



Potential of electrodialytic techniques in brackish desalination and recovery of industrial process water for reuse



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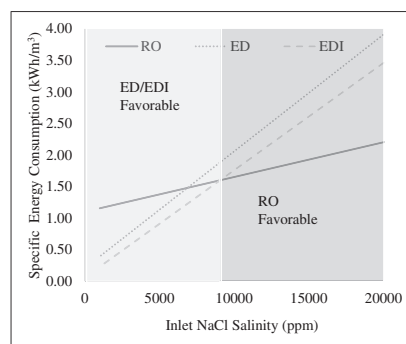
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HIGHLIGHTS

- Electrodialysis and electrodeionization of brackish water was conducted.
- Systems demonstrated low specific energy consumption for low inlet salinity feeds.
- Competitive electrodeionization techniques are discussed for desalination.

GRAPHICAL ABSTRACT



Comparison of SEC for ED, ED, and RO separation processes. At low inlet salinities, ED and EDI are favorable while at high salinities RO becomes favorable. This suggests two regimes where the ideal separation process can be determined from feed conditions.

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ABSTRACT

Large demands for water in industry and consumer markets have led to the development of seawater desalination plants worldwide. Electrodialysis allows the removal of ions at a much lower specific energy consumption than pressure-driven systems and holds the potential to move the desalination industry to greater water yields, lowering the degree of water wasted and energy required for separations. This study investigates the use of traditional electrodialysis as well as electrodeionization for the removal of contaminant ions from brackish water as well as samples from industrial sources. Results indicated that conventional electrodeionization can successfully remove ion contaminants from brackish water at specific energy consumptions of approximately 0.9–1.5 kWh/m³ water recovered with high water productivity at 40–90 L/m² h. Ion-exchange resin wafer electrodeionization showed greater promise with specific energy consumption levels between 0.6–1.1 kWh/m³ water recovered and productivity levels between 10–40 L/m² h. From these results, electrodialysis and electrodeionization have demonstrated viability as alternatives to pressure-driven membrane systems for brackish water desalination.

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1. Introduction

With the ever increasing demand for water due to population growth and global industrialization, potable water production from seawater and brackish sources is an issue that must be addressed to limit global water scarcity. Water production is one of the largest topics and industries that have gained worldwide attention and significant research efforts in the scientific community [1–3]. Typically, the production of water occurs through seawater desalination and water reclamation. With global efforts for water recovery improving over the past few decades, focus has shifted to developing sustainable methods for seawater desalination [4,5]. Significant research on desalination has occurred in order to develop better methods which maximize water productivity while minimizing energy requirements, fouling, and cost [6–9]. Typical desalination and water reclamation occurs through membrane filtration or multi-stage flash distillation (MSF). MSF produces high quality water with high output volumes; however, the process is energy intensive [10,11]. Therefore, novel membrane processes for desalination and wastewater recovery have been implemented in several countries in order to modernize water production methods. The most common membrane techniques used in these plants are reverse osmosis (RO), forward osmosis (FO), and ultrafiltration (UF).

Reverse osmosis (RO) is the most common desalination process, due to its high salt rejection and ease of operation [12,13]. However, several problems persist with RO, including propensity of membranes to fouling and limitations on water recovery [14,15]. As such, UF membranes are often used to pre-treat water solutions before RO operations [16–18]. State-of-the-art RO operations can operate between 20–40 L/m² h with specific energy consumption (SEC) levels at approximately 1.5–4 kWh/m³ water recovered [1,19,20]. The cost of energy and membranes in these plants account for approximately 2–5% and 10–15% of the total capital cost respectively with membrane replacement costs at \$0.10–0.30/m³ water produced [21,22]. The thermodynamic limits of RO are currently 1.06 kWh/m³ at 50% water recovery, demonstrating that further optimization of RO will have minimal impact on the industry [1]. For most countries, these levels are suitable for commercial and consumer demand. Unfortunately, as time progresses and water scarcity becomes a greater issue in developing and developed countries, greater water recoveries are needed at or below the current specific energy consumption (SEC) levels. In order to meet these future demands, new membrane techniques must be employed.

Forward osmosis (FO) has gained much attention recently due to advances in draw solutions and regeneration techniques [21,23,24]. Recent FO research in desalination investigated the incorporation of FO technology with RO for improved water productivity through retentate recovery [23,25,26]. Additionally, pressure recovery devices have been designed to reduce overall SEC by RO and FO pumps [27,28]. Current state-of-the-art suggests that FO process requires 1.3–8 kWh/m³ water produced [26,29,30]. Limitations associated with FO technology include draw solution recovery, membrane fouling, and concentration polarization [27].

Electrodialysis (ED) and electrodeionization (EDI) offer great potential for increased water productivity in desalination. Electrodialysis is the use of electrical current to drive ions in solution from one solution to another [31]. This allows salt water solutions to be desalted using electrical power with little additional energy required. Electrodeionization (EDI) is a similar process in which current is used to drive ions from a solution; however, the major difference is the addition of ion exchange resins to reduce solution resistance limitations for the separation process [32]. EDI process is also advantageous in that the resins used during operation are self-regenerating. A small portion of the energy used during separation is also consumed to regenerate the resin charged groups, allowing continuous operation of EDI systems without need to recover resin performance. Many studies has been conducted in the use of ED and EDI in the food and beverage industry [33–

35], the formation of acids and basis [36,37], and the development of specialty chemicals [38,39]. However, work conducted on the use of ED in the desalination industry, specifically when considering brackish water, has resulted in SEC levels ranging anywhere from 1–15 kWh/m³ water treated with common values over 10 kWh/m³. In addition, ion exchange membranes are more typically 2–3 times more expensive than RO membranes [40]. At these SEC levels and capital costs, ED and EDI are uncompetitive with RO and FO. Some research has been done on the applicability of ED in the desalination of high salinity feeds, however, production of potable water at lower salinities has yet to be fully considered [41]. With the development and maturity of RO, additional membrane techniques such as ED and EDI can be investigated for potential desalination applications. Table 1 summarizes the typical water productivity and SEC of each desalination technique.

This study investigated the applicability of ED and EDI techniques for water desalination and process water recovery. To our knowledge, this is the first study that compares the treatment of brackish water from industrial and drinking source waters by EDI and ED to current RO technologies. Sodium chloride was used as a model salt for brackish water desalination experiments. Brackish drinking water sources were also tested and the differences in productivity and water quality were discussed and compared to RO to determine commercial viability of ED and EDI. Additional contaminants were considered to determine the influence of contaminants on water productivity and SEC for the ED and EDI processes. Results suggest that while ED may be limited by high SEC levels and low salinity feeds, the benefits of EDI can overcome this obstacle through novel membranes and thinner materials which can lead to a cost-effective process for water desalination and recovery of contaminated process water.

2. Experimental

2.1. ED and EDI experimentation

Experiments were conducted with a Micro-Flow cell ED stack from Electro-Cell North America, a pilot TS-2 EDI stack from EURODIA, and a pilot EUR2B-10 ED stack from EURODIA. Table 2 shows the characteristics of each stack. In EDI, solution compartments are filled with ion exchange resin which enhances ion transport and solution conductivity at low ion concentrations. To minimize stack thickness and ensure resin retention, ion exchange resin wafers were used in experiments in lieu of ED flow spacers. For EDI experiments, resin wafers were produced through a combination of anion exchange resin, cation exchange resin, polymer, and sucrose according to previous synthesis methods with imaging available in prior publications [47–49]. Fig. 1 shows a process schematic for ED and EDI. For both ED and EDI, experiments were duplicated in order to confirm experimental results. Sodium chloride was used as a model contaminant because most desalination efforts are focused on the decreasing sodium and chloride to levels below 500 ppm as total dissolved solids (TDS) per EPA regulations on potable drinking water [43]. In the dilute chamber, sodium chloride began at 5000–50,000 ppm while the concentrate chamber had sodium chloride at a 0.1 N concentration (~5844 ppm). Current was introduced into the

Table 1
Current desalination output and SEC for brackish water treatment.

Separation method	Water productivity (L/m ² h)	SEC (kWh/m ³)
Ultrafiltration [42] ^a	>50	0.07
Reverse osmosis [43]	10.2–43.7	3–7
Forward osmosis [26,29,44]	3–8	1.5–8
Electrodialysis [45,46]	10–45	1–15
Electrodeionization [46]	7–40	0.2–1.5

^a Desalination pretreatment only.

Table 2

Membrane, ED, and EDI system characteristics [44].

Membrane	Resistivity ($\Omega \cdot \text{cm}^2$)	Burst strength (MPa)	Permselectivity	Thickness (mm)	Ion exchange capacity (meq/g)
AMX	2.4	≥ 0.25 MPa	0.98	0.14	1.4–1.7
CMX	3.0	≥ 0.40 MPa	0.98	0.17	1.5–1.8
ED cell characteristics					EDI cell characteristics
Intermembrane distance (mm)	0.5				0.5
Membrane area (cm^2)	64				10
Anode material	Pt/Ir				Pt/Ti
Cathode material	Ti				Pt/Ti

system and samples were taken while pH, conductivity, and mass fluctuations were recorded. An Orion PerpHecT LogR Model 330 pH meter was used to measure pH while a VWR Traceable® Expanded Range Conductivity Meter was used to record conductivity. Experiments continued until the diluate chamber had a TDS concentration below 500 ppm evidenced by electrical conductivity and confirmed by ion chromatography or atomic absorption.

In order to better determine the efficacy of EDI for brackish water treatment, brackish desalination plant source waters were taken from California and treated using EDI. Well 1 (well 84 sample) was treated for 110 min, Well 2 (well 57 sample) was treated for 60 min, and Well 3 (well 82 sample) was treated 80 min in a pilot EDI consisting of 2 cells with a total potential of 10 V across the EDI stack with ion-exchange resin wafers to get their final ion conductivity values to

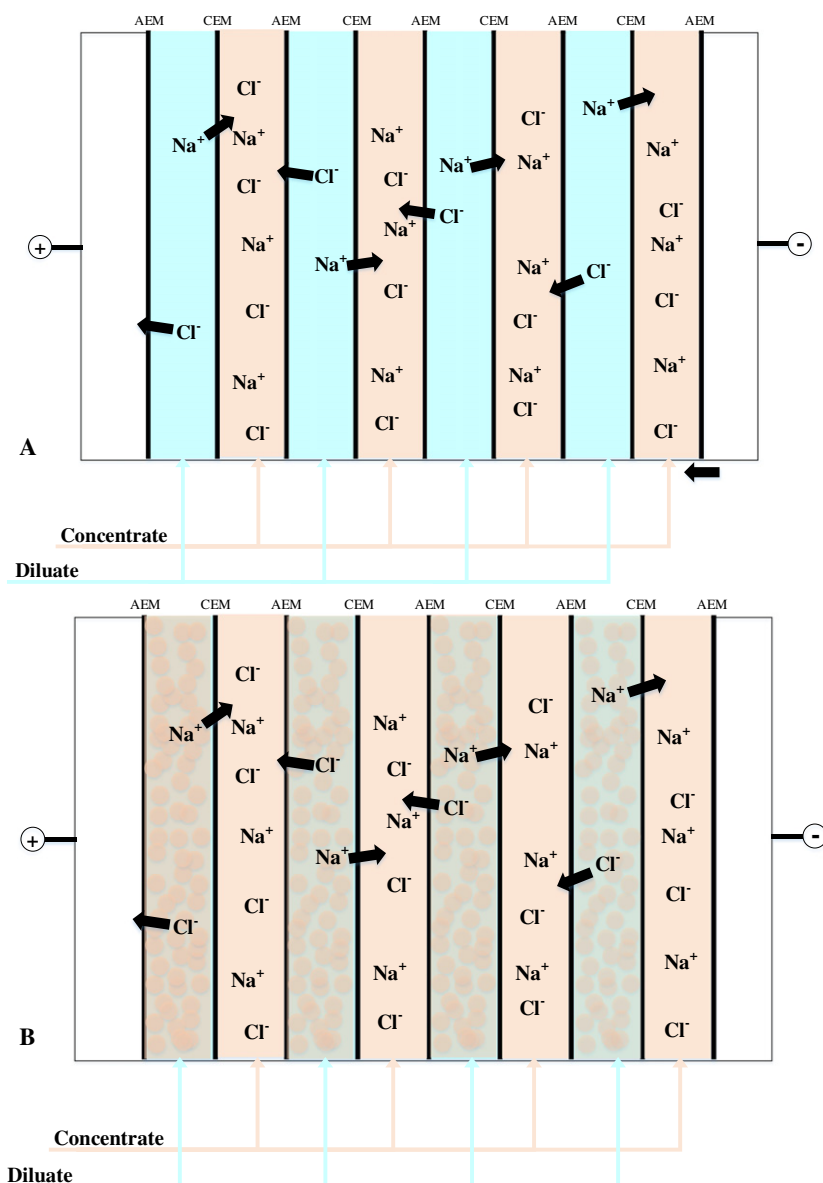


Fig. 1. ED (A) and EDI (B) schematic. For EDI experiments, a resin-wafer was placed in the diluate compartments. AEM = anion exchange membrane. CEM = cation exchange membrane.

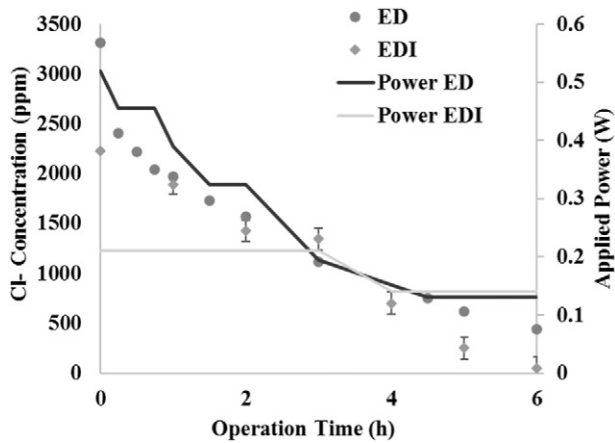


Fig. 2. ED/EDI performance in bench system.

$\leq 300 \mu\text{S/cm}$. Ion concentrations, conductivity, and TDS were analyzed before and after each experiment.

2.2. Analysis of water samples

Samples were analyzed for chloride content via ion chromatography using a Metrohm-850 IC Professional IC equipped with an MSM suppressor and an IC anion column. From conductivity and chromatography results, ion depletion from experiments was determined and used to calculate SEC and water productivity. Sodium concentration was measured using Atomic Absorption (AA) analysis on a GBC Model 933 system.

2.3. Determination of desalination SEC and maximum water productivity

SEC was calculated using Eq. (1) which incorporated the ion removal rate, current efficiency, and voltage applied to the ED stack.

$$\text{SEC} = \frac{VIJ_s}{\eta} \quad (1)$$

where V is the voltage, I is the current, J_s is the ion flux through the membrane and η is the system current efficiency. Water productivity was calculated according to Eq. (2).

$$W = \frac{V_s}{At} \quad (2)$$

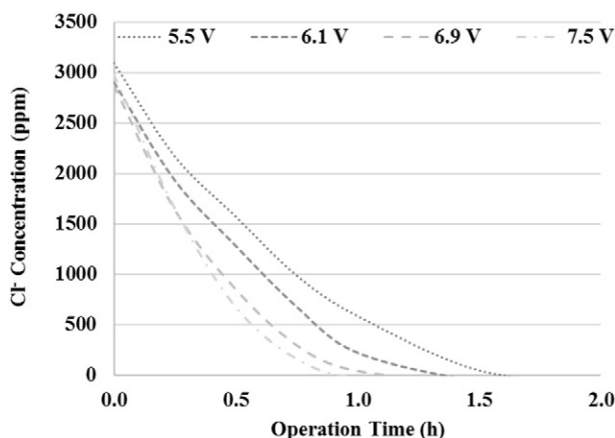


Fig. 3. Ion removal from diluate stream with EDI TS-2 pilot system.

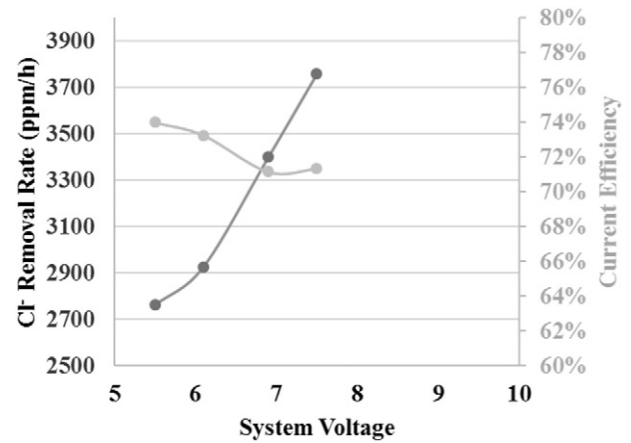


Fig. 4. Influence of power applied on brackish water desalination in EDI.

where V_s is the diluate sample volume, A is the active membrane surface area, and t is system operation time.

3. Results and discussion

3.1. Desalination through ED and EDI

Desalination through ED produced water with TDS < 500 ppm using an estimated $0.8\text{--}1.5 \text{ kWh/m}^3$ water produced with water productivity of $45 \text{ L/m}^2 \text{ h}$. EDI consumed $0.48\text{--}1.01 \text{ kWh/m}^3$ with water productivity of $13\text{--}40 \text{ L/m}^2 \text{ h}$. Fig. 2 shows the results from ED and EDI operation with the lab-scale system. Although, ED had a higher starting concentration of salt in these experiments, ED and EDI performed were similarly until chloride concentrations dropped below 500 ppm. Here, low ion concentrations in the diluate compartment reduced current efficiency and ion removal in ED. In EDI ion removal continued with no reduction of performance at low solution conductivities. Ion exchange wafers did result in higher operation voltages due to wafer regeneration and water splitting at the resin surfaces, yet overall SEC was lower due to greater contaminant removal at low concentrations and a more stable current driving force.

Fig. 3 shows the performance of the pilot scale EDI TS-2 system. As the voltage and current applied increases, water productivity increased as well as SEC. Fig. 4 shows the performance of the TS-2 system SEC with regards to system voltage and ion transfer rate. For the voltage range tested, increasing the system voltage increased the chloride ion transfer rate. However, current efficiency slightly decreased as the system voltage was increased. At higher voltages, water splitting and other

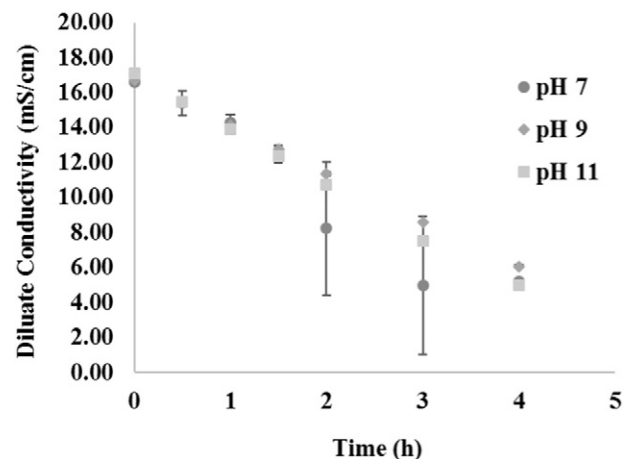


Fig. 5. EDI treatment of brackish water containing alkali contaminants.

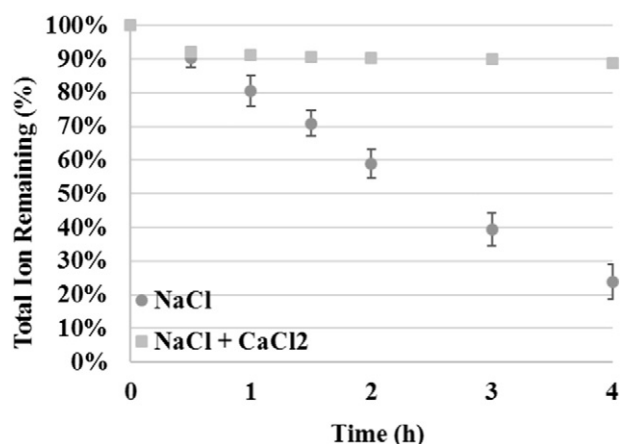


Fig. 6. EDI treatment of brackish water containing divalent contaminants.

detrimental phenomenon can occur within the system, limiting the benefit of increasing the system voltage. Thus, ideal EDI operation would occur before limiting current density occurs, ensuring high ion transport with reasonable SEC.

3.2. Brackish water testing and influence of alkali and divalent contaminants

Treatment of brackish water can result in changes in fouling and scaling as well as process conditions. The influence of pH and divalent ions through addition of calcium on EDI performance is shown in Figs. 5 and 6. Variation of pH on feed solution resulted in no effect in ion transport rate. However, it is important to note that high pH can lead ion transport competition between target anions and OH^- [50]. Thus, pH control is advised to ensure optimal EDI performance. Addition of calcium ions resulted in a decrease in current efficiency from 95% to 27% as evidenced in Fig. 5. This is due to the increase in electroosmotic drag force caused by the calcium ions due to increased ion strength and water co-transport. In addition, high concentrations of divalent ions can lead to the formation of precipitates [51]. Therefore, novel strategies are needed in ED and EDI separations to mitigate the issues caused by the presence of divalent ions.

In order to better determine the efficacy of EDI for brackish water treatment, groundwater samples were taken from three drinking water treatment plant intakes in Perris, CA and treated using EDI. Well 1 (well 84 sample) was treated for 110 min, well 2 (well 57 sample) was treated for 60 min, and well 3 (well 57 sample) was treated for 80 min in a pilot EDI consisting of 2 cells with a total potential of 10 V across the EDI stack with ion-exchange resin wafers to get obtain a final ion conductivity below 300 $\mu\text{S}/\text{cm}$. Ion concentrations, conductivity, and TDS were analyzed before and after each experiment. The results of EDI treatment on well samples are shown in Table 3. For all cases, EDI treatment resulted in significant reduction of salts and divalent ions with average ion removals ranging from 61–99%. Notably, TDS levels were decreased below the 500 mg/L threshold and the average bromide removal was 95%. As these were high bromide waters (>1 mg/L),

formation of brominated disinfection byproducts is a concern during chlorine disinfection [52], thus the EDI process may be helpful in controlling formation of these compounds. SEC for these experiments were high (6.7 kWh/m^3). However, for an optimized industrial scale system, the SEC decreases to 0.8 kWh/m^3 . Nitrate levels for this water were below detectable limit. Sulfate concentrations were low and were retained in the diluate after treatment. Ideal membranes would limit the retention of nitrate and sulfate. In order for EDI to become competitive for desalination and brackish water treatment, larger and more economical systems are needed as well as membranes that can ensure the removal of harmful contaminants such as nitrate and sulfate.

3.3. Potential of ED and EDI on desalination of brackish and seawaters

Current state-of-the-art ED and EDI are uncompetitive against RO and other pressure-driven membrane processes for seawater desalination due to limitations on current density and ion selectivity. However, experiments have shown that there may be brackish water sources where ED and EDI are more economical than pressure-driven membrane processes. In order to determine the efficacy for ED and EDI at low and high inlet salinities, several experiments were conducted with varied inlet NaCl concentrations and SEC and potable water productivity was calculated. Comparison of the results with the reported RO SEC and potable water productivity [43,53], a trend emerges between inlet NaCl concentration and SEC. Fig. 7 demonstrates this phenomenon. As the feed salinity decreases, EDI becomes more competitive at ca. 9000 ppm while ED becomes competitive at ca. 7000 ppm. The data suggests that there exists two regions for desalination, an area at low salinity where ED/EDI is favored and another region at moderate and high salinities where RO is favored. It is also important to note that organics have a strong propensity to foul ED and EDI membranes. However, pretreatment systems that are in place to protect RO membranes would result in similar mitigation of ED and EDI fouling. In addition, requiring only a partial removal of salts from contaminated waters makes ED more economical due to operation limited during high efficiency regimes as demonstrated by McGovern et al. [54].

Water productivity is another important aspect of seawater and brackish water desalination. A comparison of SEC and water productivity is shown in Fig. 8. For separation at low salinities (<9000 ppm), EDI demonstrated limited water productivity while ED showed high water productivity with a higher SEC. These results indicated that current SEC and water productivity for ED and EDI are economical at low salinity feeds. However, at high salinities, ED and EDI possess high SEC which makes them unviable for use in water recovery, thus ED and EDI are viable options for brackish water production so long as feed salinities are <9000 ppm. Significant reductions in ED SEC are unlikely as these systems currently operate at high current efficiencies (>80%). However, research in improving EDI membranes and systems would yield greater water productivities with moderate increases in SEC. Thus, next generation EDI is capable of competing with pressure-driven systems. It is also important to note that ED and EDI allow for more varied water output, making them viable alternatives for applications where complete ion depletion is not necessary. For these instances, ion selectivity can be crucial for economical separations. Thus, additional research on the development of selective ion exchange membranes would be of benefit

Table 3
EDI water treatment of industrial well sources.

	Na^+	K^+	Ca^{2+}	Mg^{2+}	F^-	Cl^-	Br^-	σ (mS/cm)	TDS (mg/L)	Nitrate ^a	Sulfate (ppm)
Well 1 feed	590.34	5.68	41.37	187.33	0.58	1148.91	2.47	4.35	2780.00	BDL	6.138
Well 1 posttreatment	56.45	0.00	0.90	3.65	0.18	81.64	0.08	0.34	215.00	BDL	182.53
Well 2 feed	121.16	3.18	36.78	144.23	0.38	423.07	1.29	1.83	1170.00	BDL	5.138
Well 2 posttreatment	43.88	0.00	1.56	5.17	0.20	63.76	0.06	0.28	179.00	BDL	64.08
Well 3 feed	151.05	5.89	50.56	183.39	0.30	564.92	1.17	2.28	1460.00	BDL	3.105
Well 3 posttreatment	41.37	0.24	2.39	7.63	0.10	65.25	0.07	0.30	189.00	BDL	50.96

^a BDL = below detectable limit.

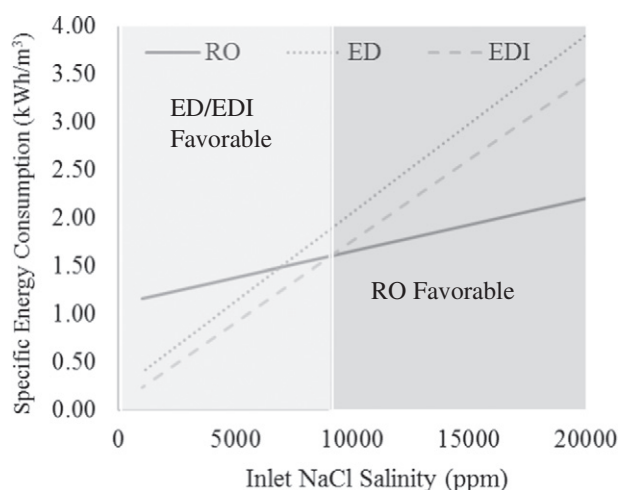


Fig. 7. Comparison of SEC for RO, ED, and EDI based on inlet NaCl salinity. RO data obtained from [43,53].

to mitigate the loss of separation efficiency when divalent ions and metal ions are present in solution (Fig. 6).

4. Conclusion

Through this study, desalination of brackish water using ED and EDI techniques were investigated. Influence of divalent ions and alkali contaminants were also studied in order to obtain greater understanding on the recovery of potable water from real industrial water sources and seawater systems. ED and EDI both operated at energy levels ≤ 1 kWh/m³, ideal for water treatment. EDI demonstrated superior performance for water recovery of low salinity feeds while ED resulted in superior water productivity. However, most potable water only requires reduction of TDS to <500 mg/L, giving current state-of-the-art ED technology an advantage for water production. EDI can become advantageous when selectivity of contaminants is crucial and when high ion depletion is desired, due to less degradation and fouling of membranes at higher voltages. Results indicate that EDI can overcome productivity limitations for low salinity feeds through novel membranes leading to a cost-effective process for brackish water desalination. Future research much investigate the development of novel, robust membranes with high ion selectivity and mechanical properties if ED and EDI technology plan to augment pressure-driven membrane separations in the desalination and water treatment industry.

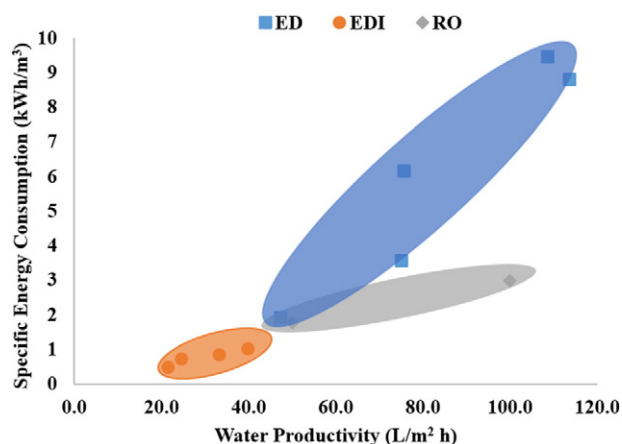


Fig. 8. Comparison of SEC and water productivity for brackish water desalination [43,53].

Nomenclature

A	active membrane area
EDI	electrodeionization
ED	electrodialysis
I	system current
FO	forward osmosis
J_s	ion flux
LCD	limiting current density
MSF	multi-stage flash desalination
RO	reverse osmosis
SEC	specific energy consumption
T	operation time
TDS	total dissolved solids
V	system voltage
V_s	system diluate volume
H	current efficiency

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