stand for the second prototype.

A box cutter was used to score along the dotted lines and cut along solid lines. The scored regions were folded up and masking tape was used to keep the cardboard in place to support the PVC piping. Two circles with a diameter of 6.0 cm were cut from thick cardboard, and a hole was cut through one of the cardboard circles to fit the bottom part of the TDS meter; this cardboard was used to hold the TDS meter upright during experimentation.

Equipment Calibration:

To calibrate the salinometer (HM Digital TDS-EZ Water Purity Meter, accuracy of 1 ppm, increments of 10 ppt, donated by William Ellis), three measurements were taken at each of numerous settings of various amounts of non-iodized NaCl (Price Chopper Brand) dissolved in 60mL of distilled water. The salt was measured on a digital scale (American Weight Scale AWS-100 Digital Scale, donated by Massachusetts Academy of Math and Science) and stirred into the water with a plastic drinking straw. Three measurements were recorded and averaged on Microsoft Excel 2010 and used to determine a calibration factor.

Membrane Preparation:

Scissors were used to cut five circular pieces with a diameter of 6.35 cm from each of the following: a flat sheet SWC5 Sea Water Reverse Osmosis (SWRO) Membrane (donated by Hydranautics), and a TM820V SWRO membrane (donated by Toray Membranes). The membranes were stored at 16.7°C in closed plastic containers and submerged in distilled water, which was replaced weekly. Before usage, the SWC5 membrane samples were gently rinsed in tap water by hand. Between trials, each membrane piece was submerged 100mL of distilled water for at least 1 hour. After usage, the membranes were stored in separate containers.

Solution Preparation:

All settings and trials were conducted inside at 20 degrees Celsius. For each trial, the feed and draw solutions were pre-mixed by measuring a set amount of non-iodized NaCl (Price Chopper Brand) and sucrose (Stop and Shop Table Sugar) and adding distilled water (Price

Chopper Brand). To prepare the feed and draw solution, non-iodized NaCl and sucrose respectively were mixed with distilled water to achieve the mass of solute to volume of solution ratios listed in Table 2.

Table 2: Table of solute : solvent ratios of solutions used in experiment.

Solution, Setting	solute mass, m_f or m_d (g)	solvent volume v_{H2O} (mL)	solution volume v_S (mL)
Feed, 1-5	1	150	150
Draw, 1	35	162	150
Draw, 2	45	168	150
Draw, 3	55	169	150
Draw, 4	65	172	150
Draw, 5	75	177	150

The feed solute was non-iodized table salt (NaCl), the draw solute was table sugar ($C_{12}H_{22}O_{11}$), and the solvent was distilled water (H_2O). The solvent volume was determine based on how much was necessary to achieve a solution with a total volume of 150 mL.

Experiment Procedure:

Before each trial, the PVC piping was rinsed, dried, and assembled. A membrane was secured in the union with membrane side facing the gasket of the union. 150 mL of the draw solution and the feed solution were measured in a standard 250 mL graduated cylinder. A TDS meter was used to take 3-4 measurements of each solution, and the arithmetic mean of the measurements were recorded on Microsoft Excel. The draw solution was poured into the side of the device that the membrane faced, and the feed solution was poured into the opposite side. After 90 minutes, the solutions were poured into separate containers, stirred with a plastic straw, and measured 3-4 times with the TDS meter. The arithmetic mean of the final measurements were recorded on Microsoft Excel.

Data Analysis:

The following calculations were performed using the data collected for both the draw solution and the feed solution and for both membranes. For each trial, the change in salinity for each solution was calculated as the difference between the initial salinity and the final salinity. These arithmetic mean of these differences were calculated across all trials of each setting. The average changes in salinity were then graphed in terms of the initial concentration of the draw solution of each setting. A Pearson's *r* correlation was used to analyze the relationship between the salinity change and the initial concentration of the draw solution.

For each trial, the total amount of salt diffusion was calculated based on the change in salinity and the solution volume. The amount of salt diffusion was then used to calculated the average water flux over the 90 minute period. The arithmetic mean of the average water fluxes of all trials was calculated for each setting, and the relationship between these means and the corresponding initial concentration of the draw solution were graphed and analyzed with an ANOVA test.

Results

The relationship between the initial concentration of the draw solution and the average change in salinity of the feed solution was graphed and analyzed with a Pearson's *r* correlation (Figure 5). Similarly, the relationship between the initial concentration of the draw solution and the average change in salinity of the draw solution was graphed and analyzed with a Pearson's *r* correlation (Figure 6). Finally, the average water flux was calculated and the relationship between the initial concentration of the draw solution and the calculated average water flux was graphed and analyzed with an ANOVA statistical test (Figure 7).

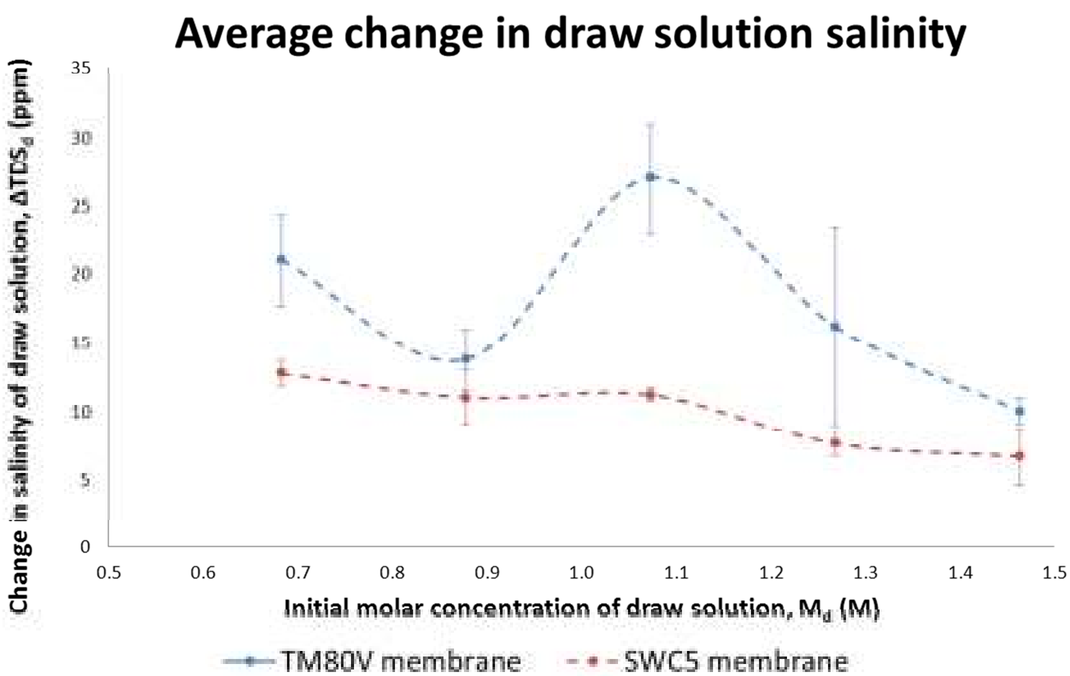

Figure 5: Graph displaying the average salinity changes of the draw solution; the arithmetic mean of all trials for each of 5 settings. The blue and red bars represent the standard deviation of the data. The Pearson's *r*-correlation was calculated for data about TM80V (r = -0.468) and SWC5 (r = -0.952).

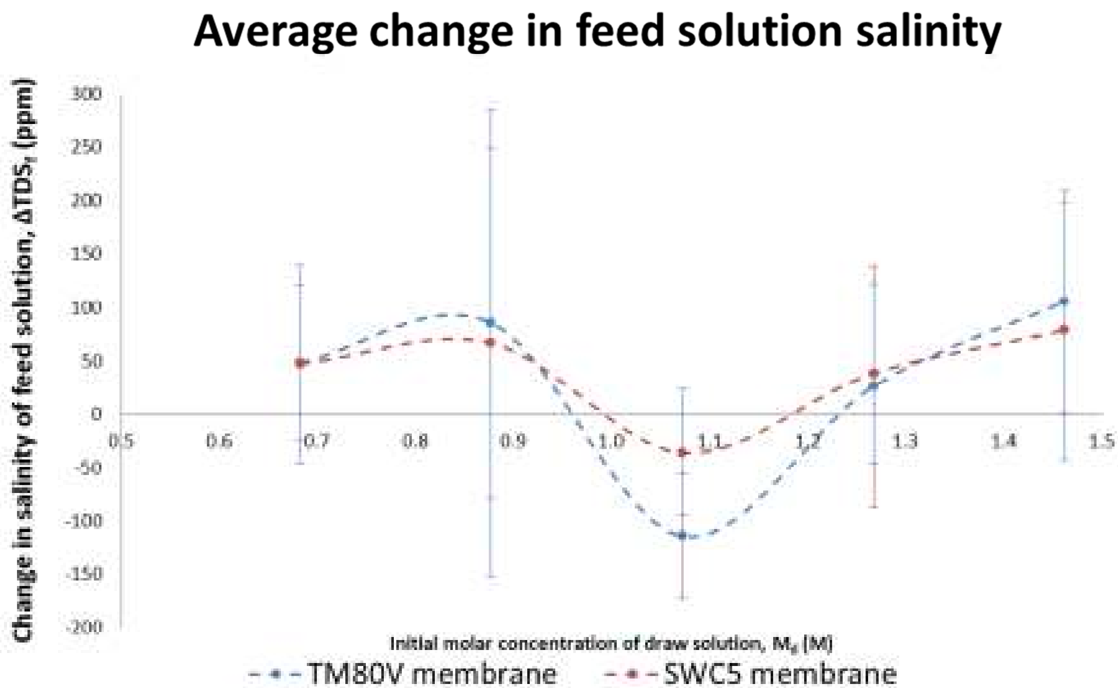

Figure 6: Graph displaying the average salinity changes of the feed solution; the arithmetic mean of all trials for each of 5 settings. The blue and red bars represent the standard deviation of the data. The Pearson's *r*-correlation was calculated for data about TM80V (r = 0.101) and SWC5 (r = 0.123).

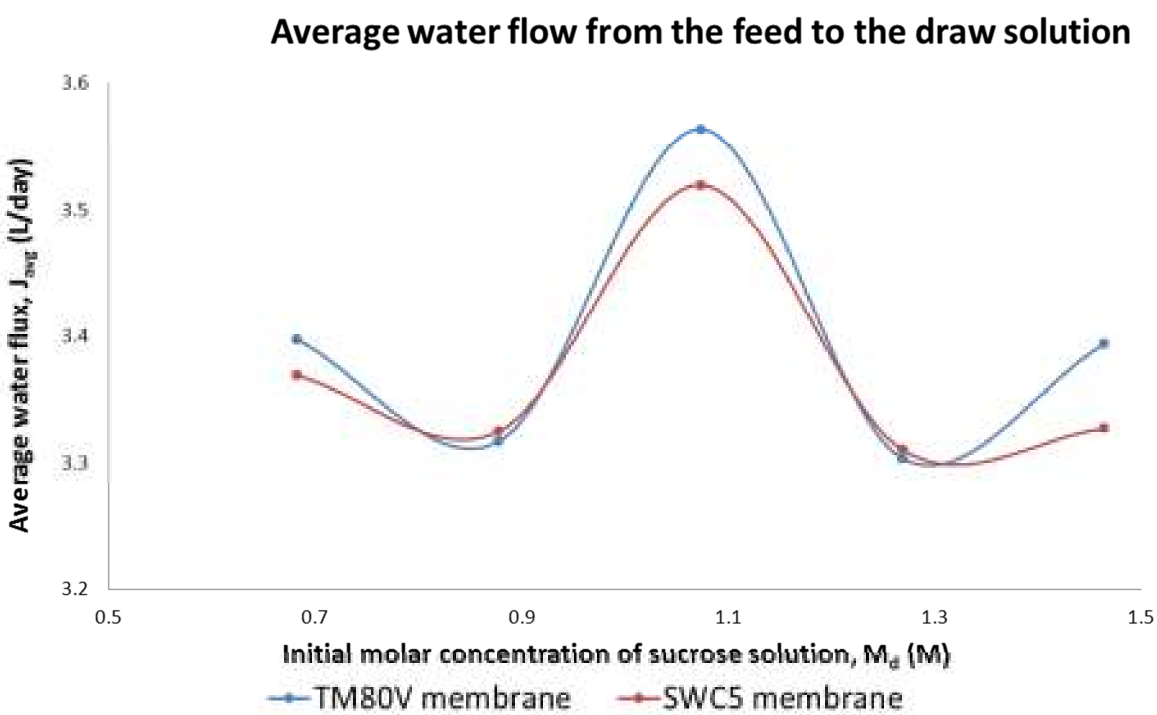

Figure 7: Graph comparing water flow and initial draw solution concentration. The arithmetic mean of the water flow calculated for each trial was averaged across all trials for each of 5 settings. The Pearson's *r*-correlation was calculated for data about TM80V (r = -0.031) and SWC5 (r = -0.181).

Data Analysis and Discussion

Although no conclusive mathematical trends were found between the initial concentration of the draw solution and the change in measured salinity of either the draw solution (Figure 5) or the feed solution (Figure 6), the TM80V and SWC5 membranes yielded similar TDS meter measurements. A Pearson's *r* correlation was performed on the measured data. Weak negative correlations between the draw solution initial molarity, M_d, and the change in draw solution TDS measurements, ΔTDS_d, were found (r = -0.47, -0.95 for data collected with the TM80V and SWC5 membranes, respectively); similarly, weak positive correlations between the draw solution initial molarity, M_d, and the change in draw solution TDS measurements, ΔTDS_f , were found (r = 0.10, 0.12 for data collected with the TM80V and SWC5 membranes, respectively). The data suggests that there was significantly greater salt and water diffusion on the third setting than the other settings from testing both the TM80V membrane and the SWC5 membrane to a lesser extent; hence, the water flux calculated for the third setting was an outlier among the settings.

The data did not support the alternative hypothesis that increasing the initial concentration of the draw solution would increase the water flux; an ANOVA test was performed to show that the results supports the null hypothesis (p = 0.120). The results neither corroborate or contradict results of past studies in the field. For example, McCutcheon, McGinnis, and Elimelech (2007) have tested the effect of osmotic pressure on the water flux using ammonia-carbon dioxide (NH_4-CO_2) draw solutions of various concentrations and found strictly increasing relationships. In contrast, the relationship between the initial concentration of the draw solution and the average water flux was found to be greatest on setting of the median initial concentration in this study.

Conclusions

The data supported the null hypothesis that the concentration of the $C_{12}H_{22}O_{11}$ solution increases does not affect the average water flux due to forward osmosis for 1.5 hours across a semipermeable membrane from a 150mL NaCl solution to the 150mL $C_{12}H_{22}O_{11}$ sucrose solution. The low cost and convenience of both Further engineering is needed to design a filter with a greater membrane surface area in order to apply forward osmosis to small scale desalination.

Limitations and Assumption

Numerous limitations were encountered throughout the project. A major limitation was that the equipment to directly measure the water flux was not available. Instead, a HM-Digital TDS meter was used to measure the conductivity of the solution and estimate the NaCl content of the solution, which was then used to calculate water flow. Measuring the water flow directly would eliminate rounding errors accumulated throughout the calculations and would better support the results. Another limitation was that reverse osmosis membranes were used instead of membranes designed for forward osmosis. Furthermore, numerous draw solutions and numerous devices were unable to be tested due to financial and temporal limitations.

In addition, several assumptions were made regarding the membranes, the process, and the results. It was assumed that the membranes did not experience any physical or biological damage before or during experimentation, and all membrane samples of the same type performed identically. In particular, it was assumed that the salt rejectivities of the SWC-5 and TM80V membranes were 99.8% and 99.8%, respectively, which correspond with the maximum salt rejectivities of the membranes as claimed by the manufacturers, and it was assumed that no sucrose passed through any membrane. Furthermore, it was assumed that the draw solution initially had no salt, despite non-zero TDS meter readings, and the hydraulic pressures on either side of the membrane were assumed to be equal.

Sources of error include human error while mixing the solutions and miscalculation of the water flux. A potential sources of non-human error is membrane damage. Discoloration was observed on the TM80V membrane used on the third setting; membrane damage during this setting would account for the considerable diffusion salt and water because these values exceeded corresponding data of all other settings. Results may have been affected by inaccurate TDS meter measurements resulting from air bubbles trapped in the solution or miscalibration. During TDS meter calibration, it was observed that as salinity increased, the difference between the expected salinity and the TDS meter reading increased; thus, calculations for higher settings may underestimate final feed solution salinity and water flux.

Future Experimentation and Applications

The prevalence of sucrose and the versatility of PVC piping make these inexpensive materials suitable for small scale filtration in developing countries. Developing countries often lack of funding for large desalination facilities or new water infrastructure, and an increase in groundwater and well contamination has forced many people to drink water that is detrimental to their health. However, the results from this experiment show that a better filter design is necessary to increase water flow; filters could be engineered with an increased membrane surface area or a non-zero change in hydraulic pressure.

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