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Letter

Integrating Divalent-Selective Electrodialysis in Brackish Water Desalination

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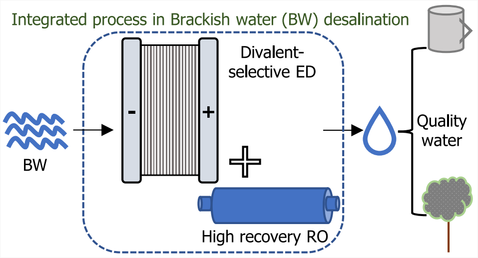

ABSTRACT: Brackish water desalination is imperative for meeting water demands in arid regions far from the seashore. Reverse osmosis, the leading desalination technology, removes nearly all calcium and magnesium ions, which are essential in drinking and irrigation water. Multistep process schemes combining reverse osmosis with ion-selective membrane processes can maintain or reintroduce these minerals without external chemical addition. Previous efforts emphasized membrane processes that retain multivalent ions, focusing primarily on nanofiltration and monovalent-selective electrodialysis. The potential of processes where monovalent ions are retained and divalent preferentially transported through the membrane has not been studied systematically. Here, we explored applying divalent-selective electrodialysis to transfer calcium and magnesium from the influent into the brackish water reverse osmosis permeate. This novel concept enables chemical-free remineralization of the reverse osmosis permeate while reducing membrane scaling by sparingly soluble calcium salts. We tested this concept experimentally using commercial membranes and natural brackish water, evaluated the product water based on quality criteria for domestic and agricultural use, and assessed the techno-economic feasibility. We found that water suitable for potable use and irrigation can be attained at a reasonable cost, depending on current density. These findings highlight the need for more research on divalent-selective electrodialysis and offer future directions.

KEYWORDS: *Ion−ion selectivity, selective ion-exchange membranes, mineral recovery, reverse osmosis pretreatment, reverse osmosis post-treatment, circular desalination, water softening*

■ INTRODUCTION

Population growth, increased living standards, urbanization, and changing water consumption patterns have driven increased demand for freshwater.[1] According to a UNESCO report, global water use has risen by about 1% yearly in the past 40 years.[2] Such trends lead to global water scarcity, exacerbated by climate change and contamination of freshwater sources.[3] Most water resources are saline (e.g., oceans and brackish groundwater) and unsuitable for drinking or irrigation purposes, requiring desalination to remove the salt. Seawater, the primary source for desalination, is inaccessible within inland areas, where brackish water (BW) is often exploited as an alternative source.

Reverse osmosis (RO) stands out as the dominant desalination technology, accounting for 69% of desalinated water in 2018;[4] however, it is not without its limitations. RO rejects almost all salts (>99% rejection of NaCl),[5] creating low-salinity permeate and high-salinity brine. Each of these two streams is associated with a different major drawback. The high salt rejection by RO also depletes the permeate from minerals essential for human health and plant growth. As a result, the water cannot be supplied directly for domestic and agricultural uses.[6] In the brine, precipitation of sparingly soluble salts can cause scaling, impair desalination performance, and shorten membrane lifespan.

To avoid the consequences of mineral scaling, the water recovery ratio is decreased, thus increasing brine production. In 2018, global brine production was estimated to be 22 million m^3 day^{-1}, requiring the development of brine management strategies.[4] Inland brine can adversely affect the environment or incur a heavy economic burden due to the high cost of current brine treatment technologies.[7,8] Minimizing the brine volumes can reduce the costs and land footprint of the membrane desalination system and more efficiently utilize the brackish water source.

Different RO pretreatment, interstage, and post-treatment processes were suggested and applied to overcome the limitations of brackish water RO (BWRO). Pretreatment approaches for increasing the recovery ratio include chemically enhanced seeded precipitation with antiscalants,[9] CO_2 stripping for alkaline species precipitation with minimal chemical addition,[10] and ion exchange to reduce scale-inducing ions.[11] Once inorganic scaling is eliminated, the brine can be

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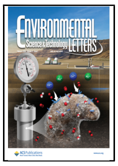

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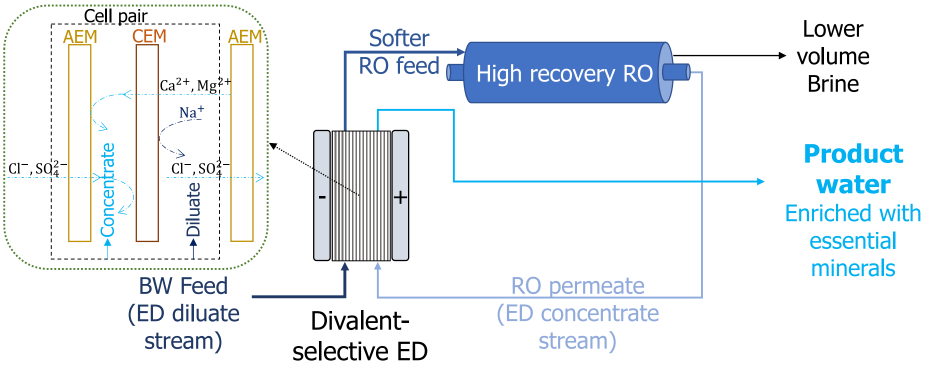

Figure 1. Divalent-selective electrodialysis (ED) integration in brackish water (BW) desalination by reverse osmosis (RO). The ED unit performs pretreatment and post-treatment in a single step. The ED-diluate compartment receives the BW feed, while the ED-concentrate receives the RO permeate. Divalent ions preferentially pass through the membranes to the concentrate (RO permeate) stream upon applying electrical potential. Consequently, the RO feed is softened, reducing the scaling of RO and enabling higher water recovery (or lower brine volume). Concurrently, the RO permeate is enriched with essential Ca^{2+}, Mg^{2+}, and SO_4^{2-} ions.

further treated by membrane separation methods, such as membrane distillation,[12] forward osmosis, and RO-based processes.[7,13−15] Post-treatment methods to meet water quality regulations include direct dosage of chemicals and dissolution of calcite ($CaCO_3$) or dolomite ($CaMg(CO_3)_2$).[6] Blending the desalinated water (RO permeate) with other water sources was also suggested,[16] but this practice often impairs water quality. Although effective, these methods require adding chemicals, which is disadvantageous from a circular economy perspective. Recently, multistep separation processes were suggested for minimizing chemical consumption by using minerals originating in the source water. However, these processes have relatively high energy demand.[17,18] This work introduces a chemical-free low-energy process based on a single electrodialysis (ED) step, which transfers hardness directly from the brackish feed to the permeate in one step.

ED is an alternative desalination technique in which ions move in opposite directions according to their charge under applied voltage. Driving the ions through ion-exchange membranes with high selectivity for counterion (opposite charge to the membrane) passage creates an ion-depleted stream (diluate) and an ion-enriched stream (concentrate). Depending on the membrane characteristics and operational parameters (such as current density), the transport rate of different counterions can differ, enabling separation between counterions. Due to the increased affinity of counterions of higher charge to ion exchange membranes, many commercial cation-exchange membranes have intrinsic selectivity to divalent cations.[19,20] Nevertheless, recent studies focused almost exclusively on monovalent selective membranes, which preferentially transport monovalent ions over divalent ions.[21−27] Specifically, BW desalination by monovalent-selective ED can maintain essential Ca^{2+} and Mg^{2+} ions in the desalinated stream[26,28,29] and prevent calcium from scaling in the brine. However, due to a permselectivity-conductivity trade-off − inflicting a higher energy demand[30,31] − and the high cost of ion-exchange membranes, this process is still economically inferior to BWRO.

Here, we propose a novel approach that combines *divalent-selective* ED (DVS-ED) with BWRO desalination. DVS-ED has the potential to transfer divalent ions directly from the BW feed into the BWRO permeate, thus achieving two goals: (1) supplementing the desalinated water with essential minerals and (2) decreasing the scaling potential in the RO step, therefore, increasing water recovery and reducing the brine volume. In our proposed scheme (Figure 1), DVS-ED uses the BW feed (before RO) as the ED diluate stream and the BWRO permeate as the ED concentrate stream. Divalent Ca^{2+}, Mg^{2+}, and SO_4^{2-} ions are preferentially transported to the concentrate compartment containing the BWRO permeate solution. Controlling the duration (in a batch process) or the number of ED stages (in a continuous process) allows stopping the process after a desired amount of divalent ions is translocated. After the DVS-ED step, the softer ED diluate stream continues to a high recovery BWRO, producing more permeate and less brine. At the same time, the final concentrate stream is enriched with tunable concentration of divalent ions, adjusted for potable water, irrigation water, or both. Therefore, the DVS-ED step can be considered a simultaneous pretreatment and post-treatment for BWRO.

■ MATERIALS AND METHODS

Analytical grade reagents and DI water were used to prepare the concentrate streams and electrode rinse for the ED experiments. Natural BW (see the SI) was used as the diluate. Fumasep FKS-PET-130 (Fumatech BWT GmbH, Germany) and PC SK (PCCell GmbH, Germany) were the cation-exchange membranes (CEMs). FAD-PET-75 (Fumatech BWT GmbH, Germany) was the anion-exchange membrane (AEM). Further details are in the Supporting Information (Figure S1 and Table S1).

Electrodialysis batch experiments were conducted in a BED 1−4 bench-scale electrodialyzer (PCCell GmbH, Germany) in constant current mode and 23 ± 0.5 °C. The current, voltage, electrical conductivity (EC), and pH were monitored continuously. The ion composition of the diluate and concentrate streams—sampled periodically based on EC reduction—was determined by inductively coupled plasma−atomic emission spectroscopy. See the Supporting Information for more details.

■ RESULTS AND DISCUSSION

Low Current Density Promotes Divalent Selectivity.

To explore the integration of divalent-selective ED (DVS-ED) in BW desalination by RO, we conducted a series of ED experiments with natural brackish water as the ED diluate and simulated RO permeate (100 mg L^{-1} NaCl) as the ED concentrate. Ion fluxes were calculated from the ion concentrations, measured sequentially in both streams. The trend of ion concentrations in Figure 2 (a representative ED experiment) points to divalent-selective ion transport. The decrease in Ca^{2+} and Mg^{2+} normalized concentrations in the diluate was sharper (Figure 2A) than that of Na$^+$, which translates to higher depletion rates and indicates preferential transport of these divalent cations. Despite the similarity between Ca^{2+} and Mg^{2+}, Ca^{2+} migrated through the membrane at a higher rate, which may be attributed to its higher molecular affinity toward the sulfonic cation exchange groups.[32,33] Since Na$^+$ was the predominant cation in the BW (Table S2 and Figure S2), its absolute flux was the highest, as indicated by the increasing Na$^+$ concentration in the concentrate stream (Figure 2B) and its depletion in the diluate stream (Figure S2A). Still, the concentration-normalized fluxes of the divalent cations were higher, thus facilitating the enrichment of the concentrate stream (RO permeate) with these essential minerals.

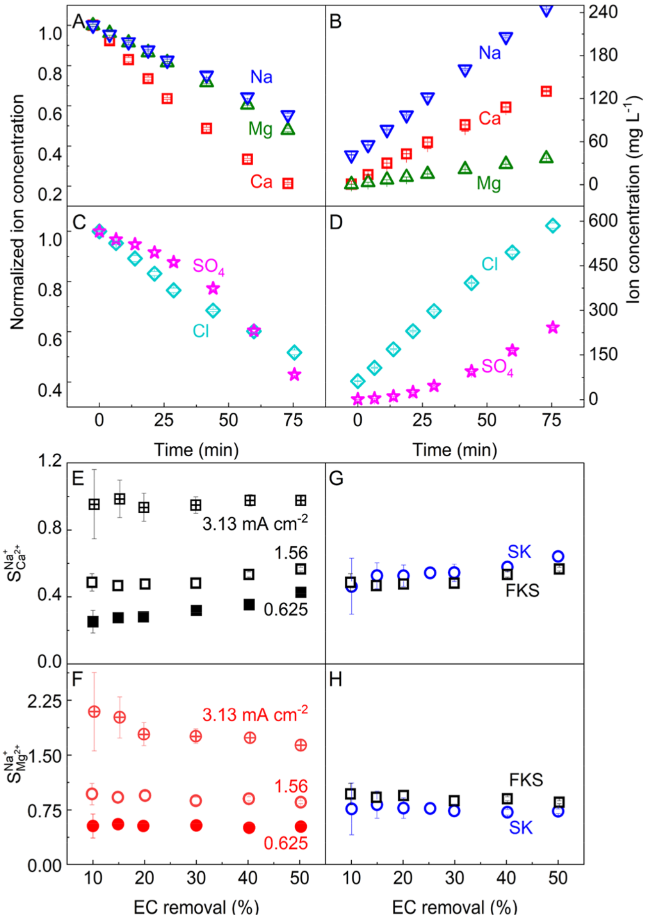

Figure 2. Transport of major cations from the (A) diluate to the (B) concentrate and transport of major anions from the (C) diluate to the (D) concentrate as a function of time. The applied current was 1.56 mA cm^{-2}. The ion concentrations in the diluate are normalized to their initial concentration, while in the concentrate, the concentrations are presented in mg L^{-1}. Error bars represent the standard deviation of ion normalized concentrations (analytical replicates; n = 3–4). Selectivity values (separation factor, removal percentage ratio, for additional data see the SI) for (E) Na$^+$ over Ca^{2+} and (F) Na$^+$ over Mg^{2+} at applied currents of 0.625 mA cm^{-2}, 1.56 mA cm^{-2}, and 3.13 mA cm^{-2} as a function of electrical conductivity (EC) removal. Selectivity values (separation factor) for (G) Na$^+$ over Ca^{2+} and (H) Na$^+$ over Mg^{2+} with different cation-exchange membranes (CEMs PC SK and FKS-PET-130) as a function of EC removal. Selectivity value error bars represent the error in selectivity calculation according to the standard deviation of ion concentrations (analytical replicates; n = 4). In all the experiments, initial solutions contained brackish water on the diluate side and ca. 100 mg L^{-1} NaCl on the concentrate side. FKS-PET-130 was used as the CEM, and FAD-PET-75 was used as the anion-exchange membrane (AEM), except in (E) and (F), where also PC SK was tested as the CEM.

We chose FAD-PET-75 as the AEM to facilitate efficient SO$_4^{2-}$ transport (Figure 2C–D). While typical AEMs preferentially transport Cl$^-$ over SO$_4^{2-}$, this membrane showed similar depletion rates for these two anions under the applied experimental conditions (Figure 2C–D). Interestingly, the SO$_4^{2-}$ depletion rate increased for higher EC removal (Figure 2C), illustrating the impact of solution composition on selectivity, also corroborated by the increase in the permeate concentration (Figure 2D). FAD-PET-75 favorably transports SO$_4^{2-}$ over Cl$^-$ compared to standard AEM membranes (e.g., AEM FAS-PET-130, see properties in Table S1), likely due to its more open structure or higher water uptake, as indicated by its lower area resistance and (counter/co-ion) permselectivity. A higher concentration of divalent cations and anions in the product water, relative to the monovalent Na$^+$ and Cl$^-$, is vital for optimal water quality.

The applied current significantly influenced the selectivity between monovalent and divalent cations. Notably, a transition from divalent to monovalent selective ion transport was observed at a higher current density. Figures 2E and 2F illustrate this selectivity switch, marked by increased Na/Ca and Na/Mg separation factors (S) at higher current density. The separation factor S, a practical measure of selectivity, is the monovalent to divalent cation depletion ratio from the diluate stream; thus, a lower S value indicates a higher divalent ion selectivity. Specifically, $S < 1$ indicates divalent-selective transport, while $S > 1$ points to monovalent-selective transport. The best divalent selectivity (S in the range 0.2–0.4) was recorded at the lowest current density (0.625 mA cm^{-2}). However, at this low current density, the area resistance of the ED cell was the highest (~4000 Ω cm^2), which is energetically unfavorable. We attribute the high resistance to the low applied voltage, which approached the minimal voltage required to initiate water electrolysis in the electrodes. The standard deviation in S calculation was higher initially and subsequently decreased as the experiment progressed. The initial variability arises from the relatively small changes in diluate cation concentration. As a result, even minor analytical errors can substantially impact the calculated S.

The dependency of selectivity on current density suggests that at lower currents, the mass transport is governed by membrane affinity (i.e., ion partitioning), whereas ion mobility is the dominant factor at higher currents. An interplay between these two factors determines the selectivity. Specifically, Na$^+$ ions are more mobile than divalent cations but have lower affinity to the membranes,[34,35] which aligns with the increase in both $S_{\mathrm{Ca}}^{\mathrm{Na}}$ and $S_{\mathrm{Mg}}^{\mathrm{Na}}$ with current density. Among the divalent cations, the affinity of Ca^{2+} to the membrane is higher;[19,32] therefore, $S_{\mathrm{Ca}}^{\mathrm{Na}}$ (Figure 2E) was significantly lower than $S_{\mathrm{Mg}}^{\mathrm{Na}}$ (Figure 2F) at equal current densities. Accordingly, the transition from divalent selectivity to monovalent selectivity was more pronounced for $S_{\mathrm{Mg}}^{\mathrm{Na}}$ (in 3.13 mA cm^{-2}, Figure 2F). Operating the ED at the lowest current density of 0.625 mA

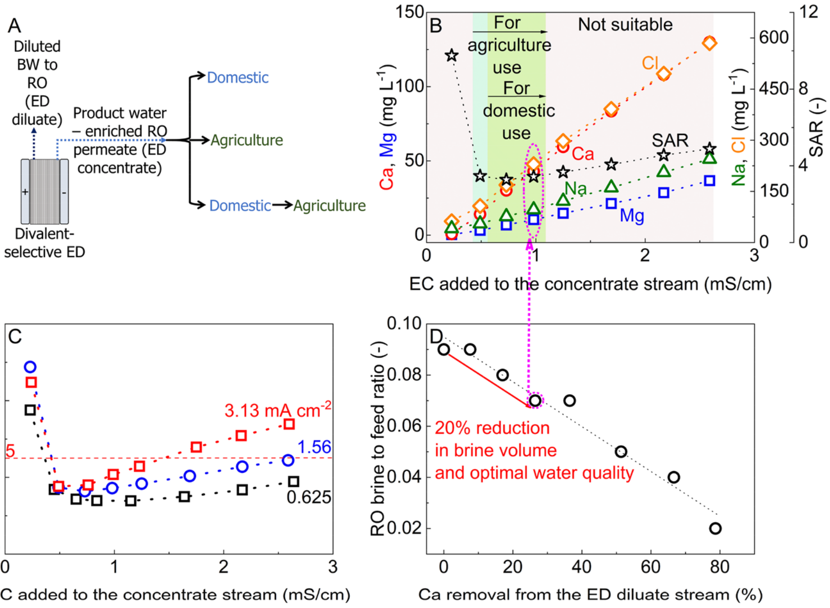

Figure 3. (A) Possible applications for the remineralized product water exiting the divalent-selective ED process. (B) Essential minerals and sodium absorption rate (SAR) evolution during the ED process as a function of electrical conductivity (EC) added to the concentrate stream and the limitation for domestic use and agriculture. The circled data points at EC 0.98 mS cm^{-1} represent the optimal water quality according to the Israeli water quality regulations for unlimited irrigation and household use. (C) SAR values during the ED process as a function of EC added to the concentrate stream at different applied current densities (0.625 mA cm^{-2}, 1.56 mA cm^{-2}, and 3.13 mA cm^{-2}). (D) Reverse osmosis (RO) brine-to-feed ratio limited by gypsum precipitation (assumed to occur at saturation index of 0.4) as a function of % Ca removal from the ED diluate stream. The saturation index was calculated using PHREEQC simulation (pitzer.dat database), mimicking desalination by RO via stepwise H_2O removal. For ~40 mg L^{-1} removal of Ca (~26.5%), a 22% brine volume reduction can be achieved. This point corresponds to an optimal water quality (marked in Figure 3B) suitable for agriculture and domestic use. The analysis was conducted for the current density of 1.56 mA cm^{-2}. The CEM was FKS-PET-130, and the AEM was FAD-PET-75.

cm^{-2} resulted in the highest divalent selectivity but may be economically impractical due to the high electric resistance and large membrane surface area required. Therefore, the intermediate current density, 1.56 mA cm^{-2}, was chosen for further testing.

The commercial CEMs showed similar divalent selectivity in ED applied to natural brackish water. Two commercial membranes, PC SK and FKS-PET-130, from different manufacturers, PCCell and Fumatech, respectively, were tested at a current density of 1.56 mA cm^{-2}. Both membranes preferentially transported divalent cations over monovalent ions, with S_{Ca}^{Na} and S_{Mg}^{Na} lower than unity in all cases (Figure 2G-H). A slight advantage of FKS-PET-130 in separating Ca^{2+} from Na^+ and for SK in separating Mg^{2+} from Na^+ was observed. Since regulations currently require minimal concentrations of Ca^{2+} but not Mg^{2+}, the water quality analysis below focused on the results of the FKS-PET-130 CEM.

Divalent-Selective ED Enables the Production of High-Quality Water for Domestic and Agricultural Uses and Minimizes RO Brine. Ca^{2+} and Mg^{2+} are essential to human and soil health, which is implicated in water quality standards and regional regulations. In Israel,[36] for example, the health regulations for desalinated water mandate Ca^{2+} concentrations to be between 32–48 mg L^{-1}, while for Mg^{2+}, a recommendation of 20–30 mg L^{-1} is standing. The World Health Organization (WHO) recommends Mg^{2+} concentration above 10 mg L^{-1} in its report.[37] Despite recommendations, Mg^{2+} addition to desalinated water is not currently implemented. Since desalinated water can be used for irrigation directly or indirectly (Figure 3A), a low SAR (eq S2) should be maintained for soil preservation (SAR < 5 according to Israeli regulations).[38] Dissolved Ca^{2+} and Mg^{2+} contribute to a lower SAR, while Na^+ increases it. EC and Cl^- are also regulated for irrigation use.[38] Herein, based on our experimental results, we assess the water reuse potential unlocked by DVS-ED according to the Israeli regulations[36,38] and WHO recommendation[37] regarding Mg^{2+} concentration in desalinated water (values are in Table S4).

Our analysis suggests that integrating DVS-ED with BWRO (as illustrated in Figure 1) enables meeting domestic water supply regulations by adjusting the cation composition of the RO permeate (Figure 3A-C). In the ED experiments, ions from the BW (the ED diluate) migrated to the simulated BWRO permeate (the ED concentrate). Consequently, the EC of the BWRO permeate (and all ion concentrations) increased with time and is used in the horizontal axis of Figure 3B–C to depict the progression of the ED experiment. Due to the CEM divalent selectivity, Ca^{2+} was preferentially transported through it. At an added EC of 0.8 ms cm^{-1} (Figure 3B), the Ca^{2+} concentration surpassed the minimum required by the Israeli regulations for domestic water (32 mg L^{-1}), while the EC and Cl^- did not exceed their maximums (1.4 mS cm^{-1}, 250 mg L^{-1}, respectively). With further EC addition to the permeate, the Mg^{2+} concentration exceeded the minimum recommended by the WHO (10 mg L^{-1}) while maintaining submaximum EC and Cl^-. With an additional Ca^{2+} increase, the ionic composition achieved at this point (EC 0.98 mS cm^{-1}, Ca 42.9 ± 0.3 mg L^{-1}, Mg 10.5 ± 0.1 mg L^{-1}, Na 96.8 ± 1.0 mg L^{-1}, Cl 230 ± 2 mg L^{-1}) was the most suitable for drinking water.

In addition to domestic use, water quality suitable for agriculture was achieved during the DVS-ED experiments.

Since the BWRO permeate comprises mainly NaCl, it is detrimental to soil structure and, therefore, unsuitable for irrigation. At low EC addition (~0.2 mS cm^{-1}), the SAR value in the simulated BWRO permeate still exceeded the maximum (SAR = 5) for the three current densities tested (Figure 3C). However, at an added EC of ~0.5 mS cm^{-1}, the SAR dropped sharply due to preferential enrichment with divalent cations, and the treated water was suitable for irrigation for 1.56 mA cm^{-2}, given the low EC and chlorides. With further EC addition, the SAR reached a minimum value, which was lower—and at lower EC— as the current density decreased. The following increase in SAR was sharper for higher current density because of lower divalent selectivity (Figure 2E-F). For the case of 1.56 mA cm^{-2}, after EC addition of 0.73−0.98 mS cm^{-1}, the ion composition of the treated BWRO permeate met the criteria for both domestic and agricultural use (Figure 3B). The high water quality enabled by DVS-ED is critical for reusing desalinated water for irrigation—after domestic consumption—in the form of treated wastewater or graywater.

An additional benefit to the DVS-ED step is the reduction of scaling potential in the BWRO step, mainly due to Ca reduction in the feed. Lower scaling permits a higher recovery ratio and lower brine volume for the subsequent RO stage, which we quantified here via PHREEQC simulations (SI, Table S5), considering gypsum ($CaSO_4 \cdot 2H_2O$) as the limiting scalant (carbonate mineral precipitation can be controlled by reducing the pH). We found that the brine-to-feed volume ratio decreased linearly with Ca removal (also accompanied by SO_4^{2-} depletion) from the BWRO feed (Figure 3D). Specifically, based on the data points representing an optimal product water quality (circled in Figure 3B), we estimated ~22% brine volume reduction (circled in Figure 3D) could be attained. This result demonstrates the potential of DVS-ED as a dual-function pretreatment and post-treatment step.

Although this work was mainly focused on permeate quality, DVS-ED can also facilitate a higher recovery ratio by further removing Ca^{2+} from the BWRO feed (Figure 3D). For example, a second DVS-ED step could be envisioned, which selectively removes Ca^{2+} and Cl^- from the diluate exiting the first DVS-ED step (Figure 1), producing Ca-poor BWRO feed and $CaCl_2$-rich concentrate. In this case, the CEM is divalent selective, while the AEM is monovalent selective to block SO_4^{2-} and avoid $CaSO_4$ scaling in the ED concentrate. Various process designs and stack configurations can be imagined for a range of desalination scenarios and water quality requirements. The DVS-ED concept thus opens new directions for interesting and potentially cost-effective treatment schemes promoting sustainable desalination.

Techno-Economic Feasibility and Research Needs. The techno-economic analysis reinforces the practical relevance of integrating DVS-ED in BWRO. Within the framework of the proposed process scheme, we estimated the main cost components—electricity and capital costs, including membranes, stack, and auxiliaries[39]—for the optimal scenario that produces water with ion composition suitable for both agriculture and domestic use (circled data points at EC 0.98 mS cm^{-1} marked in Figure 3B). A detailed description of the parameters and calculations used in the analysis is provided in the SI (eqs S3−S9, Tables S6−S7). The overall cost of the DVS-ED process was 0.103 \$ m^{-3}, which is 4−21% of the BWRO desalination cost (in the range of 0.5−2.5 \$ m^{-3}).[40] At this cost, reduced scaling potential and remineralization of the BWRO permeate can be achieved without external chemical addition.

The cost breakdown underscores the critical need for cheaper and more selective membranes. Based on the estimated specific energy consumption (SEC), expenses on electricity amount to 0.005 \$ m^{-3}, only ~5% of the total cost. Purchasing the ion-exchange membranes, stack, and auxiliary equipment (0.048 \$ m^{-3}) and periodically replacing the membranes (0.051 \$ m^{-3}) contributed most significantly to the overall cost in this scenario. Reducing the replacement period to 4−6 years will lead to an increase of 7−31% in the overall cost. In a hypothetical scenario where the membrane cost is 25, 50, and 75% lower, the total cost would decrease by 24, 48, and 72%, respectively. A similar cost reduction can be obtained in an alternative hypothetical scenario, where the divalent selectivity is maintained at a higher current density (e.g., at 3.13 mA cm^{-2}), resulting in a lower membrane surface area requirement.

Our findings point to two promising research paths for advancing the application of DVS-ED. One is to develop low-cost divalent selective membranes that will enable the ED unit to operate at a low current density and high membrane area, as tested here on a small scale. Heterogeneous ion membranes, a low-cost alternative to the homogeneous membranes used herein, are a promising direction.[41−43] A second path is to develop membranes that maintain higher divalent selectivity at high current densities, which can be addressed by modifying the ion exchange chemistry, water content, and structure.[44−47] Advances in both paths would enhance DVS-ED techno-economic efficiency in an additive manner. As most current research in this field tends heavily toward monovalent-selective ion exchange membranes, our results and analysis call for more research directed toward divalent selective membranes for electrodialysis applications.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.estlett.3c00861.

> Materials, membrane configuration and properties, brackish water content used as feed in the ED diluate compartment, detailed methods, and experimental conditions, and equations for separation factor and performance of electrodialysis. Ions' transport and selectivity values as a function of time and electrical conductivity (EC) removal. Regulations values, PHREEQC code and output to assess the propensity of mineral precipitation during the concentration of the softer brackish water (ED diluate stream) used as a feed to RO. Calculation methods of SEC, required membrane area, and costs for preliminary economic analysis (PDF)

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Notes

The authors declare no competing financial interest.

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