NOVEL APPLICATIONS OF MONOVALENT SELECTIVE ELECTRODIALYSIS FOR THE TREATMENT OF IRRIGATION WATERS

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EXTENDED ABSTRACT

Reverse osmosis (RO) is the most widely used desalination technology for the treatment of irrigation source water and wastewater. Brackish groundwater, seawater, and agricultural effluent often contain both monovalent ions damaging to crops (Na^+, Cl^-) and divalent ions beneficial for crops (Ca^{2+}, Mg^{2+}, SO_4^{2-}). RO removes both types of ions. These beneficial ions must then be reintroduced to the desalinated water through the addition of fertilizer. Monovalent selective electrodialysis (MSED) demonstrates greater potential to align with the needs of the agriculture sector. MSED preferentially removes monovalent ions relative to multivalent ions, defined as monovalent selectivity, via selective ion-exchange membranes. MSED operates at a significantly higher water recovery than RO. In the treatment of irrigation source water, MSED's selective removal may reduce fertilizer requirements and associated costs, while its greater recovery saves water and decreases the volume of brine for disposal. In the treatment of agricultural wastewater, MSED's selective removal of sodium, the biggest barrier to water reuse, may help greenhouses achieve minimal liquid discharge. Despite the possible economic and environmental benefits of MSED, the technology has not been commercially employed for the treatment of agricultural water. This study investigates the membrane performance and economics of MSED for the treatment of irrigation source water and wastewater. Experiments are conducted on two types of MSED membranes to characterize the key system parameters as a function of feedwater composition. The experimentally-determined system parameters then serve as inputs to our MSED cost model.

Keywords: Monovalent selective electrodialysis, agriculture, greenhouses, seawater, brackish groundwater, wastewater

I. INTRODUCTION

Greenhouses have begun adopting desalination technologies to optimize their source water (brackish water, seawater) and effluent treatment. Reverse osmosis (RO) is the most widely implemented technology in the greenhouse sector as a result of its commercial availability and cost effectiveness. Monovalent selective electrodialysis (MSED), a variant of conventional electrodialysis (ED) presents an alternative to RO for the treatment of agricultural source water and wastewater. Key advantages offered by MSED relative to RO, both of which are membrane-based technologies, include the following:

- MSED removes monovalent ions damaging to crops (Na^+, $Cl^−$) while preserving divalent ions beneficial for crops (Ca^{2+}, Mg^{2+}, SO_4^{2-}) in the desalinated source water. This selective removal reduces fertilizer requirements and associated costs. In RO systems, which remove all ions from solution, key nutrients already present in the feedwater must be reintroduced into the desalinated water by addition of fertilizer.
- MSED can achieve a higher water recovery than RO, increasing water savings and decreasing brine volume for disposal and/or reuse. Previously conducted studies suggest that it can operate at over 90% recovery for brackish solutions [1], compared to RO's 70-75% [2], at a similar energy consumption rate and 66-86% for seawater solutions [3, 4, 5], compared to RO's 40-50% [6], at a greater energy consumption rate.
- MSED shows potential to remove nitrate ($NO_3^−$), a monovalent ion, from greenhouse effluent in order to reduce nitrogen pollution in water for disposal.
- The higher chemical and mechanical stability of MSED membranes results in an average lifetime exceeding that of RO membranes by 2-3 years [1].
- MSED experiences less membrane fouling or scaling than RO. The frequent cycling of diluate and concentrate streams in MSED systems helps combat the effects of concentration polarization.

Since the 1960s, MSED has been used to concentrate sodium chloride from seawater or seawater brine for salt production in [7]. The technology, however, has not been commercially deployed for the treatment of brackish water, seawater, or wastewater for agriculture, despite its promise to better align with greenhouse industry needs in comparison to RO. In this abstract, we investigate four possible MSED applications in greenhouses and compare the performance to that of RO: 1) brackish groundwater (BGW), 2) seawater (SW), 3) wastewater for reuse, and 4) wastewater for disposal.

II. METHODS

The MSED stack (Figure 1) contains two types of monovalent selective membranes, cation exchange membranes (CEM) and anion exchange membranes (AEM). CEMs allow for the passage of monovalent cations and reject multivalent cations and all anions. AEMs allow for the passage of monovalent anions and reject multivalent anions and all cations. Spacers lie between the membranes, as well as the membranes and electrodes, to configure the flow. A potential difference applied across the stack drives the separation process, with anion migration towards the anode and cation migration towards the cathode. MSED yields a brine stream concentrated in monovalent ions and a fresher product stream rich in multivalent nutrients for crops.

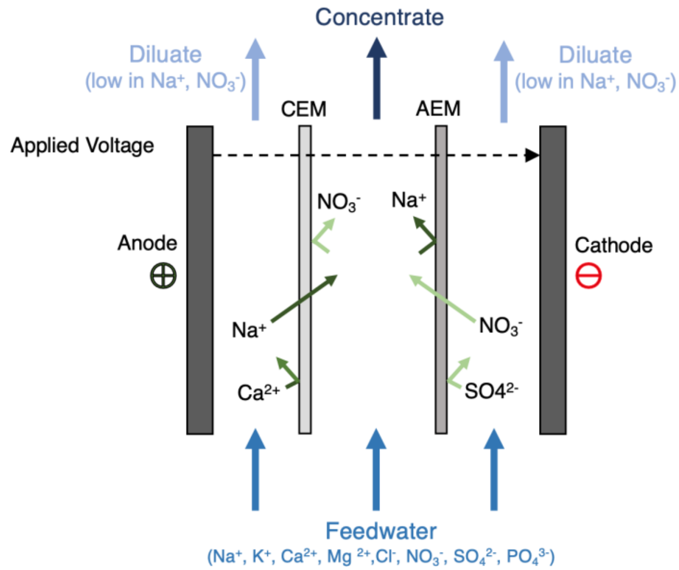

Figure 1: A simplified MSED stack composed of two electrodes, CEM and AEM. Potassium, chloride, magnesium and phosphate, not shown here, exhibit the same behavior as sodium, nitrate, calcium and sulfate, respectively. A cell pair includes a CEM, AEM, diluate channel and concentrate channel.

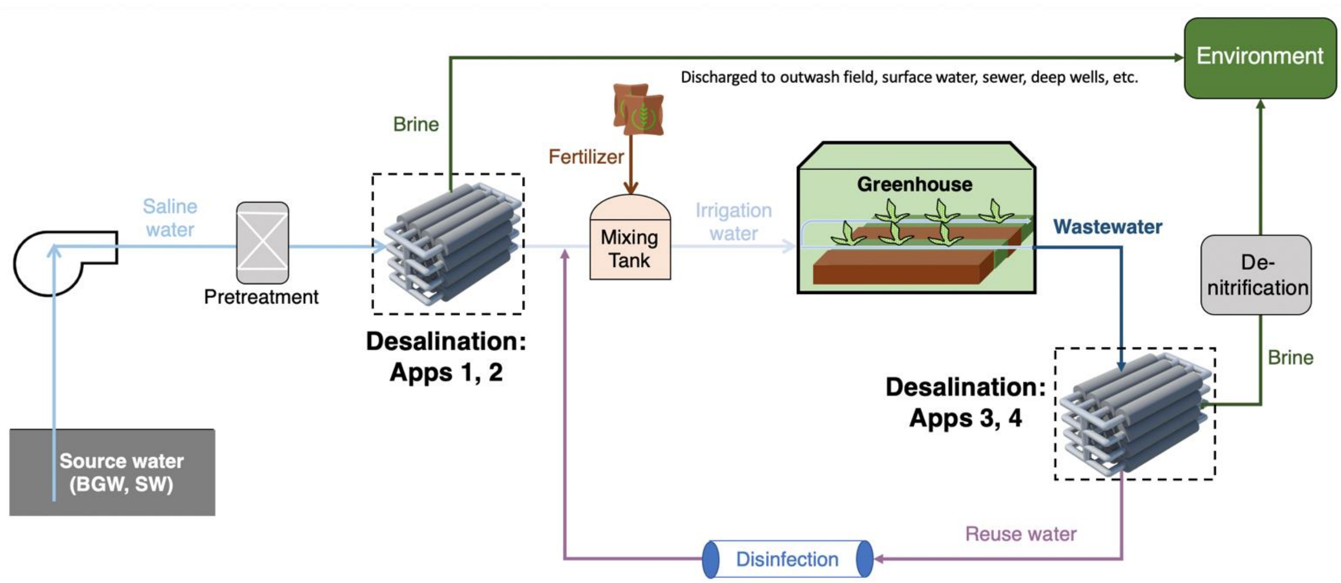

Figure 2: Four desalination applications in the greenhouse water cycle: 1) source water treatment, 2) SW source water treatment, 3) wastewater treatment for reuse, and 4) wastewater treatment for disposal.

Figure 2 shows the points of use of the four novel applications of MSED within the greenhouse water cycle. Each application corresponds to a water type with a particular salinity range, ionic composition and/or end use (Table 1). Composition differences influence MSED system performance. Experiments were conducted on multiple compositions of BGW, SW and wastewater and on two types of membranes (widely-used Neosepta ACS/CMS membranes and novel Fujifilm Type 16 membranes) using an MSED experimental set-up. The set-up utilizes a

PCCell ED200 stack containing 10-15 cell pairs, or a total active membrane area of 0.43-0.64 m^2, and 20-30 spacers of 0.5 mm and 2 end-spacers of 1 mm thickness. It is a batch configuration consisting of diluate, concentrate, and electrode rinse circuits. The diluate, concentrate, and electrode rinse containers can hold up to 1 liter, 4 liters, and 4 liters, respectively. Simulated water containing nitrate, sodium, calcium, potassium, magnesium, chloride, sulfate and/or phosphate serves as feedwater in the diluate and concentrate. Sodium sulfate (0.2 M) is used as the electrode rinse to stabilize pH. Centrifugal pumps (Iwaki, model MD-55R (T)) circulate the three streams at a flowrate of 95 L/h. The power supply (GW-INSTEK GPR-60600) applies a current less than 70% of the limiting current, the standard in real-world ED systems, to induce ion transport and separation across the stack. Feed and product water quality is measured using an inductively coupled plasma optical emission spectrometer (ICP-OES).

Table 1: Four potential MSED applications. Each application corresponds to a feedwater type of particular total dissolved solids (TDS) range, ionic constituents, composition variation with location and end use (irrigation, disposal). The constituents in light and dark green are primary and secondary macronutrients for crops, respectively, while those in red are harmful to crops.

Application	Feedwater	End use	Composition variation	TDS	Constituents
1	Brackish water (BGW)	Irrigation	Significant	1,000 – 10,000	Na^+, Ca^{2+}, SO_4^{2-}, Cl^-, Mg^{2+}
2	Seawater (SW)	Irrigation	Minimal	~ 35,000	
3	Agricultural wastewater	Irrigation (reuse)	Significant	< 4,000	Na^+, K^+, SO_4^{2-}, Cl^-, PO_4^{3-}, Mg^{2+}, NO_3^-, Ca^{2+}
4	Agricultural wastewater	Disposal			

Ion transport numbers $T_{cp,j}^{s}$ are calculated based on the change in concentration of each ion species in the diluate compartment as a function of time during the desalination process:

$$T_{cp,j}^{s} = \frac{\Delta C_{j,d} F}{N_{cp} i A_{mem} \Delta t} \qquad (1)$$

where $\Delta C_{j,d}$ is the change in concentration of salt species j in the diluate tank measured by the ICP, F is Faraday's constant, N_{cp} is the number of cell pairs, i is the limiting current density of the stack, A_{mem} is the total membrane area, and Δt is the time interval over which the concentration varies.

To quantify the ability of an MSED membrane to selectively remove monovalent sodium relative to multivalent ions, we define a membrane permselectivity *P*. This metric corresponds to the ratio of multivalent (*mult*) to monovalent (*mon*) transport numbers, normalized by their initial ion concentrations at $t = 0$:

$$P_{mult/mon} = \frac{T_{mult}/w_{mult,0}}{T_{mon}/w_{mon,0}} \qquad (2)$$

The closer *P* is to unity, the less monovalent selective the membranes. Consequently, lower permselectivities denote better rejection of monovalent ions and allude to a more efficient MSED system. Table 2 shows the *P* ratios determined to analyze the performance of each considered MSED application.

Table 2: Each application corresponds to a feedwater type of particular TDS range, ionic constituents, composition variation with location and end use (irrigation, disposal). The constituents in light and dark green are primary and secondary macronutrients for crops, respectively, while those in red are harmful to crops.

Application	Feedwater	End use	Permselectivity ratio
1	Brackish water (BGW)	Irrigation	$P = \frac{Na^+ \; Cl^-}{Ca^{2+} \; Mg^{2+} \; SO_4^{2-}}$
2	Seawater (SW)	Irrigation	$P = \frac{Na^+ \; Cl^-}{Ca^{2+} \; Mg^{2+} \; SO_4^{2-}}$
3	Agricultural wastewater	Irrigation (reuse)	$P = \frac{Na^+ \; Cl^- \; K^+ \; NO_3^-}{Ca^{2+} \; Mg^{2+} \; PO_4^{3-} \; SO_4^{2-}}$
4	Agricultural wastewater	Disposal	$P = \frac{Na^+ \; Cl^- \; K^+ \; NO_3^-}{Ca^{2+} \; Mg^{2+} \; PO_4^{3-} \; SO_4^{2-}}$

III. RESULTS

A summary of MSED performance results for the various feedwaters is given in Figure 3. MSED membranes demonstrate notable selectivity towards monovalent ions in all cases. However, a decrease in CEM performance is observed for wastewater treatment as a result of competitive transport between two dominant monovalent cations in wastewater (Na^+, K^+), unlike SW and BGW which contain one dominant monovalent cation (Na^+). Overall, Fujifilm membranes outperform Neosepta membranes at lab-scale, while having only one-third the cost. Fujifilm membranes, which are still under development, are expected to cost proportionally less at the commercial-scale. MSED membranes typically comprise 30% of total capital expenses. Consequently, Fujifilm membranes are recommended for use in MSED systems.

Based on the experimentally determined MSED performance, we conducted comparative cost analyses of MSED and RO to identify the potential for MSED adoption in greenhouses. Figures 4 and 5 provide an overview of this comparison, including the net savings or extra costs of MSED and suggested next steps in the MSED commercialization process. Greenhouses are considered the beachhead market for MSED implementation, because of their widespread use of desalination and their need to optimize growing conditions.

The results indicate that MSED should be adopted in place of RO for the treatment of BGW, the primary source water for irrigation. MSED technology can save farmers an average of 4,400 $/ha annually at current MSED membrane prices (~180 $/m^2). An MSED pilot test in a greenhouse is required to verify the technology's performance at scale prior to global adoption. In contrast, MSED costs an average of 12,000 $/ha more annually than RO for SW treatment as a result of higher capital and operating expenses. With regard to wastewater treatment, we preliminarily estimate that MSED may save greenhouses using RO in their reuse loop 1,500 $/ha annually at current MSED membrane prices (~180 $/m^2).

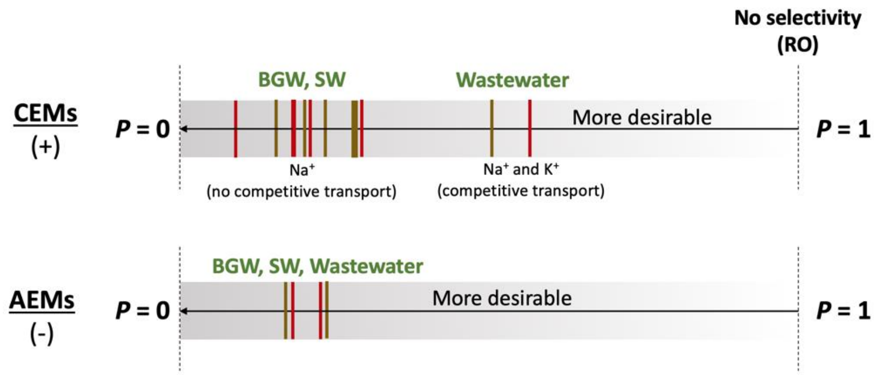

Figure 3: MSED performance spectrum for the four analyzed applications and two membrane types. Red and gold lines correspond to the Fujifilm and Neosepta membranes, respectively. Differences in performance for the treatment of brackish water and seawater versus wastewater stem from competitive monovalent transport. Sodium is present in relatively large concentrations in BGW, SW and wastewater. Potassium is present in small concentrations, if at all, in BGW and SW and large concentrations in wastewater as a result of its presence in fertilizer. Consequently, MSED membranes are transporting two, rather than one, monovalent ions when treating wastewater

Application	Tailor nutrients to increase crop yields	Low fertilizer need	Low water wastage	Low energy need (OpEx)	Low capital investment (CapEx)	Next steps for greenhouse adoption of MSED
RO (Baseline)	✗	✗	✗	✓	✓	
MSED (BGW) Net savings: $4.4k	✓	✓ Savings: +$5.4k	✓	✓ Added costs: +$1k	✓	Pilot in large vegetable greenhouse (e.g., CA)
MSED (SW) *current membrane cost* Net extra cost: $12k	✓	✓ Savings: +$9k	✓	✗ Added costs: +$21k	✗	MSED cost reduction (e.g., lower SEC, membrane cost)
MSED (SW) *projected membrane cost* Net extra cost: $4k	✓	✓ Savings: +$5.4k	✓	✗ Added costs: +$13k	✓	Cheaper Fujifilm membranes commercially available
MSED (wastewater for reuse) Net savings: $1.5k	✓	✓ Savings: +$3k	✓	✓ Added costs: +$1.5k	✓	Detailed cost analysis to verify economics before piloting

Figure 4: Overview of MSED and RO cost comparisons for applications 1 to 3 with suggested next steps for commercialization. All numbers are average annual values per ha. A cost analysis of application 4 was not conducted, as the baseline in that case is conventional denitrification using nitrifying/denitrifying bacteria rather than RO.

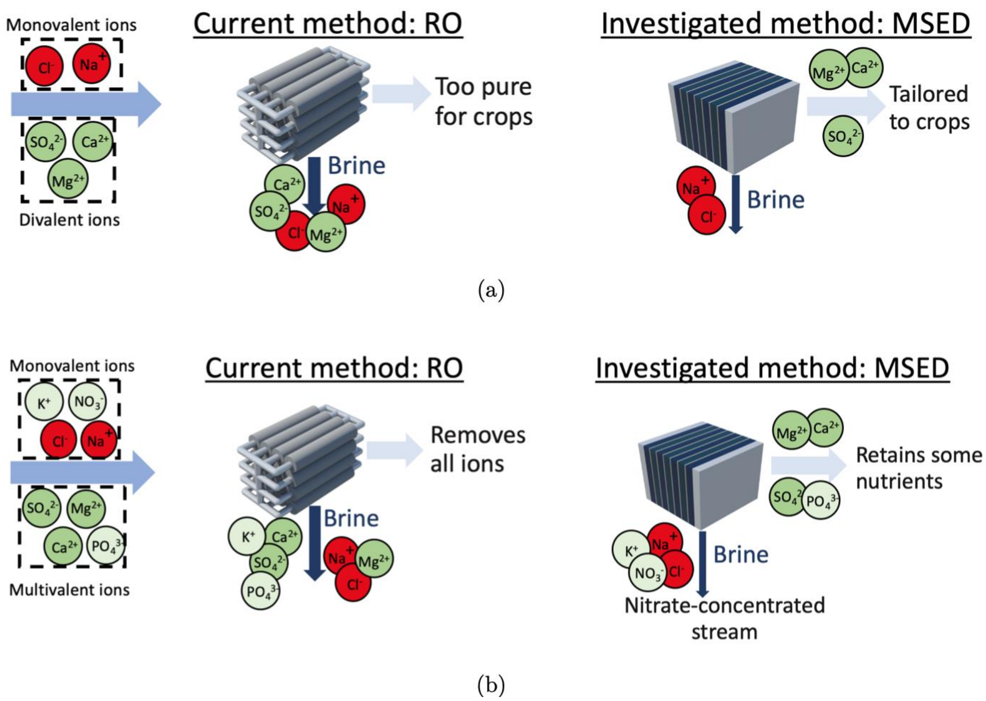

Figure 5: Advantage of MSED relative to RO for (a) applications 1 and 2 and (b) application 3.

VI. REFERENCES

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