

Treatment of greenhouse wastewater for reuse or disposal using monovalent selective electro dialysis

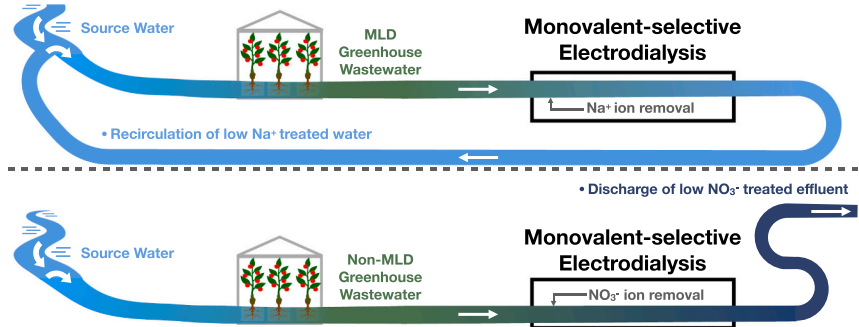
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HIGHLIGHTS

- Characterized MSED Neosepta and Fujifilm membranes for various GH effluents
- Determined cation-exchange membrane selectivity towards sodium for increased reuse
- Evaluated anion-exchange membrane selectivity towards nitrate before disposal
- Investigated sensitivity of membrane selectivity to composition
- Identified three GH cases for MSED adoption as alternative to RO or denitrification

GRAPHICAL ABSTRACT



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ABSTRACT

Minimal liquid discharge (MLD) in greenhouses minimizes the volume of discharged wastewater, thereby increasing the volume of effluent that may be reused. Sodium accumulation in wastewater is often considered the main bottleneck to achieving 100% reuse. Consequently, greenhouses have begun adopting reverse osmosis (RO), the most commonly used desalination technology for wastewater treatment. RO removes ions from wastewater indiscriminately, including multivalent nutrients to crops (Ca^{2+} , Mg^{2+} , SO_4^{2-} , PO_4^{3-}). In contrast, monovalent selective electro dialysis (MSED) selectively removes monovalent sodium while retaining multivalent nutrients in solution. For greenhouses that have not achieved MLD, MSED has an alternative application of reducing levels of nitrate, a monovalent ion and agricultural pollutant, in wastewater for disposal. This paper investigates the monovalent selectivity and potential of the widely-used Neosepta MSED membranes and the new Fujifilm MSED membranes to treat wastewater in greenhouses for reuse or discharge. Eight effluent compositions are tested as feedwater in a laboratory MSED system. Both membranes demonstrate selectivity towards sodium and nitrate across the tested compositions. Fujifilm cation-exchange membranes remove two to six sodium ions, compared to Neosepta's two to eight, for every magnesium ion. Fujifilm anion-exchange membranes remove two to seven nitrate ions, compared to Neosepta's two to six, for every sulfate ion.

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| Nomenclature | | w | Concentration, meq |
|----------------------|---|----------------------|---|
| <i>Roman symbols</i> | | z | Valence |
| A_m | Membrane area, m^2 | <i>Greek symbols</i> | |
| C | Concentration, $mol \cdot m^{-3}$ | π | Osmotic pressure, bar |
| D | Diffusion coefficient, $m^2 \cdot s^{-1}$ | σ | Spacer shadow effect |
| E | Donnan potential, V | <i>Subscripts</i> | |
| F | Faraday constant, $C \cdot mol^{-1}$ | c | Concentrate |
| h | Channel height, m | cu | Counter ion |
| i | Current density, $A \cdot m^{-2}$ | d | Diluate |
| I | Current, A | div | Divalent |
| J | Flux, $mol \cdot m^{-2} \cdot s^{-1}$ | f | Final |
| k | Electrical conductivity, $S \cdot m^{-1}$ | j | Ion species |
| L_j | Membrane ion permeability, $m \cdot s^{-1}$ | lim | Limiting |
| L_w | Membrane water permeability, $s \cdot m^{-1}$ | m | membrane |
| m | Slope | mon | Monovalent |
| M | Molar mass, $mg \cdot mol^{-1}$ | o, i | Initial |
| m_j | Ion mass, kg | r | Rinse |
| N_{cp} | Number of cell pairs | s | Salt |
| P | Permselectivity | w | Water |
| Q | Volume flow rate, $m^3 \cdot s^{-1}$ | <i>Superscripts</i> | |
| r | Solute ratio | cp | Cell pair |
| \bar{R} | Resistance | <i>Acronyms</i> | |
| Re_D | Reynolds number | AEM | Anion exchange membrane |
| S | Salinity | CEM | Cation exchange membrane |
| Sc | Schmidt number | ED | Electrodialysis |
| Sh | Sherwood number | MSED | Monovalent selective electrodesalination |
| T | Transport number | RO | Reverse osmosis |
| t_{cu} | Integral counter ion transport number | TDS | Total dissolved solids, $mg \cdot L^{-1}$ |
| t | Process time, s | | |
| V_{el} | Electrode potential, V | | |
| V_{stack} | Stack potential, V | | |

1. Introduction

The dominant user of global water supplies is agriculture, which consumes approximately 69% of freshwater withdrawn [1]. Greenhouse horticulture has emerged as a modern solution to irrigation needs: it lowers water and land use for irrigated agriculture, increases process control for creating favorable growing conditions independent of the surrounding environment, and enables containment of agricultural pollutants. A key objective in optimizing greenhouse operations is minimal liquid discharge (MLD). High-tech greenhouses, particularly in the Netherlands, have begun to adopt MLD irrigation systems to reduce their environmental footprint and operational costs [45]: MLD minimizes the volume of greenhouse wastewater disposed into the environment, thereby maximizing the volume of water reused to grow crops.

In order to achieve MLD, greenhouses must recirculate wastewater through a disinfection stage to prevent the spread of crop disease or biofilm growth and often through a treatment stage to remove constituents detrimental to crop growth, before blending with freshwater and fertilizer for irrigation (Fig. 1). Two primary issues exist with greenhouse water recirculation systems. First, water recirculation may lead to a loss of process control regarding source water quality [46]. Because residual fertilizer concentration levels in wastewater constantly fluctuate, the mixing of fertilizer-enhanced freshwater and untreated effluent makes it difficult to maintain a stable irrigation water composition without continuous adjustment of the fertilizer addition rate. Second, ionic constituents in the source water that are not absorbed by crops accumulate in the reuse loop [3,4]. Sodium accumulation is considered the main bottleneck in greenhouse recirculation systems due to crop intolerance for sodium [5].

To reduce sodium levels and generate reused water of consistent

quality, greenhouses have begun piloting reverse osmosis (RO), the most widely used desalination technology, in their recirculation loop [46,6] (Fig. 1(a)). RO removes all ion constituents from the wastewater stream, including monovalent sodium that is harmful to crops and various plant nutrients that are both monovalent (K^+ , NO_3^-) and multivalent (Ca^{2+} , Mg^{2+} , SO_4^{2-} , PO_4^{3-}) in nature. The removal of nutrients already present in the reuse water results in greater fertilizer requirements to convert source water to irrigation water.

Monovalent selective electrodesalination (MSED) is an alternative membrane process for desalination that better fits the needs of greenhouses. MSED allows for the selective removal of monovalent ions, such as sodium, while keeping multivalent solutes in solution. Consequently, MSED may be implemented at the greenhouse water outlet to prevent sodium accumulation in effluent prior to recirculation to achieve MLD (Fig. 1(b)). Although MSED, like RO, extracts monovalent nutrients in addition to sodium, the technology critically retains multivalent nutrients, unlike RO, resulting in lower fertilizer requirements and greater cost savings. Other key advantages of MSED, compared to RO, are its inherently lower brine production, longer membrane lifetime, and lower sensitivity to membrane fouling [7]. MSED operates at a recovery of over 90% compared to RO's 80% [7].

In greenhouses that have not achieved MLD, another viable application of MSED is the removal of nitrate, the primary agricultural pollutant, from greenhouse wastewater for disposal (Fig. 1(d)). Stringent regulations on reducing nitrate levels in agricultural effluent exist around the world, including the European Union's Nitrates Directive and the National Pollutant Discharge Elimination System in North America. Similar to the reuse application, MSED separates greenhouse effluent into two outlet streams: a discharge stream low in monovalent nitrate and sodium that is ready for disposal and a low volume brine

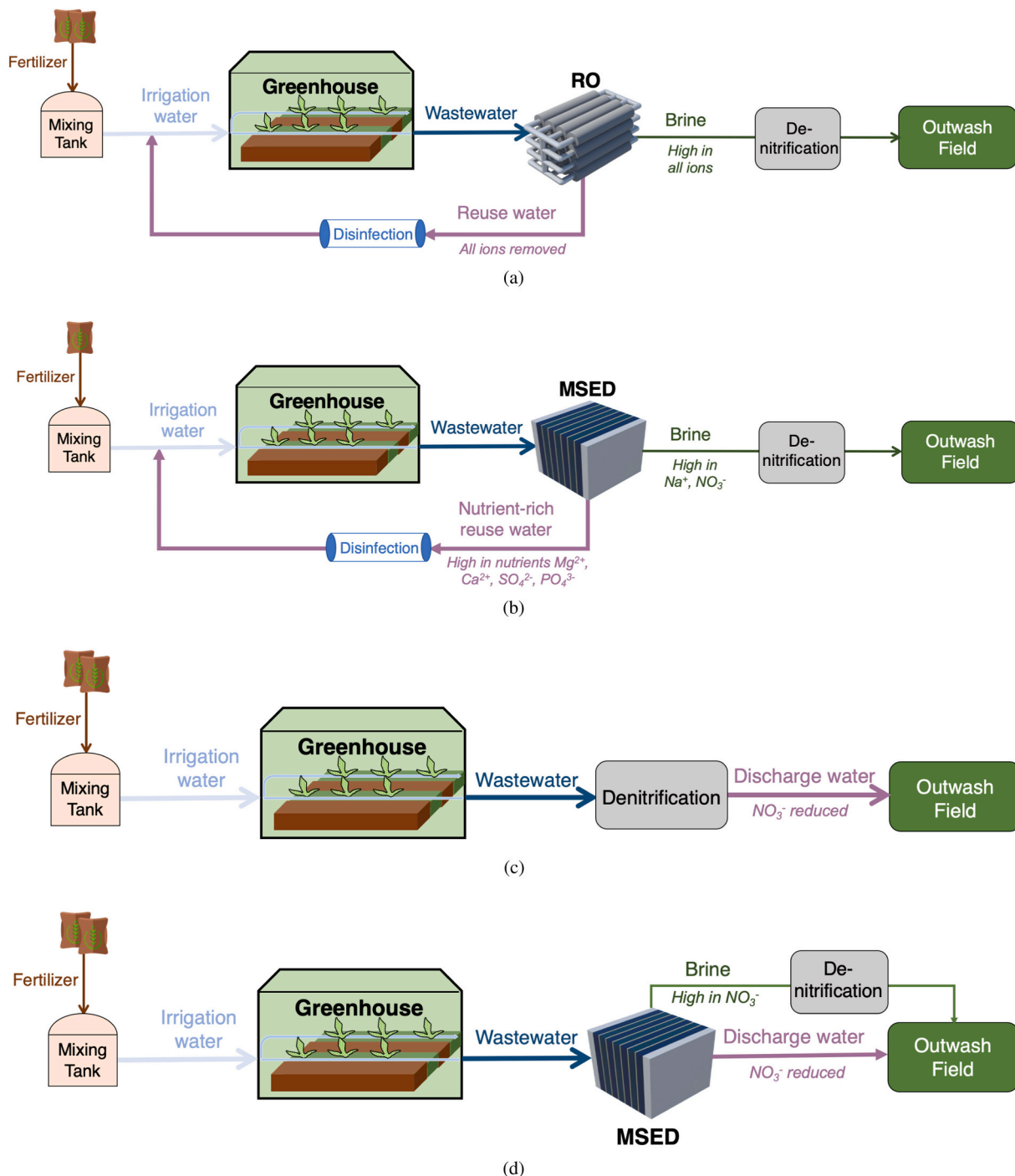


Fig. 1. Water cycle of greenhouse using (a) RO for wastewater reuse, (b) MSED for wastewater reuse, (c) conventional denitrification prior to wastewater discharge, and (d) MSED for nitrate removal from wastewater prior to discharge. (a) RO removes all ions including already present nutrients from wastewater for reuse. (b) MSED selectively removes sodium and nitrate while retaining other nutrients in the reuse loop. In both cases, the desalination brine undergoes denitrification before disposal. A lower volume (< 10%) and more concentrated brine leaves the MSED than RO system. (c,d) MSED yields a discharge water stream ready for disposal and a brine stream of much lower volume that undergoes denitrification before disposal. There may be the possibility of nitrate recovery from MSED brine for fertilizer use.

stream that undergoes conventional denitrification before disposal. The conventional process involves biological denitrification of wastewater in large reaction basins, trickling filters, or artificial wetlands. Such treatment increases capital costs, such as land use, and operating costs, such as permits and continuous effluent monitoring and reporting. The over 90% reduction in the amount of water subject to denitrification through MSED implementation may greatly decrease the associated denitrification costs. According to a recent study [8], MSED adoption for

nitrogen removal from municipal wastewater, through reducing ammonium levels, is an order of magnitude less expensive on a per kilogram nitrogen removed basis than existing denitrification technologies in both capital and operating expenses. In addition, the concentrated-nitrate stream leaving the MSED system provides the opportunity to recover nitrates for fertilizer use. Pastushok et al. [9] recently applied capacitive deionization (CDI) to domestic wastewater to recover nitrates in the form of concentrate for fertilizer production.

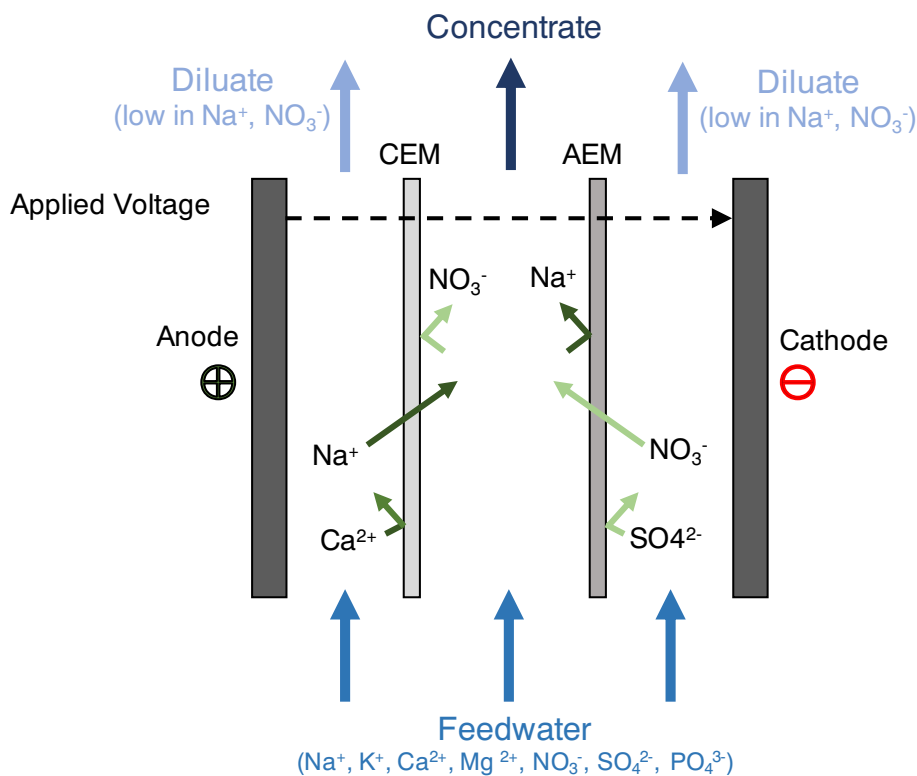


Fig. 2. A simplified MSED stack containing two electrodes, CEM and AEM. Greenhouse effluent serves as feedwater. An applied voltage across the electrodes yields from the effluent a diluate stream low in sodium for reuse and low in nitrate for disposal. Potassium, magnesium and phosphate, not shown here, will exhibit the same behavior as sodium, calcium and sulfate, respectively.

Since the 1960s, MSED has been used to concentrate sodium chloride from seawater brine for salt production in Japan [10]. MSED has not been commercially implemented in greenhouses to treat brackish source water or wastewater, which have much lower salinities than seawater brine. Consequently, MSED membranes on the market, such as the most commonly used Neosepta ACS/CMS membranes (Astom Corporation), have been designed for high salinity applications. Fujifilm Corporation recently manufactured MSED membranes for low salinity applications (Fujifilm Type 16 membranes) that are not yet commercially available. Aligned with industry use, the literature has mainly investigated the monovalent selectivity of MSED for concentrated seawater salinities [11,12,13]. More recent studies have been conducted on recovery of nutrients, particularly ammonium and phosphate, from industrial and municipal wastewaters [8,14,15,16] and removal of sodium or nitrate from groundwater [17,18,19,20,21]. Ahdab et al. [20,21] concluded that the Neosepta CMS/ACS membranes and Fujifilm Type 16 membranes are selective towards sodium for 16 diverse BGW compositions. To our knowledge, no prior literature considers removing sodium and nitrate from greenhouse effluent. Because water composition greatly influences membrane performance, groundwater and wastewater, which substantially differ in ionic composition (e.g., groundwater contains minimal amounts of nitrate, phosphate and potassium, unlike wastewater), should be considered distinct points of use for MSED within greenhouses.

This paper reports the first analysis of the selective removal of sodium (application A) and nitrate (application B) from various greenhouse effluents for two sets of MSED membranes: the widely-used Neosepta ACS/CMS MSED membranes and the new Fujifilm Type 16 MSED membranes. We conduct experiments on eight effluent compositions, based on data from the literature [22,23] and interviews conducted with greenhouse operators in the Netherlands and North America [24,25,26], to determine ion transport number, membrane selectivity, membrane resistance and limiting current density. MSED

adoption for the treatment of greenhouse wastewater may improve environmental footprint, increase fertigation process control and reduce capital and operational costs through increasing wastewater reuse or nitrate removal from wastewater for disposal.

2. Methods

An MSED system comprises two types of monovalent selective ion-exchange membranes, a cation exchange membrane (CEM) and anion exchange membrane (AEM), positioned in alternating order between two electrodes to enable the separation of a feed stream into a diluate stream and a concentrate stream. CEMs and AEMs contain negatively charged and positively charged groups, respectively, embedded in their polymer matrix [7]. Donnan exclusion induces selective charge-based migration of ionic species [27]. AEMs allow for the passage of monovalent anions and reject divalent anions and all cations. CEMs allow for the passage of monovalent cations and reject divalent cations and all anions. Various parameters influence membrane performance, including the hydrophobicity of the matrix polymer, the concentration and type of fixed charges in the polymer, and the density of the polymer network [7].

Spacers lie between the membranes, as well as the membranes and electrodes, to configure the flow. An applied potential difference across the electrodes drives ion transport across the membranes, with anion migration towards the anode and cation migration towards the cathode. Fig. 2 shows this process for an MSED system with two membranes treating greenhouse effluent. While the ionic composition of effluent may vary, the primary constituents include calcium, magnesium, sodium, potassium, sulfate, nitrate and phosphate. Calcium, magnesium, potassium, nitrate and phosphate are nutrients for crops, while sodium is detrimental to crops [28,29]. MSED can serve a dual purpose in increasing reuse through the removal of sodium over time (application A) and pretreating discharge water through the removal of nitrate

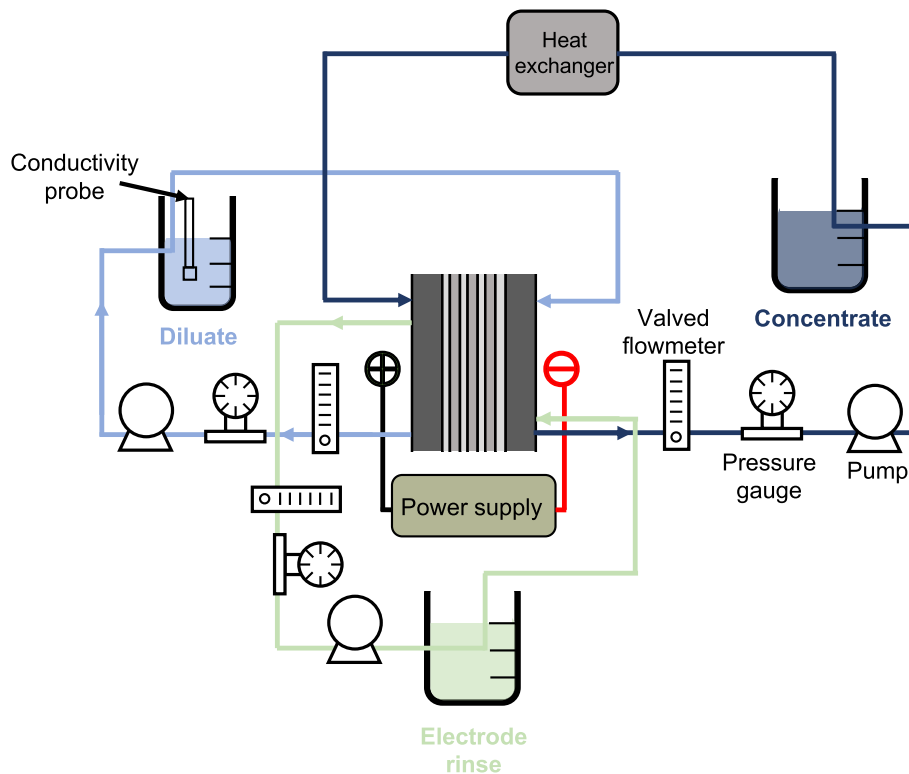


Fig. 3. MSED set-up consisting of a diluate, concentrate, and rinse circuit feeding an ED200 stack.

(application B). Consequently, in the cases of reuse and disposal, MSED yields a product stream low in sodium, nitrate and potassium, but high in calcium, magnesium, and sulfate.

Net salt and water transport across the membrane in each compartment of the MSED stack can be written as:

$$J_{s,j} = \frac{T_{s,j}^{cp} i}{zF} - L_j (C_{j,c,m} - C_{j,d,m}) \quad (1)$$

$$J_w = \frac{T_w^{cp} i}{F} + L_w (\pi_{j,c,m} - \pi_{j,d,m}) \quad (2)$$

where J is flux in $\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$, s denotes salt, w denotes water, T is a transport number, F is Faraday's constant, L is the membrane permeability in $\text{m}\cdot\text{s}^{-1}$ for the salts and in $\text{s}\cdot\text{m}^{-1}$ for the water, z is the ion valence, c denotes concentrate, d denotes diluate, m is membrane, C is a concentration in $\text{mol}\cdot\text{m}^{-3}$, and A_m is the membrane area in m^2 . The subscript j indicates an ion species in the greenhouse effluent that migrates across the series of ion exchange membranes. The applied current density i depends on the applied voltage, Donnan potentials and ohmic resistances for the membranes, diluate, and concentrate. The salt flux in Eq. 1 is a function of ion migration (first term) and ion diffusion (second term). The water flux in Eq. 2 is a function of electro-osmosis (first term) and water diffusion (second term).

In order to characterize the MSED membranes, we experimentally determine the ion transport numbers, membrane selectivity, membrane resistance, and limiting current density. The methods for calculating limiting current density and membrane resistance can be found in Appendix A.

2.1. Experimental set-up

The MSED experimental set-up, which operates in a batch configuration, is composed of 3 flow circuits (diluate, concentrate, electrode rinse) that feed into a PCCell ED200 stack (Fig. 3). The stack contains 10 membrane cell pairs (total active membrane area of 0.43 m^2), 20 spacers

Table 1

Detailed specification of Neosepta CMS/ACS membranes. Electrical resistance is measured on AC after equilibration with a 0.5 M NaCl solution at 25°C [18,30].

| | 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 |

of 0.5 mm thickness and 2 end spacers in the electrode stream 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 greenhouse effluent produced by dissolving calcium, magnesium, sodium, potassium, sulfate, nitrate, and phosphate (Appendix B). Diluate water composition is measured using an inductively coupled plasma optical emission spectrometer. 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 LPH. 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. Two sets of membrane are tested: Neosepta ACS/CMS membranes and Fujifilm Type 16 membranes. Table 1 includes Neosepta membrane specifications. The Fujifilm membranes, which are not commercially available, do not have a

Table 2

Greenhouse effluent cation compositions analyzed for MSED application A using the Fujifilm and Neosepta membranes.

| Label | Fujifilm | | | | Neosepta | | | |
|--------|------------|-----------|---------------|---------------|------------|-----------|---------------|---------------|
| | r_{Na^+} | r_{K^+} | $r_{Ca^{2+}}$ | $r_{Mg^{2+}}$ | r_{Na^+} | r_{K^+} | $r_{Ca^{2+}}$ | $r_{Mg^{2+}}$ |
| Comp 1 | 0.31 | 0.47 | 0.16 | 0.05 | 0.28 | 0.49 | 0.18 | 0.05 |
| Comp 2 | 0.27 | 0.41 | 0.26 | 0.07 | 0.28 | 0.40 | 0.27 | 0.06 |
| Comp 3 | 0.22 | 0.34 | 0.34 | 0.09 | 0.20 | 0.34 | 0.37 | 0.09 |
| Comp 4 | 0.27 | 0.41 | 0.23 | 0.09 | 0.24 | 0.42 | 0.27 | 0.08 |
| Comp 5 | 0.43 | 0.26 | 0.24 | 0.07 | 0.45 | 0.24 | 0.24 | 0.07 |
| Comp 6 | 0.44 | 0.44 | 0.07 | 0.05 | 0.44 | 0.44 | 0.07 | 0.05 |
| Comp 7 | 0.14 | 0.23 | 0.47 | 0.16 | 0.12 | 0.22 | 0.50 | 0.16 |
| Comp 8 | 0.22 | 0.29 | 0.38 | 0.11 | 0.22 | 0.28 | 0.38 | 0.11 |

Table 3

Greenhouse effluent anion compositions analyzed for MSED application B using the Fujifilm and Neosepta membranes.

| Label | Fujifilm | | | Neosepta | | |
|--------|--------------|-----------------|-----------------|--------------|-----------------|-----------------|
| | $r_{NO_3^-}$ | $r_{SO_4^{2-}}$ | $r_{PO_4^{3-}}$ | $r_{NO_3^-}$ | $r_{SO_4^{2-}}$ | $r_{PO_4^{3-}}$ |
| Comp 1 | 0.30 | 0.70 | 0 | 0.31 | 0.69 | 0 |
| Comp 2 | 0.28 | 0.71 | 0.01 | 0.26 | 0.73 | 0.01 |
| Comp 4 | 0.30 | 0.67 | 0.03 | 0.28 | 0.71 | 0.02 |
| Comp 5 | 0.41 | 0.57 | 0.01 | 0.42 | 0.58 | 0.01 |
| Comp 6 | 0.55 | 0.43 | 0.02 | 0.55 | 0.44 | 0.01 |

specifications datasheet.

2.2. Greenhouse effluents analyzed

Greenhouse effluent composition will vary depending on source water composition, soil composition, and crop type. In this analysis, we select eight feedwater compositions based on the literature [22,23] that represents average compositions of greenhouses treating various crops (Comps 3–5) and interviews conducted with a cucumber greenhouse (Comp 2, Comp 8) in the Netherlands, a tomato greenhouse in Canada (Comp 6, Comp 7) and a vegetable/gerbera greenhouse in California (Comp 1) (these growers requested to remain anonymous [24,25,26]). The collected data indicates that the total dissolved solids (TDS) of greenhouse effluent typically ranges from 1500 to 3500 mg/L. The dominant anions are sulfate and nitrate, while the dominant cations are sodium, potassium, magnesium, and calcium. Consequently, we investigate the impact of cation solute ratios r_{j^+} and anion solute ratios r_{j^-} on MSED membrane performance¹:

$$r_{j^+} = \frac{C_{j^+}}{\sum_{j^+} C_{j^+}} \quad (3)$$

$$r_{j^-} = \frac{C_{j^-}}{\sum_{j^-} C_{j^-}} \quad (4)$$

where j^+ represents each cation species, j^- represents each anion species, and C denotes ion concentration in the diluate in mg/L. The cation compositions analyzed for application A using the Neosepta and Fujifilm MSED membranes can be found in Table 2. The anion compositions analyzed for application B using the Fujifilm and Neosepta membranes

¹ We define solute ratio in terms of C_j (mg/L), rather than w_j (meq/L), in order to develop transport number fits as a function of measured ion concentrations C_j . For wastewater compositions considered in this study, the correlation coefficients of solute ratio calculated using C_j and w_j is equal to 1 for anions and is greater than 0.97 for cations. Consequently, observed trends as a function of solute ratio will be the same using either concentration basis. Appendix C includes permselectivity results on an equivalent concentration basis.

can be found in Table 3. Complete composition data can be found in Appendix B. The average TDS across all compositions is 2397 ± 478 mg/L.

2.3. Transport number and membrane selectivity

To determine ion transport numbers, we conducted constant current tests, in which we measure the mass of ions transported across the membranes in a fixed amount of time. Simulated greenhouse effluent served as feedwater 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 $0.7i_{lim}$, a typical operating limit in commercial ED systems [31]. Based on Eq. 1, the ion transport number can be written as:

$$T_{sj}^{cp} = \frac{\Delta w_j F}{i \Delta t A_m N_{cp}} \quad (5)$$

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 Eq. 1, which is nearly three orders of magnitude less than the ion migration term [21], is neglected. This trend has been verified even for high salinity applications by McGovern et al. [32].

Membrane permselectivity P serves as a metric to quantify a membrane's ability to selectively remove monovalent relative to divalent ions. We define it as the ratio of divalent to monovalent transport number, normalized by initial ion concentration at $t=0$:

$$P_{mon}^{div} \equiv \frac{T_{div}/w_{div,o}}{T_{mon}/w_{mon,o}} \quad (6)$$

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.

3. Results

This section contains results for ion transport number and membrane permselectivity for Neosepta ACS/CMS and Fujifilm Type 16 MSED membranes used for applications A and B in greenhouses. These results are compared to previous studies we conducted on MSED desalination of brackish groundwater in greenhouses [20,21]. Appendix A contains results for limiting current density and membrane resistance. The determined system parameters represent a bench-scale setup and may differ at larger scale. Consequently, pilot studies in greenhouses are necessary to fully characterize MSED systems for real-world applications.

3.1. Application A: sodium removal for wastewater reuse

Experimental results for cation transport number and CEM monovalent selectivity are determined for eight greenhouse effluent solutions. First, we explore trends in normalized cation concentration as a function of time in a given experiment. Second, the relationship between cation transport number and solute ratio is investigated. Third, we determine whether the Neosepta and Fujifilm CEMs are monovalent selective towards sodium for increased wastewater reuse and discuss the influence of effluent composition on selectivity.

3.1.1. Transient cation concentration

Across the considered greenhouse effluents, normalized cation concentration linearly varies with desalination process time in a given experiment for Fujifilm and Neosepta CEMs (Fig. 4). This trend is consistent with the literature [33,34] and suggests that the migration term in the transport equation dominates over the diffusion term. In addition, due to the selectivity of the membranes, divalent ion

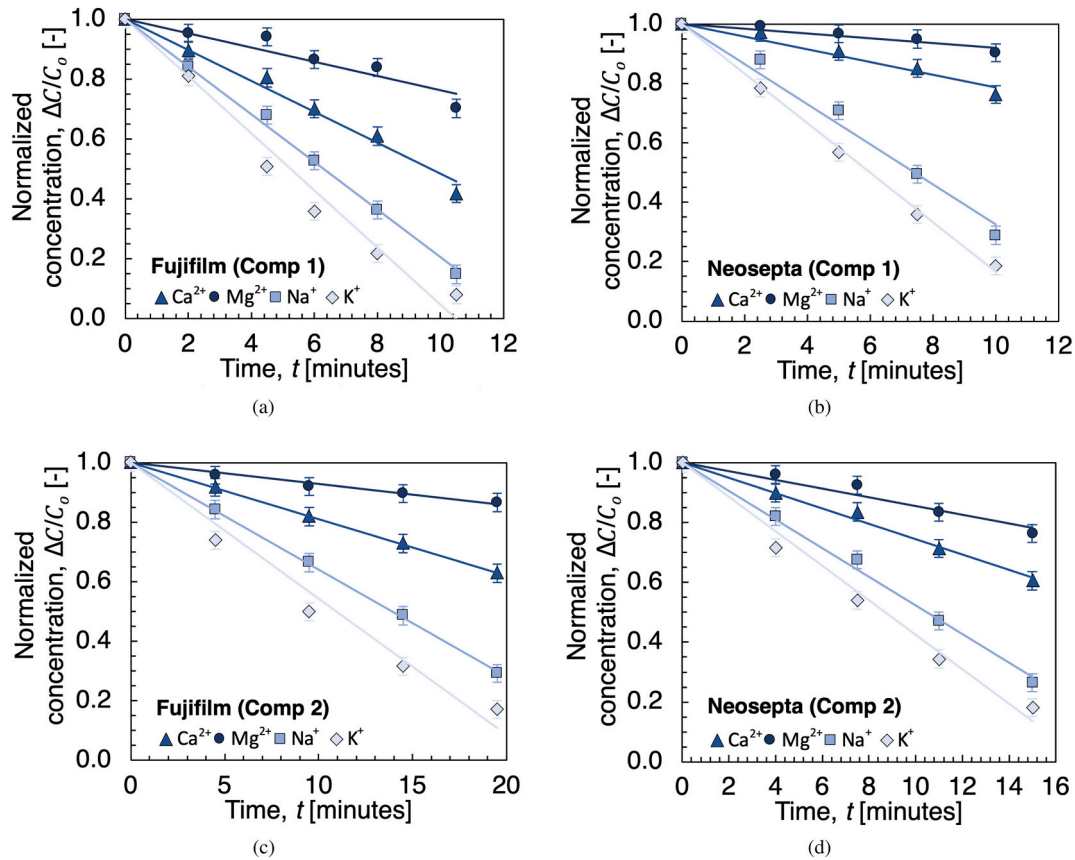


Fig. 4. Normalized cation concentration (Ca^{2+} , Mg^{2+} , Na^+ , K^+) of Neosepta and Fujifilm CEMs as a function of desalination process time for two effluent compositions (Comp 1, Comp 2).

concentrations decrease at a slower rate than monovalent ion concentrations. The order presented in the ion concentration-time slopes increase with decreasing hydration energy: magnesium (1904 kJ/mol), calcium (1592 kJ/mol), sodium (405 kJ/mol), potassium (321 kJ/mol) [35,36]. Ions must partly or fully shed their hydration shell in order to cross the membranes. Consequently, a larger hydration energy corresponds to a lower ion removal over time.

3.1.2. Cation transport number

Figs. 5 and 6 illustrate that calcium, sodium and potassium transport numbers vary linearly with calcium, sodium and potassium ion solute ratios, respectively, for Fujifilm CEMs ($r^2 > 0.85$) and Neosepta CEMs ($r^2 > 0.71$). Differences in transport number slopes suggest that Neosepta CEMs may be more sensitive to calcium solute ratio, less sensitive to sodium solute ratio and comparably sensitive to potassium solute ratio relative to Fujifilm CEMs. No trends in magnesium transport number with solute ratio are observed, because magnesium transport number is calculated based on minor changes in measured ion concentration (e.g., $\Delta C_{\text{Mg}^{2+}} = 3 \text{ mg/L}$ on average for Comp 1).

Consistent with trends in the literature [18], the sum of the monovalent transport $T_{\text{Na}+\text{K}}$ and sum of the divalent transport $T_{\text{Ca}+\text{Mg}}$ inversely vary with total monovalent solute ratio $r_{\text{Na}+\text{K}}$ (Fig. 7). At a given monovalent solute ratio (i.e., effluent composition), a higher monovalent transport corresponds to a lower divalent transport, because the sum of the cation transport numbers is equivalent to a relatively fixed transport efficiency across compositions: $T_{\text{cation, Fujifilm}} = 0.52 \pm 0.05$ and $T_{\text{cation, Neosepta}} = 0.60 \pm 0.03$. The difference in these values suggests that Neosepta CEMs have a greater capacity than Fujifilm CEMs for cation transport over a given amount of time.

3.1.3. CEM permselectivity

Neosepta and Fujifilm CEMs demonstrate selectivity towards monovalent ions for eight effluent compositions (Tables C.1 and C.2). Across all compositions, Fujifilm CEMs average a $P_{\text{Na}^+\text{Ca}^{2+}}$ of 0.59 ± 0.16 , compared to Neosepta's 0.48 ± 0.16 , and a $P_{\text{K}^+\text{Ca}^{2+}}$ 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. Fujifilm CEMs average a $P_{\text{Na}^+\text{Mg}^{2+}}$ of 0.34 ± 0.18 , compared to Neosepta's 0.32 ± 0.17 , and a $P_{\text{K}^+\text{Mg}^{2+}}$ 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. For a given composition, differences in ion hydration energy largely account for differences in permselectivity. A higher magnesium hydration energy results in a lower magnesium removal rate and correspondingly lower magnesium permselectivity ($P_{\text{K}^+\text{Mg}^{2+}}$, $P_{\text{Na}^+\text{Mg}^{2+}}$) compared to calcium permselectivity ($P_{\text{K}^+\text{Ca}^{2+}}$, $P_{\text{Na}^+\text{Ca}^{2+}}$). Similarly, a higher sodium hydration energy results in a lower sodium removal rate and correspondingly higher divalent permselectivity relative to sodium ($P_{\text{Na}^+\text{Ca}^{2+}}$, $P_{\text{Na}^+\text{Mg}^{2+}}$) than potassium ($P_{\text{K}^+\text{Ca}^{2+}}$, $P_{\text{K}^+\text{Mg}^{2+}}$). Whether these selectivity ranges are large enough to retain enough nutrients, while mitigating sodium accumulation, for substantive fertilizer savings requires a complete techno-economic analysis that also considers the water savings offered by MSED (further discussed in Section 4).

Fig. 8 shows the breakdown of Neosepta and Fujifilm cation permselectivity by effluent composition. In comparison to the Fujifilm CEMs, Neosepta CEMs demonstrate a lower permselectivity (i.e., superior

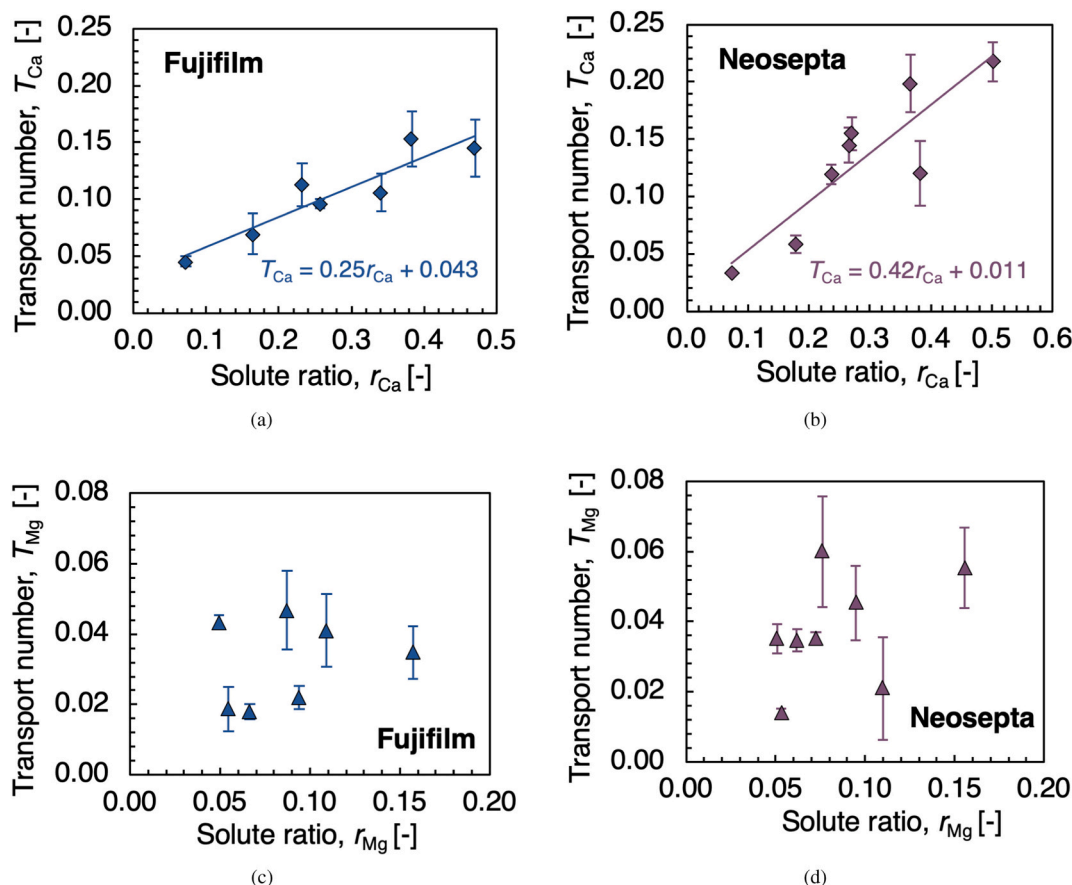


Fig. 5. Divalent transport number of calcium and magnesium as a function of ion solute ratio for Fujifilm and Neosepta CEMs.

monovalent selectivity) for sodium and potassium relative to calcium for five effluent compositions (Comp 1, Comp 5, Comp 6, Comp 7, Comp 8), comparable selectivity for two compositions (Comp 2, Comp 4) and inferior selectivity for one composition (Comp 3). Neosepta CEMs also show better monovalent selectivity than Fujifilm CEMs for sodium and potassium relative to magnesium for five effluent compositions (Comp 1, Comp 5, Comp 6, Comp 7, Comp 8) and inferior selectivity for three compositions (Comp 2, Comp 3, Comp 4). Fig. 9 shows no trends in permselectivity with monovalent ion solute ratio (i.e., composition), with the exception of $P_{Na^+}^{Mg^{2+}}$ and $P_{Na^+}^{Ca^{2+}}$ as a function of r_{Na} for Fujifilm CEMs ($r^2 = 0.68$).

These results differ from previous studies [20,21], in which we observed a linear relationship between solute ratio and permselectivity ($r^2 > 0.85$) and superior monovalent selectivity for 16 brackish feedwaters composed of one monovalent cation (Na^+ , Ca^{2+} , Mg^{2+}). In contrast, the analyzed greenhouse effluents are composed of two monovalent cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+}). Consequently, the difference in behavior may stem from the role of competitive monovalent transport and the presence of additional ionic constituents in wastewater. The large concentration of potassium, which has a lower hydration energy, in wastewater decreases the number of transfer sites available for sodium [35] and results in the preferential removal of potassium relative to sodium (Fig. 4, Tables C.1-C.2). Fig. 10 shows a comparison of the average CEM permselectivity for wastewater and brackish groundwater. Additional feedwaters should be investigated to conclusively determine the influence of competitive monovalent transport on permselectivity.

Disparities in Fujifilm and Neosepta CEM performance for the tested effluent compositions may result from differences in intrinsic membrane properties, including the concentration and type of functional groups in the matrix polymer and the hydrophobicity and density of the polymer network [7]. While some of this data has been publicized for the

commercially available Neosepta membranes (Table 1), it has not been publicized for the Fujifilm membranes, which are not commercially available.

3.2. Application B: nitrate removal for wastewater disposal

Experimental results for anion transport number and AEM monovalent selectivity are determined for six greenhouse effluent solutions. First, we explore trends in normalized anion concentration as a function of time in a given experiment. Second, the relationship between anion transport number and solute ratio is investigated. Third, we determine whether the Neosepta and Fujifilm AEMs can selectively remove nitrate from greenhouse discharge water. We also discuss the influence of effluent composition on selectivity.

3.2.1. Transient anion concentration

Across the considered greenhouse effluents, normalized anion concentration linearly varies with desalination process time in a given experiment for Fujifilm and Neosepta AEMs (Fig. 11). This trend is consistent with the literature [20,21,18]. The concentration of sulfate, a divalent ion, decreases at a slower rate than the concentration of nitrate, a monovalent ion, reflecting the monovalent selectivity of both membranes. Phosphate, a multivalent ion, does not linearly vary with time. Because the initial phosphate concentration of 19 ± 3.4 mg/L is very low, changes in measured phosphate concentration are minor and more sensitive to measurement error. Sulfate and phosphate have larger hydration energies of 1145 kJ/mol and 2835 kJ/mol, respectively, relative to nitrate's 328 kJ/mol [36]. Because ions must partly or fully shed their hydration shell in order to cross the membranes, a larger hydration energy usually corresponds to a lower ion removal over time.

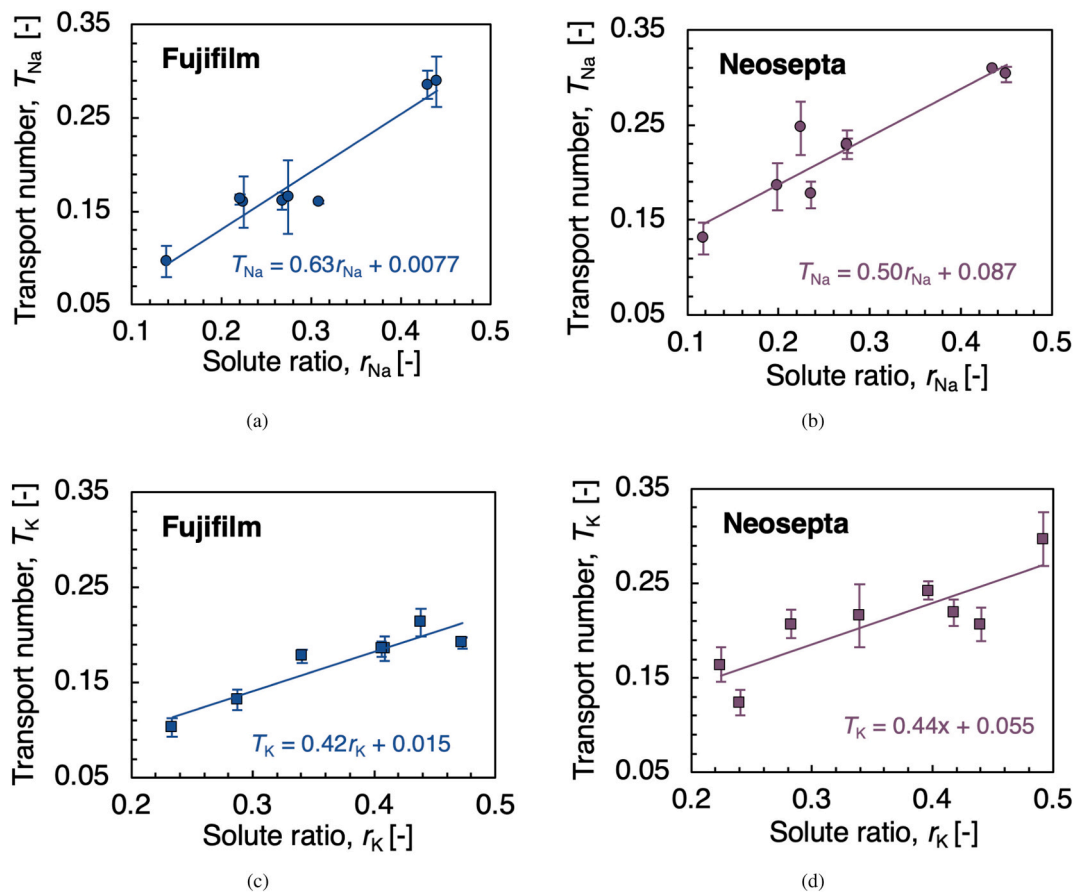


Fig. 6. Monovalent transport number of sodium and potassium as a function of ion solute ratio for Fujifilm and Neosepta CEMs.

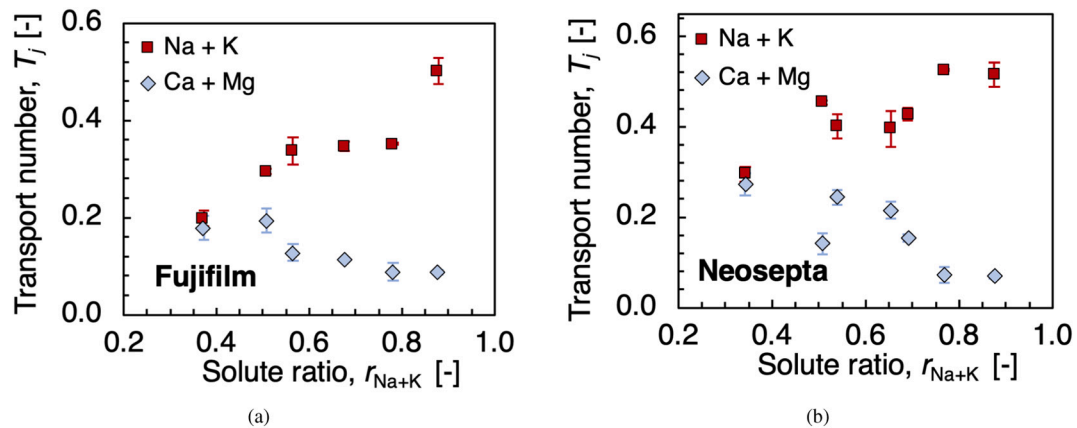


Fig. 7. Sum of divalent (T_{Ca+Mg}) and monovalent (T_{Na+K}) transport numbers as a function of total monovalent cation solute ratio (r_{Na+K}) for Fujifilm and Neosepta CEMs.

3.2.2. Anion transport number

Figs. 12 and 13 illustrate that sulfate and nitrate transport numbers vary linearly with sulfate and nitrate ion solute ratios, respectively, for Fujifilm AEMs ($r^2 > 0.77$) and Neosepta AEMs ($r^2 > 0.88$). Differences in transport number slopes suggest that Neosepta AEMs may be less sensitive to sulfate solute ratio and more sensitive to nitrate solute ratio relative to Fujifilm AEMs. This trend in Neosepta AEMs is the inverse of that in Neosepta CEMs, which appear more sensitive to monovalent and less sensitive to divalent cations. No trends in phosphate transport number with solute ratio are observed, because phosphate transport number is calculated based on minor changes in measured ion

concentration (e.g., $\Delta C_{PO4^{3-}} = 1.5$ mg/L on average for Comp 5).

Consistent with trends in the literature [18], the sums of the monovalent transport T_{NO3} and of the multivalent transport $T_{SO4+PO4}$ inversely vary with total monovalent solute ratio r_{NO3} (Fig. 14). At a given monovalent solute ratio (i.e., effluent composition), a higher monovalent transport corresponds to a lower divalent transport, because the sum of the anion transport numbers is equivalent to a relatively fixed transport efficiency across compositions: $T_{anion,Fujifilm} = 0.51 \pm 0.04$ and $T_{anion,Neosepta} = 0.60 \pm 0.03$. The difference in these values suggests that Neosepta AEMs have a greater capacity than Fujifilm AEMs over a given amount of time for anion transport, similar to Neosepta CEM capacity.

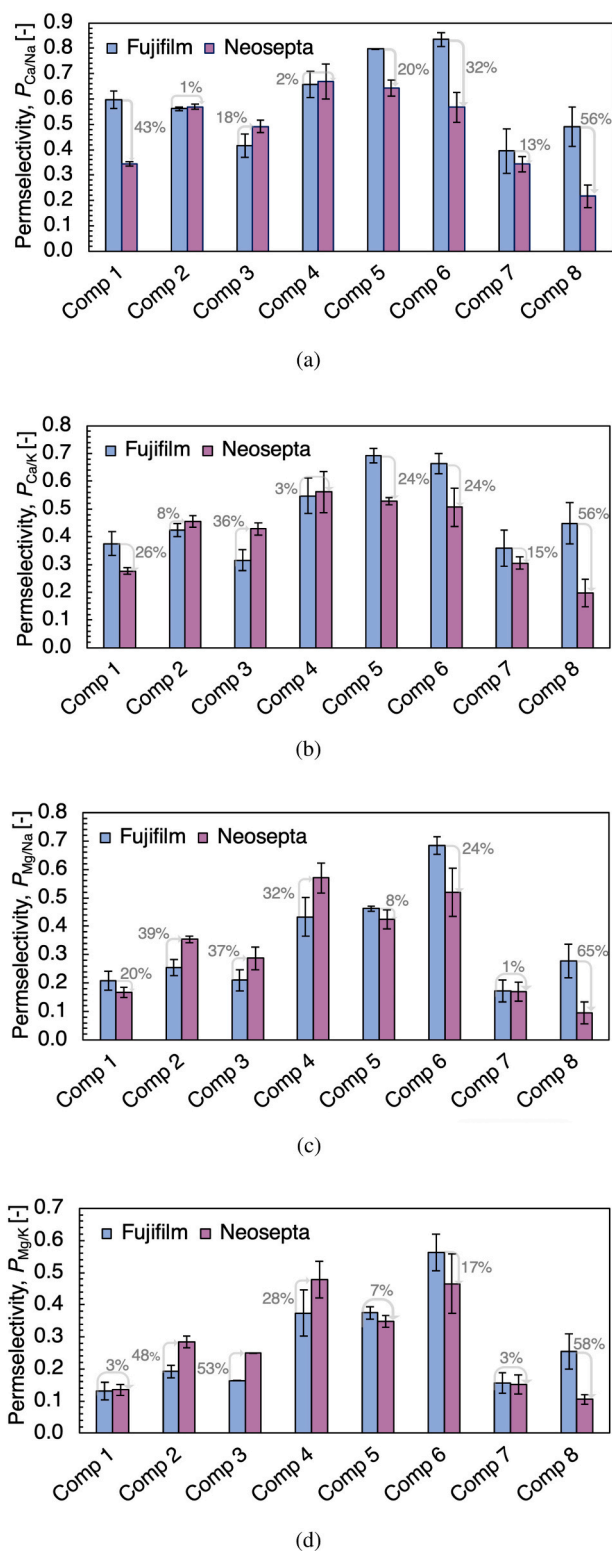


Fig. 8. Comparison of Fujifilm and Neosepta CEM permselectivity for (a) calcium relative to sodium, (b) calcium relative to potassium, (c) magnesium relative to sodium, and (d) magnesium relative to potassium, including percent difference between membrane performance. A lower permselectivity value corresponds to better membrane performance.

3.2.3. AEM permselectivity

Neosepta and Fujifilm AEMs demonstrate selectivity towards monovalent nitrate for six effluent compositions (Table C.3) and thus potential for MSED adoption by greenhouses as effectively a pretreatment step to the typical denitrification process of greenhouse wastewater. Across compositions, Fujifilm AEMs remove a factor of 2.3–6.5 more nitrate than sulfate and 1.1–4.0 more nitrate than phosphate. Neosepta AEMs remove a factor of 2.3–6.4 more nitrate than sulfate and 4.6–7.1 more nitrate than phosphate. Fig. 15 illustrates the breakdown of Neosepta and Fujifilm anion permselectivity by effluent composition. Neosepta AEMs demonstrate better monovalent selectivity than Fujifilm AEMs for sulfate relative to nitrate for three effluent compositions (Comp 1, Comp 4, Comp 6), comparable selectivity for one composition (Comp 5), and inferior selectivity for one composition (Comp 2). Neosepta AEMs also show better monovalent selectivity for phosphate relative to nitrate for all four tested effluent compositions (Comp 2, Comp 4, Comp 5, Comp 6). As with the CEMs, disparities in Fujifilm and Neosepta AEM performance for the tested effluent compositions may result from differences in intrinsic membrane properties.

Fig. 16 shows linear trends in sulfate permselectivity with nitrate solute ratio for Fujifilm AEMs ($r^2 = 0.97$) and Neosepta AEMs ($r^2 = 0.72$) and no trends in phosphate permselectivity as a result of its presence in low concentrations. This trend differs from the CEMs, which do not exhibit a linear relationship between permselectivity and solute ratio with the exception of calcium relative to sodium permselectivity ($r^2 = 0.68$). A possible explanation for this disparity in behavior is the influence of competitive monovalent transport on permselectivity trends. The greenhouse effluents tested on the AEMs contain one monovalent ion (NO_3^-), while those tested on the CEMs contain two monovalent ions (Na^+ , K^+). In previous studies [20,21], we similarly found a linear relationship between solute ratio and permselectivity for Neosepta and Fujifilm AEMs and CEMs tested on brackish feedwaters composed of one monovalent cation and anion (Na^+ , Cl^- , Ca^{2+} , Mg^{2+} , SO_4^{2-}). Analyzed waters containing one monovalent anion and/or cation (i.e., brackish feedwaters tested on CEMs and AEMs, greenhouse effluents tested on AEMs) also demonstrate superior monovalent selectivity relative to waters containing two monovalent cations (i.e., greenhouse effluents tested on CEMs) in which these ions compete for migration across the membranes (Fig. 10). Additional feedwaters should be investigated to conclusively determine the influence of competitive monovalent transport on permselectivity. Furthermore, the AEMs exhibit inferior monovalent selectivity on average when treating wastewater compared to brackish water, although the AEM disparity is smaller than that of the CEM (Fig. 17). The salinity range of wastewater and brackish water is comparable. Consequently, these trends suggest that the Fujifilm and Neosepta membranes are less tolerant of nitrate, potassium and phosphate, which are not primary constituents in brackish water.

4. Implications

A broad decision-making framework regarding the usefulness of MSED for effluent treatment in a given greenhouse is shown in Fig. 18. The primary consideration is whether a greenhouse has or is striving to implement MLD. A variety of factors impact the incentive for and degree of difficulty in MLD implementation. Source water composition, soil composition, and crop type influence greenhouse effluent composition and subsequent treatment requirements to enable reuse. Technology advancements impact the optimization and control of greenhouse operations. Brine regulations motivate greenhouses to reduce the volume of water and pollutant levels before discharge into the environment. Because these factors largely vary by geography, location is a key indicator of possible hurdles to or incentives for 100% reuse. For instance, TDS and ionic composition of brackish groundwater (BGW), often source water for greenhouses, differ notably with location (Fig. 19(a) and (c)); BGW may contribute to soil salinization and higher concentrations of problematic constituents in greenhouse effluent particularly

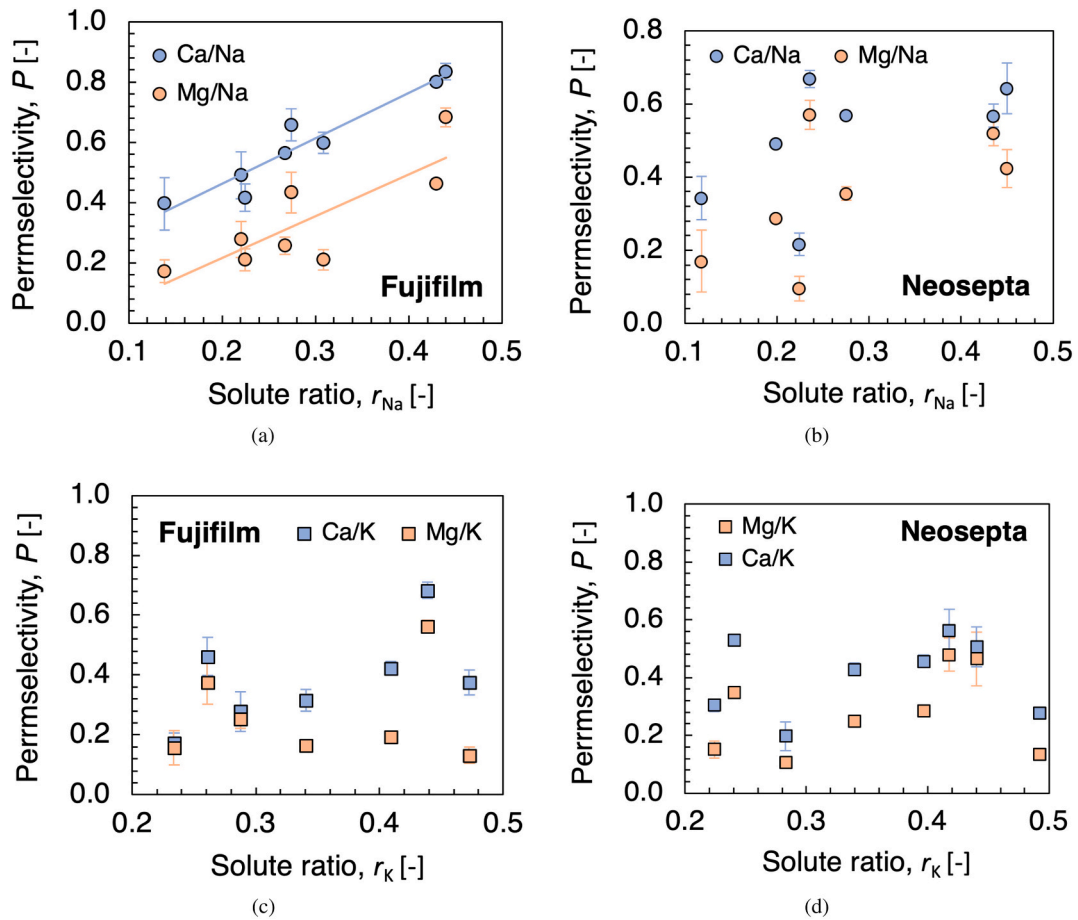


Fig. 9. Calcium and magnesium selectivity as function of sodium and potassium solute ratios for Fujifilm and Neosepta CEMs. These trends are also observed when calcium and magnesium selectivity are plotted as a function of total monovalent solute ratio (i.e., r_{Na+K}).

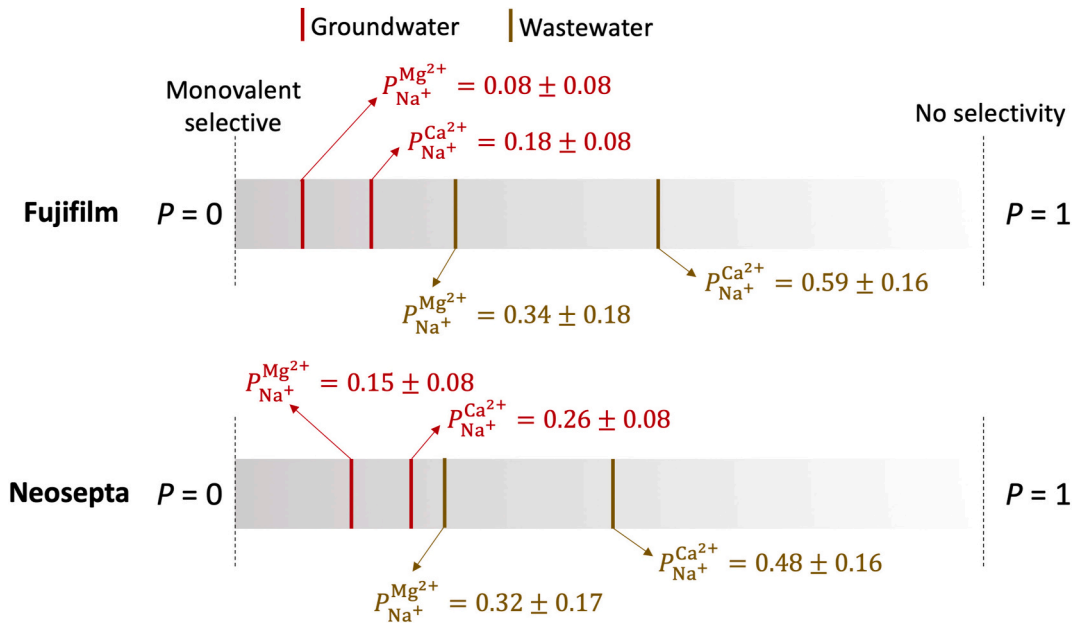


Fig. 10. Comparison of average permselectivity values for 16 brackish groundwater compositions (red) [20,21] and 8 wastewater compositions (brown) for Fujifilm and Neosepta CEMs. A lower permselectivity corresponds to greater monovalent selectivity and membrane performance.

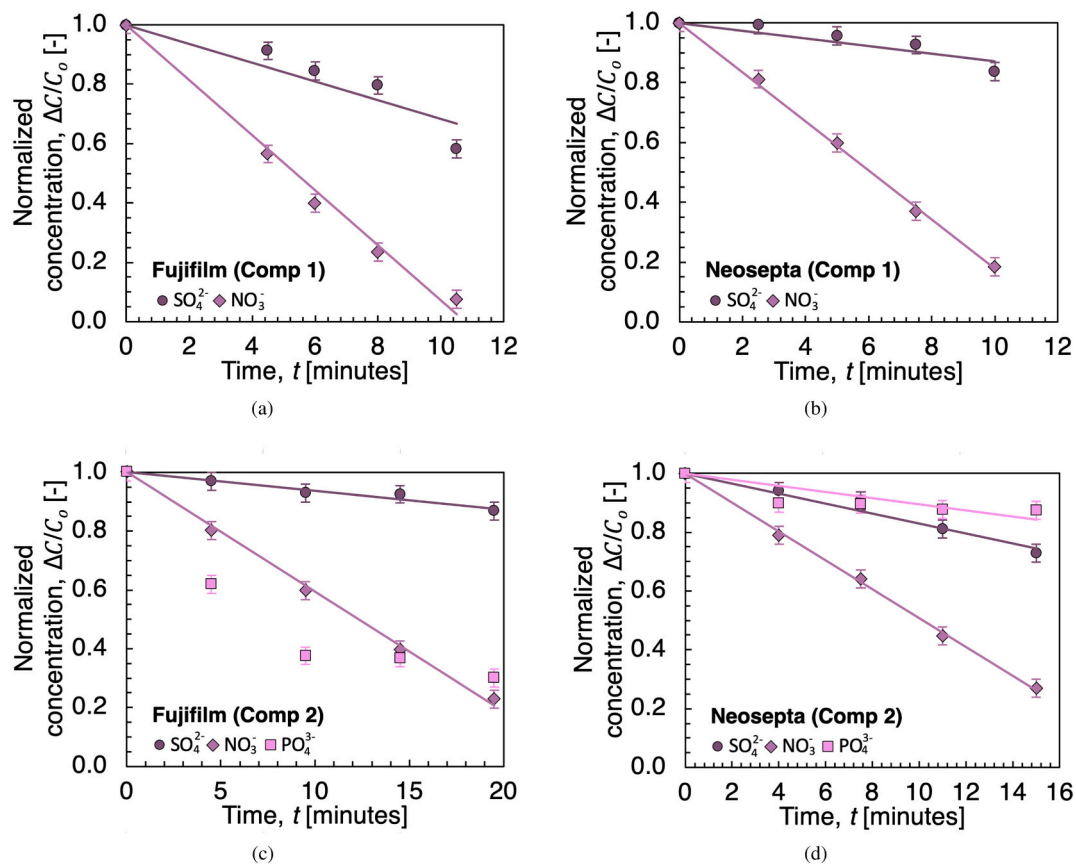


Fig. 11. Normalized anion concentration (NO_3^- , SO_4^{2-} , PO_4^{3-}) of Neosepta and Fujifilm AEMs as a function of desalination process time for two effluent compositions (Comp 1, Comp 2). Comp 2 contains phosphate in addition to sulfate and nitrate.

if untreated [45,4]. Fig. 19(b) reflects the overlap of some major greenhouses in California with brackish source water. In addition, compared to other regions, the Netherlands greenhouse sector is very technologically advanced [37] and has largely achieved MLD [38].

Based on greenhouse MLD capacity, we identify three potential avenues for MSED adoption, as shown in Fig. 18:

1. A greenhouse utilizes RO in the recirculation loop to remove sodium in order to achieve MLD: MSED may serve as a desalination technology replacement that removes detrimental monovalent ion constituents (Na^+) while retaining secondary nutrients (Ca^{2+} , Mg^{2+} , SO_4^{2-}) that would otherwise be removed by RO and have to be reintroduced as fertilizer in source water. A complete investigation of the trade-offs between MSED and RO adoption is necessary to determine the MSED payback period. MSED costs include higher capital and operating expenses. MSED benefits include desalination brine reduction due to its higher recovery operation of over 90% compared to RO's 80% [7] and fertilizer savings due to its nutrient retention ability depending on membrane type. The experimentally determined membrane permselectivities in this study may be used to provide a first-round approximation of fertilizer savings and sodium reduction.
2. A greenhouse does not use any desalination treatment and experiences sodium accumulation as the biggest barrier to wastewater reuse: similar to avenue 1, MSED may remove sodium while retaining secondary nutrients, thereby increasing water and fertilizer savings. In this case, the costs of not reusing wastewater (i.e., of sodium accumulation) would be weighed against the MSED capital and operating costs and savings.
3. A greenhouse disposes of wastewater containing problematic levels of nitrate: MSED may serve as a more cost-effective alternative to the

conventional denitrification processes by reducing capital and operating expenses [8]. A cost-benefit analysis accounting for the difference in MSED and conventional expenses must be conducted to quantify the feasibility of MSED adoption. The experimentally determined AEM permselectivities in this study may be used to provide a first-round approximation of nitrate reduction.

In all three cases, the nitrate-rich brine stream generated by MSED may provide the possibility of recovering nitrate as concentrate for fertilizer use [9]. Depending on future work around nitrate recovery, the cost and benefits of this process would also need to be included in the techno-economic analyses.

Should a greenhouse opt to implement MSED, both the Neosepta ACS/CMS and Fujifilm Type 16 MSED membranes show potential to further optimize greenhouse operations through sodium removal, particularly relative to magnesium, and nitrate removal. While the Neosepta membranes overall demonstrate moderately superior selectivity for sodium and nitrate relative to the Fujifilm membranes, the Neosepta membranes cost substantially more than the Fujifilm membranes at the lab scale ($A_m < 10 \text{ m}^2$): Fujifilm cost per membrane area is approximately $\$162/\text{m}^2$ [39] in comparison to Neosepta membrane cost of $\$503/\text{m}^2$ [40]. This significant price difference, relative to the moderate difference in membrane performance, preliminarily suggests that the Fujifilm membranes may have a competitive edge over the Neosepta membranes. Pilot scale testing and a detailed techno-economic analysis must be conducted to verify this hypothesis.

5. Conclusions

Neosepta ACS/CMS and Fujifilm Type 16 MSED membranes were tested on eight model greenhouse effluent solutions to characterize

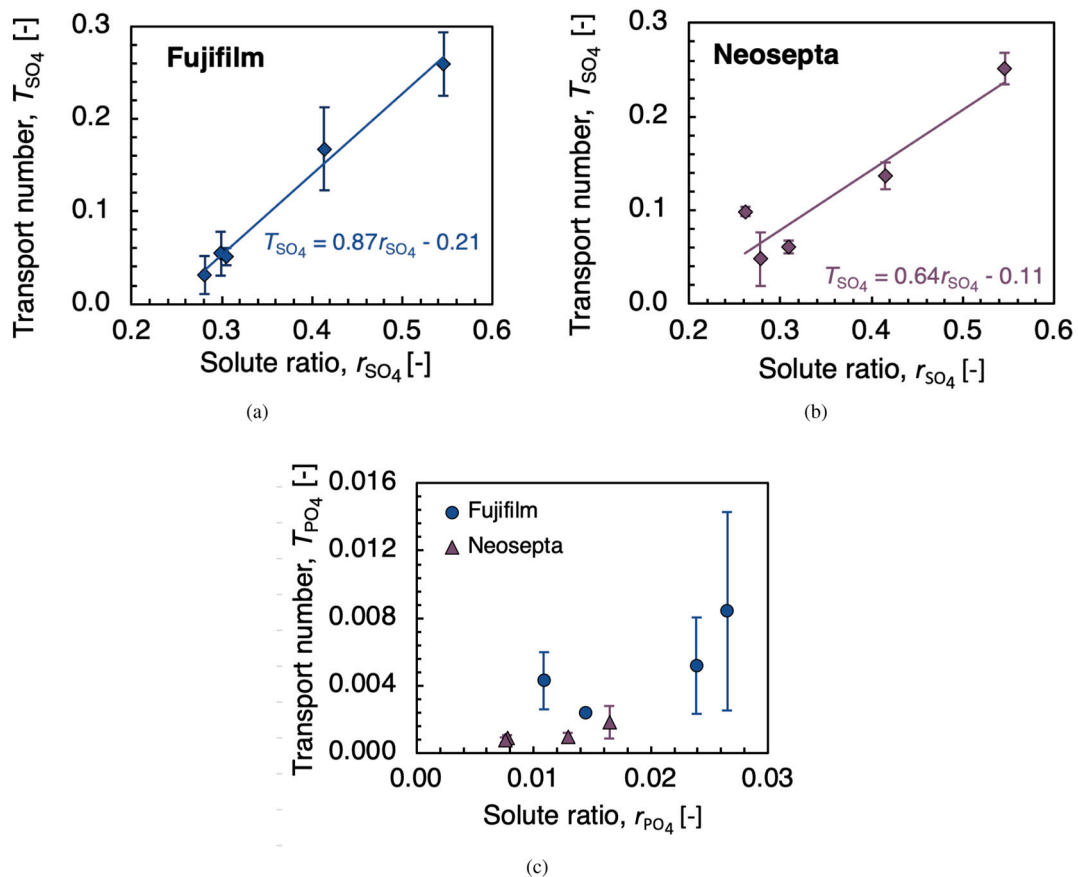


Fig. 12. Multivalent anion transport numbers of sulfate and phosphate as a function of anion solute ratio for Fujifilm and Neosepta AEMs.

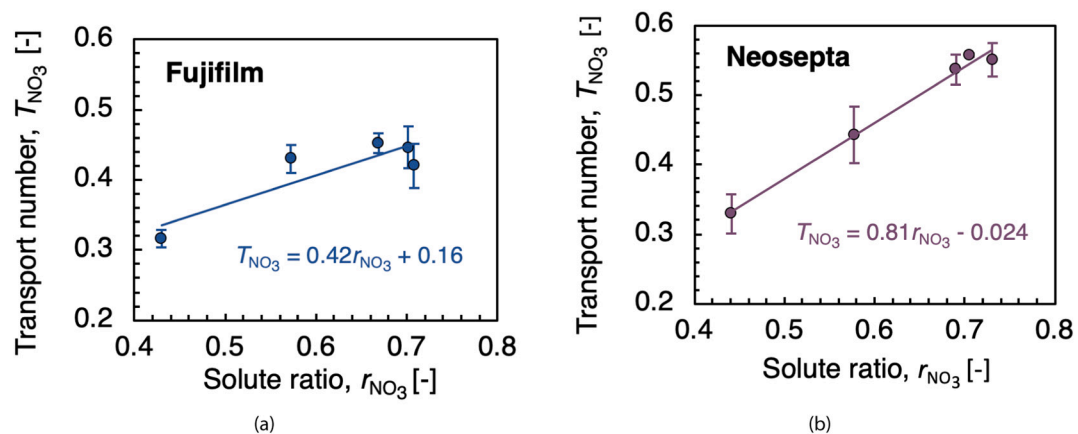


Fig. 13. Monovalent anion transport number of nitrate as a function of nitrate solute ratio for Fujifilm and Neosepta AEMs.

membrane selectivity and the potential to treat greenhouse wastewater for reuse (i.e., sodium removal) or disposal (i.e., nitrate removal). The following conclusions have been reached:

1. Across the tested greenhouse effluents, the Neosepta CEMs remove 1.6 to 3.2 sodium ions for every calcium ion and 2.4 to 7.6 sodium ions for every magnesium ion. The Neosepta AEMs remove 2.3 to 6.4 nitrate ions for every sulfate ion and 4.6 to 7.1 nitrate ions for every phosphate ion.
2. Across the tested greenhouse effluents, the Fujifilm CEMs remove 1.3 to 2.3 sodium ions for every calcium ion and 2.0 to 6.2 sodium ions for every magnesium ion. The Fujifilm AEMs remove 2.3 to 6.5

nitrate ions for every sulfate ion and 1.1 to 4.0 nitrate ions for every phosphate ion.

3. The Neosepta membranes demonstrate moderately superior selectivity overall relative to the Fujifilm membranes. The significant difference in capital costs of the membranes, despite the minimal difference in performance, at the bench-scale indicates that the Fujifilm membranes may be a more desirable choice for greenhouses adopting MSED.
4. The three cases that demonstrate potential for MSED adoption in greenhouse effluent treatment are: 1) greenhouses that use RO for sodium reduction in wastewater to achieve MLD; 2) greenhouses that do not use a desalination technology but sodium accumulation in

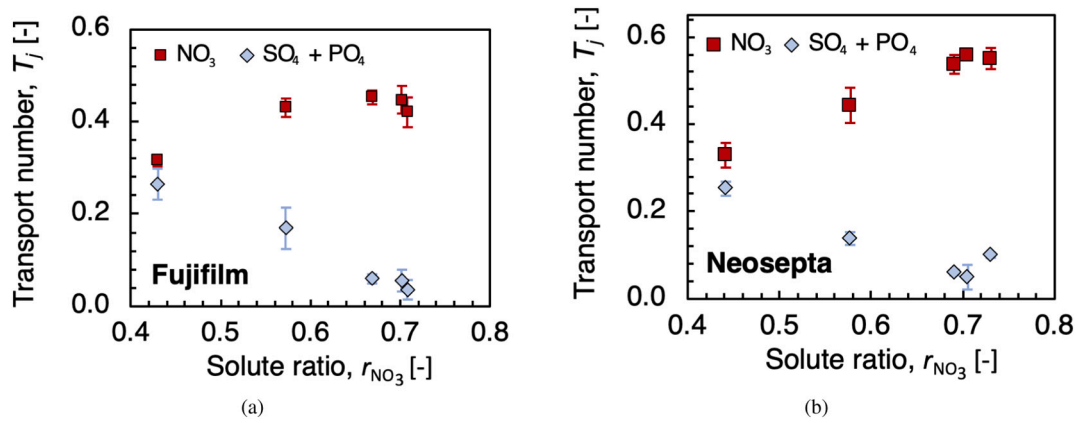


Fig. 14. Sum of monovalent (T_{NO_3}) and multivalent ($T_{SO_4+PO_4}$) transport numbers as a function of the total monovalent solute ratio (r_{NO_3}) for Fujifilm and Neosepta AEMs.

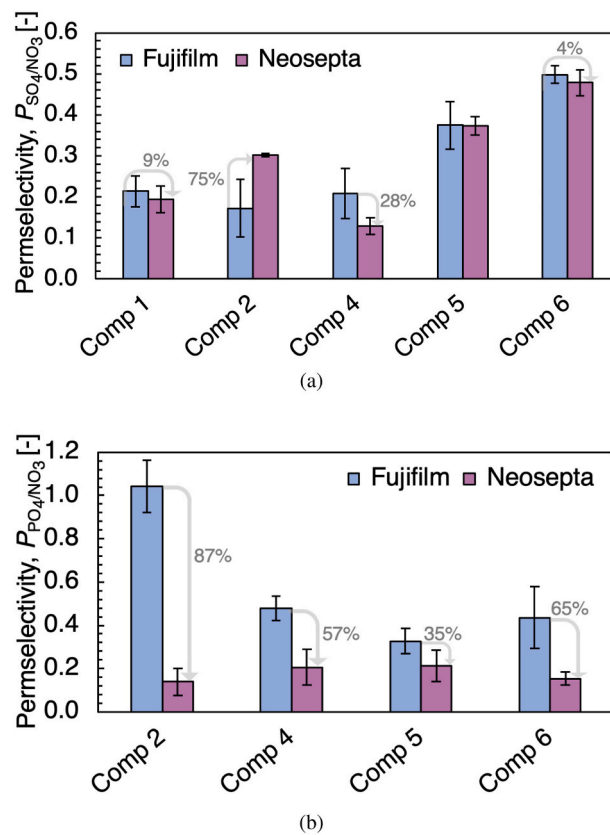


Fig. 15. Comparison of Fujifilm and Neosepta AEM permselectivity for (a) sulfate relative to nitrate and (b) phosphate relative to nitrate, including percent difference between membrane performance.

wastewater prevents 100% reuse; and 3) greenhouses with high levels of nitrate in wastewater to be discharged. Detailed cost-benefit analyses of these three scenarios must be conducted in order to quantify the economic feasibility of MSED for greenhouses. The monovalent selectivities measured in this study may serve as the basis for estimating sodium and nitrate reduction, as well as fertilizer savings, offered by MSED.

CRedit authorship contribution statement

Yvana Ahdab: Conceptualization, Methodology, Validation, Formal

analysis, Investigation, Writing, Visualization.

Georg Schikking: Validation, Investigation, Writing – Review & Editing, Visualization.

Danyal Rehman: Conceptualization, Writing – Review & Editing.

John Lienhard: Supervision, Writing – Review & Editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

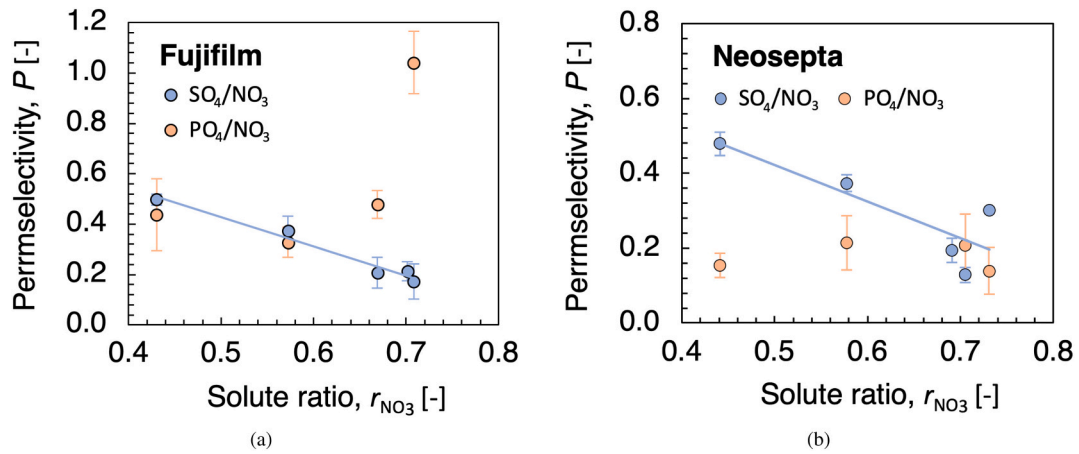


Fig. 16. Sulfate and phosphate selectivity as function of nitrate solute ratio for Fujifilm and Neosepta AEMs.

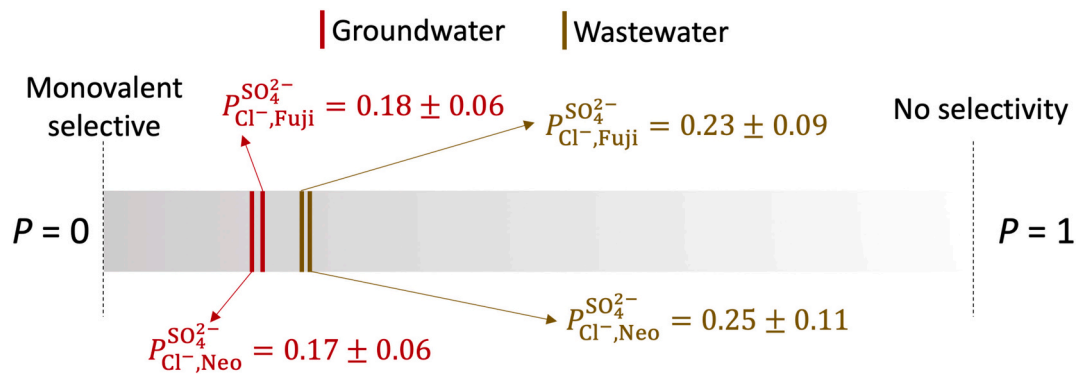


Fig. 17. Comparison of average permselectivity values for 16 brackish groundwater compositions (red) [20,21] and 8 wastewater compositions (brown) for Fujifilm (Fuji) and Neosepta (Neo) AEMs. A lower permselectivity corresponds to greater monovalent selectivity and membrane performance.

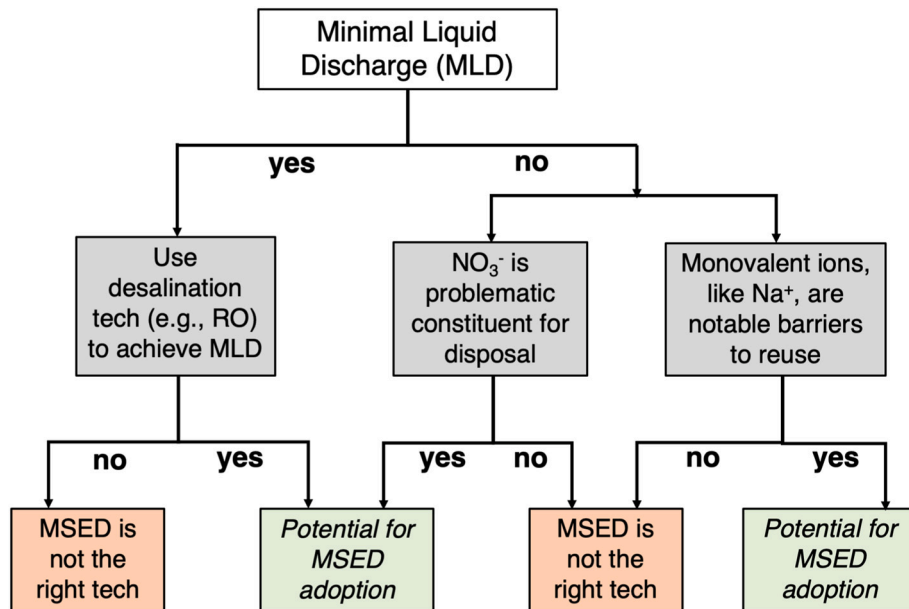


Fig. 18. Flowchart providing a decision-making framework for greenhouses regarding the potential of MSED adoption for wastewater treatment for reuse or disposal.

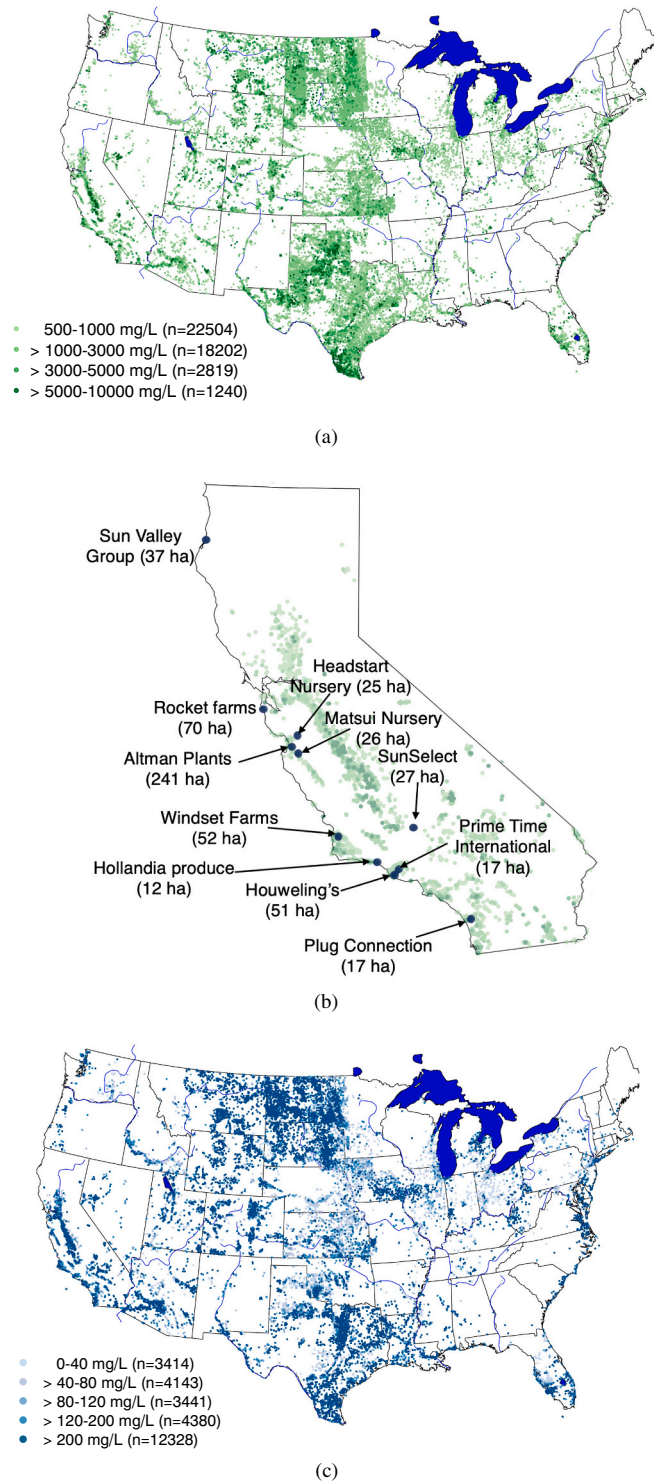


Fig. 19. (a) TDS of 45,000 brackish groundwater samples across the U.S., (b) TDS of BGW samples overlaid with selected major greenhouses in California, and (c) sodium levels in 28,000 BGW samples across the U.S. Each dot corresponds to a sample. Data was acquired from the U.S. Geological Survey [41] and GreenhouseGrower.com [42].

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Appendix A. Limiting current density and membrane resistance

This section includes results for the limiting current density and membrane resistance of the Neosepta and Fujifilm membranes that were determined in our previous studies on MSED groundwater desalination [20,21].

A.1. Methods

We model the MSED stack as an electric circuit comprised of ohmic terms \bar{R} , Donnan potentials E_{AEM} and E_{CEM} , and electrode potential V_{el} :

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

where N_{cp} is number of cell pairs, r denotes the rinse solution, and σ denotes a spacer shadow effect of 0.72 ± 0.09 [21]. 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. Because greenhouse effluent composition varies, the membrane resistance and limiting current density will not be known for every effluent that might enter an MSED system. Therefore, we evaluate these parameters for NaCl solutions with comparable salinities. The NaCl results serve as a lower bound on membrane resistance and limiting current density of a more general, multi-ionic effluent composition.

At each conductivity, the membrane resistance was determined using the slope of a linear fit of V_{stack} versus the applied current from Eq. (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 Brown method [43] 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.

A.2. Results

Membrane resistance is usually determined at standard conditions, i.e., in 0.5 M (29 g/kg) NaCl solution [33]. However, greenhouse effluent typically contains a much lower salinity (1.5–3.5 g/kg). Consequently, we evaluate Neosepta and Fujifilm membrane resistance for NaCl solutions ranging from 0.8–10 g/L. Consistent with the literature [33,34], we observe that membrane resistance sharply increases with decreasing salinity (Fig. A.1), suggesting that resistive losses in the MSED stack are greater in more dilute solutions [44]. 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.

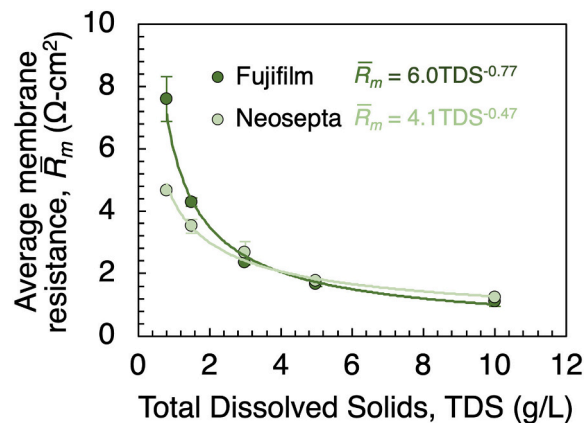


Fig. A.1. CEM and AEM resistance of Neosepta and Fujifilm membranes for NaCl solutions containing TDS ranging from 0.8–10 g/L. Values obtained for Neosepta match those in the literature ($\bar{R}_m = 1.8 - 3.8 \Omega\text{-cm}^2$) [18].

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. The limiting current density for NaCl solutions represents a minimum of that of any multi-ionic effluent composition, due to the presence of additional cations other than sodium in wastewater that carry the current. Fig. A.2 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.

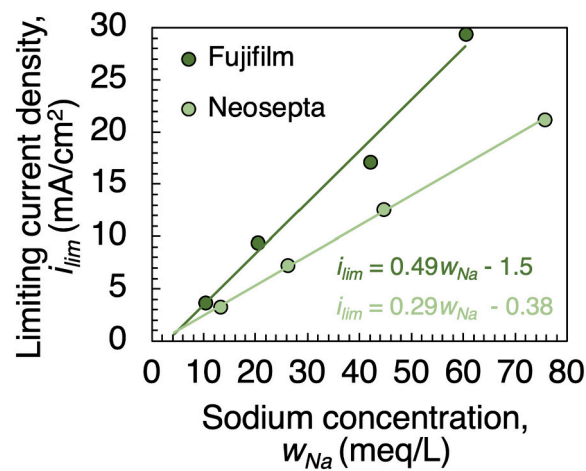


Fig. A.2. Limiting current density of Neosepta and Fujifilm membranes as a function of sodium concentration in the diluate for various dilutions of NaCl solutions.

Appendix B. Analyzed greenhouse effluent feedwater and desalinated product water compositions

Figs. B.1 and B.2 include feedwater and product water composition breakdowns of Comps 1–6 by cations and anions for Fujifilm and Neosepta membranes, respectively.

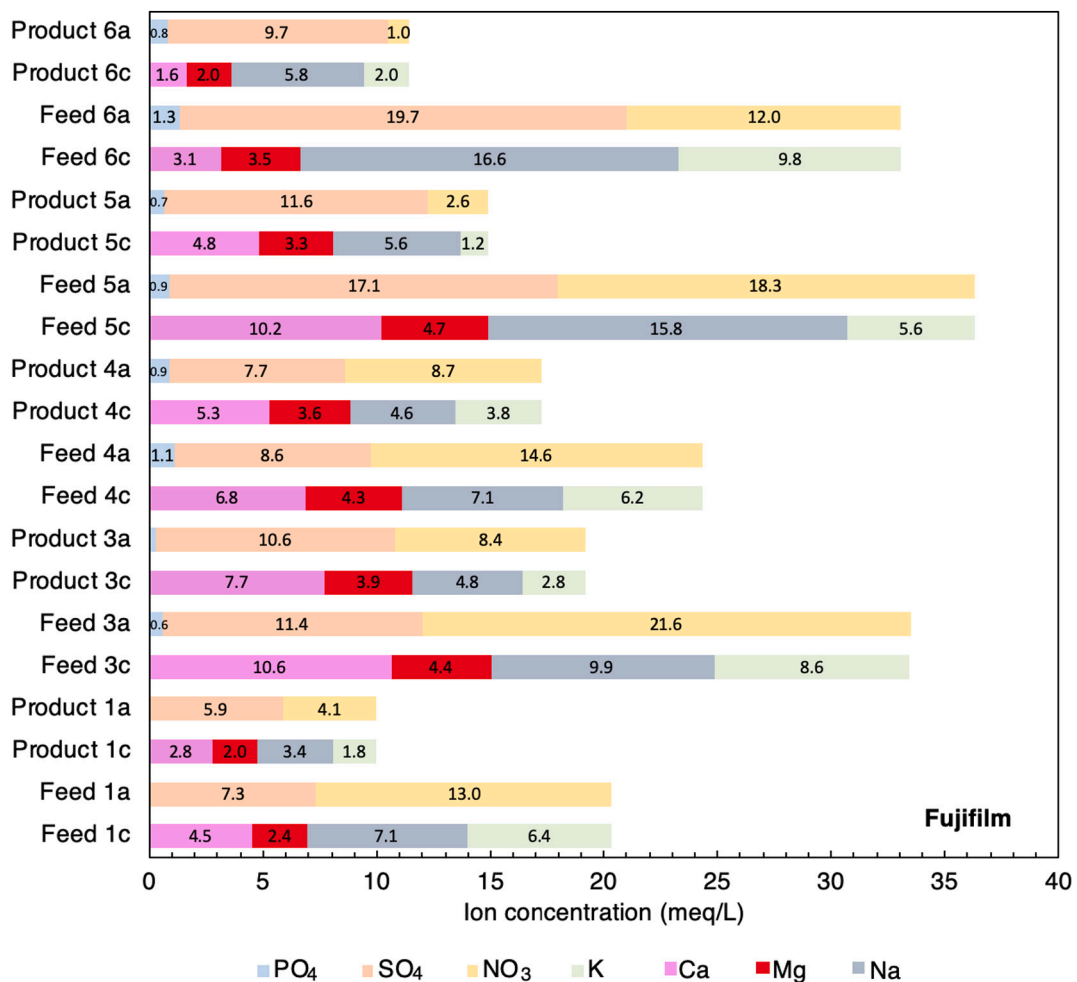


Fig. B.1. Ionic composition breakdown of Comps 1–6 for Fujifilm Neosepta membranes. Feed indicates feedwater composition. Product indicates product water composition. Cations and anions correspond to c and a, respectively.

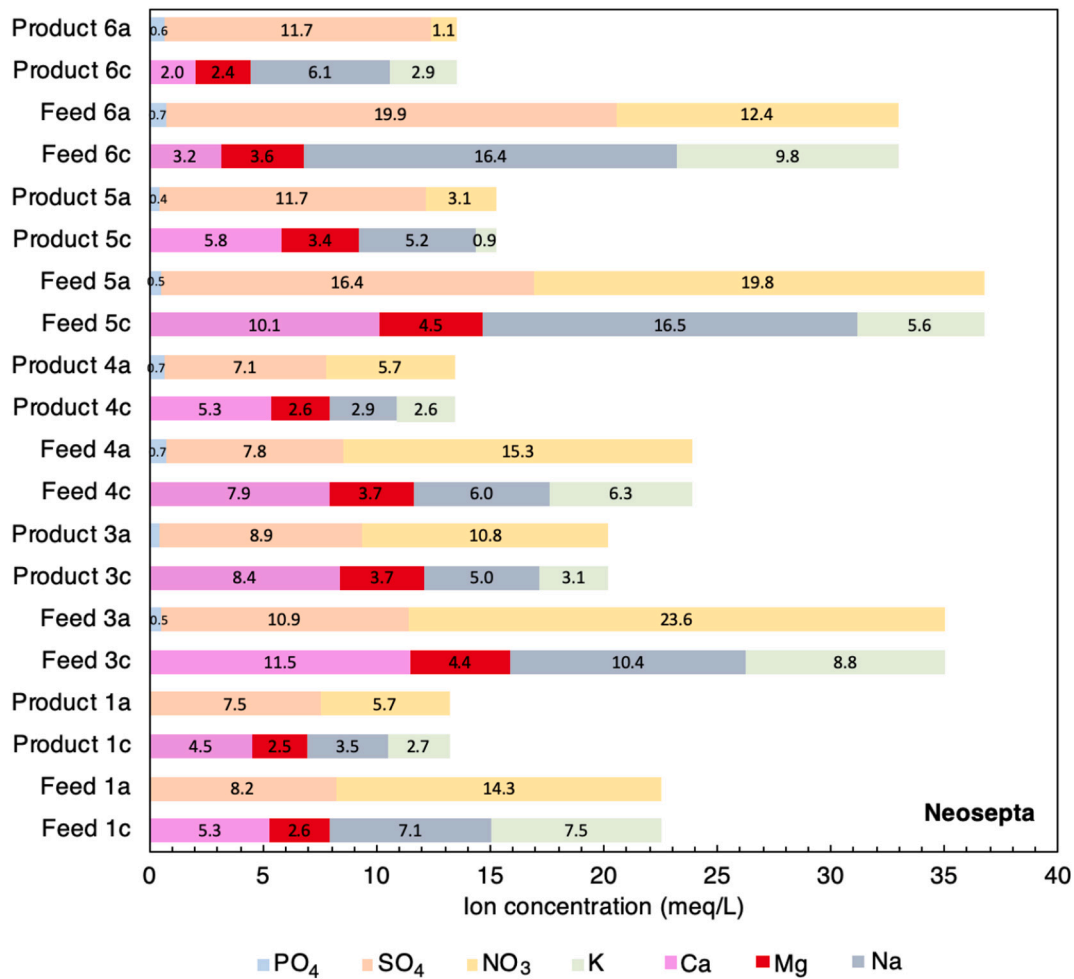


Fig. B.2. Ionic composition breakdown of Comps 1–6 for Neosepta membranes. Feed indicates feedwater composition. Product indicates product water composition. Cations and anions correspond to c and a, respectively.

Appendix C. Additional permselectivity results

This appendix contains numerical values of permselectivity and permselectivity trends with solute ratio defined on an equivalent concentration basis.

C.1. Permselectivity values

Tables C.1–C.3 include permselectivity values for all tested effluent compositions.

Table C.1

Permselectivity of calcium and magnesium relative to sodium and potassium of Fujifilm CEMs for eight effluent compositions. We define an additional permselectivity of monovalent potassium, a nutrient for crops, relative to monovalent sodium as $P_{Na^+}^{K^+} \equiv \frac{T_K/w_{K,o}}{T_{Na^+}/w_{Na,o}}$; a $P_{Na^+}^{K^+}$ value greater than one indicates more potassium than sodium ions are removed.

| Composition | $P_{Na^+}^{Ca}$ | $P_{Na^+}^{Mg}$ | P_K^{Ca} | P_K^{Mg} | $P_{Na^+}^K$ |
|-------------|-----------------|-----------------|-------------|-------------|--------------|
| Comp 1 | 0.60 ± 0.06 | 0.21 ± 0.03 | 0.38 ± 0.04 | 0.13 ± 0.03 | 1.59 ± 0.24 |
| Comp 2 | 0.56 ± 0.02 | 0.26 ± 0.03 | 0.42 ± 0.03 | 0.19 ± 0.03 | 1.33 ± 0.03 |
| Comp 3 | 0.42 ± 0.05 | 0.16 ± 0.04 | 0.16 ± 0.04 | 0.23 ± 0.01 | 1.32 ± 0.18 |
| Comp 4 | 0.66 ± 0.05 | 0.43 ± 0.07 | 0.55 ± 0.06 | 0.37 ± 0.07 | 1.20 ± 0.26 |
| Comp 5 | 0.80 ± 0.002 | 0.46 ± 0.01 | 0.69 ± 0.03 | 0.37 ± 0.02 | 1.15 ± 0.11 |
| Comp 6 | 0.83 ± 0.03 | 0.68 ± 0.03 | 0.66 ± 0.04 | 0.56 ± 0.06 | 1.26 ± 0.14 |
| Comp 7 | 0.40 ± 0.09 | 0.17 ± 0.04 | 0.36 ± 0.07 | 0.16 ± 0.03 | 1.10 ± 0.26 |
| Comp 8 | 0.49 ± 0.08 | 0.28 ± 0.06 | 0.45 ± 0.07 | 0.25 ± 0.06 | 1.09 ± 0.30 |

Table C.2

Permselectivity of calcium and magnesium relative to sodium and potassium of Neosepta CEMs for eight effluent compositions. We define an additional permselectivity of monovalent potassium, a nutrient for crops, relative to monovalent sodium as $P_{Na^+}^{K^+} \equiv \frac{T_K/W_{K,o}}{T_{Na}/W_{Na,o}}$; a $P_{Na^+}^{K^+}$ value greater than one indicates more potassium than sodium ions are removed.

| Composition | $P_{Na^+}^{Ca}$ | $P_{Na^+}^{Mg}$ | $P_{K^+}^{Ca}$ | $P_{K^+}^{Mg}$ | $P_{Na^+}^{K^+}$ |
|-------------|-----------------|-----------------|----------------|----------------|------------------|
| Comp 1 | 0.34 ± 0.01 | 0.17 ± 0.02 | 0.28 ± 0.01 | 0.13 ± 0.02 | 1.24 ± 0.04 |
| Comp 2 | 0.57 ± 0.01 | 0.35 ± 0.01 | 0.46 ± 0.02 | 0.28 ± 0.02 | 1.25 ± 0.08 |
| Comp 3 | 0.49 ± 0.02 | 0.29 ± 0.04 | 0.43 ± 0.02 | 0.25 ± 0.01 | 1.15 ± 0.29 |
| Comp 4 | 0.67 ± 0.07 | 0.57 ± 0.05 | 0.56 ± 0.07 | 0.48 ± 0.06 | 1.19 ± 0.06 |
| Comp 5 | 0.64 ± 0.03 | 0.42 ± 0.03 | 0.53 ± 0.01 | 0.35 ± 0.02 | 1.22 ± 0.13 |
| Comp 6 | 0.57 ± 0.06 | 0.52 ± 0.09 | 0.52 ± 0.07 | 0.46 ± 0.09 | 1.12 ± 0.37 |
| Comp 7 | 0.34 ± 0.03 | 0.17 ± 0.03 | 0.30 ± 0.02 | 0.15 ± 0.03 | 1.12 ± 0.12 |
| Comp 8 | 0.22 ± 0.04 | 0.10 ± 0.04 | 0.20 ± 0.05 | 0.11 ± 0.02 | 1.10 ± 0.18 |

Table C.3

Permselectivity of sodium and phosphate relative to nitrate of Fujifilm and Neosepta AEMs for 5 effluent compositions. Phosphate permselectivity is evaluated based on small changes in measured ion concentration (e.g., $\Delta C_{PO_4^{3-}} = 1.5$ mg/L on average for Comp 5), which may account for the Fujifilm $P_{SO_4^{2-}}^{NO_3^-}$ outlier for Comp 2. Comp 1 does not contain any phosphate.

| Composition | Fujifilm | | Neosepta | |
|-------------|--------------------------|--------------------------|--------------------------|--------------------------|
| | $P_{SO_4^{2-}}^{NO_3^-}$ | $P_{PO_4^{3-}}^{NO_3^-}$ | $P_{SO_4^{2-}}^{NO_3^-}$ | $P_{PO_4^{3-}}^{NO_3^-}$ |
| Comp 1 | 0.21 ± 0.03 | 0 | 0.20 ± 0.03 | 0 |
| Comp 2 | 0.17 ± 0.07 | 1.04 ± 0.12 | 0.30 ± 0.01 | 0.14 ± 0.06 |
| Comp 4 | 0.21 ± 0.06 | 0.48 ± 0.06 | 0.13 ± 0.02 | 0.21 ± 0.08 |
| Comp 5 | 0.37 ± 0.06 | 0.33 ± 0.06 | 0.37 ± 0.02 | 0.21 ± 0.07 |
| Comp 6 | 0.50 ± 0.02 | 0.44 ± 0.14 | 0.48 ± 0.03 | 0.15 ± 0.03 |

C.2. Permselectivity trends on an equivalent concentration basis

We define cation solute ratio $r_{j^+, \text{meq}}$ and anion solute ratio $r_{j^-, \text{meq}}$ on an equivalent concentration basis as:

$$r_{j^+, \text{meq}} = \frac{w_{j^+}}{\sum_{j^+} w_{j^+}} \quad (\text{C.1})$$

$$r_{j^-, \text{meq}} = \frac{w_{j^-}}{\sum_{j^-} w_{j^-}} \quad (\text{C.2})$$

where j^+ represents each cation species, j^- represents each anion species, and w denotes ion concentration in the diluate in meq/L. For wastewater compositions considered in this study, the correlation coefficients of solute ratio calculated using C_j (mass basis) and w_j (equivalent basis) is equal to 1 for anions and is greater than 0.97 for cations. Consequently, observed trends as a function of solute ratio are the same using either concentration basis. Figs. C.1 and C.2 show permselectivity as a function of solute ratio based on equivalent concentration.

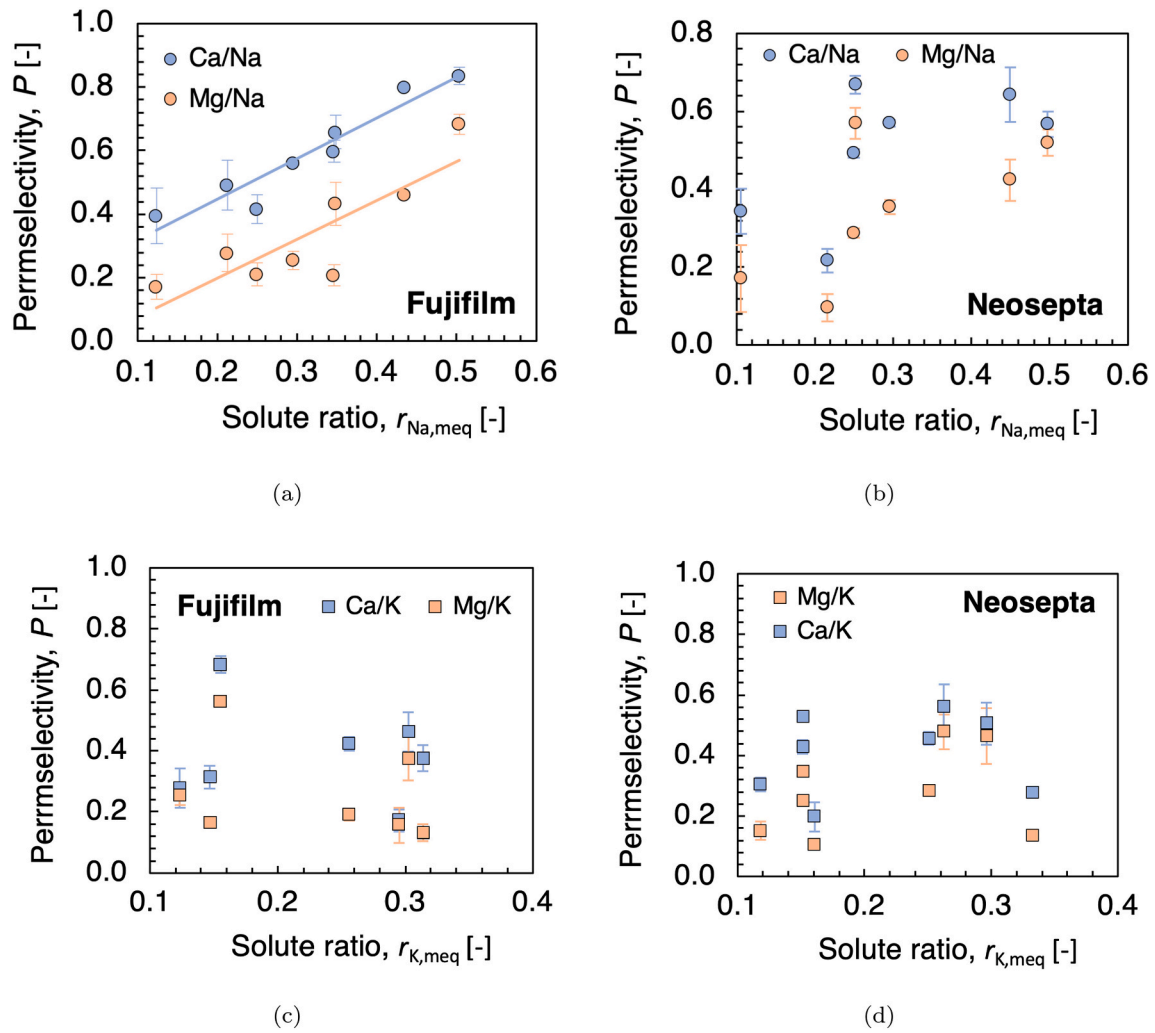


Fig. C.1. Calcium and magnesium selectivity as function of sodium and potassium solute ratios, derived from equivalent concentrations, for Fujifilm and Neosepta CEMs. These trends are also observed when calcium and magnesium selectivity are plotted as a function of total monovalent solute ratio (i.e., r_{Na+K}).

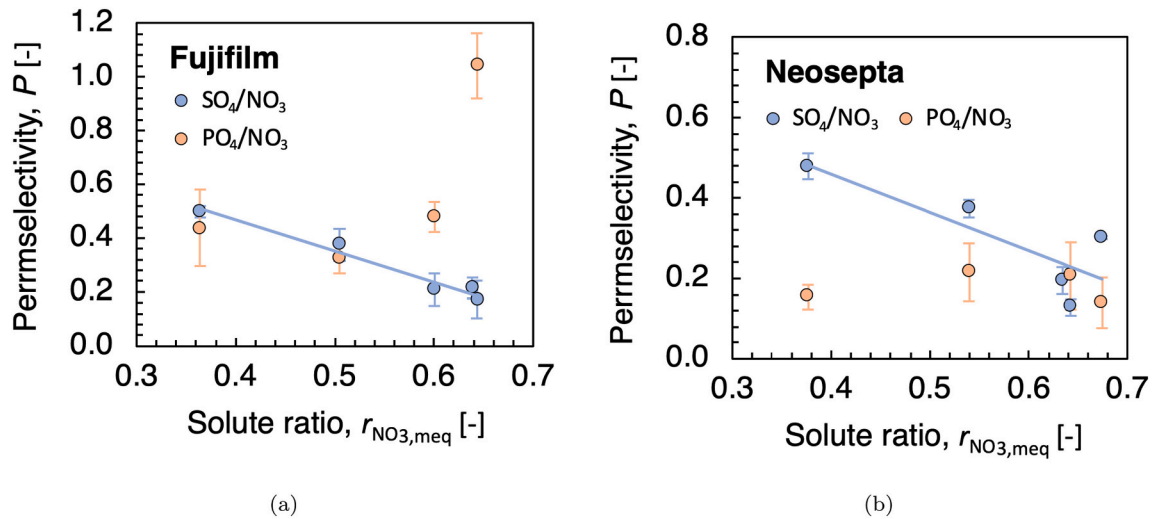


Fig. C.2. Sulfate and phosphate selectivity as function of nitrate solute ratio, derived from equivalent concentrations, for Fujifilm and Neosepta AEMs.

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