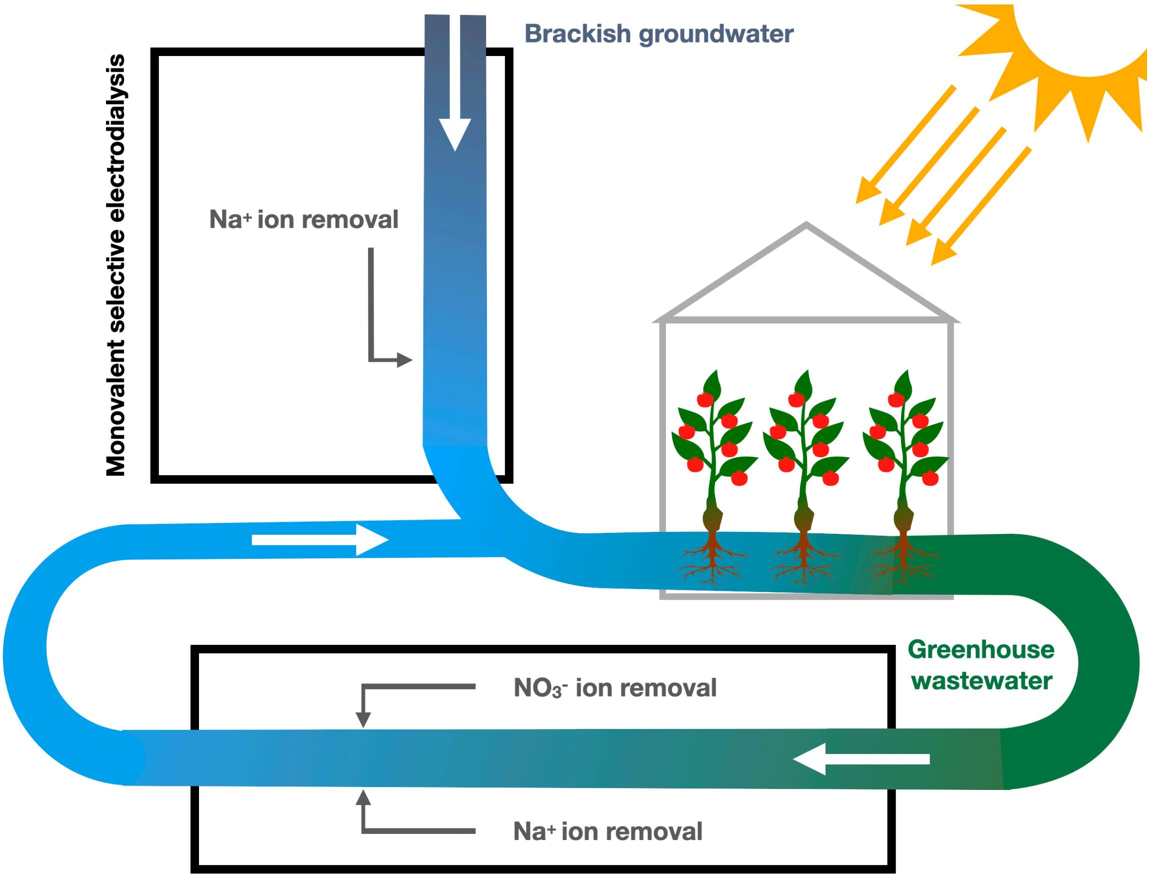
Monovalent selective electrodialysis in greenhouses

An analysis of brackish groundwater and greenhouse wastewater treatment



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Water and Environmental Engineering
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by

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Picture on front page: Flowchart of MSED applications in greenhouse systems. Chart by Georg Schücking.

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Preface

This thesis was written in in partial fulfillment of the requirements for the degree of Master of Science in Water Resources Engineering at Lund University. I collected the experimental data presented in this work during a nine month research visit to John H Lienhard V's group at the Massachusetts Institute of Technology (MIT) in Cambridge, MA. My thanks go to John Lienhard, who made this project possible and whose continued support throughout my stay in the U.S. allowed me to finish my work at MIT despite uncertain periods of campus lockdowns and major restrictions due to the COVID-19 pandemic. I would also like to to thank Yvana Ahdab for introducing me to this research topic and for her immense help and advice during all parts of my project work. Thanks to all other members of my research group at MIT for welcoming me into the laboratory and helping me navigate a new country, city, and area of scientific research.

I want to thank Åsa Davidsson at the Water and Environmental Engineering Division for being a very supportive and knowledgable supervisor throughout the different stages of my thesis project, as well as the International Offices at the Faculty of Engineering in Lund and at MIT, who helped me plan my visit. Thanks to the Crafoord Foundation and the German Agency for International Cooperation (GIZ) for supporting me through their scholarship programs.

Lastly, I want to express my thanks and gratitude to my friends Kuba and Skyler and everyone that made my time in the U.S. so special and memorable.

Summary

Water use in greenhouse can be optimized by switching to alternative sources of irrigation water and building zero-liquid discharge systems that recirculate greenhouse effluent. The use of brackish groundwater (BGW) has become a popular option for greenhouses that have adopted reverse osmosis (RO) to reduce the salinity of their source water. Similarly, RO has emerged as the most commonly used desalination technology for wastewater treatment. In either case, desalination treatment is necessary to remove monovalent sodium ions, which occur naturally in BGW and can build up in reuse loops when other ions and part of the water are consumed by the crops.

During RO treatment, ions are removed indiscriminately, including multivalent nutrients that support and encourage crop growth, leading to increased fertilizer use as the multivalent ions have to be reintroduced to the irrigation water. Unlike RO, monovalent selective electrodialysis (MSED) selectively removes monovalent sodium while retaining multivalent nutrients in the solution. This allows for the targeted removal of sodium ions without an inversely proportional increase in required fertilizer use. MSED can furthermore remove monovalent nitrate, a major environmental pollutant, from greenhouse wastewater, allowing for the safe discharge of treated effluent.

This thesis analyzes the experimentally determined monovalent selectivity of Fujifilm MSED membranes for 13 BGW compositions, as well as their ability to treat eight greenhouse effluent compositions with a focus on nitrate and sodium removal. In addition, the latter experiments were also conducted for a set of Neosepta MSED membranes. The Fujifilm membranes analyzed showed better BGW desalination performance (i.e. higher monovalent selectivity) than has been reported for Neosepta membranes. In the BGW experiments, solute ratio was found to influence selectivity, as the highest selectivity was observed at the lowest solute ratios. In the greenhouse effluent experiments, Neosepta membranes outperformed those manufactured by Fujifilm, as Neosepta membranes removed more nitrate and sodium.

List of abbreviations

Abbreviation	Definition
AEM	anion exchange membrane
BGW	brackish groundwater
CEM	cation exchange membrane
ED	electrodialysis
EU	European Union
IDE-JETRO	Institute of Developing Economies, Japan External Trade Organization
MSED	monovalent selective electrodialysis
RO	reverse osmosis
TDS	total dissolved solids
U.S.	United States
ZLD	zero liquid discharge

Contents

1 Introduction

The high water demand of agriculture (accounting for 70% of freshwater withdrawals worldwide (IDE-JETRO, 2011)) as well as increasing water stress due to global population and economic growth, and freshwater source contamination (Chen et al., 2018) have created the need for a more efficient water utilization in this sector. One promising approach to keep up with the growing demand for irrigation water is an increased focus on greenhouses as opposed to conventional open-field crop cultivation. Greenhouses have a lower water consumption at a higher crop yield (Barbosa et al., 2015), while further allowing for a higher degree of parameter control throughout the cultivation process. A common source of irrigation water in agriculture is groundwater, as it is widely accessible through wells or preexisting water supply systems (Siebert et al., 2010). The chemical composition of irrigation water strongly impacts a plant's growth and general physiological development. Specifically the prevalence of increased concentrations of monovalent ions in irrigation water can hinder plant growth and crop production. At present, greenhouse operators therefore ensure ideal water conditions via the removal of all dissolved salts in brackish groundwater (BGW) using reverse osmosis (RO), a process constrained by high running costs due to the energy required to run RO membranes (Greenlee et al., 2009). RO treated groundwater further requires the addition of fertilizers to achieve irrigation quality. Moreover, improper RO brine management can result in damage to natural ecosystems (Winters et al., 1979). Apart from source water treatment, a key component in optimizing greenhouses is zero liquid discharge (ZLD). This technology, which was pioneered in the Netherlands, reduces the environmental footprint of greenhouse horticulture while simultaneously lowering operational costs (Thompson et al., 2018). The wastewater volume discharged into the environment is minimized (ideally to zero) and the amount of water reused is maximized.

Monovalent selective electrodialysis (MSED) presents a novel treatment technology that can potentially improve ZLD operation and serve as a more efficient alternative to RO because MSED aims to only remove monovalent ions, retaining di-and multivalent ions in the irrigation water. Previous studies suggest that greenhouses may achieve an annual 168% cost reduction by treating their source water with MSED instead of RO (Ahdab et al., 2020a). Savings are thus greater than operating costs leading to a net gain. Although MSED has been used to concentrate sodium chloride from saltwater in Japan since the 1960s (Kawate et al., 1983), little research has been conducted to determine possible alternative applications such as brackish water desalination or the treatment of greenhouse effluent to remove monovalent nitrate or improving recirculation systems with sodium build-up. Consequently, the market standard for monovalent selective ion exchange membranes is designed for higher salinity applications since the research to date has prioritized seawater and concentrated seawater salinities for salt production applications (Saracco and Zanetti, 1994; Saracco, 1997; Luo et al., 2018).

1.1 Aim

The purpose of this thesis is to investigate the suitability of MSED to be used for:

A) The desalination of BGW for irrigating greenhouse crops

B1) The treatment of greenhouse effluent to remove nitrate

B2) Greenhouse reuse water treatment for sodium removal to achieve ZLD

The experiments conducted compare two sets of MSED membranes on their performance for BGW (application A) and greenhouse effluent (applications B1 and B2) treatment. The individual membrane performance is determined by a comparative permselectivity analysis for the respective feedwaters. The results, which are also published in two journal articles that I co-wrote during my Master's work (Ahdab et al., 2020b,c), are evaluated with reference to current greenhouse water treatment technologies to outline possible paths towards MSED implementation.

2 Background

2.1 Monovalent electrodialysis

Electrodialysis (ED) is an ion separation process driven by a potential difference applied across a stack of several ion exchange membrane cells with an aqueous salt solution permeating through them. Each cell consists of an anion exchange membrane (AEM) and an adjacent cation exchange membrane (CEM), which are separated by a spacer to allow flow across the cell. AEMs and CEMs have charged surfaces that repel cations and anions, respectively. The current, induced by a direct voltage power supply, forces cations to shift towards the anode and anions towards the cathode. If a feedwater containing ions of different valency passes through an ED stack, water is desalinated as all ions are removed from the stream between two ion exchange membranes in a single stack, resulting in a product or diluate stream of pure water and a brine stream with an increased ionic concentration.

MSED on the other hand has monovalent selective ion exchange membranes, which are semipermeable, ideally only allowing for the passage of monovalent ions in order to selectively remove them from the feedwater. As a stack contains several cation exchange membranes (CEMs) and anion exchange membranes (AEMs), a single monovalent ion may pass through one membrane with the opposite charge, but will then be unable to pass through the next membrane because it will have the same charge as the ion. Figure 2.1 depicts this process in which ion transport occurs perpendicular to the direction of water flow.

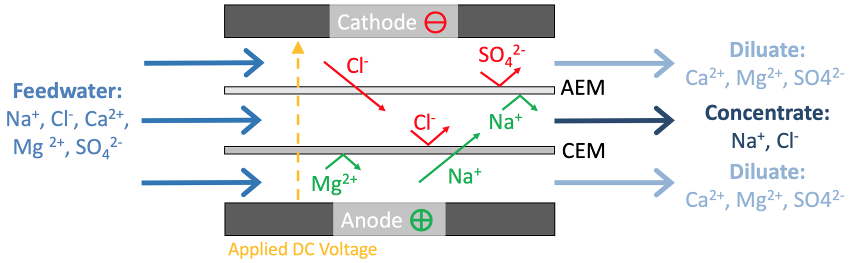


Figure 2.1: Simplified conceptual MSED stack with a single membrane cell (modified from Rehman et al., 2019).

Desalination can play a crucial role in ensuring that irrigation water quality requirements are met. The process involves the treatment of water through the removal of dissolved solids that would otherwise make the water source unsuitable for irrigation applications. Because water quality is central to crop growth, advanced agriculture sectors, such as hydroponics and greenhouses, have begun to use RO to treat their source water.

Since MSED was originally developed for the production of sea salt (Kawate et al., 1983), the literature has predominantly focused on MSED membranes selectivity at high salinities (Saracco and Zanetti, 1994; Saracco, 1997; Luo et al., 2018). Studies examining MSED at lower salinities (e.g. brackish groundwater conditions) show varying degrees of monovalent membrane selectivity for different available membranes. CSO/ASV membranes (Asahi Glass) were found to have selectivity towards monovalent ions (Cohen-Tanugi and Grossman, 2012), while the CR67 membrane (Suez Water Technologies & Solutions) selectively removed divalent ions (Jiang et al., 2019). However, monovalent selectivity for the CR67 membrane could be improved by adding a polyethyleneimine coating layer (Jiang et al., 2019). For Neosepta CMS/ACS membranes (Astom Corporation) selectivity towards both monovalent ions (Ahdab et al., 2020a) and divalent ions (Cohen-Tanugi and Grossman, 2012) has been reported. Due to Ahdab et al.'s greater variation in feedwaters analyzed (16 compared to one by Cohen-Tanugi and Grossman), it seems plausible that Neosepta CMS/ACS membranes exhibit greater monovalent selectivity than found by Cohen-Tanugi and Grossman. Recently, Fujifilm has developed a new type of MSED membranes (Type 16) specifically for salinities in the brackish range. Both Neosepta CMS/ACS membranes and Fujifilm Type 16 MSED membranes were used in the experiments for this thesis (see Chapter 3.2 for a description of the experimental set-up).

2.2 Greenhouse source water

The choice of source water for greenhouses largely depends on the local availability and cost of water and its quality. Common sources of greenhouse irrigation water include surface freshwater, rainwater, tapwater, groundwater, and seawater, which have varying pretreatment needs. Groundwater is a popular choice due its wide availability and low cost. In order not to damage crops, irrigation water requires high chemical water quality, i.e. concentrations of dissolved minerals in the water that support optimal plant growth.

Along with sunlight, air (carrying carbon dioxide), and water, the prevalence of minerals in the soil-water interface constitutes one of the fundamental environmental conditions necessary for plant life. Essential minerals are commonly defined by subcategories of macro-and micronutrients, based on their molar concentration in plant cells, where the cumulative concentration of all micronutrients is less than the concentration of the least common macronutrient. Epstein (1972) identifies nitrogen, potassium, calcium, magnesium, phosphorous, sulfur, and silicon as macronutrients and chlorine, iron, boron, manganese, sodium, zinc, copper, nickel, and molybdenum as micronutrients.

While nutrients are essential for crop growth, it is the dose that makes the poison. Exposure to overly nutrient-rich water can interfere with the nutrient uptake process of crops, resulting in lower yields and potentially loss of crops. High concentrations of sodium in irrigation water causes plant tissue necrosis, leading to reduced growth or die-off (Taiz and Zeiger, 2002). Moreover, soil quality may be affected by the introduction of sodium-rich water if sodium ions absorb to clay aggregates and subsequently accumulate in the soil. The osmotic pressure of a soil solution is further increased by high salinities in the root zone, causing decreased rates of water absorption by crops, negatively affecting seed germination along with overall plant growth and yield (Phocaides, 2007). The resilience of crops to sodium exposure and salinity varies, but in the context of greenhouse agriculture, eggplants are among the most sodium sensitive crops, whereas tomatoes are most resilient (Voogt and Sonneveld, 1997).

2.2.1 Brackish groundwater

Groundwater is a preferred irrigation water source for many growers because it is accessible at a low cost and independent of municipal waterworks or precipitation. Although 69.5% of all groundwater withdrawals in the U.S. in 2015 were used for plant irrigation (Dieter et al., 2018), BGW only accounted for close to 3% of all groundwater withdrawals in 2015. BGW could be used at a significantly higher rate since 29% of the country's grid cell volume between 0 m and 914 m (3,000 ft) below ground level contain water with ionic concentrations in the brackish range (Stanton et al., 2017).

Ionic concentrations in groundwater originate from mineral weathering or the dissolution of organic and inorganic salts. The weathering process consists of two subprocesses, during which hydrogen ions are produced[I] and consumed (Svensson, 2011). Hydrogen production takes place after carbon dioxide gas from the air or from bacterial-mediated respiration in the soil reacts with water, producing carbonic acid (see equation 2.1), which in turn dissociates into hydrogen cations and bicarbonate anions (see equation 2.2) that themselves can dissociate further into carbonate (see equation 2.3).

$$\mathrm{CO_2(g) + H_2O \rightleftharpoons H_2CO_3} \tag{2.1}$$

$$\mathrm{H_2CO_3 \rightleftharpoons H^+ + HCO_3{}^-} \tag{2.2}$$

$$\mathrm{HCO_3{}^- \rightleftharpoons H^+ + CO_3{}^{2-}} \tag{2.3}$$

This is a simplification of the reaction order, for a more detailed description of the carbonate equilibrium in water, see Fetter (2014, Chapter 9). While the reactions caused by carbon dioxide and water are the main source of hydrogen ions in groundwater, other sources include but are not limited to the oxidation of sulphuric minerals (i.e. pyrite, FeS_2), ammonium oxidation, and iron oxidation by nitrates (Svensson, 2011).

An increased concentration of H^+ radicals reduces the pH to acidic conditions, inducing the hydrolysis of minerals (Earle, 2016). Hydrolysis is a process in which a larger mineral breaks down into ions that go into solution with water and a smaller mineral (e.g. clay). Feldspars, a group of aluminium silicates that constitute over half of the earths crust by mass, are an example of a mineral group that may undergo hydrolysis resulting in ion transport to the groundwater. Similarly, oxidation can chemically weather other minerals (e.g. olivine) (Earle, 2016).

Another source of dissolved minerals in groundwater is direct dissolution. Salts that occur naturally in soil/aquifer systems dissolve in water until an equilibrium i.e. saturation is reached. Halite (NaCl), like many inorganic salts, has a high solubility of 360 kg/m^3 [II] (Seidell and Linke, 1958). Halite dissolution is the main source of Na^+ and Cl^- in groundwater (Svensson, 2011).

[I] Hydrogen ions are not actually dissolved as H^+, but prevail in the form of H_3O^+.

[II] at a pH of 7, a temperature of 25° *C* and a total pressure of 1 *bar*

The major ions in groundwater are cations calcium, magnesium, sodium, and potassium and anions bicarbonate, carbonate, and chloride. Other ions may be considered in groundwater analysis if the ion balance of the major cations and anions does not equal to zero. The exact concentration of different ions in groundwater varies depending on the soil passage time and the contact period, resulting in higher rates of total dissolved solids (TDS) in confined and less permeable aquifers (i.e. clay). Brackish groundwater TDS ranges from 1000 mg/L to 10000 mg/L, while seawater TDS levels are greater than 30000 mg/L. This difference is due to the oceans' position at the end point of any soil passage, where dissolved ions inevitably accumulate over a geological time period, resulting in high TDS levels in seawater. Seawater can also turn previously fresh groundwater brackish by seawater intrusion, which typically occurs in coastal regions as an effect of unsustainable rates of groundwater extraction through wells. Pumping water from an aquifer at a rate higher than the rate of natural replenishment via percolation may create an artificial hydraulic gradient (cone of depression), which can draw saltwater from a nearby shore into the aquifer (Fetter, 2014). The subsequent effect of seawater intrusion is that groundwater and seawater mix, which raises the overall TDS into the brackish range. Due to these two geological processes, the availability of BGW is highest along coastlines and where long geological passage has caused the percolating water to take up higher concentrations of minerals.

The Netherlands have a long history of innovation in the field of greenhouse technology. This is exemplified by the development and early implementation of modern cultivation methods including hydroponical fertigation systems, soil sensors and continuous water quality monitoring, artificial lighting, and drip irrigation (Thompson et al., 2018). While these advancements have allowed Dutch farmers to maximize their yield per area, making the Netherlands the fourth largest vegetable exporter world-wide by revenue (World Bank, 2020), there continues to be a strong reliance on BGW to irrigate crops (Thompson et al., 2018; Ros and Zuurbier, 2017). Seawater intrusion in the Westland region where the majority of Dutch greenhouses, are located has created a need for farmers to desalinate their well-water or to use other water sources. A more cost-efficient BGW desalination method would drive down the cost of food production and lower dependence on intermittent water sources, i.e. rainwater and tapwater. Figure 2.2 shows how the Westland's groundwater is impacted by seawater intrusion. The hydraulic gradient, which correlates to the regional topography, draws seawater into the aquifer that local greenhouse operators use to produce irrigation water.

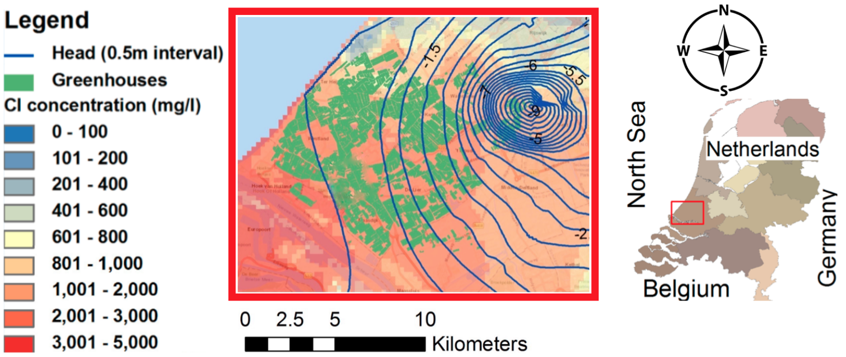
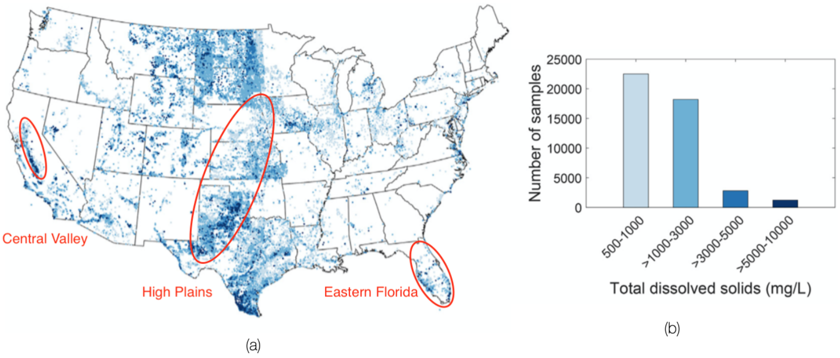


Figure 2.2: Map of greenhouse locations in the Westland region with hydraulic heads and groundwater salinity (modified from Ros and Zuurbier, 2017).

The U.S. present another case study for BGW use. Several agricultural hubs in the U.S., including the Californian Central Valley, the High Plains east of the Rocky Mountains mountain range, and Eastern Florida, are projected to face extreme water stress by 2050. Utilizing the water from BGW aquifers offers a solution to the impending water security crises in these regions. The correlation of BGW prevalence and the three mentioned areas is displayed in figure 2.3 on the next page. Unlike the aforementioned Westland region of the Netherlands, U.S. BGW supplies remain largely untapped, which is likely to change as freshwater resources become more scarce.



(a)

(b)

Figure 2.3: (a) Map of BGW distribution as determined through the analysis of USGS groundwater datasets. (b) Histogram showing the number of samples, classified by four TDS color-coded brackets with reference to (a) (modified from Rehman et al., 2019).

2.3 Greenhouse water cycle

The fertigation process in greenhouses involves the addition of fertilizer to irrigation water to provide optimal growing conditions to the crops. One of the constituents added to the irrigation water stream is a source of nitrogen in the form of nitrate or ammonium, which is biologically transformed into nitrate (Taiz and Zeiger, 2002). Since irrigation water contains higher amounts of fertilizer than are absorbed by the crops, the surplus concentrations wash out to the greenhouse effluent. While greenhouses used to discharge their effluent directly into the environment, recent regulations in the European Union (e.g. Nitrates Directive and Water Framework Directive) and the U.S. (e.g. National Pollutant Discharge Elimination System) on the disposal of nitrate among other constituents have led to the emergence of two greenhouse wastewater treatment approaches. In the first approach, wastewater is biologically denitrified using large reaction basins or artificial wetlands. The main drawback of this low-tech solution is its high land use and limited process control options in the case of artificial wetland treatment (Gruyer et al., 2013). The alternative treatment approach of reusing the wastewater as irrigation water requires that a recirculation system continuously pumps effluent water back into the irrigation stream. To prevent the spread of crop pathogens or biofilm growth on irrigation nozzles, the effluent water needs to be disinfected before being reused. Recirculating the effluent wastewater has the added benefit of enabling ZLD systems, which are an industry goal due to the environmental risks caused by nutrients leaching out from agricultural growing facilities and associated discharge permits. The Netherlands have set guidelines to phase out any greenhouse effluent discharge by 2027 in order to prevent negative environmental impacts of Dutch greenhouses, which cover 10,000 ha of the country's area.

Despite the benefits of reusing greenhouse wastewater, there are some inherent problems that need to be addressed. One reported issue with recirculation loop is the accumulation of minerals not used by the plants, specifically the build up of dissolved sodium ions in the system (Baas and Berg, 1999; Voogt and van Os, 2012; Stanghellini et al., 2005). Over time, this effect can result in sodium concentrations in the feedwater exceeding the threshold levels that crops can withstand without damage. In order to sustain the desired growing conditions, greenhouse operators are currently left to either discharge the effluent once sodium accumulation becomes apparent or to desalinate the reuse water using RO. The latter approach has the disadvantage of high energy demands and the need for more fertilizer addition as RO removes all dissolved minerals. Another problem in this context is optimal nitrate level in the feedwater. Mixing recirculated reuse water with fresh source water prior to the addition of fertilizer can make it more difficult to reach the desired nitrate levels in the irrigation water.

2.4 MSED in greenhouses

MSED may serve as an alternative technology to RO with greater potential of tailoring reuse water to irrigation needs. There are several advantages to using MSED instead of RO. Most importantly, the selective removal of monovalent ions which are detrimental to crops (sodium in particular) using MSED, while retaining divalent ions favorable to crops in the product water stream, results in lower fertilizer needs. Corresponding cost savings can hence make MSED favorable over RO (Ahdab et al., 2020a). Furthermore, the high water recovery of MSED, which can exceed 90% for brackish solutions (Strathmann, 2010), leads to water savings and less brine volume for disposal and/or reuse. Another advantage of MSED membranes is their long lifetime compared to RO. According to Strathmann (2010) MSED membranes can be used 2-3 years longer than RO membranes due to their high chemical and mechanical stability. The physical robustness of the membranes additionally results in increased fouling resilience compared to RO.

Figure 2.4 shows three examples of MSED applications that could improve the greenhouse water process. Application A refers to the desalination of BGW to be used as greenhouse irrigation water. For greenhouses with a conventional effluent discharge set-up but limited available land (application B1 in Figure 2.4), MSED presents an alternative nitrate removal strategy to biological treatment that potentially allows for the recovery of nitrate for use in fertilization. Application B2 in Figure 2.4 highlights the combined nitrate and sodium removal capabilities of MSED in greenhouses with implemented reuse loops. Primary market research has shown that greenhouse operators are looking for a solution to the problems associated with sodium accumulation in particular.

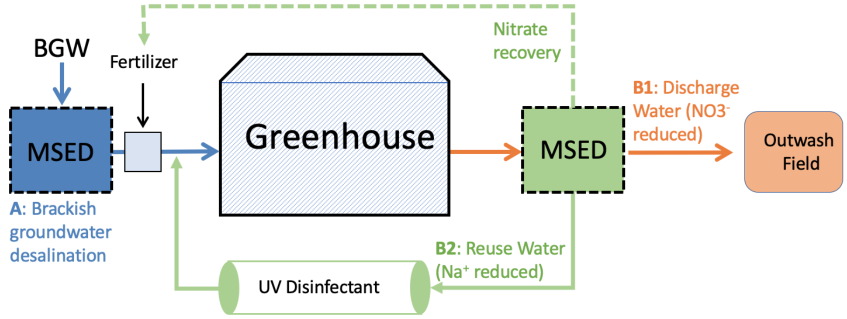


Figure 2.4: The greenhouse water cycle with three highlighted possible MSED applications (**A**: BGW desalination, **B1**: sodium reduction in the reuse loop, **B2**: nitrate removal from discharge water)

3 Materials and methods

I conducted three series of experiments to determine the performance of two MSED membranes sets via monovalent selectivity analysis. My work included the selection of feedwaters to test through literature review and interviews with growers (resulting in the compositions shown in Chapter 3.1), conducting the experiments outlined in Chapter 3.2 using a previously built MSED desalination set-up, and the analysis of experimental results. Throughout this process, I received substantial feedback and support from other members of my research group, particularly with regard to the experimental workflow and the physical grounds for result evaluation (Chapter 3.3).

3.1 Waters analyzed

The two types of greenhouse waters analyzed in this thesis are BGW as greenhouse source water (application A in Figure 2.4 on page 11) and greenhouse wastewater (applications B1 and B2 in Figure 2.4 on page 11). Due to the variation in individual ion concentrations for all water analyzed, the impact of cation solute ratios r_{j^+} and anion solute ratios r_{j^-} on MSED membrane performance is investigated:

$$r_{j^+} = \frac{C_{j^+}}{\sum\limits_{j^+} C_{j^+}} \tag{3.1}$$

$$r_{j^-} = \frac{C_{j^-}}{\sum\limits_{j^-} C_{j^-}} \tag{3.2}$$

where j^+ represents all cation species, j^- represents all anion species, and C denotes ion concentration in the diluate in mg/L.

Application A compositions are based on samples from a U.S. Geological Survey (USGS) major-ions dataset (Qi and Harris, 2017) at four dilutions between $1500 - 10000$ mg/L (compositions $\mathrm{A}_1, \mathrm{A}_2,$ and A_3) and the composition used by Cohen-Tanugi and Grossman (2012) (composition A_4). The ion concentrations and solute ratios of the resulting compositions are listed in Table 3.1 on the next page and Table 3.2 on the following page, respectively.

Table 3.1: TDS in mg/L and ion concentrations in eq/L of 13 BGW compositions tested in the MSED experiments (application A).

Label	TDS	Na^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}
Comp. A_1	1295	14	8.4	3.3	17	8.4
Comp. A_1	2858	24	15	5.7	30	15
Comp. A_1	4408	38	23	8.9	47	23
Comp. A_1	10396	97	59	23	120	59
Comp. A_2	1483	8.3	11	5.3	22	2.6
Comp. A_2	2895	18	24	12	48	5.6
Comp. A_2	4756	28	37	18	74	8.7
Comp. A_2	7814	64	85	41	170	20
Comp. A_3	1450	16	2.7	3.3	9.5	12
Comp. A_3	2683	32	5.4	6.7	19	25
Comp. A_3	4276	53	9.0	11	32	42
Comp. A_3	8491	123	21	26	74	96
Comp. A_4	2564	32	6.7	6.7	33	10

Table 3.2: Solute ratios of 13 BGW compositions tested in the MSED experiments (application A).

Label	r_{Na^+}	$r_{Ca^{2+}}$	$r_{Mg^{2+}}$	r_{Cl^-}	$r_{SO_4^{2-}}$
Comp. A_1	0.60	0.32	0.08	0.60	0.40
Comp. A_2	0.40	0.46	0.14	0.86	0.14
Comp. A_3	0.78	0.13	0.09	0.36	0.64
Comp. A_4	0.78	0.14	0.08	0.70	0.30

Greenhouse effluent composition is hyperlocal due to its dependance on various factors including source water composition, soil composition, and crop type. The experiments were conducted using composition data from literature (Saxena and Bassi, 2012; Eveleens, 2016), as well as data collected through interviews with growers in the Netherlands and North America. Ten interviews were conducted to find suitable greenhouse effluent composition data with two datasets being used for the generation of the feedwater compositions (Tielemans, 2020; van het Hof, 2020). Another composition dataset that was used had been shared by a Californian greenhouse operator (Everbloom Nursery, 2018) during a previous market analysis.

The datasets in the literature represent average values for vegetable producing greenhouses, while the datasets shared by greenhouses were selected after comparing data from different greenhouses. The collected data indicates that the TDS of greenhouse effluent typically ranges from $1500 - 3500$ mg/L. The ion compositions analyzed for application B1 and B2 can be found in Table 3.3 (for Fujifilm experiments) and Table 3.4 on the following page, respectively. The average TDS across all compositions is 2397 ± 478 mg/L. Ion solute ratios are shown in Tables 3.5 and 3.6 on page 17.

Table 3.3: Fujifilm feedwater composition data of the five effluent compositions for which both cation and anion concentration measurements were taken. All concentration measurements are in mg/L.

Label	TDS	Na^+	K^+	Ca^{2+}	Mg^{2+}	NO_3^-	SO_4^{2-}	PO_4^{3-}
Comp. B_1	1681	162	250	91	29	805	344	0
Comp. B_2	2797	227	335	213	53	1337	546	19
Comp. B_4	1948	163	241	137	52	906	413	36
Comp. B_5	2830	363	220	204	57	1137	821	29
Comp. B_6	2605	383	381	63	43	746	948	41

Table 3.4: Neosepta feedwater composition data of the five effluent compositions for which both cation and anion concentration measurements were taken. All concentration measurements are in mg/L.

Label	TDS	Na^+	K^+	Ca^{2+}	Mg^{2+}	NO_3^-	SO_4^{2-}	PO_4^{3-}
Comp. B_1	1876	164	293	106	32	886	396	0
Comp. B_2	2869	238	343	230	54	1464	524	16
Comp. B_4	1938	138	245	159	45	952	376	22
Comp. B_5	2888	380	217	203	55	1229	788	15
Comp. B_6	2613	377	382	64	44	770	953	22

Table 3.5: Greenhouse effluent anion compositions analyzed for MSED application B1 using the Fujifilm and Neosepta membranes.

	Fujifilm			Neosepta		
Label	$r_{\mathrm{NO_3}^-}$	$r_{\mathrm{SO4_2}^-}$	$r_{\mathrm{PO_4}^{3-}}$	$r_{\mathrm{NO_3}^-}$	$r_{\mathrm{SO4_2}^-}$	$r_{\mathrm{PO_4}^{3-}}$
Comp. B_1	0.30	0.70	0	0.31	0.69	0
Comp. B_2	0.28	0.71	0.01	0.26	0.73	0.01
Comp. B_4	0.30	0.67	0.03	0.28	0.71	0.02
Comp. B_5	0.41	0.57	0.01	0.42	0.58	0.01
Comp. B_6	0.55	0.43	0.02	0.55	0.44	0.01

Table 3.6: Greenhouse effluent cation compositions analyzed for MSED application B2 using the Fujifilm and Neosepta membranes.

	Fujifilm				Neosepta			
Label	r_{Na^+}	r_{K^+}	$r_{\mathrm{Ca}^{2+}}$	$r_{\mathrm{Mg}^{2+}}$	r_{Na^+}	r_{K^+}	$r_{\mathrm{Ca}^{2+}}$	$r_{\mathrm{Mg}^{2+}}$
Comp. B_1	0.31	0.47	0.16	0.05	0.28	0.49	0.18	0.05
Comp. B_2	0.27	0.41	0.26	0.07	0.28	0.40	0.27	0.06
Comp. B_3	0.22	0.34	0.34	0.09	0.20	0.34	0.37	0.09
Comp. B_4	0.27	0.41	0.23	0.09	0.24	0.42	0.27	0.08
Comp. B_5	0.43	0.26	0.24	0.07	0.45	0.24	0.24	0.07
Comp. B_6	0.44	0.44	0.07	0.05	0.44	0.44	0.07	0.05
Comp. B_7	0.14	0.23	0.47	0.16	0.12	0.22	0.50	0.16
Comp. B_8	0.22	0.29	0.38	0.11	0.22	0.28	0.38	0.11

3.2 Experimental set-up

The experiments were conducted with an MSED set-up, operating in a batch configuration. Two sets of membrane are tested: Neosepta ACS/CMS membranes and Fujifilm Type 16 membranes. Table 3.7 on page 19 includes Neosepta membrane specifications. The Fujifilm membranes, which are not commercially available, do not have a specifications datasheet. The set-up is comprised of 3 flow circuits (diluate, concentrate, electrode rinse) feeding into a PCCell ED200 stack, which contains 15 membrane cell pairs (total active membrane area of 0.64 m^2), 30 spacers of 0.5 mm thickness and 2 end spacers in the electrode streams of 1 mm thickness for the experiments for application A. Since there already exists data on Neosepta ACS/CMS groundwater desalination performance (Ahdab et al., 2020a), only Fujifilm Type 16 was tested for application A. Experiments for applications B1 and B2 were conducted on the same set-up but with a smaller stack of 10 membrane cell pairs (total active membrane area of 0.43 m^2), 20 spacers of 0.5 mm thickness and 2 end spacers in the electrode streams of 1 mm thickness. The diluate and concentrate containers have a 1 L and 4 L feedwater capacity, respectively, and the electrode container has a 4 L rinse capacity. The feedwater is simulated BGW and greenhouse effluent produced by dissolving calcium, magnesium, sodium, potassium, sulfate, nitrate and phosphate in deionized water. Samples of diluate water composition at different intervals of the desalination process are measured using an inductively coupled plasma optical emission spectrometer (ICP-OES). The electrode rinse contains sodium sulfate (0.2 M) for pH stabilization. Centrifugal pumps (Iwaki, model MD-55R (T)) and valved-flowmeters together generate a constant flow in the three streams of 95 L/h. The flow channel height is 0.5 mm. The power supply (GW-INSTEK GPR-60600) applies a voltage to drive ion transport and separation across the stack. A heat exchanger regulates the concentrate temperature; the stack then serves as a second heat exchanger to maintain a diluate temperature of 25°C. Figure 3.1 depicts a schematic blueprint of the set-up, excluding the subsequent diluate sample analysis in the ICP-OES.

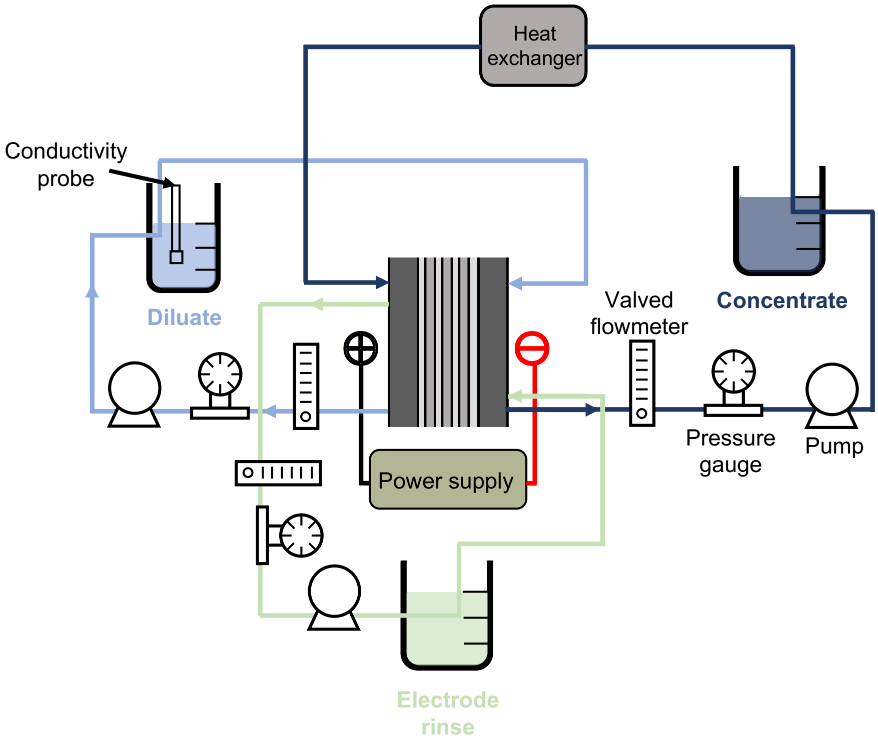


Figure 3.1: MSED set-up consisting of a diluate, concentrate, and rinse circuit feeding an ED200 stack.

Table 3.7: Detailed specification of Neosepta CMS/ACS membranes. Electrical resistance is measured on AC after equilibration with a 0.5N-NaCl solution at 25°C (ASTOM Corporation, 2013; Cohen-Tanugi and Grossman, 2012).

	CMS	ACS
Type	Strong acid (Na type)	Strong base (Cl type)
Functional group	Sulfonic acid	Ammonium
Characteristics	Monovalent cation permselectivity	Monovalent anion permselectivity
Resistance ($\Omega\cdot\text{cm}^2$)	1.8	3.8
Burst strength (MPa)	≥ 0.10	≥ 0.15
Thickness (mm)	0.15	0.13
Temperature (°C)	≤ 40	≤ 40
pH	0–10	0–8

3.3 Transport number and membrane selectivity

Although there is variation in the ionic composition of greenhouse effluent and greenhouse source water i.e. BGW, the major constituents are calcium, magnesium, sodium, potassium, and sulfate in either case. Greenhouse effluent additionally contains phosphate, nitrate, depending on the fertilizer applied and greenhouse specifications ammonium. Net salt (ion) and water transport across the membrane in each compartment of the MSED stack can be written as:

$$J_{s,j} = \frac{T_{s,j}^{cp} i}{zF} - L_j (C_{j,c,m} - C_{j,d,m}) \tag{3.3}$$

$$J_w = \frac{T_w^{cp} i}{F} + L_w (\pi_{j,c,m} - \pi_{j,d,m}) \tag{3.4}$$

where J is flux in mol·m^{-2}·s^{-1}, s denotes salt, w denotes water, T is a transport number, F is Faraday's constant, L is the membrane permeability in m·s^{-1} for the salts and in s·m^{-1} for the water, z is the ion valence, c denotes concentrate, d denotes diluate, m is membrane, C is a concentration in mol·m^{-3}, and

A_m is the membrane area in m^2. The subscript j indicates an ion species in the greenhouse water (effluent or BGW) that migrates across the series of ion exchange membranes. The salt flux (Equation 3.3 on the preceding page depends on ion migration $(\frac{T^{cp}_{s,j} i}{zF})$ and ion diffusion $(L_j(C_{j,c,m} - C_{j,d,m})$, while the water flux (Equation 3.4 on the previous page) is a function of electro-osmosis $(\frac{T^{cp}_{w} i}{F})$ and water diffusion $(L_w(\pi_{j,c,m} - \pi_{j,d,m})$. Further, the applied current density i depends on Donnan potentials and ohmic resistances for the membranes, diluate, and concentrate. The membrane characterization presented in this thesis is based on the experimental determination of ion transport number, membrane selectivity, membranes resistance, and limiting current density. The determination of membrane resistance and limiting current density are outlined in Appendix A.1.

To determine ion transport numbers, constant current tests were conducted, in which the mass of ions transported across the membranes in a fixed amount of time was measured. Simulated BGW and greenhouse effluent served as feedwaters in the diluate and concentrate circuits. A minimum of three tests per feedwater composition were run to ensure repeatability. The applied current in all tests did not exceed $0.7 i_{lim}$, a typical operating limit in commercial ED systems (Cobban and Faller, 1995). Based on Equation 3.3, the ion transport number can be written as:

$$T^{cp}_{s,j} = \frac{\Delta w_j F}{i \Delta t A_m N_{cp}} \tag{3.5}$$

where Δw_j is the change in ion concentration in milliequivalents relative to the initial ion concentration at $t = 0$, N_{cp} is the number of cell pairs, and A_m is the membrane area in m^2. Using the Hittorf method, the ion diffusion term in Equation 3.3, which is nearly three orders of magnitude less than the ion migration term (Ahdab et al., 2020a), is neglected. This trend has been verified even for high salinity applications by McGovern et al. (2014).

Membrane permselectivity P serves as a metric to quantify a membrane's ability to selectively remove monovalent relative to multivalent ions. The definition used for this thesis is the ratio of multivalent to monovalent transport number, normalized by initial ion concentration at $t = 0$:

$$P_{mon}^{mult} \equiv \frac{T_{mult}/w_{mult,o}}{T_{mon}/w_{mon,o}} \tag{3.6}$$

The closer P is to zero, the more monovalent selective a membrane is. In other words, lower permselectivities indicate better removal of monovalent ions and a more efficient MSED system.

4 Results

All data presented in this section were collected using the bench-scale MSED system outlined in Section 3.2 on page 17.

4.1 Application A: sodium removal from BGW

Fujifilm membranes were analyzed for 13 diverse BGWs to characterize their monovalent selectivity. Throughout the experiments monovalent ion removal was achieved. Figure 4.1 shows the relative change in sodium concentration compared that of divalent cations in solution over time. The trend depicted suggests that membrane selectivity is highest at desalination start and decreases towards the end of each experiment. This effect is consistent with findings in literature (Cohen-Tanugi and Grossman, 2012; Ahdab et al., 2020a).

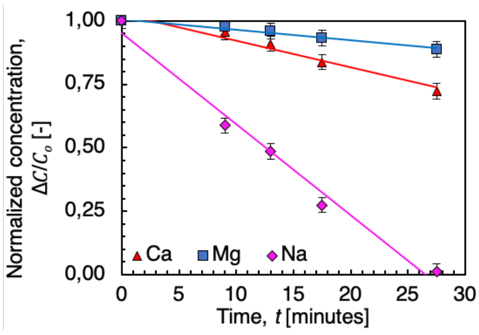


Figure 4.1: Normalized cation concentration as a function of desalination process time for a 10000 mg/L BGW solution.

The selectivities found for each of the 13 BGW solutions are shown in Table 4.1 on the following page. The average magnesium permselectivity is 0.08 ± 0.04, representing a factor of $8.3 - 26$ removal of sodium relative to magnesium. Calcium selectivity is 0.18 ± 0.08 on average (removal of $3.7 - 10$ times more sodium than calcium). Average sulfate permselectivity across all compositions is 0.18 ± 0.12, corresponding to a factor of $3.3 - 20$ removal of chloride relative to sulfate. The maximum standard deviation σ from the average values is 25% for cations and 33% for anions.

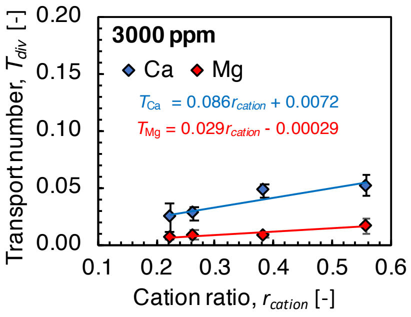
There is a linear relationship between solute ratio and transport numbers at constant TDS. Figure 4.2 on page 25 shows that monovalent transport numbers of sodium and chloride decrease with anion and cation solute ratio, while

Table 4.1: Calcium, magnesium and sulfate permselectivity for 13 BGW compositions. The first two columns correspond to BGW composition.

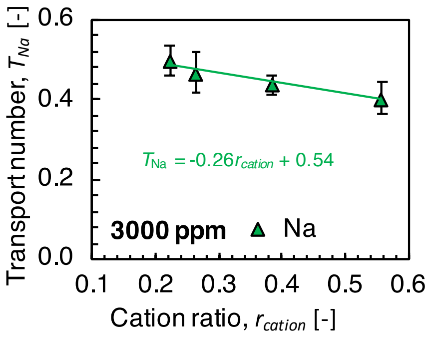
Solute ratio	TDS (mg/L)	$P_{\text{Na}}^{\text{Ca}}$	$P_{\text{Na}}^{\text{Mg}}$	$P_{\text{Cl}}^{\text{SO}_4}$
Comp. A_1	1295	0.21 ± 0.03	0.09 ± 0.02	0.21 ± 0.02
	2858	0.14 ± 0.03	0.06 ± 0.02	0.18 ± 0.10
	4408	0.19 ± 0.03	0.09 ± 0.02	0.16 ± 0.02
	10396	0.16 ± 0.04	0.09 ± 0.03	0.27 ± 0.02
Comp. A_2	1483	0.18 ± 0.02	0.05 ± 0.002	0.10 ± 0.01
	2895	0.10 ± 0.05	0.06 ± 0.004	0.12 ± 0.01
	4756	0.19 ± 0.02	0.10 ± 0.002	0.15 ± 0.008
	7814	0.22 ± 0.02	0.09 ± 0.003	0.10 ± 0.01
Comp. A_3	1450	0.13 ± 0.03	0.07 ± 0.02	0.22 ± 0.04
	2683	0.22 ± 0.03	0.10 ± 0.01	0.28 ± 0.01
	4276	0.22 ± 0.02	0.05 ± 0.007	0.23 ± 0.01
	8491	0.21 ± 0.01	0.09 ± 0.002	0.18 ± 0.02
Comp. A_4	2564	0.20 ± 0.02	0.08 ± 0.02	0.11 ± 0.02

divalent transport numbers increase. High solute ratios correlate to reduced monovalent transport because monovalent ions have to compete with more divalent ions to cross the membranes. At lower solute ratios, the opposite effect can be observed: monovalent transport is increased and divalent transport is decreased as fewer divalent ions compete with monovalent ions to cross the membranes. Due to the proportional relationship of permselectivity to the transport number ratio (see Equation 3.6 on page 21), trends in permselectivity at fixed TDS reflect those seen in transport numbers. Cation permselectivity decreases with cation solute ratio increase and anion anion permselectivity increases with anion higher solute ratios.

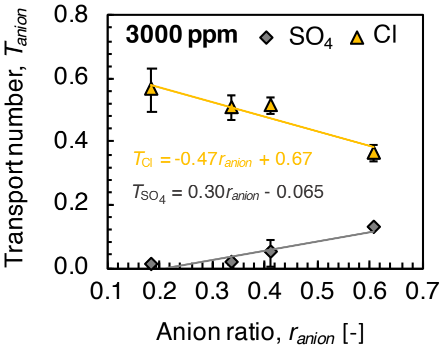
Membrane selectivity seems not to be influenced by salinity, as transport numbers in the compositions A_1, A_2, and A_3 are unaffected by differences in salinity and no trend was detected (see Figure 4.3 on page 26 and Figures A.3 on page X and A.4 on page XI). The error bars in the figure also show that transport number variation is minimal across the BGW salinity range. Due to the relationship of transport number to selectivity, no trends in permselectivity with initial salinity are found either (see Table 4.1).



(a)

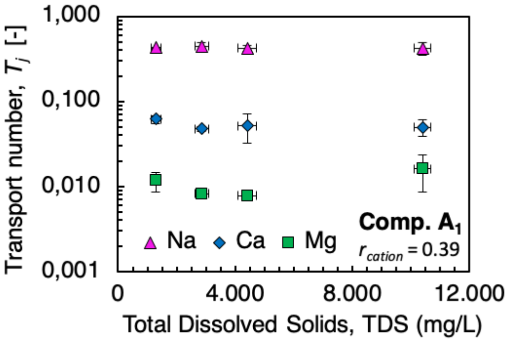


(b)

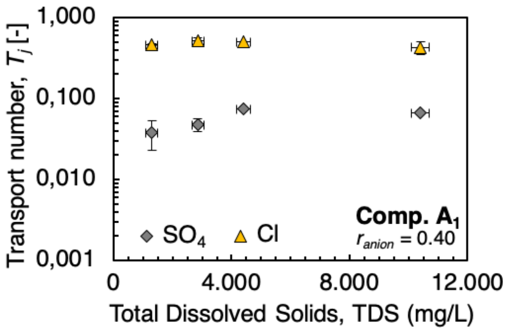


(c)

Figure 4.2: (a) Divalent cation and (b) sodium transport numbers as a function of cation solute ratio for BGWs containing a TDS of 3000 mg/L. (c) Anion transport numbers as a function of anion solute ratio for BGWs containing a TDS of 3000 mg/L.



(a)

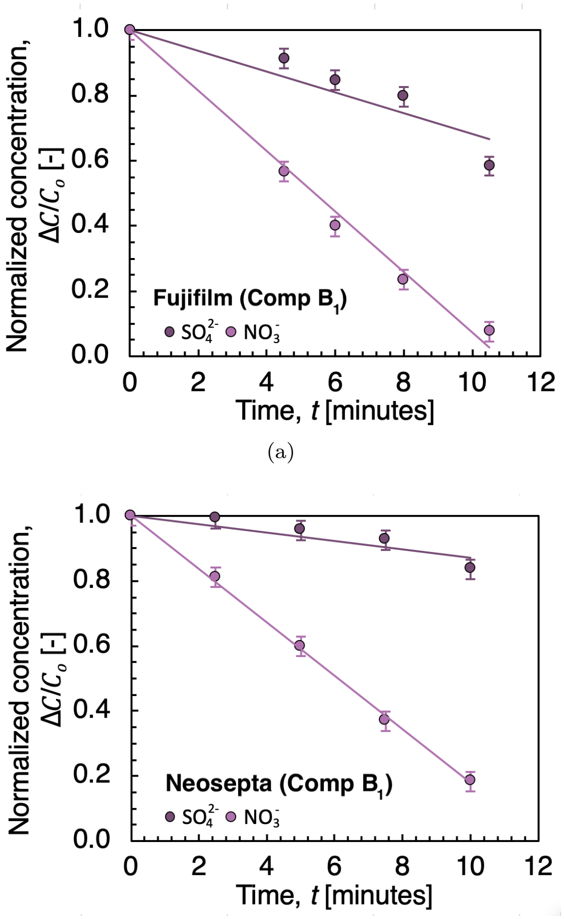


(b)

Figure 4.3: Cation (a) and anion (b) transport numbers on a logarithmic scale as a function of TDS for composition A_1.

4.2 Application B1: nitrate removal from greenhouse effluent

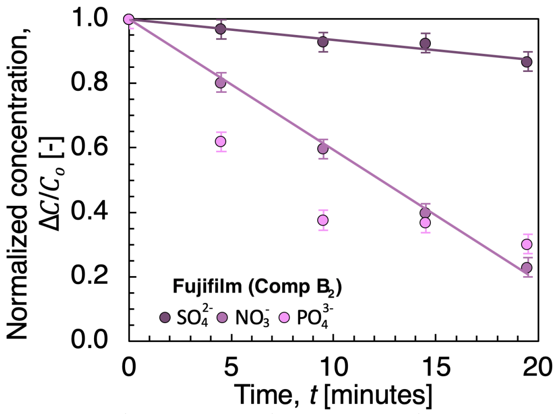
Both Fujifilm and Neosepta AEMs remove nitrate at an increased rate compared to divalent sulphate. This trend is depicted in Figures 4.4 on the next page and 4.5 on page 28. Phosphate however, shows a non-linear removal (see Figure 4.5 (a)) throughout the Fujifilm experiments. This observation could not be made for Neosepta (see Figure 4.5 (b)).



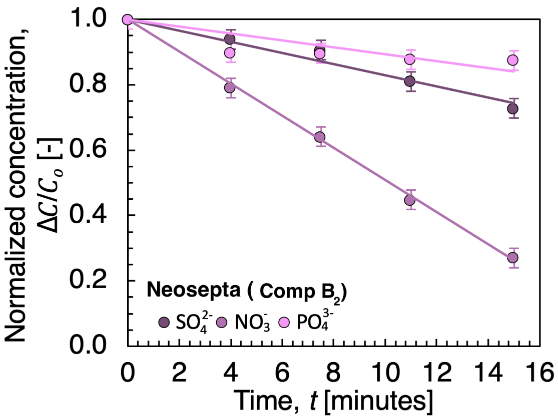
(a)

(b)

Figure 4.4: Normalized anion concentration (NO_3^-, SO_4^{2-}) of Neosepta and Fujifilm AEMs as a function of desalination process time for composition B_1.



(a)



(b)

Figure 4.5: Normalized anion concentration $(NO_3^-, SO_4^{2-}, PO_4^{3-})$ of Neosepta and Fujifilm AEMs as a function of desalination process time for composition B_2).

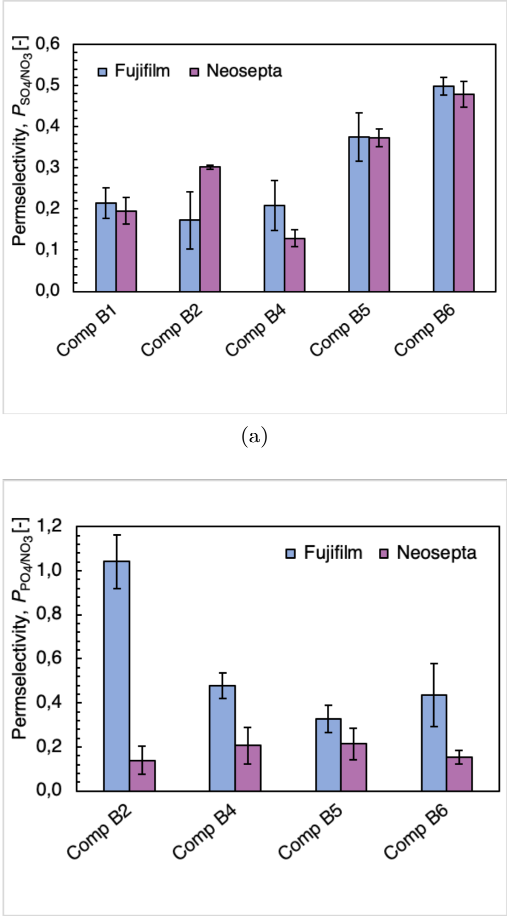
Table 4.2 on the next page shows the permselectivities of the two AEM sets for each composition analyzed for application B1. The average permselectivity over all Fujifilm AEMs is 0.29 ± 0.14 of sulfate relative to nitrate and 0.30 ± 0.14 for the Neosepta AEMs. Phosphate relative to nitrate permselectivities were 0.57 ± 0.32 for Fujifilm AEMs and 0.18 ± 0.04 for Neosepta AEMs on average. Fujifilm permselectivities corresponds to a factor $2.3 - 6.5$ removal of nitrate relative to sulfate and $1.1 - 4.0$ removal of nitrate relative to phosphate. Neosepta permselectivities represent a factor of $2.3 - 6.4$ removal of nitrate relative to sulfate and $4.6 - 7.1$ removal of nitrate relative to phosphate.

Neosepta AEMs demonstrate better monovalent selectivity than Fujifilm

Table 4.2: Permselectivity of sulphate and phosphate relative to nitrate of Fujifilm and Neosepta AEMs for 5 effluent compositions.

	Fujifilm		Neosepta	
Composition	$P_{\mathrm{SO}_4}^{\mathrm{NO}_3}$	$P_{\mathrm{PO}_4}^{\mathrm{NO}_3}$	$P_{\mathrm{SO}_4}^{\mathrm{NO}_3}$	$P_{\mathrm{PO}_4}^{\mathrm{NO}_3}$
Comp. B_1	0.21 ± 0.03	0	0.20 ± 0.03	0
Comp. B_2	0.17 ± 0.07	1.04 ± 0.12	0.30 ± 0.01	0.14 ± 0.06
Comp. B_4	0.21 ± 0.06	0.48 ± 0.06	0.13 ± 0.02	0.21 ± 0.08
Comp. B_5	0.37 ± 0.06	0.33 ± 0.06	0.37 ± 0.02	0.21 ± 0.07
Comp. B_6	0.50 ± 0.02	0.44 ± 0.14	0.48 ± 0.03	0.15 ± 0.03

AEMs for sulfate relative to nitrate for three effluent compositions, comparable selectivity for one composition, and inferior selectivity for one composition. Neosepta AEMs remove more sulfate than nitrate by the following percentages on average compared to Fujifilm AEMs in a given composition (Figure 4.6 (a)): composition B_1 (9%), composition B_4 (38%), and composition B_6 (4%). Neosepta AEMs remove an average of 75% less sulfate than nitrate compared to Fujifilm AEMs in composition B_2 and an equivalent amount of sulfate in composition B_5. The Fujifilm permselectivities also have a larger error than those of the Neosepta for each composition. Furthermore, Neosepta AEMs demonstrate far better monovalent selectivity than Fujifilm AEMs for phosphate relative to nitrate for all four tested effluent compositions. Neosepta AEMs remove more phosphate than nitrate by the following percentages on average compared to Fujifilm AEMs in a given composition (Figure 4.6 (b)): composition B_2 (87%), composition B_4 (57%), composition B_5 (35%), and composition B_6 (65%).



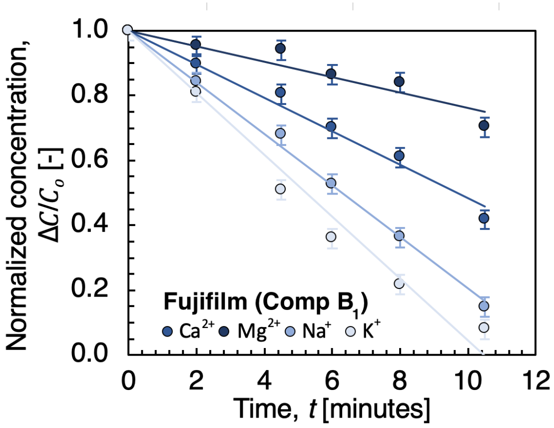
(a)

(b)

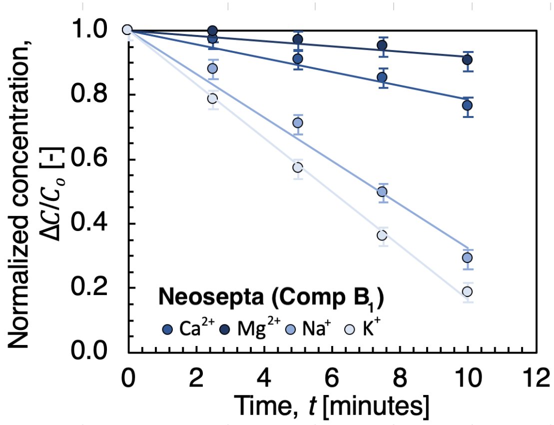
Figure 4.6: Comparison of Fujifilm and Neosepta AEM permselectivity for (a) sulfate relative to nitrate and (b) phosphate relative to nitrate, including percent difference between membrane performance.

4.3 Application B2: sodium removal from greenhouse effluent

As for application B1, selective monovalent ion removal was also achieved for the cations considered in MSED application B2. The decrease in ion concentration, shown in Figures 4.7 on the following page and 4.8 on page 32, reveals that potassium ions are removed at a higher rate than sodium for both the Fujifilm and Neosepta CEMs.

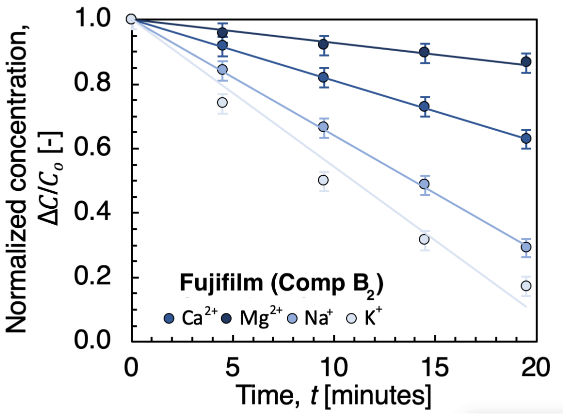


(a)

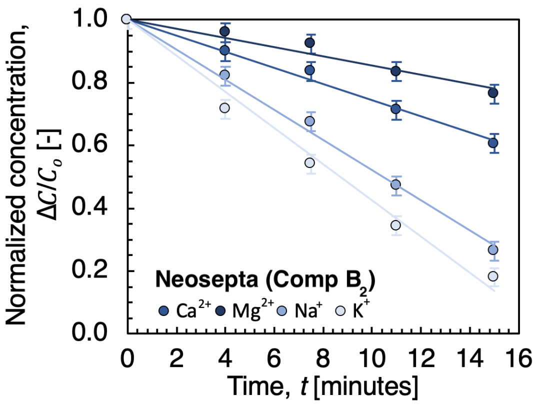


(b)

Figure 4.7: Normalized cation concentration $(\mathrm{Ca}^{2+}, \mathrm{Mg}^{2+}, \mathrm{Na}^{+}, \mathrm{K}^{+})$ of Neosepta and Fujifilm CEMs as a function of desalination process time for effluent composition B_1.



(a)



(b)

Figure 4.8: Normalized cation concentration $(Ca^{2+}, Mg^{2+}, Na^{+}, K^{+})$ of Neosepta and Fujifilm CEMs as a function of desalination process time for effluent composition B_2.

The individual permselectivities for all of the compositions are shown in Table 4.3 on the following page and Table 4.4 on the next page. Across all compositions, Fujifilm CEMs average a calcium relative to sodium permselectivity of 0.59 ± 0.16, compared to Neosepta's 0.48 ± 0.16, and a calcium relative to potassium permselectivity of 0.48 ± 0.14, compared to Neosepta's 0.41 ± 0.12. Fujifilm permselectivities correspond to factors of $1.3 - 2.3$ removal of sodium and $1.6 - 3.0$ removal of potassium relative to calcium. Neosepta permselectivities correspond to factors of $1.6 - 3.2$ removal of sodium relative and 1.9–3.6 removal of potassium relative to calcium. In addition, Fujifilm CEMs average a magensium relative to sodium permselectivity of 0.34 ± 0.18, compared to Neosepta's 0.32 ± 0.17 , and a magensium relative to potassium permselectivity of 0.28 ± 0.15, compared to Neosepta's 0.28 ± 0.14. Fujifilm permselectivities correspond to factors of $2.0 - 6.2$ removal of sodium and $2.4 - 7.9$ removal of potassium relative to magnesium. Neosepta permselectivities correspond to factors of $2.4 - 7.6$ removal of sodium relative and $2.0 - 6.7$ removal of potassium relative to magnesium.

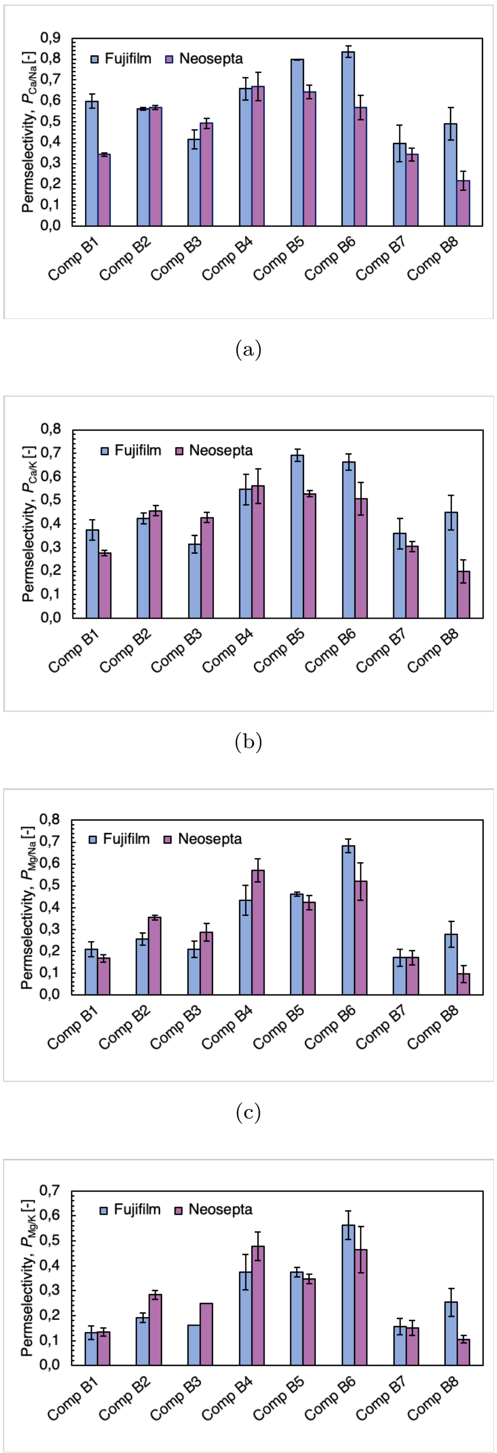
Table 4.3: Permselectivity of calcium and magnesium relative to sodium and potassium of Fujifilm CEMs for 8 effluent compositions.

Composition	$P_{\mathrm{Na}}^{\mathrm{Ca}}$	$P_{\mathrm{Na}}^{\mathrm{Mg}}$	$P_{\mathrm{K}}^{\mathrm{Ca}}$	$P_{\mathrm{K}}^{\mathrm{Mg}}$
Comp. B_1	0.60 ± 0.06	0.21 ± 0.03	0.38 ± 0.04	0.13 ± 0.03
Comp. B_2	0.56 ± 0.02	0.26 ± 0.03	0.42 ± 0.03	0.19 ± 0.03
Comp. B_3	0.42 ± 0.05	0.16 ± 0.04	0.16 ± 0.04	0.23 ± 0.01
Comp. B_4	0.66 ± 0.05	0.43 ± 0.07	0.55 ± 0.06	0.37 ± 0.07
Comp. B_5	0.80 ± 0.002	0.46 ± 0.01	0.69 ± 0.03	0.37 ± 0.02
Comp. B_6	0.83 ± 0.03	0.68 ± 0.03	0.66 ± 0.04	0.56 ± 0.06
Comp. B_7	0.40 ± 0.09	0.17 ± 0.04	0.36 ± 0.07	0.16 ± 0.03
Comp. B_8	0.49 ± 0.08	0.28 ± 0.06	0.45 ± 0.07	0.25 ± 0.06

Table 4.4: Permselectivity of calcium and magnesium relative to sodium and potassium of Neosepta CEMs for 8 effluent compositions.

Composition	$P_{\mathrm{Na}}^{\mathrm{Ca}}$	$P_{\mathrm{Na}}^{\mathrm{Mg}}$	$P_{\mathrm{K}}^{\mathrm{Ca}}$	$P_{\mathrm{K}}^{\mathrm{Mg}}$
Comp. B_1	0.34 ± 0.01	0.17 ± 0.02	0.28 ± 0.01	0.13 ± 0.02
Comp. B_2	0.57 ± 0.01	0.35 ± 0.01	0.46 ± 0.02	0.28 ± 0.02
Comp. B_3	0.49 ± 0.02	0.29 ± 0.04	0.43 ± 0.02	0.25 ± 0.01
Comp. B_4	0.67 ± 0.07	0.57 ± 0.05	0.56 ± 0.07	0.48 ± 0.06
Comp. B_5	0.64 ± 0.03	0.42 ± 0.03	0.53 ± 0.01	0.35 ± 0.02
Comp. B_6	0.57 ± 0.06	0.52 ± 0.09	0.52 ± 0.07	0.46 ± 0.09
Comp. B_7	0.34 ± 0.03	0.17 ± 0.03	0.30 ± 0.02	0.15 ± 0.03
Comp. B_8	0.22 ± 0.04	0.10 ± 0.04	0.20 ± 0.05	0.11 ± 0.02

Neosepta CEMs demonstrate better monovalent selectivity than Fujifilm CEMs for sodium and potassium relative to calcium for five effluent compositions, comparable selectivity for two compositions and inferior selectivity for one composition. Neosepta CEMs remove more sodium than calcium by the following percentages on average compared to Fujifilm CEMs in a given composition (Figure 4.9 (a)): composition B_1 (43%), composition B_5 (20%), composition B_6 (32%), composition B_7 (13%) and composition B_8 (56%). Neosepta CEMs remove less sodium than calcium by the following percentages compared to Fujifilm CEMs in a given composition: composition B_2 (1%), composition B_3 (18%) and composition B_4 (2%). Similarly, Neosepta CEMs remove more potassium than calcium by the following percentages on average compared to Fujifilm CEMs in a given composition (Figure 4.9 (b)): composition B_1 (26%), composition B_5 (24%), composition B_6 (24%), composition B_7 (15%) and composition B_8 (56%). Neosepta CEMs remove less potassium than calcium by the following percentages on average compared to Fujifilm CEMs in a given composition: composition B_2 (8%), composition B_3 (36%) and composition B_4 (3%). Moreover, Neosepta CEMs show better monovalent selectivity than Fujifilm CEMs for sodium and potassium relative to magnesium for five effluent compositions and inferior selectivity for three compositions. Neosepta CEMs remove more sodium than magnesium by the following percentages on average compared to Fujifilm CEMs in a given composition (Figure 4.9 (c)): composition B_1 (20%), composition B_5 (8%), composition B_6 (24%), composition B_7 (1%) and composition B_8 (65%). Neosepta CEMs remove less sodium than magnesium by the following percentages on average compared to Fujifilm CEMs in a given composition: composition B_2 (39%), composition B_3 (37%) and composition B_4 (32%). Similarly, Neosepta CEMs remove more potassium than calcium by the following percentages on average compared to Fujifilm CEMs in a given composition (Figure 4.9 (d)): composition B_5 (7%), composition B_6 (17%), composition B_7 (3%) and composition B_8 (58%). Neosepta CEMs remove less potassium than calcium by the following percentages on average compared to Fujifilm CEMs in a given composition: composition B_1 (3%), composition B_2 (48%), composition B_3 (53%) and composition B_4 (28%).



(a)

(b)

(c)

(d)

Figure 4.9: Comparison of Fujifilm and Neosepta CEM permselectivity for (a) calcium relative to sodium, (b) calcium relative to potassium, (c) magnesium relative to sodium, and (d) magnesium relative to potassium, including percent difference between membrane performance.

5 Discussion

Considering the permselectivity results from all three applications, membrane performance appears to differ depending on the feedwater composition. The investigation of Fujifilm type 16 MSED membranes for application A (BGW desalination) shows that the membranes used in the experiments are sensitive to feedwater solute ratio but not to differences in salinity. Compared with Neosepta AMS/CMS membranes, which were previously characterized by Ahdab et al. (2020a) for the same BGW compositions, the Fujifilm CEMs allow for significantly higher monovalent cation selectivity during BGW desalination. Calcium and magnesium permselectivities are 28% and 47%, respectively, lower than those of Neosepta membranes on average. Table 5.1 on the following page shows the difference between the membranes' cation selectivities for four of the BGW compositions analyzed, where Composition A_1, Composition A_2, and Composition A_3 values are averaged across their four tested salinities, since no trends in permselectivity with TDS are observed for either membrane set. Moreover, a higher selectivity (i.e. lower removal rate) of calcium compared to magnesium was found (see Table 4.1 on page 24). This result may be caused by calcium's lower hydration energy (1592 kJ/mol) compared to magnesium (1904 kJ/mol), as ions must partly or entirely shed their hydration shell to traverse the membranes (Firdaous et al., 2007; Burgess, 1999). The same trend was observed in the results for application B2 (see Table 4.4 on page 33 and Figures 4.7 on page 31 and 4.8 on page 32), suggesting that hydration energy is the governing factor for ion removal order. The superior performance of Fujifilm CEMs could not be confirmed by the results for application B2, which also looked at monovalent cation selectivity. Neosepta CEMs predominately delivered lower permselectivities than Fujifilm CEMs in the experiments for application B2 (see Table 4.3 on page 33). A possible explanation for this discrepancy are differences in cation solute ratio in the feedwater, with sodium solute ratios being higher in the application A experiments ($0.60 - 0.78$) compared to applications B1 and B2 ($0.14 - 0.44$). Furthermore, the calcium phosphate salt dissolved in the feedwaters for applications B1 and B2 precipitated to an increased degree throughout the MSED system causing membrane scaling. CEM performance in the greenhouse effluent experiments may have been affected by this condition.

Results for application B1 further suggest non-linear removal of phosphate during the Fujifilm experiments (see Figure 4.5 on page 28). The low feedwater concentrations of phosphorous (19 ± 3.4 mg/L) may explain this difference in Neosepta and Fujifilm phosphate reduction rates. At a constant absolute measurement uncertainty, the relative uncertainty for phosphate, which with had a very low initial concentration, is higher than for the other ions.

Table 5.1: Cation permselectivities of Neosepta and Fujifilm membranes for four solute ratios (Composition A_1, Composition A_2, Composition A_3, Composition A_4) and for all 13 analyzed BGWs. The Neosepta data was reprinted from Ahdab et al. (2020a).

	$P_{\mathrm{Na}}^{\mathrm{Ca}}$		$P_{\mathrm{Na}}^{\mathrm{Mg}}$	
	Fujifilm	Neosepta	Fujifilm	Neosepta
Comp. A_1	0.17 ± 0.03	0.26 ± 0.03	0.08 ± 0.02	0.14 ± 0.02
Comp. A_2	0.17 ± 0.05	0.23 ± 0.03	0.08 ± 0.02	0.13 ± 0.03
Comp. A_3	0.20 ± 0.04	0.27 ± 0.04	0.08 ± 0.02	0.17 ± 0.03
Comp. A_4	0.20 ± 0.03	0.27 ± 0.04	0.08 ± 0.04	0.16 ± 0.04
All BGWs	0.18 ± 0.08	0.26 ± 0.06	0.08 ± 0.04	0.15 ± 0.06

For all three applications, The Fujifilm AEM's performance is slightly worse for than that of the Neosepta membrane. A comparison between the experimentally determined Fujifilm AEM permselectivities and compared with data from the literature for Neosepta is found in Table 5.2

Table 5.2: Anion permselectivities of Neosepta and Fujifilm membranes for four solute ratios (Composition A_1, Composition A_2, Composition A_3, Composition A_4) and for all 13 analyzed BGWs. The Neosepta data was reprinted from Ahdab et al. (2020a).

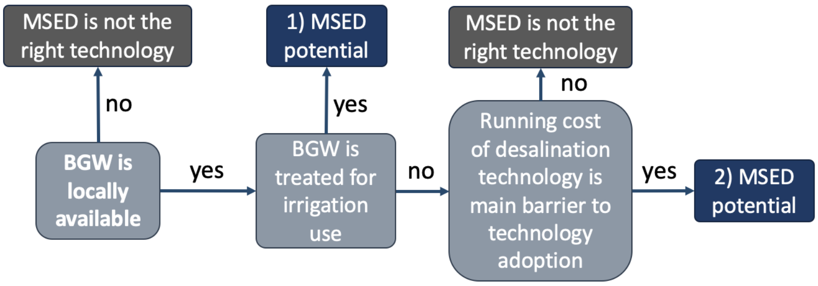
	$P_{\mathrm{Cl}}^{\mathrm{SO_4}}$	
	Fujifilm	Neosepta
Comp. A_1	0.20 ± 0.06	0.15 ± 0.04
Comp. A_2	0.12 ± 0.06	0.15 ± 0.03
Comp. A_3	0.23 ± 0.08	0.20 ± 0.06
Comp. A_4	0.11 ± 0.04	0.16 ± 0.04
All BGWs	0.18 ± 0.12	0.17 ± 0.06

5.1 Implications

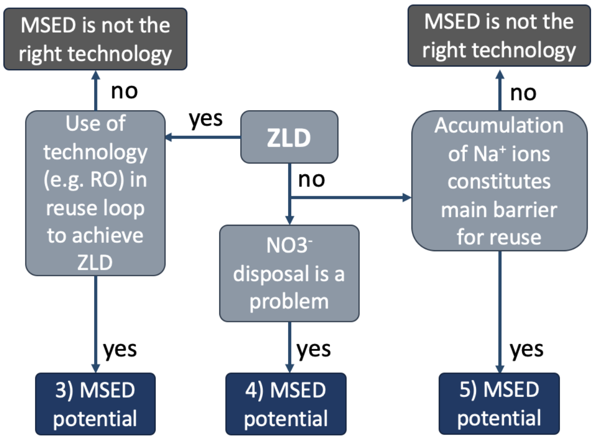
The successful removal of monovalent ions in the experiments for all three applications investigated suggests that for each case an implementation would physically achieve the respective goal of sodium (applications A and B2) and nitrate removal (application B1). As mentioned in Chapter 1, RO is currently the most commonly used method for BGW desalination. The added benefit of using MSED over RO stems from the lower fertilizer needs created through the retained multivalent ion concentrations in monovalent selective desalination.

Depending on local greenhouse conditions and needs, MSED should be considered as a treatment option. Figure 5.1 on the following page depicts a guide that could help determine where MSED could be a useful treatment method based on the results of this thesis. First, BGW presents an ideal application option for this technology. MSED adoption is a viable option for greenhouses that already use RO-desalinated BGW to irrigate their crops due to the fertilizer savings created by MSED (Ahdab et al., 2020a). While RO's capital expenditure and operating costs are lower than those of MSED, the fertilizer savings along with water savings due to MSED's higher water recovery rate (Strathmann, 2010) can make up for these costs. Generally, the benefits of implementing MSED are greater for larger greenhouses because the adoption cost relative to operating costs are lower and absolute savings are higher. Greenhouses that are reluctant to desalinate BGW due to the costs associated with operating an additional water treatment technology would therefore benefit from MSED adoption, as MSED reduces running costs in this scenario.

Similarly to its use in BGW desalination, the application of RO in the reuse loop to prevent sodium accumulation can be replaced by MSED. The cost reduction is lower than in the previous case because only 70% of the source water are reused in ZLD systems (Tielemans, 2020). In greenhouses without a ZLD water reuse system, MSED could enable a closed loop irrigation approach at a lower cost than RO. Another possible use of MSED in the greenhouse context is the treatment or pretreatment of greenhouse wastewater. The removal of sodium and nitrate, which could otherwise cause environmental pollution constitutes a significant water quality improvement. MSED cannot serve as the sole effluent treatment method however, as pathogens and other environmental ionic pollutants (e.g. phosphate) are not removed by this technology.



(a)



(b)

Figure 5.1: (a) Outline of possible paths to MSED implementation for application A. (b) Outline for possible paths to MSED implementation for applications B1 and B2.

The membrane permselectivities that were experimentally determined in this thesis indicate that MSED implementation may be feasible in several greenhouse applications, but larger scale pilot studies will be required to determine economic feasibility.

6 Conclusions

In this work Fujifilm Type 16 and Neosepta ACS/CMS MSED membranes were tested on eight model greenhouse effluent solutions. The Fujifilm membranes were additionally tested on 13 BGW solutions. The experiments aimed at characterizing membrane selectivities and determining the potential of MSED for BGW desalination for greenhouse irrigation water production and greenhouse wastewater treatment for safe discharge (nitrate removal) or reuse (sodium removal). The following conclusions have been reached:

1. Fujifilm CEMs can selectively remove monovalent ions from groundwater in the brackish range. Compared with Neosepta CEM data in the literature, Fujifilm on average removed 62% more sodium ions relative to calcium ions and 150% more sodium ions relative to magnesium ions for the same BGW compositions.

2. Experimentally determined sodium removal from greenhouse effluent was achieved at a higher rate by Neosepta CEMs than by Fujifilm CEMs. Neosepta on average removed 81% more sodium ions relative to calcium ions and 2% more sodium ions relative to magnesium ions for the same greenhouse effluent compositions than Fujifilm CEMs.

3. Fujifilm CEM performance is linked to cation solute ratio and independent of feedwater salinity. Selectivities were highest for low solute ratios and lowest for high solute ratios.

4. Both Fujifilm and Neosepta AEMs can selectively remove nitrate from greenhouse wastewater. Across the tested feedwater compositions, the Neosepta membranes showed better performance with regard to nitrate removal. Neosepta AEMs on average removed 222% more nitrate ions relative to sulfate ions than Fujifilm AEMs, while Fujifilm AEMs on average removed 1% more nitrate ions relative to phosphorous ions for the same greenhouse effluent compositions than Fujifilm AEMs.

5. The monovalent ion removal for BGW desalination, greenhouse wastewater treatment, and greenhouse reuse water treatment suggests that MSED application is possible for all three proposed cases. Based on the presented

selectivity results for Fujifilm and Neosepta MSED membranes, Fujifilm membranes seem better suited for BGW desalination, whereas Neosepta membranes had more promising results for applications in greenhouse effluent treatment for discharge or reuse.

7 Future Work

Based on the results of this thesis, there are several open questions that remain to be answered through future research. The foremost recommendation is that system parameter variation, which can have numerous reasons (e.g. differences in operating conditions, ion transport characteristics, and systems configuration) is considered prior to MSED adoption. The evaluation of the real world performance of MSED in greenhouses has to subsequently be examined through on-site pilot studies. Moreover, an experimental analysis of BGW desalination using Fujifilm MSED in the higher salinity range (10000 – 15000 mg/L) may improve the understanding of the influence of salinity on CEM performance. Another possible area of future research is the experimental study of co-ion (i.e., ions with the same electric charge as the membrane) and counter ion (i.e., ions with an electric charge opposite to the membrane) effects on monovalent selectivity. An investigation of co-ion influence would require the analysis of feedwaters with constant counter-ion ratios and varying co-ion ratios. Further comparative studies into the performance of different types of MSED membranes would also serve a better understanding of performance differences between products from different manufacturers and help create customized solutions for MSED applications.

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A Appendix

A.1 Membrane resistance and limiting current density

The MSED stack acts as an electric circuit comprised of ohmic terms $\bar{r}$, Donnan potentials E_{AEM} and E_{CEM}, and electrode potential V_{el}:

$$V_{stack} = i\left[N_{cp}\left(2\bar{r}_m + \frac{\bar{r}_d}{\sigma} + \frac{\bar{r}_c}{\sigma}\right) + \bar{r}_m + 2\bar{r}_r\right] + N_{cp\left(E_{AEM}+E_{CEM}\right)+V_{el}} \quad \text{(A.1)}$$

where N_{cp} is number of cell pairs, r denotes the rinse solution, and σ denotes the spacer shadow effect of 0.72 ± 0.09 (Ahdab et al., 2020a). The circuit resistances can be written as the ratio of flow channel height h to electrical conductivity k:

$$\bar{r} = \frac{h}{k} \quad \text{(A.2)}$$

Membrane resistance and limiting current density are calculated by performing current-voltage tests at constant diluate and concentrate conductivity ($k_d = k_c = k$) for NaCl solutions containing a TDS of 800, 1500, 3000, 5000, and 10,000 mg/L. The CEM and AEM resistances are assumed to be equivalent. At each conductivity, the membrane resistance is determined using the slope of a linear fit of V_{stack} versus the applied current from Equation A.1:

$$m = (2N_{cp} + 1)\bar{r}_m + \frac{2N_{cp}h}{\sigma k} + \frac{2h_r}{\sigma k_r} \quad \text{(A.3)}$$

The Cowan and Brethod method (Cowan and Brown, 1959) was employed to determine the limiting current density. At each conductivity, the MSED stack electrical resistance ($\Delta V_{stack}/I$) was plotted as a function of the inverse of applied current ($1/I$). The inverse of the limiting current ($1/I_{lim}$) corresponds to the minimum point at which the electrical resistance begins increasing.

Membrane resistance is usually determined at standard conditions, i.e., in 0.5 M (29 g/kg) NaCl solution (Dlugolkecki et al., 2010). However, greenhouse effluent typically contains a much lower salinity (1.5 – 3.5 g/kg). Consequently, Neosepta and Fuijfilm membrane resistance is evaluated for NaCl solutions ranging from 0.8 – 10 g/L. Consistent with the literature (Dlugolkecki et al., 2010; Strathmann, 2004), membrane resistance increases sharply with decreasing salinity (Figure A.1), suggesting that resistive losses in the MSED stack are greater in more dilute solutions (Geise et al., 2013). In comparison to Neosepta membranes, Fujifilm membranes experience larger resistive losses at TDS $<$ 3 g/L and lower resistive losses at TDS $>$ 3 g/L. Consequently, in the salinity range of interest for greenhouse effluents, Neosepta membranes possess the advantage of decreased resistive losses.

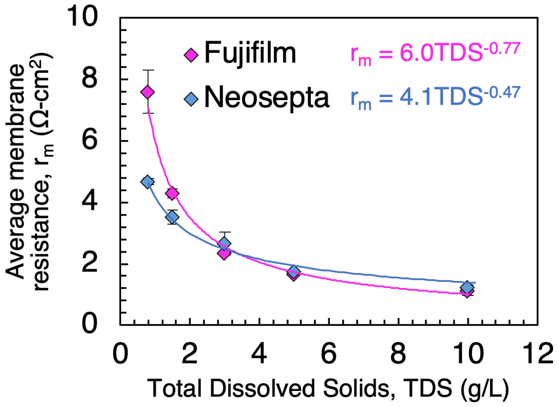


Figure A.1: CEM and AEM resistance of Neosepta and Fujifilm membranes for NaCl solutions containing TDS ranging from 0.8 – 10 g/L. Values obtained for Neosepta match those in the literature (r_m = 1.8 – 3.8 Ω-cm^2) (Cohen et al., 2018).

MSED membrane performance, i.e. permselectivity, worsens when the applied current is near or above the limiting current. Therefore, quantifying the limiting current is necessary to optimize MSED system performance. Figure A.2 on page IX illustrates the linear dependence of limiting current density on sodium concentration in NaCl solutions for Neosepta and Fujifilm membranes. Fujifilm membranes possess the advantage of tolerating a higher operating current without impeding membrane performance at a given sodium concentration. Greenhouse effluent has a higher current density than NaCl solutions as a result of other cations, in addition to sodium, that carry the current. In multi-ionic effluent solutions, monovalent selective CEMs first remove monovalent ions, such as sodium, from the boundary layer adjacent to the membrane before removing divalent ions. Consequently, the limiting current no longer depends solely on sodium concentration.

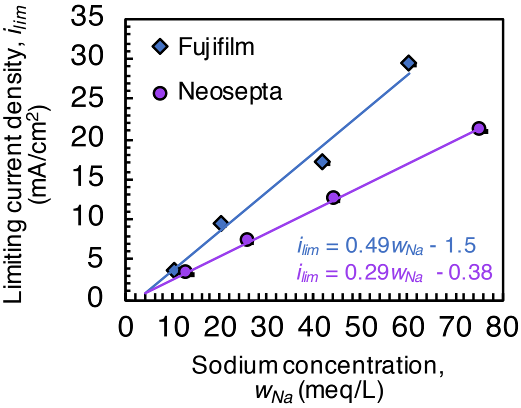
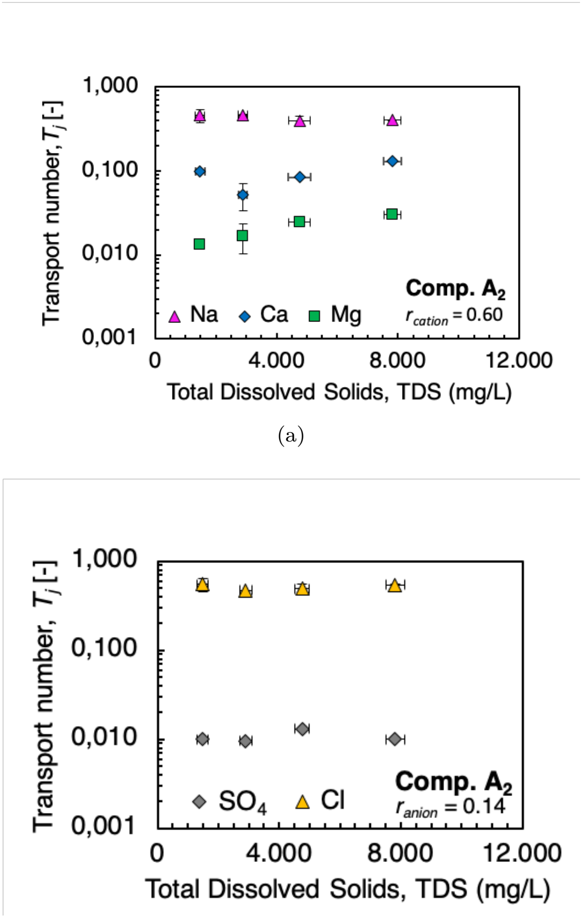


Figure A.2: Limiting current density of Neosepta and Fujifilm membranes as a function of sodium concentration in the diluate for various dilutions of NaCl solutions.

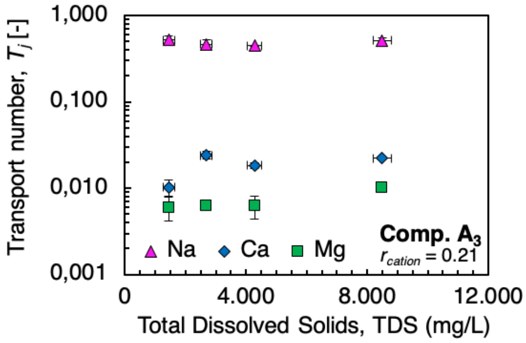
A.2 Figures



(a)

(b)

Figure A.3: Cation (a) and anion (b) transport numbers on a logarithmic scale as a function of TDS for Comp. A_2.



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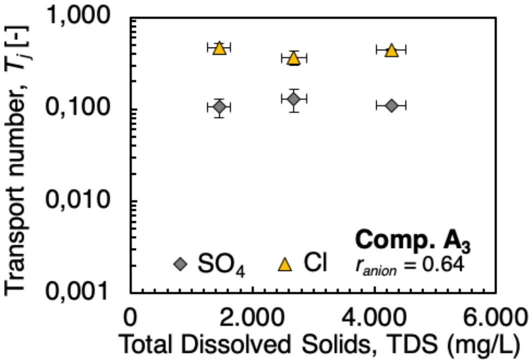

(b)

Figure A.4: Cation (a) and anion (b) transport numbers on a logarithmic scale as a function of TDS for Comp. A_3.

B Popular science summary

Greenhouses can play an important role in ensuring food security in many areas with non-optimal conditions for conventional open field agriculture. One crucially important condition is access to high quality irrigation water. This thesis describes the analysis of a new treatment technology that can be used to improve the quality of water used in greenhouses.

While it may seem obvious that growers in areas with hot and dry climates will find it difficult to find water to irrigate their crops, this can also become a problem in places where water seems to be abundant because the groundwater that is often pumped into greenhouses to irrigate crops heavily varies in quality. Groundwater slowly moves through the layers of soil and rock before being pumped back to the surface. During this time, minerals, which are essential for crop growth, are dissolved from the surrounding underground environment. The problem is that plants are also very sensitive to certain minerals in groundwater. Increased concentrations of sodium ions, which we ingest every day as table salt (sodium chloride), are a common ingredient in groundwater that can cause lower crop yields or the death of plants. Greenhouses therefore often remove all minerals from their groundwater using a membrane technology known as reverse osmosis. All the beneficial minerals that plants need to grow are subsequently reintroduced to the treated groundwater as fertilizer. The technology discussed in this thesis, called monovalent selective electrodialysis or MSED, can selectively remove a small number of dissolved minerals including sodium from groundwater. This reduces the need to use a lot of fertilizer after treating the groundwater. The experiments conducted for this thesis show that MSED works and that the technology can be used as an alternative to conventional groundwater treatment.

After crop irrigation, the resulting greenhouse wastewater is either treated and discharged or recirculated and reused. Water reuse lowers groundwater needs, but it can also cause sodium to be trapped in the reuse loop as it is not utilized by the plants. Over time sodium concentrations increase until they exceed the threshold that crops can withstand and the reuse water has to be discharged to prevent crop loss. To avoid the discharge of reuse water, MSED can be used to continuously remove sodium from the recirculated wastewater.

In this thesis greenhouse wastewater was tested to see if MSED could remove sodium from such compositions. It was found that this is possible. Another aspect investigated was the removal of nitrate, which enters the greenhouse water cycle as added fertilizer, using MSED. While nitrate encourages crop growth, it is also considered an environmental pollutant that can pose health risks if it leaches into the drinking water supply. The experiments on greenhouse wastewater treatment using MSED showed that nitrate can also be removed by this technology.

Based on the results presented in this thesis, several avenues to MSED implementation in greenhouses are discussed. MSED groundwater treatment can be useful when old technologies that cannot selectively remove sodium are currently in use or when groundwater is currently not utilized for irrigation due to high treatment costs. Moreover, water reuse in greenhouses can be made more efficient using MSED. Greenhouses can even consider implementing this new technology to replace biological nitrate removal treatment steps, which use a lot of space and do not allow a high degree of process control. While more research into case-specific aspects of MSED use in greenhouses and economic feasibility have to be done prior to any major changes throughout the greenhouse sector, this work suggests that MSED could play an important role in optimizing future food production.