



Selective removal of arsenic and monovalent ions from brackish water reverse osmosis concentrate



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HIGHLIGHTS

- Arsenic was effectively removed by coagulation with ferric salts.
- Adsorption with ferric sludge provides a “waste treat waste” method for arsenic removal.
- Coagulant dose requirement for RO concentrate was higher than low salinity water.
- Increase in current density does not affect significantly selectivity of monovalent anions over di-, multi-valent anions.
- Transport of divalent cations increases with increase in current density.

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ABSTRACT

Concentrate disposal and management is a considerable challenge for the implementation of desalination technologies, especially for inland applications where concentrate disposal options are limited. This study has focused on selective removal of arsenic and monovalent ions from brackish groundwater reverse osmosis (RO) concentrate for beneficial use and safe environmental disposal using in situ and pre-formed hydrous ferric oxides/hydroxides adsorption, and electrodialysis (ED) with monovalent permselective membranes. Coagulation with ferric salts is highly efficient at removing arsenic from RO concentrate to meet a drinking water standard of 10 µg/L. The chemical demand for ferric chloride however is much lower than ferric sulfate as coagulant. An alternative method using ferric sludge from surface water treatment plant is demonstrated as an efficient adsorbent to remove arsenic from RO concentrate, providing a promising low cost, “waste treat waste” approach. The monovalent permselective anion exchange membranes exhibit high selectivity in removing monovalent anions over di- and multi-valent anions. The transport of sulfate and phosphate through the anion exchange membranes was negligible over a broad range of electrical current density. However, the transport of divalent cations such as calcium and magnesium increases through monovalent permselective cation exchange membranes with increasing current density. Higher overall salt concentration reduction is achieved around limiting current density while higher normalized salt removal rate in terms of mass of salt per membrane area and applied energy is attained at lower current density because the energy unitization efficiency decreases at higher current density.

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1. Introduction

1.1. Concentrate management and treatment

Groundwater is progressively becoming an important source of drinking water as surface water resources are depleted. In the

United States, an estimated 26% of fresh water used comes from groundwater and nearly 44% of the population depend on groundwater for their drinking water supply [1,2]. This is without regard to other uses such as agricultural irrigation. Groundwater in many areas can have characteristically high ionic strength due to seawater infiltration, irrigation, or overdraft that results in increased salt concentration in aquifers [3]. In addition, the presence of natural and anthropological contaminants such as arsenic, selenium, nitrate, naturally occurring radioactive materials, petroleum byproducts, and pesticides requires groundwater to be treated prior to potable use. Desalting technologies such as reverse osmosis (RO) membrane processes are principal methods for treating

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brackish groundwater as they are effective at removing almost all dissolved constituents. The primary shortfall of RO is the management and disposal of the highly saline concentrate laden with accumulated pollutants. While ocean disposal is widely used in coastal areas, inland communities are confronted with more challenging disposal issues. Management of the concentrate depends on the source water's quantity and quality, geography and geology, regulations, costs, and potential environmental impacts [4].

Current inland RO concentrate disposal options include surface water discharge, sewer discharge, deep well injection, evaporation ponds, irrigation and zero liquid discharge using thermal evaporators and crystallizers [4,5]. Surface water discharge, sewer discharge and deep well injection are convenient but have risks of contaminating water sources and habitats, and interfering with downstream treatment facilities (via fouling, scaling and inhibition of biological processes due to increased salinity and individual ions). Disposal of large amounts of RO concentrate is a waste of water resources and some disposal options are cost prohibitive for inland communities [5,6]. As permitting requirements for concentrate disposal become more stringent, developing new methods for treatment and beneficial use of RO concentrate is crucial to keeping costs and environmental damage down. Treatment of RO concentrate can convert the waste stream to additional water for beneficial use (e.g., irrigation) that is otherwise scarce in arid climates. Potential treatment concerns include contaminants concentrated from feed water, added process chemicals (e.g., acids, disinfectants, coagulants, and antiscalant), and heavy metals introduced by natural dissolution of rocks, agricultural runoff, and mining activities [7,8]. Consequently, removal of these contaminants from RO concentrate in a cost-effective manner remains a challenge.

Several treatment technologies have been investigated to improve concentrate management and recovery, including dewaporation [9], membrane distillation [10], forward osmosis [10], electrodialysis [11,12], electrodialysis reversal [13], electrodialysis metathesis [14], and various intermediate precipitation followed by secondary RO processes [15–19]. These processes can achieve up to 90% additional water recovery (depending on the feed water quality) for desalination of concentrates. New research trends are striving to recover salts and other valuable products and energy from concentrate [20–22].

Previous studies have focused on improving overall water recovery and providing fresh water; however, these technologies are often costly and energy intensive. A cost effective alternative is to treat concentrate by selective removal of specific constituents (e.g., arsenic, nitrate, or monovalent ions), and partially reduce salt level to meet water quality requirements of target applications. Electrodialysis (ED) and electrodialysis reversal (EDR) are commonly used methods of desalinating water whereby charged membranes separate the ions from water, driven by applied electrical potential [23]. One of the benefits of this method is the selectivity of removing monovalent ions (e.g., Na^+ , Cl^- , and NO_3^-) over multivalent ions using monovalent permselective ion exchange membranes [24,25]. This allows the modification of ionic composition in product water for beneficial uses, including irrigation and stream flow augmentation. ED and EDR processes can be controlled to partially reduce the total dissolved solids (TDS) concentration of the concentrate rather than produce water with very low TDS. This will minimize the complexity of product water blending and stabilization, and allow more options for concentrate management and disposal.

Compared to RO membranes, ED and EDR membranes require less pre-treatment and are more tolerant to waters with higher silica, hardness, suspended solids, and organics concentrations [26–28]. Therefore, ED and EDR offer significant advantages over secondary RO and can operate at substantially lower cost and higher water recovery when treating RO concentrates. Post treatment such

as disinfection is required if the ED product water is used for drinking water.

1.2. Arsenic removal

Arsenic is a carcinogenic metalloid that occurs in groundwater mainly naturally or due to anthropogenic activities. Organic species of arsenic such as monosodium methanearsonate and disodium methanearsonate are not commonly found in aquifers except for areas with heavy industrial pollution [29]. Inorganic arsenic species can have several different oxidation states ($-3, 0, +3, +5$). In groundwater, natural arsenic occurs as arsenate, As(V), or the more mobile arsenite, As(III) [30,31]. Speciation depends largely on water chemistry and exposure of the source to air, which influences the oxidation state of arsenic. The World Health Organization's guideline for arsenic in drinking water was lowered from $50 \mu\text{g/L}$ to $10 \mu\text{g/L}$ in 1993. The European Union followed suit in 1998 and the United States in 2001 [32]. In the United States, elevated levels of groundwater arsenic ($>10 \mu\text{g/L}$) are found primarily in the West and Midwest, parts of Texas, and the Northeast [33].

Several techniques exist to lower aqueous arsenic concentrations in groundwater. These include coagulation/precipitation, RO, ion exchange, adsorption, and nanofiltration [34–41]. Metal salts such as ferric chloride or ferric sulfate have been known to more effectively remove As(V) from solution than aluminum salts when followed with sedimentation and filtration [42–44]. The higher solubility of alum than metal salts over a wider pH range causes alum to stay in solution instead of precipitating out [45]. The selectivity of As(V) to ferric salts is related to the solution's concentration and pH [46]. For ferric iron specifically, selective removal of arsenate occurs when hydrolyzed iron precipitates, forming porous structures known as hydrous ferric oxides that arsenic species readily bind to. The exact mechanism for the adsorption to the oxides is not entirely agreed upon, but it is thought that ligand exchange of arsenate to the hydroxyl functional groups is the driving force of the reaction [47] and is more effective near pH of 6–7 [48]. Removal of arsenic from high ionic strength solutions has been successful using synthetic solutions but more research is needed that utilizes non-artificial source water.

1.3. Objectives

The main objective of the current study was to develop cost effective technologies to treat RO concentrate with high arsenic concentrations to facilitate concentrate disposal and beneficial use. Following analysis of the arsenic species, bench-scale experiments were conducted to evaluate arsenic removal by different ferric salt coagulants and an adsorbent under a variety of operating conditions. Electrodialysis was then used to further remove TDS and monovalent ions from the concentrate in an effort to modify the salt composition to bring the water quality to suitable agricultural irrigation use or stream flow augmentation.

2. Experimental

2.1. Water quality analysis and methods

RO concentrate was collected from a groundwater desalination plant (Table 1). Initially, deep well injection was used to dispose of the concentrate, but recently, arsenic levels (as arsenate) have exceeded the discharge permit of $10 \mu\text{g/L}$. The high TDS level ($>10,000 \text{ mg/L}$) and high sodium adsorption ratio (22) make the concentrate unsuitable for beneficial use such as irrigation. Selective removal of arsenic and excess salts (mainly sodium and chloride) from the RO concentrate can provide additional water for

Table 1
Major constituents in the RO concentrate.

Analyte	Concentration
Al ³⁺	0.14 mg/L
As ⁵⁺	0.029 mg/L
Ba ²⁺	0.51 mg/L
Ca ²⁺	717 mg/L
Fe ³⁺	0.14 mg/L
K ⁺	122 mg/L
Li ⁺	0.76 mg/L
Mg ²⁺	177 mg/L
Na ⁺	2491 mg/L
SiO ₂	152 mg/L
Sr ²⁺	20.5 mg/L
Zn ²⁺	0.14 mg/L
F ⁻	2.9 mg/L
Cl ⁻	5056 mg/L
NO ₂ ⁻	19.8 mg/L
PO ₄ ³⁻	61 mg/L
SO ₄ ²⁻	1263 mg/L
pH	7.9
EC	18 mS/cm
Alkalinity	350 mg/L CaCO ₃
TDS ^a	10,860 mg/L
TOC	1.5 mg/L

^a Measured.

agricultural and irrigation use, and minimize deep well injection of RO concentrate.

Common anions (fluoride, chloride, bromide, phosphate, sulfate and nitrate) were analyzed by ion chromatography (ICS-90, Dionex, Sunnyvale, CA). Metals and other elements were analyzed by an inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Optima 5300, Perkin-Elmer, Fremont, CA). Organic concentration was quantified with a total organic carbon (TOC) analyzer (Shimadzu TOC-L, Kyoto, Japan). Determination of arsenic species and concentration were measured by inductively coupled plasma mass spectrometry (ICP-MS, Perkin Elmer Nexion 300Q, Waltham, MA) using a Dionex AG guard column and AS-16 analytical column (IonPac[®], Dionex, Sunnyvale, CA). Only inorganic arsenic species as As(V) were detected and no As(III) was found; therefore, oxidation of the samples prior to coagulation was unnecessary.

All samples were diluted to levels suitable for analysis for the different analytical instruments. General sample collection and handling were in accordance with the guidelines of Section 1060 in Standard Methods [49]. Water samples were filtered using a Pall Supor[®] 0.45 μm hydrophilic polyethersulfone membrane when applicable.

Conductivity was measured by a conductivity meter (Model 431-61, Cole-Parmer, Vernon Hills, IL), and all pH measurements taken on a pH meter with temperature gauge (Oakton 300 Series, Eutech Instruments, Singapore). Alkalinity was measured by digital titrator (Hach Company, Lot A5187, Loveland, CO) using sulfuric acid standard solution. Total dissolved solids were measured by evaporation of 0.45 μm filtered water at 180 °C.

2.2. Bench-scale testing systems

The water treatment was a two-step process with coagulation/precipitation for arsenic removal followed by ED for monovalent ions removal. To simplify the bench-scale study, we used raw RO concentrate for all experiments.

2.2.1. Bench-scale testing for arsenic removal

A series of jar testing were conducted to investigate the impact of coagulants, dosing, and pH on arsenic removal. Reagent grade ferric sulfate and ferric chloride (Fisher Chemical Co., Fairlawn, NJ) were selected as coagulants based on their effectiveness in high

ionic strength solutions reported in the literature [50,51]. pH was adjusted using 1 N HNO₃ or 1 N NaOH solutions. In addition to conventional coagulants, ferric sludge collected from a local drinking water treatment plant (with ferric sulfate as primary coagulant) was used as coagulant and adsorbent to remove arsenic from RO concentrate. Freshly dewatered ferric sludge by filter press was used directly in the testing without further treatment. The total solids concentration of the dewatered sludge was approximately 18%, and arsenic was not present in the source water of the treatment plant and sludge.

During jar testing rapid mixing was conducted at 200 rpm (round per minute) for 1 min immediately after coagulant addition. Flocculation was conducted at 30 rpm for 20 min and sedimentation for 30 min. Adsorption experiments were designed using a column packed with 25 mL dewatered sludge. During this preliminary study, the concentrate was added to the column and allowed to flow freely through with a hydraulic retention time of approximately 20 min.

2.2.2. ED testing

The ED bench testing used a single stage ED-1 electrodiolysis stack from Electrosynthesis (Lancaster, NY). Sixteen pairs of ion exchange (IX) membranes provided a total surface area of 0.16 m² with an individual membrane area of 0.01 m². The stack was integrated in a lab-scale ED-unit that provided the flow for three compartments (feed, concentrate, and electrode rinse) and the electrical power. The feed and concentrate streams were operated with a flow of 0.96 L per minute (15.2 gallons per hour, gph) and each of the rinsing compartments ran 0.1 M Na₂SO₄ solution with a flow of 2 L per minute (32 gph). The working pressure was 14–27 kPa (2–4 pounds per square inch, psi).

The ED unit was operated in a once-through mode, with 15 L of RO concentrate in a feed container. The water was split equally and flowed through the feed and concentrate channels (i.e., simulating 50% ED recovery). Diluate and concentrate were combined in the feed container and recirculated to the ED unit. NEOSEPTA monovalent permselective membranes (ACS and CMX-S) manufactured by ASTOM (Japan) were used in the study. ACS is a strongly basic anion exchange membrane having a thickness of 130 μm and an electrical resistance of 3.8 Ω cm² in 0.5 M NaCl. CMX-S is a strongly acidic cation exchange membrane having a thickness of 150 μm and an electrical resistance of 3.8 Ω cm² in 0.5 M NaCl.

Unit and stack voltages, current and current density, pH, conductivity, and pressure were monitored continuously throughout the testing. The permeability of salts through cation exchange and anion exchange membranes (CEM and AEM) was measured by analyzing samples collected from each stream (feed, concentrate and diluate) at certain time intervals. The ED performance under different operating conditions was assessed based on concentration reduction, product water composition, and normalized salt removal rate. The relevant equations are listed below.

The feed water recovery is the percentage of feed water that becomes diluate and is given by

$$\text{Recovery (\%)} = \frac{Q_d}{Q_f} \times 100 \quad (1)$$

where Q_d is the diluate flow and Q_f is the feed flow (diluate plus concentrate, L/h). The percent removal of a constituent in a feed solution is often expressed as concentration reduction calculated by

$$\text{Percent removal (\%)} = \left(1 - \frac{C_d}{C_f}\right) \times 100 \quad (2)$$

where C_d is the diluate or product water concentration (g/L) and C_f is the feed concentration (g/L). The same calculation applies to the

removal of arsenic from water during coagulation and adsorption experiments.

For ED operation, the desalination energy is directly related to current density, which is defined as

$$\text{Current density (A/m}^2\text{)} = \frac{I}{S_1} \quad (3)$$

where I is the current through the ED stack (amps) and S_1 is the membrane surface area of a single pair (m^2).

The normalized salt removal rate is given as grams of salt removed per m^2 of membrane area per watt hour (Wh) of energy used. The normalized removal rate allows the comparison of salt removal using different ED stacks and under different operating conditions, such as with different membrane area, flow rate, and applied energy. It also allows the extrapolation of bench-scale results to estimate the energy consumption and salt removal for pilot testing. For once-through mode operation,

$$\text{Normalized salt removal (kg/m}^2\text{/kwh)} = \frac{(C_f - C_d) \times Q_d}{S \times I \times V} \quad (4)$$

where V is the applied voltage to the ED stack (volts), S is the membrane area of the stack (m^2).

In this study, electrical conductance (EC) or conductivity was used as an indicator for total dissolved solids. To convert EC to TDS, the TDS/EC ratio (g/L per mS/cm) was estimated based on the measured EC and calculated TDS values. TDS was calculated based on the sum of total cations and anions. The measured TDS of the RO concentrate was slightly higher than the calculated TDS (approximately 7.8%).

3. Results and discussion

3.1. Selective removal of arsenic from RO concentrate

Arsenic was removed from the RO concentrate using 3 different coagulants: ferric chloride solution, ferric sulfate solution, and iron sludge. Both ferric chloride and ferric sulfate coagulants show increased arsenic removal with increasing dose at ambient operating pH of 7.6 (Fig. 1). For ferric chloride, 80% removal of arsenic occurs at an Fe:As molar ratio of 410 or greater ($\geq 9 \text{ mg/L as Fe}^{3+}$), achieving $6 \mu\text{g/L}$ arsenic concentration in the treated water. Ferric sulfate also removes greater than 80% of arsenic beginning at molar Fe:As ratios of 820 ($18 \text{ mg/L as Fe}^{3+}$). Removal results show that both ferric chloride and sulfate metal salts successfully produce enough hydrous ferric oxides/hydroxides to decrease

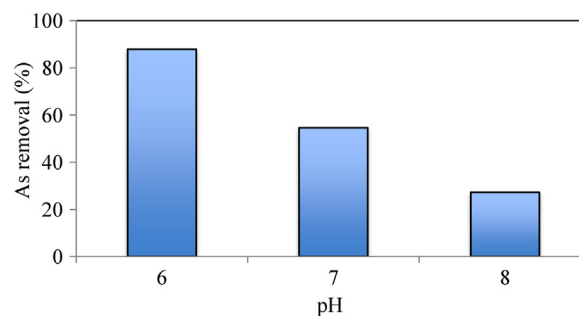


Fig. 2. Removal of arsenic using ferric chloride coagulant (Fe:As molar ratio 273 and $6 \text{ mg/L as Fe}^{3+}$) at different pH values.

arsenic concentrations to below $10 \mu\text{g/L}$; however, more ferric sulfate coagulant is required than ferric chloride.

Using ferric chloride as coagulant at Fe:As molar ratio of 273 (6 mg/L Fe^{3+}), arsenic removal increased significantly from 27% to 55%, and up to 88% with pH decreasing from 8 to 7, and down to 6, respectively (Fig. 2). This corresponds to the literature findings in high ionic strength solutions [51,52]. Lowering pH reduces competition of hydroxide ions for hydrous ferric oxides surface sites and thus the affinity of arsenic to ferric coagulants is not inhibited. The decreased pH is also thought to have increased the positive charge on the hydroxide surface, which increased the affinity for As(V) to bind.

In this study the Fe/As molar ratios appear high for the removal of arsenic from RO concentrate compared to low salinity water or synthetic solutions reported in the literature, which could be attributed to the feed water chemistry. Sancha reviewed the coagulation technology for arsenic removal in various surface and groundwater treatment plants in Chile [53]. To meet the drinking water standard of $10 \mu\text{g/L}$, an Fe:As molar ratio ranging from 47 to 65 was required to remove $400 \mu\text{g/L}$ arsenic in surface water with TDS between 700 and 800 mg/L . A similar Fe:As ratio of 53 was reported for groundwater with arsenic concentration of $70 \mu\text{g/L}$ and TDS concentration of $730\text{--}790 \text{ mg/L}$ [53]. Using synthetic solution prepared with sodium chloride, sodium bicarbonate, and disodium hydrogen arsenate, Mercer and Tobiason [51] found that arsenic removal was more successful at higher ionic strength and lower pH solutions. At lower ionic strengths, electrostatic interactions have a greater influence on colloids and subsequently reduce floc formation. Increased TDS concentration is thought to reduce electrostatic repulsions and provide more opportunities for particles to come in contact with the coagulant. However, this study finds that the demand of iron dose in real RO concentrate is much higher than in both synthetic solution [51] and low salinity water [53]. Using FeCl_3 solution as the coagulant, 80% removal of arsenic was achieved at an Fe:As molar ratio of 410 in RO concentrate compared to 10:15 in synthetic solutions [51]. This infers competition of other constituents in RO concentrate for the adsorption capacities of hydrous ferric oxides/hydroxides. Previous studies have found that chloride, sulfate, phosphate, fluoride, silicate, and organic species can compete with arsenate and arsenite for adsorption on ferrihydrite and other adsorbents [54]. It was reported that the impact of competing species on the adsorption of arsenic to iron hydroxide was in the order of phosphate > humic acid > silicate > sulfate. The RO concentrate has high concentrations of chloride (5050 mg/L), sulfate (1260 mg/L), and silicate (150 mg/L), but trace level of arsenic ($30 \mu\text{g/L}$); the competition of these constituents could be remarkable, resulting in decreased arsenic removal and significantly higher dose of coagulants.

Ferric sludge is found ineffective for removing arsenic using flocculation/coagulation/filtration method. The ratio of Fe:As is in

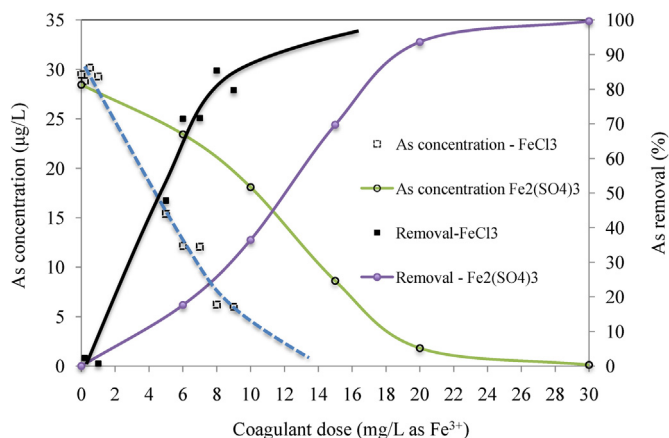


Fig. 1. Removal of arsenic using ferric chloride and ferric sulfate as coagulants at ambient pH 7.6. Standard deviation of arsenic concentration in duplicate samples was approximately $0.1 \mu\text{g/L}$.

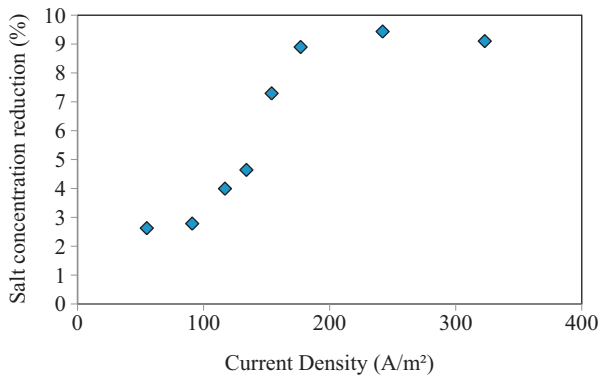


Fig. 3. Salt removal as a function of current density during ED desalination of RO concentrate.

the range of 456 and 2279. It was observed during the jar testing that the sludge condensed and amassed at the bottom of the jar and was not evenly distributed during mixing. It is likely that because the conglomerated sludge is not distributed throughout the water solution, there is not enough hydrolyzed iron in solution to destabilize and aggregate the dissolved arsenic. However, when using ferric sludge as adsorbent in column experiments at ambient pH, the removal efficiency increases to $86.7 \pm 0.9\%$ and the arsenic concentration was reduced to below $3.2 \mu\text{g/L}$. It implies that the pre-formed ferric sludge can provide active sites for adsorption of dissolved arsenic by surface complexation or ligand exchange. A recent study by Gibbons and Gagnon [55] reported that using ferric sludge to treat low salinity arsenic groundwater achieved the highest adsorptive capacity for arsenic of 43 g/kg. A column adsorption experiment showed ferric residual solids achieved arsenic removal of >26,000 bed volumes before breakthrough past $10 \mu\text{g As/L}$ [55]. These studies demonstrated that ferric sludge, an industrial waste with high availability and low costs, could be a promising adsorbent for arsenic removal. However, the form of the sludge may make it difficult to use in a column configuration. More research is required for better design of adsorption reactors and investigating the competition of a variety of constituents in highly saline concentrate. Leaching of other contaminants, including pathogens, from sludge to treated water should be examined as well.

3.2. Determine the limiting current density of ED system

The limiting current density (LCD) in the ED process is an important parameter that determines the electrical resistance and the current utilization. Usually, LCD depends on membrane and solution properties as well as on the ED stack construction and various operational parameters such as the flow velocity of the diluate solution and water temperature. In this study the LCD in the ED unit treating the RO concentrate was measured using the method first proposed by Cowan and Brown [56] where the LCD is calculated by the voltage divided by the current as opposed to solely the inverse current. The LCD is determined at an Ohm value of 12.2Ω , which corresponds to a unit voltage of 24 V and a current density above 154 A/m^2 .

Fig. 3 illustrates the salt concentration reduction in the 1-stage ED process as a function of current density. Salt concentration reduction increases with increasing current density then levels off at 9.4%. It infers that the operating current density could be approximately 190 A/m^2 , slightly higher than the limiting current density estimated for the RO concentrate using the 1-stage bench-scale ED unit. Further increase of the current density did not result in the improvement of salt removal because of the decrease in current efficiency of the ED stack.

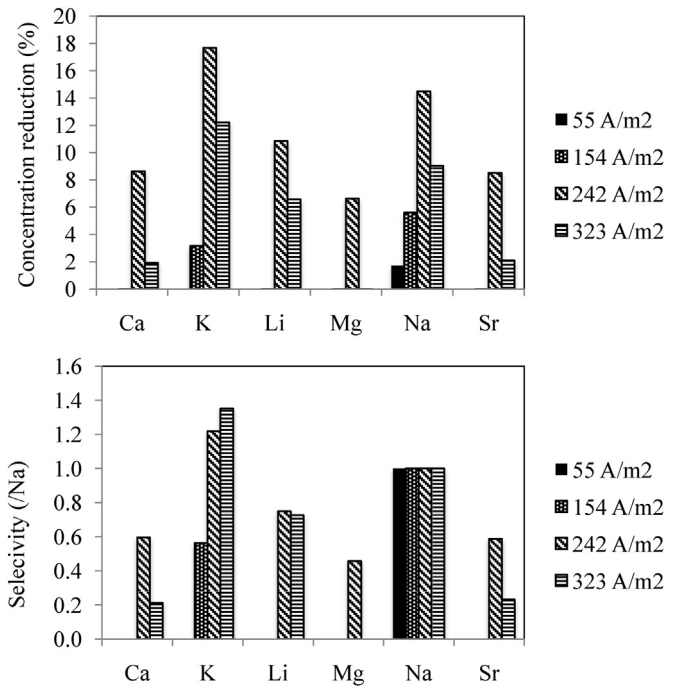


Fig. 4. Cations removal and selectivity under different current densities during ED desalination of RO concentrate.

3.3. Selective removal of monovalent ions from RO concentrate

Removal of cations and anions under different current densities was determined based on the samples taken throughout the ED testing using IC, ICP-AES, and ICP-MS analysis (Figs. 4 and 5). Under low current density (55 A/m^2), the total concentration reduction of cations was less than 2%, mainly as sodium. Removal efficiency begins to increase near the limiting current density (154 A/m^2 or a unit voltage of about 20 V). The highest removal rates for potassium (K^+), calcium (Ca^{2+}), sodium (Na^+), and strontium (Sr^{2+}) are seen at a current density of 242 A/m^2 or a unit voltage of 30 V. Higher current

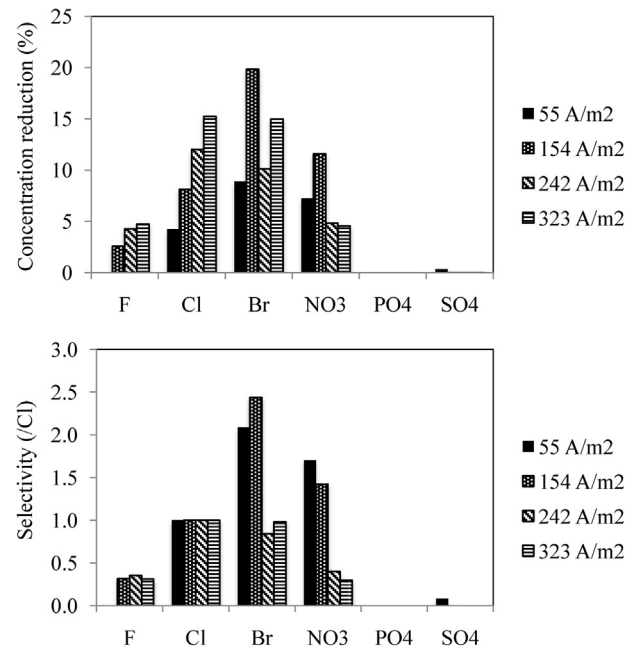


Fig. 5. Anions removal and selectivity under different current densities during ED desalination of RO concentrate.

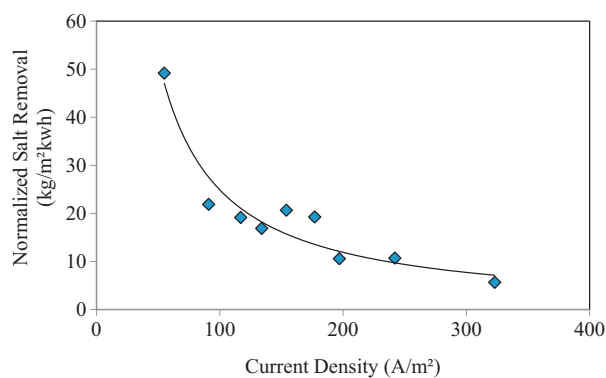


Fig. 6. Normalized salt removal as a function of current density for ED desalination of RO concentrate.

density of 323 A/m² did not result in higher cation concentration reduction, due to the energy used for water hydrolysis.

The removal of anions exhibits similar trend as cations, concurrently increasing with current density but decreasing at high current density of 323 A/m² (Fig. 5). Chloride and fluoride removal increased over the course of the experiment while nitrate showed the highest removal at a current density of 154 A/m². There was little to no transport of phosphate and sulfate through the membranes, which corresponds to the high selectivity of the monovalent permselective membranes used for the ED experiments.

The selectivity of individual ions compared to sodium and chloride was calculated based on the percent removal of cations and anions against the percent removal of sodium and chloride at different current densities. These parameters show the selective removal efficiency of cations and anions with the same charge using the specific ED membranes. Removal of monovalent cations was high as expected though there is some removal of divalent ions. At current densities between 55 and 154 A/m², the selectivity of removing sodium was the highest (Fig. 4). However, the selectivity of potassium surpasses sodium at current densities of 242 and 323 A/m². This corresponds to findings by Zhang et al. and is attributed to the fact that potassium has a lower hydrated ionic radius and a higher molar conductivity and therefore it diffuses faster than sodium through the ED membranes [11]. Yet, the overall removal selectivity of monovalent cations over divalent cations by CEM decreases with the increase in current density. This phenomenon has been observed consistently during our ED studies, and treating other types of RO concentrate and brackish groundwater.

For monovalent anions, the removal selectivity of bromide and nitrate was higher than chloride at current densities of 55 and 154 A/m², but less than chloride at higher current densities (Fig. 5). The removal selectivity of fluoride was consistently lower than chloride. AEM exhibit high selectivity to reject monovalent anions over divalent and trivalent anions (sulfate and phosphate). There was no transport of phosphate detected over the range of studied current densities while the transport of small amount of sulfate was detected only at 55 A/m². Therefore, the selectivity between monovalent anions and multivalent ions was not impacted by current density.

The removal efficiencies reported in this study are not absolute values; they depend on applied current density, membrane area, and flow rates. Therefore, normalized salt removal rate in terms of mass of salt removed per membrane area per kilowatt hour was calculated and illustrated in Fig. 6. The normalized salt removal rate decreases with the increase in current density, indicating that the energy efficiency reduces at higher applied unit voltage. The maximum salt removal rate of 50 kg salt/m² kWh was achieved at a current density of 55 A/m².

4. Conclusion

As energy and water needs increase worldwide, it becomes necessary to increase the recovery of water in both drinking and wastewater treatment facilities. For inland communities, especially in arid places, employing environmentally responsible and economically sustainable solutions for concentrate management and water use is essential. Efforts to recover clean water from membrane desalination concentrates are becoming more important as new inland freshwater sources become scarce. The benefits of improving recovery include a more viable water source, high quality of water, a reduction in waste volume, and potential extraction of valuable salts from the concentrate.

Ferric salt coagulants have been proven successful in removing arsenic from high ionic strength RO concentrate. While both ferric chloride and ferric sulfate removed over 80% of arsenic from RO concentrate (achieving arsenic concentration below 6 µg/L in treated water), ferric chloride required less materials and is therefore a potentially more cost effective method. Ferric sludge from water treatment plant was also efficient at removing arsenic as adsorbent during column testing. Using ferric sludge to treat RO concentrate may provide a promising technology for arsenic removal at low costs. Due to the high salinity level in RO concentrate and competition of other constituents for hydrous ferric oxides adsorption sites such as sulfate and silica, the requirement of coagulant dose for RO concentrate is expected to be higher than the chemical demand for water with low salinity.

Electrodialysis with monovalent permselective membranes exhibited high selectivity to remove monovalent ions from RO concentrate. ED can effectively remove monovalent ions such as sodium, chloride, and nitrate over divalent and multivalent ions in RO concentrate, resulting in an adjusted sodium adsorption ratio and reduced chloride concentration in the ED product water. Increase in current density had little impact on the high selectivity of monovalent anions over divalent anions but the transport of divalent cations through the monovalent permselective CEM increased with increasing current density. High salt reduction was achieved around the limiting current density of 190 A/m² while the highest energy use exhibited at low current density, approximately 50 kg salt/m² kWh at the current density of 55 A/m².

Three separate streams will be produced in the process to be disposed of, or used, in different manners. The coagulated sludge containing arsenic can be disposed of in landfill. The ED product stream containing multivalent ions, such as calcium and magnesium, is beneficial to the agricultural industry and can be made available as an application to farmland. And finally, the ED concentrate stream containing monovalent ions, such as sodium and chloride, and low arsenic concentration, can be disposed of using deep-well injection.

Although the ED treated the RO concentrate without any pretreatment, membrane fouling and scaling was not observed during the laboratory testing because of the low reduction of organics, silica, and hardness. This study demonstrated the feasibility of using coagulation and adsorption, and ED to selectively remove arsenic and monovalent ions from RO concentrate. Pilot study is required to further investigate the overall salt reduction, arsenic removal, water recovery, and economic effectiveness.

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