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Emerging investigator series: Capacitive Deionization for Selective Removal of Nitrate and Perchlorate: Impacts of Ion Selectivity and Operating Constraints on Treatment Costs

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Water Impact Statement

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**Emerging investigator series: Capacitive Deionization for Selective
Removal of Nitrate and Perchlorate: Impacts of Ion Selectivity and Operating
Constraints on Treatment Costs**

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Abstract

Treating toxic monovalent anions such as NO_3^- or ClO_4^- in drinking water remains challenging due to the high capital and environmental costs associated with common technologies such as reverse osmosis or ion exchange. Capacitive deionization (CDI) is a promising technology for selective ion removal due to high reported ion selectivity for these two contaminants. However, the impacts of ion selectivity and influent water characteristics on CDI life cycle cost have not been considered. In this study we investigate the impact of ion selectivity on CDI system cost with a parameterized process model and technoeconomic analysis framework. Simulations indicate millimolar concentration contaminants such as nitrate can be removed at costs in the range of $\$0.01\text{--}0.30 \text{ m}^{-3}$ at reported selectivity coefficient ranges ($S = 6\text{--}10$). Since perchlorate removal involves micromolar scale concentration changes, higher selectivity values than reported in literature ($S > 10$ vs $S = 4\text{--}6.5$) are required for comparable treatment costs. To contextualize simulated results for CDI treatment of NO_3^- , CDI unit operations were sized and costed for three cases studies based on existing treatment facilities in Israel, Spain, and the United States, showing that achieving a nitrate selectivity of 10 could reduce life cycle treatment costs below $\$0.2 \text{ m}^{-3}$.

Water Impact Statement

Cost-effective treatment of ionic pollutants such as NO_3^- or ClO_4^- remains a major challenge. In this study, we investigate for the first time, the cost of capacitive deionization (CDI) systems for treatment of NO_3^- or ClO_4^- using a full-scale sizing and costing framework. Across three case studies for selective NO_3^- removal, CDI could achieve treatment at below $\$0.4 \text{ m}^{-3}$.

1. Introduction

Nitrate is a common water contaminant which has been shown to cause acute toxic response and has been investigated as a potential carcinogen.¹ To avoid adverse health impacts of ingesting NO_3^- both the WHO and US EPA proscribe 10 mg-N L^{-1} maximum contaminant levels (MCLs) in drinking water.¹⁻³ Likewise, ClO_4^- toxicity in humans has been observed at very low doses, prompting an Interim Drinking Water Health Advisory of 15 $\mu\text{g L}^{-1}$ by the US EPA.^{4,5} However, the relatively low salinity of contaminated drinking water and the presence of other anions makes removal of ClO_4^- and NO_3^- difficult, particularly by technologies which lack ion-specificity.⁶⁻¹⁰ When selective ion exchange (IEX) systems are used for NO_3^- the brines used to regenerate resins incur a significant economic and environmental burden, accounting for as much as 77% of total system operating/maintenance costs.¹¹⁻¹³

Capacitive deionization (CDI) is a class of electrochemical separation technologies which has been primarily studied for brackish water desalination.¹⁴⁻¹⁸ While numerous performance metrics have been proposed to best evaluate the efficacy of CDI as compared to other desalination technologies such as reverse osmosis (RO) and electrodialysis (ED),¹⁴⁻¹⁶ only recently has a sizing framework been introduced to enable quantification of the capital and operating life cycle water costs ($\text{\$ m}^{-3}$) of CDI systems.¹⁹ Our recent technoeconomic analysis (TEA) of brackish groundwater desalination with CDI showed that capital and operating costs are proportional to the influent concentration and target concentration reduction (Δc), indicating applications in low salinity water, which require lower concentration reduction, would be far less expensive. Since CDI is an electrochemical separation process, ion-selective removal presents a myriad of possible

alternative applications to water desalination.^{20–23} While CDI systems have been studied for selective removal of numerous ions,^{23–40} ClO_4^- and NO_3^- removal have been of particular interest to the CDI field.^{2,7,8,24,25,41–46}

Bare carbon CDI systems have been shown to have high selectivity for NO_3^- and ClO_4^- , up to a 6:1 and 4:1 selectivity over the more abundant Cl^- , respectively.^{2,25,42–46} Additionally, anion exchange membranes and electrode modifications have been shown to increase NO_3^- sorption.^{7,8,44,47} Because the capital cost of CDI systems are proportional to the target concentration reduction and account for the majority of total system cost, increasing ion selectivity offers promising means of reducing CDI cost for pollutant removal.¹⁹ In this study, ion selectivity is incorporated into a process model TEA framework for CDI. This ion selective TEA framework is used to elucidate the impacts of influent concentration, MCL, ion mixture, and selectivity on the costs of CDI and membrane CDI (MCDI) systems for the removal of two toxic oxyanions (ClO_4^- and NO_3^-). Lastly, we sized and costed CDI systems based on the water quality and flow/separations conditions drawn from three NO_3^- removal case-studies.

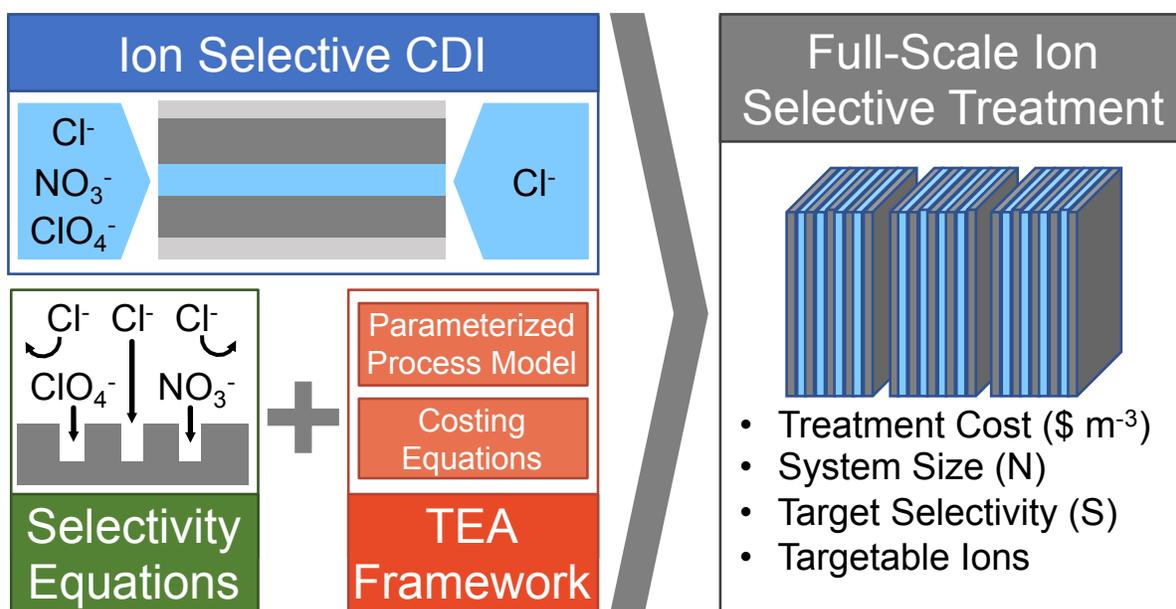


Figure 1. Ion-selectivity was incorporated in a parameterized process model-based techno-economic analysis framework. Input parameters drawn from lab-scale ion-selective CDI systems were used to evaluate selective ion removal system size and treatment cost at full-scale. Full-scale treatment costs were used to benchmark cost-effective ion selectivity and identify target ions for economic treatment.

2. Materials and Methods

2.1. Incorporating ion-selectivity within the parameterized process model and techno-economic analysis framework

Constant current CDI systems were sized for selective removal of either NO_3^- or ClO_4^- across ranges of water quality and operating/material parameters using a coupled electrochemical/hydraulic process model framework as described in Ref 6 (Fig 1). Briefly, the necessary number of hydraulically parallel cell pairs are calculated at given treatment characteristics and operating/material parameters including cell voltage limit (V, Volts), cycle time (t, sec), electrode area (A, cm^2), area-normalized equivalent series resistance

(R , $\Omega \text{ cm}^2$), specific capacitance (C , F g^{-1}), current density (i , A m^{-2}), water recovery (WR), double-layer adsorption efficiency (η_C), treatment flow (Q , L s^{-1}), and influent/effluent concentrations (c_{in}/c_{out} , equivalents L^{-1}) (Table 1). From the total number of cells pairs, total mass of active material and energy consumed per cycle are calculated to size a CDI system. In all cases, ideal energy recovery was assumed (i.e., 100% of recoverable energy during discharge was recovered). The CDI system is then costed according to size of the system determined from the parametric model.

Table 1. Selective CDI and MCDI input parameters.

Input	Symbol	Value	Unit
Voltage Limit	V	0.6	V
Total Cycle Time	t	1200	s
Electrode Area	A	70–150	cm^2
Equivalent Series Resistance	R	30–150	$\Omega \text{ cm}^2$
Influent Concentration	c_{in}	10	meq L^{-1}
Flow	Q	200	L s^{-1}
Specific Capacitance	C	40–70	F g^{-1}
Current Density	i	5–7	A m^{-2}
Pump Energy Consumption	E_P	0.1–0.3	kWh m^{-3}
CDI Charge Efficiency	η_{Cc}	0.3–0.6	
MCDI Charge Efficiency	η_{Cm}	0.8–1.0	
Water Recovery	WR	0.5–0.9	

Per Ref 6, electrodes were modelled and costed as composite electrode sheets composed of activated carbon, polymeric binder, and conductivity additive at 85:10:5 wt.%, respectively. The projected area of electrodes was varied between 70 to 150 cm^2 and the thickness of the electrodes (δ_e , μm) was determined from the electrode density and the calculated electrode mass ($\delta_e \leq 500 \mu\text{m}$ across all runs). Each cell stack was modelled and costed with 400 parallel cell pairs. The price of each stack was composed

of graphitic current collectors, electrode cost, frames/gaskets, electrode separators, and ion exchange membrane (IEM) costs for MCDI systems (Table 2). IEM costs were assumed as low-cost, cast layers as reported for commercial MCDI applications.^{48,49} Capital costs included the cell stack component and balance-of-plant costs which includes heat management equipment and power electronics. Pumping costs were estimated as 0.1–0.3 kWh m⁻³ based on cell geometry and previously reported values for comparably operated systems.^{19,50,51} Operating costs were limited to the electricity directly utilized by the CDI stack and electricity consumed by pumping. From the capital and operating costs, a discounted cash flow analysis was used to calculate the equivalent annual cost (EAC) of the system over various system lifetimes. The discount rate for capital costs was set at 3% per the U.S. EPA's Water Infrastructure Finance and Innovation Act (WIFIA) program, and the discount rate for annual operating cost was fixed at 7%. The results EAC was normalized to annual water production in order to determine water price. We refer our readers to our previous study for detailed equations governing system sizing and costing (See SI Section 2).¹⁹

Table 2. Constituent costs for selective CDI and MCDI systems.

Input	Value	Unit	Source
Carbon	20	\$ kg ⁻¹	52–54
Current Collector	5	\$ m ⁻²	55–58
Frames	2	\$ m ⁻²	58
Separator	3	\$ m ⁻²	58,59
Conductivity Additive	3.3	\$ kg ⁻¹	59
Binder	14	\$ kg ⁻¹	59
IEM	20	\$ m ⁻²	19
Balance of Plant	300	\$ kW ⁻¹	58
Electricity	0.07	\$ kWh ⁻¹	19
Cell pairs per stack	400		19

In order to incorporate ion-selective removal, the parametric process model was modified to include ion-selectivity coefficients as previously reported for both CDI and MCDI systems.^{2,43,46} For any target ion, we assume electrosorption site competition between target ion and the dominant co-ion in solution (e.g., Cl⁻, HCO₃⁻, etc.). The selectivity of target ion removal over co-ions can be calculated per a modification of the IUPAC selectivity coefficient for adsorbed ions defined by Hawks et al.²:

$$S_{T/X} = \frac{c_{ads,T}/c_{m,T}}{c_{ads,X}/c_{m,X}} \quad (1)$$

where $S_{A/B}$ is the selectivity coefficient for target species T over species X, $c_{ads,T}/c_{ads,X}$ is the adsorbed concentration of target species T over species X in mM, and $c_{m,T}/c_{m,X}$ is the mobile concentration of target species T over species X in mM. From Equation 1, the effluent concentration goal for the target species and the influent water composition can be used to calculate the final concentration of other species as follows:

$$c_X = \frac{\beta X_0}{1 + \beta} \quad (2)$$

$$\beta = \frac{S_{T/X} c_T}{T_0 - c_T} \quad (3)$$

where c_X is the final concentration of species X in mM, X_0 is the initial concentration of species X in mM, c_T is the final concentration of the target species T in mM, and T_0 is the initial concentration of the target species T in mM. Finally, the initial and target concentrations of total ionic species input to the parameterized model can be calculated as:

$$c = \sum c_i z_i \quad (4)$$

where c is the total water concentration in meq L^{-1} , c_i is the concentration of species i in mM , and z_i is the charge number of species i in mM . Unless otherwise noted, the simulated electrolyte was a binary mixture composed of the target ion (NO_3^- or ClO_4^- , at commonly reported concentration ranges) and monovalent co-ion, Cl^- . The concentration total electrolyte concentration was fixed at 10^{-2} charge equivalents per liter (10 meq L^{-1}).

2.2. Case studies of existing NO_3^- removal systems

Using the above modifications to the previously developed parameterized sizing framework, CDI systems were sized for three reported NO_3^- removal cases: (1) surface water treatment at the South Water Treatment Plant in Decatur, Illinois (Decatur); (2) ground water treatment at the Weizmann Institute of Science in Rehovot, Israel (Israel); and (3) groundwater treatment at the Falconera Water Treatment Plant in Gandia, Spain.⁶⁰ Each of these locations was selected due to existing NO_3^- removal practices and a detailed water quality report including competing anions. Each CDI system was sized according to the treatment flows reported at each location with two target effluent quality conditions, 0.7 mM NO_3^- (the US EPA MCL) and 0.35 mM NO_3^- ($\frac{1}{2}$ MCL), given the influent conditions reported for each case (Table 1). The input parameters used in all case studies were based on median values from previously reported ranges of CDI operating and material parameters with 85% water recovery and a 0.6 V operating window per experimental literature for selective ion removal (Tables 1 and 2).^{2,14,19,22,25,42,46}

Table 3. Anion composition of water across the three case studies for NO_3^- removal with CDI systems.

Ion	Concentration (meq L ⁻¹)		
	<i>Decatur</i>	<i>Spain</i>	<i>Israel</i>
NO_3^-	1.14	0.97	1.48
Cl^-	0.9	0.82	5.47
SO_4^{2-}	0.68	1.2	1.98
HCO_3^-	-	3.36	3.80
<i>Total Influent</i>	2.72	6.35	12.73

3. Results and Discussion

3.1. Impacts of water recovery and influent concentration on life cycle treatment cost

To evaluate the impacts of incorporating ion-selective removal on performance and costs, we evaluated both CDI and MCDI with a generalized binary electrolyte mixture (i.e., a 1:1 ratio of generic target ion and to generic co-ion) with no selectivity ($S = 1$). Life cycle water treatment cost was calculated for CDI systems operating at water quality and separation conditions typically observed in selective ion removal for drinking water. The systems were initially sized and costed across ranges of design parameters (cycle length, electrode projected area, current, ion removal fraction, and water recovery) and material parameters (setup resistance, specific capacitance, charge efficiency) (Table 1) for a change in total electrolyte concentration of 5 mM.

At the conditions simulated in this study, volumetric energy consumption with complete energy recovery for both MCDI and CDI varied between 0.15–0.65 kWh m⁻³, which corresponds to the previously reported ranges at similar concentration reductions ($\Delta c \leq 9$ meq L⁻¹) (Fig. S1).^{16,18,61} Similarly, productivity in the simulated systems was generally comparable to previously reported values (10–50 L m⁻³ h⁻¹) (Fig. S1).^{16,19} Since

ionic conductivity is lower in selective removal from drinking water than brackish water desalination, a lower operating current densities is required to avoid operating capacity loss due to ohmic resistance. Accordingly, the maximum productivity observed in this study was lower than that of our previous brackish water desalination TEA (50 vs. 65 L m⁻³ h⁻¹, respectively) due to the reduced maximum current density (7 vs. 25 A m⁻², respectively).¹⁹

Because selective ion removal systems often operate at lower influent concentration and concentration reduction than those for brackish water desalination ($c_{in} = 10$ vs. 50 meq L⁻¹ and $\Delta c = 5$ vs. 42.5 meq L⁻¹), the (M)CDI systems investigated in this study were able to achieve comparable system prices to previously reported capacitive brackish water deionization systems at substantially lower lifetimes.¹⁹ For example, at identical water recovery selective ion removal with CDI and MCDI systems with 12,000 cycle lifetimes cost \$0.30 m⁻³ and \$0.72 m⁻³, respectively (Figs. 2A and 2D). To achieve comparable water treatment costs for brackish water desalination, CDI and MCDI system must reach 72,000 and 144,000 cycles lifetimes, respectively.¹⁹ Increasing (M)CDI lifetime from 6,000 to 24,000 cycles reduces median system price across all water recovery conditions (Figs. 2A and 2D).

Under conditions evaluated in this study, both CDI and MCDI systems could be sized to achieve at least 0.95 water recovery, despite increased water prices beyond water recovery of 0.85 for CDI. In contrast, brackish desalination designs, which require greater concentration reduction ($\Delta c > 10$ mM), are unable to consistently achieve water recovery above 0.8 when simulated under otherwise comparable constant current operational modes.¹⁹ An inflection in water production cost is observed at a water recovery of 0.85

for all lifetimes for CDI (Figs. 2A). To achieve increased water recovery, higher discharge currents must be used when operated at a given total cycle length. Therefore, as the water recovery is increased, the total energy consumption per cycle and thus operating costs increase as well. When water recovery exceeds 0.85, increased water production ceases to offset the additional operating expenses to achieve higher water recovery and the water price begins to increase (Fig. S2). Since operating costs compose a smaller percentage of total system costs in MCDI, no local minimum in water price is observed in the water recovery ranges sampled (Fig. 2D). These results suggest that while an optimal water recovery for CDI system may exist at below the maximal achievable value (>0.95), cost-effective operation of MCDI systems will likely entail maximizing water recovery.

When evaluated at comparable lifetime and water recovery, the treatment price MCDI systems was greater than that of CDI despite improved performance due to the high cost contribution of IEMs ($>70\%$ of total costs at lifetimes less than 24,000 cycles) (Fig. 5). However, due to the carbon corrosion from parasitic processes, it will be challenging to achieve extended cycling in CDI.^{64,73,74} Conversely, MCDI has shown greater cycling stability due to reduced oxygen diffusion through IEMs, with commercial MCDI systems targeting 300,000 cycle lifetimes.^{15,63–66,75,76} As MCDI systems operate beyond 48,000 cycles (approximately 2 years of operation as simulated in this study), water price drops below that of CDI systems with optimistic 24,000 cycle lifetimes (Fig. S3).

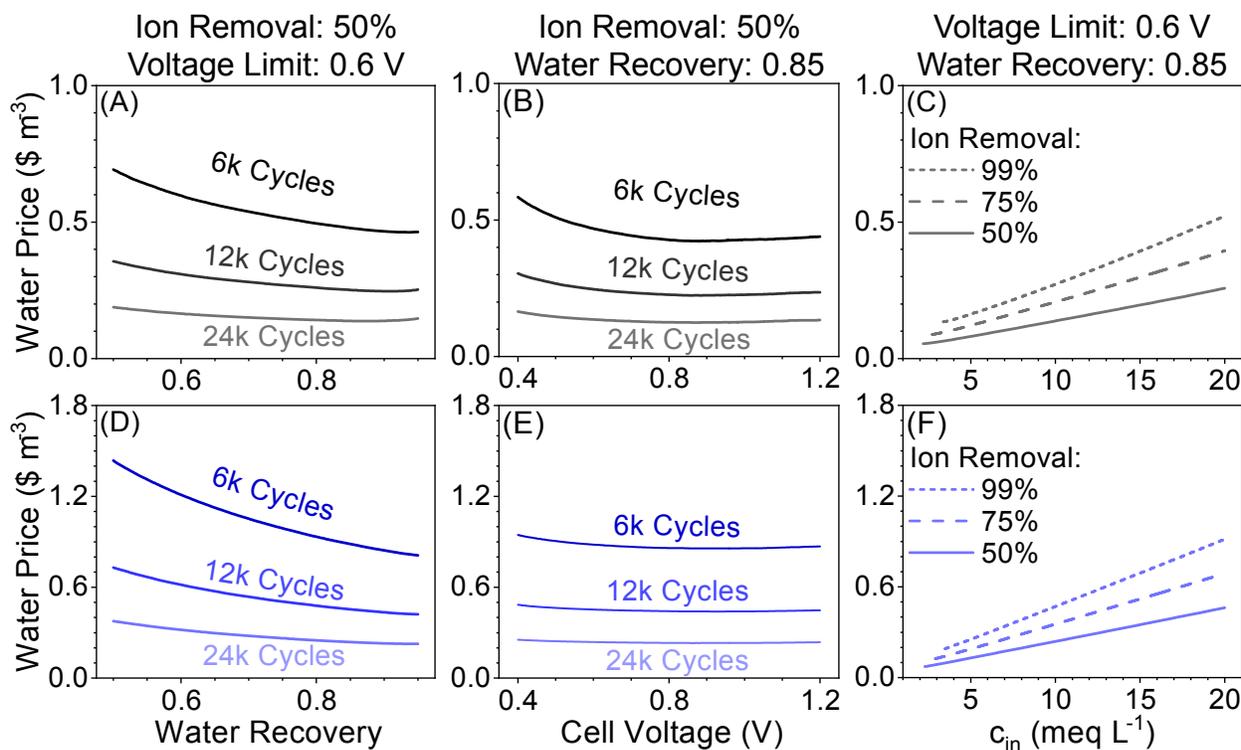


Figure 2. Median water price ranges (A, D) for CDI (A–C) and MCDI (D–F) systems as a function of water recovery and lifetime when the influent target ion (c_0) is fixed at 10 meq L⁻¹, target ion removal is 50%, cell voltage limit is 0.6 V, and ion selectivity is one. The impacts of cell voltage limit (B, E) and influent concentration and target ion removal fraction (C, F) are evaluated at optimal water recovery (0.85) and lifetime (24,000 cycles) concentration at 85% water recovery in a 1:1 mixture of the target ion and co-ion. Shaded boundaries indicate 25th–75th percentiles and lines indicate 50th percentile of price range. Increasing water recovery and system lifetime lead to lower water prices due to reduction in capital contributions to total cost. Increasing target ion removal likewise increases water price but the impact diminishes with influent concentration.

The impacts of cell voltage limit (Figs. 2B and 2E) are evaluated at optimal water recovery (0.85) and 24,000 cycle lifetimes (~1 year of operation). While constant current CDI systems are generally operated with 1.2 V voltage limits in maximize capacity for

brackish water desalination, increasing the voltage limit also increases the prevalence of parasitic reactions which reduce system lifetimes.^{62–66} Although recent studies have utilized a lower cell voltage limit of 0.6 V for selective ion removal, both CDI and MCDI were simulated from 0.4–1.2 V (Figs. 2B and 2E).^{2,22,25,42,46} For both MCDI and CDI, increasing the voltage limit from 0.4 V to 0.6 V decreased water price by nearly 25% across all system lifetimes (Figs. 2B and 2E). Because reducing the cell voltage limit reduces the available ion removal capacity of each cell, more cells are needed to achieve target effluent quality, increasing system cost. However, increasing the cell voltage has diminishing returns for reducing total system mass at the relatively low concentration reductions simulated in this study ($\Delta c = 5$ vs 10–40 meq L⁻¹ for brackish water desalination). Since energy consumption and operating costs are increased with greater voltage limits, there was little net change in system price as the voltage limit was increased beyond 0.6 V. While water prices do not significantly change at voltage limits above 0.6 V, the parametrized model utilized in this study does not account for parasitic charge transfer reactions which would adversely impact system performance and reduce system lifetimes at higher cell voltage limits, leading to higher water prices than those reported in this study.^{62,63}

Lastly, the impact of ion removal fraction and total influent ion concentration are evaluated at optimal water recovery (0.85) and 24,000 cycle lifetimes (~1 year of operation) (Figs. 2C and 2F). For both MCDI and CDI, water prices generally increase linearly with increasing influent concentration. The system size and corresponding capital cost has been shown to control total system price¹⁹ for both MCDI and CDI. Because system size is governed by the total moles of ions removed per cycle (the product of

influent concentration and ion removal fraction), increasing the ion removal fraction also increases the slopes of positive rate of change between water price and influent concentration for both CDI and MCDI (Fig. 2C and 2F). At total influent ion concentrations below 10 meq L^{-1} , both MCDI and CDI water prices for unselective removal of a generalize binary salt are comparable to or below reported NO_3^- treatment water price for RO ($\$0.67\text{--}0.82 \text{ m}^{-3}$), but only simulated CDI values are fall below those reported for ion exchange ($\$0.17\text{--}0.38 \text{ m}^{-3}$).^{13,60,67}

3.2. Impacts of selectivity on life cycle treatment cost

To evaluate the impact of ion selectivity on treatment costs for two regulated anions commonly found in drinking water, CDI systems were sized specifically for NO_3^- and ClO_4^- removal. In all cases, the total ion concentration was fixed at 10 meq L^{-1} and target-ion mole fraction was varied across concentrations typically observed for NO_3^- ($T = 0.1\text{--}1.0$, $c_0 = 1\text{--}10 \text{ mM}$) and ClO_4^- ($T = 0.001\text{--}0.01$, $c_0 = 1\text{--}10 \text{ }\mu\text{M}$) (Fig. 3). Because increasing the selectivity of a target ion reduces the total amount of ions which need to be removed per cycle, the effective concentration reduction inversely scales with selectivity (Eq. 2–4).

For both NO_3^- and ClO_4^- , increasing selectivity decreases costs, however the relative importance of selectivity varies with both concentration reduction and target-ion mole fraction. Consequently, the significance of selectivity decreased with required Δc for both target anions. For example, in non-selective operation ($S=1$), a 0.1 target ion removal fraction requires every other co-ion to undergo an identical 0.1 ion removal fraction. At a 0.5 mole fraction and selectivity coefficient of 10, a 0.1 target ion removal fraction requires co-ion removal fractions of only 0.53. Therefore, at very low Δc , any change in selectivity has a proportionally low change in Δc and equivalent system costs.

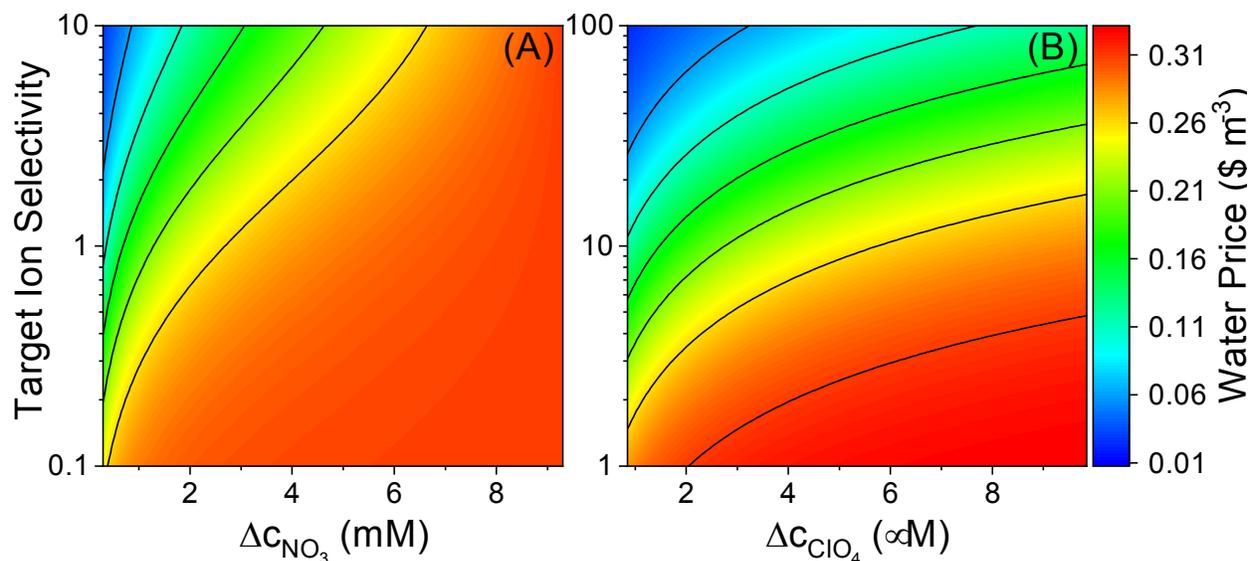


Figure 3. Impacts of ion selectivity and target ion concentration reduction on treatment cost for NO_3^- (A) and ClO_4^- (B). The total ion concentration and systems lifetimes were fixed at 10 meq L^{-1} and 24k cycles for all conditions. The target ion effluent concentration was fixed at 0.7 mM for NO_3^- and $0.15 \text{ }\mu\text{M}$ for ClO_4^- . The high percent removal (85–99%) to achieve target ClO_4^- effluent concentration requires selectivity coefficients an order of magnitude higher than those reported for either NO_3^- or ClO_4^- to reach comparable water treatment costs.

Our results suggest that CDI may be cost-competitive for selective ion removal at low to moderate mole fractions, particularly with increased selectivity. Water prices below $\$0.20 \text{ m}^{-3}$ are achievable for NO_3^- at selectivity coefficients below those experimentally observed ($S=6\text{--}10$) (Fig. 3A).^{2,68} Conversely, increasing selectivity is crucial to achieving low treatment cost toxic anions in the micromolar range such as ClO_4^- (Fig. 3B). Reducing the water price below $\$0.20 \text{ m}^{-3}$ will generally require ClO_4^- selectivity above 10, which eclipse the range of selectivity values reported in the literature for this ion at comparable concentrations to those of this study ($S=4\text{--}6.5$).⁴⁶ The significant cost difference of

selective removal between the two target ions is due to relative removal necessary to achieve regulatory concentration levels for either NO_3^- or ClO_4^- (30–90% vs 85–99%). As the necessary removal percentage increases to higher levels (>95%), treatment requires near complete deionization of influent water (i.e., $c_{\text{out}} = 0.4 \mu\text{eq L}^{-1}$ to 0.5 meq L^{-1} , depending on influent ClO_4^- concentration). These findings align with recent observations that CDI cycling behavior begins to substantially deviate from ideal behavior at high influent concentrations for ion removal levels approaching 100%.⁶⁹ Such high concentration reductions can present a substantial barrier to cost-effective CDI implementation, particularly for influent waters with total ionic content above that typically seen for drinking water. Under such conditions alternative separations technologies such as shock electrodialysis, which achieves near complete deionization, might be more cost-effective.^{70,71}

3.3. Case studies for the cost of selective capacitive deionization of nitrate

Based on the promising simulated results reported in the previous section for selective removal of NO_3^- , CDI systems were sized and costed for the three potential treatment sites that differed in target ion concentration and water composition (Table 3). In order to simplify the analysis, the selectivity constants were identically fixed across all co-ions included in the water quality table for each instance ($S_{\text{NO}_3^-/\text{Cl}^-} = S_{\text{NO}_3^-/\text{HCO}_3^-} = 1, 10$) and all other system input parameters were fixed (Table S1). Water price of sized systems was strongly dependent on concentration reduction regardless of flow rate, with Israel and Decatur case study water prices being the greatest and least, respectively (Fig. 4 and Table 3). For all case studies and target effluent qualities, the price of treating water

with CDI was below the $\$0.33 \text{ m}^{-3}$ cost of existing technologies estimated by King et al.⁷² for the State of California (Fig. 4).

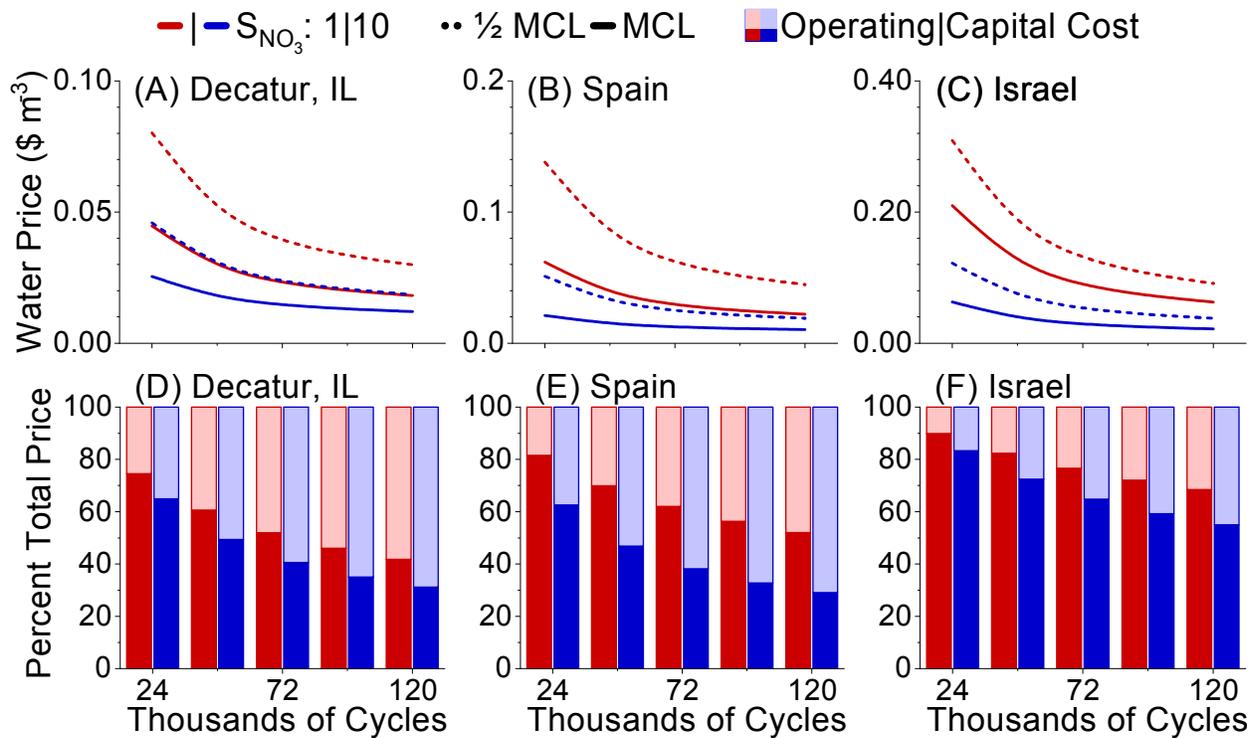


Figure 4. Water price (A–C) and operating vs capital cost contribution (D–F) for NO_3 removal with CDI systems sized for influent water quality determined by case studies located in Illinois (A, D), Spain (B, E), and Israel (C, F). Price was evaluated with target NO_3 effluent concentration set at MCL (0.7 mM, solid line) and $\frac{1}{2}$ MCL (0.35 mM, dashed line). Water price decreased as nitrate selectivity with respect to co-ions was increased from one (red) to ten (blue) due to decreased system sizes. While increasing selectivity decreases water price, this is largely due to reduced capital costs leading to lower relative capital contributions to total water price.

Since capital costs make up the majority of total cost (65–95%), the lifecycle water price for all case studies dropped approximately two- to three-fold when selectivity coefficients were increase from one to ten (Fig. 4). Conversely, decreasing the target

effluent NO_3^- concentration from 1 MCL (0.7 mM NO_3^-) to $\frac{1}{2}$ MCL (0.35 mM NO_3^-) approximately double to water price for all case studies. However, incorporating more selective materials served to offset the water price increase incurred by a more stringent product water quality limit. The relative cost improvements of increased selectivity were more pronounced at higher influent NO_3^- concentrations (Figs. 4A, C and Table 3). The cost of water treated to half MCL with $S_{\text{NO}_3^-/X} = 10$ was 1.18 times more than water treated to the MCL with no selectivity ($S_{\text{NO}_3^-/X} = 1$) for Decatur, IL (Figs. 4A), whereas for the Israel case, cost of water treated to one half the MCL with $S_{\text{NO}_3^-/X} = 10$ was 0.74 times less than water treated to the MCL with $S_{\text{NO}_3^-/X} = 1$. The Illinois and Spain case studies highlight how ion selective removal at low influent concentrations could lead to conditions in which pump and capacitor energy consumption are more influential than initial capital investment on life cycle water price (Fig. 4D–F). Therefore, while improving system lifetimes and charge efficiency are necessary to decrease the capital costs of CDI systems, increasing target ion selectivity in CDI is a promising means of either reducing treatment costs or achieving more stringent effluent quality levels without significantly increasing treatment costs.

4. Conclusions

The results of this study indicate that selective NO_3^- removal with CDI can likely be achieved economically within previously reported selectivity ranges if target cycle lifetimes can be attained.^{2,8,43} However, the removal of contaminants with lower influent concentrations or requiring high percent removal (such as ClO_4^- , Li^+ ,^{20,22,77–81} F^- ,^{24–31} Cr(VI) ,^{23,27,28,32} and As(III)/As(IV))^{23,33,34} with CDI will likely be cost-competitive only if high

selectivity can be achieved. The development of selective polymer electrodes is a promising avenue for engineering electrodes with high selectivity for target contaminants while also preventing degradation of the electrode.^{23,82,83} In addition to reducing water price by increasing selectivity, selective polymer materials may also reduce price by increasing charge and system lifetimes as previously reported.¹⁹ As is shock electro dialysis since near complete deionization is required in the micromolar concentration regime. Regardless of the target ion, CDI systems can potentially reduce treatment cost for dilute water by utilizing the intrinsic strengths of an electrochemical separations process over standard size exclusion or physio-adsorption separation.^{6,41,72}

Acknowledgments

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Supporting Information

Operating costs percentage for CDI and MCDI, model inputs for case study simulations, and design/costing equations for technoeconomic analysis framework.

Reference:

- 1 D. C. Bouchard, M. K. Williams and R. Y. Surampalli, Nitrate Contamination of Groundwater: Sources and Potential Health Effects, *Journal - American Water Works Association*, 1992, **84**, 85–90.
- 2 S. A. Hawks, M. R. Cerón, D. I. Oyarzun, T. A. Pham, C. Zhan, C. K. Loeb, D. Mew, A. Deinhart, B. C. Wood, J. G. Santiago, M. Stadermann and P. G. Campbell, Using Ultramicroporous Carbon for the Selective Removal of Nitrate with Capacitive Deionization, *Environ. Sci. Technol.*, , DOI:10.1021/acs.est.9b01374.
- 3 G. WHO, Guidelines for drinking-water quality, *World Health Organization*, 2011, **216**, 303–4.
- 4 Greer Monte A, Goodman Gay, Pleus Richard C and Greer Susan E, Health effects assessment for environmental perchlorate contamination: the dose response for inhibition of thyroidal radioiodine uptake in humans., *Environmental Health Perspectives*, 2002, **110**, 927–937.
- 5 O. US EPA, Technical Fact Sheet - Perchlorate, <https://www.epa.gov/fedfac/technical-fact-sheet-perchlorate>, (accessed 24 July 2019).
- 6 J. R. Werber, A. Deshmukh and M. Elimelech, The Critical Need for Increased Selectivity, Not Increased Water Permeability, for Desalination Membranes, *Environ. Sci. Technol. Lett.*, 2016, **3**, 112–120.
- 7 D. I. Oyarzun, A. Hemmatifar, J. W. Palko, M. Stadermann and J. G. Santiago, Ion selectivity in capacitive deionization with functionalized electrode: Theory and experimental validation, *Water Research X*, 2018, **1**, 100008.
- 8 H. I. Uzun and E. Debik, Economical approach to nitrate removal via membrane capacitive deionization, *Separation and Purification Technology*, 2019, **209**, 776–781.
- 9 K. Kannan, M. L. Praamsma, J. F. Oldi, T. Kunisue and R. K. Sinha, Occurrence of perchlorate in drinking water, groundwater, surface water and human saliva from India, *Chemosphere*, 2009, **76**, 22–26.
- 10 P. B. Hatzinger, M. C. Whittier, M. D. Arkins, C. W. Bryan and W. J. Guarini, In-Situ and Ex-Situ Bioremediation Options for Treating Perchlorate in Groundwater, *Remediation Journal*, 2002, **12**, 69–86.
- 11 L. Wang, A. Chen, A. Wang and W. Condit, *Arsenic and Nitrate Removal from Drinking Water by Ion Exchange U.S. EPA Demonstration Project at Vale, OR Final Performance Evaluation Report*, U.S. Environmental Protection Agency, Washington, DC, 2011.
- 12 J. K. Choe, A. M. Bergquist, S. Jeong, J. S. Guest, C. J. Werth and T. J. Strathmann, Performance and life cycle environmental benefits of recycling spent ion exchange brines by catalytic treatment of nitrate, *Water Research*, 2015, **80**, 267–280.
- 13 K. J. Meyer, P. D. Swaim, W. D. Bellamy, B. E. Rittmann, Y. Tang and R. Scott, Biological and Ion Exchange Nitrate Removal: Performance and Sustainability Evaluation, *Water Research Foundation, Denver*.
- 14 S. Hand, X. Shang, J. S. Guest, K. C. Smith and R. D. Cusick, Global Sensitivity Analysis To Characterize Operational Limits and Prioritize Performance Goals of Capacitive Deionization Technologies, *Environ. Sci. Technol.*, 2019, **53**, 3748–3756.

- 15 M. E. Suss, S. Porada, X. Sun, P. M. Biesheuvel, J. Yoon and V. Presser, Water desalination via capacitive deionization: what is it and what can we expect from it?, *Energy Environ. Sci.*, 2015, **8**, 2296–2319.
- 16 S. A. Hawks, A. Ramachandran, S. Porada, P. G. Campbell, M. E. Suss, P. M. Biesheuvel, J. G. Santiago and M. Stadermann, Performance metrics for the objective assessment of capacitive deionization systems, *Water Research*, 2019, **152**, 126–137.
- 17 L. Wang, J. E. Dykstra and S. Lin, Energy Efficiency of Capacitive Deionization, *Environ. Sci. Technol.*, 2019, **53**, 3366–3378.
- 18 M. Qin, A. Deshmukh, R. Epsztein, S. K. Patel, O. M. Owoseni, W. S. Walker and M. Elimelech, Comparison of energy consumption in desalination by capacitive deionization and reverse osmosis, *Desalination*, 2019, **455**, 100–114.
- 19 S. Hand, J. S. Guest and R. D. Cusick, Technoeconomic Analysis of Brackish Water Capacitive Deionization: Navigating Tradeoffs between Performance, Lifetime, and Material Costs, *Environ. Sci. Technol.*, 2019, **53**, 13353–13363.
- 20 M. E. Suss, Size-Based Ion Selectivity of Micropore Electric Double Layers in Capacitive Deionization Electrodes, *J. Electrochem. Soc.*, 2017, **164**, E270–E275.
- 21 C.-H. Hou and C.-Y. Huang, A comparative study of electrosorption selectivity of ions by activated carbon electrodes in capacitive deionization, *Desalination*, 2013, **314**, 124–129.
- 22 E. Guyes, T. Malka and M. E. Suss, Enhancing the ion size-based selectivity of capacitive deionization electrodes, *Environ. Sci. Technol.*, , DOI:10.1021/acs.est.8b06954.
- 23 X. Su, A. Kushima, C. Halliday, J. Zhou, J. Li and T. A. Hatton, Electrochemically-mediated selective capture of heavy metal chromium and arsenic oxyanions from water, *Nature Communications*, 2018, **9**, 4701.
- 24 J. Song, J. Ma, C. Zhang, C. He and T. D. Waite, Implication of Non-electrostatic Contribution to Deionization in Flow-Electrode CDI: Case Study of Nitrate Removal From Contaminated Source Waters, *Front. Chem.*, , DOI:10.3389/fchem.2019.00146.
- 25 W. Tang, P. Kovalsky, D. He and T. D. Waite, Fluoride and nitrate removal from brackish groundwaters by batch-mode capacitive deionization, *Water Research*, 2015, **84**, 342–349.
- 26 W. Tang, P. Kovalsky, B. Cao and T. D. Waite, Investigation of fluoride removal from low-salinity groundwater by single-pass constant-voltage capacitive deionization, *Water research*, 2016, **99**, 112–121.
- 27 M. S. Gaikwad and C. Balomajumder, Tea waste biomass activated carbon electrode for simultaneous removal of Cr(VI) and fluoride by capacitive deionization, *Chemosphere*, 2017, **184**, 1141–1149.
- 28 M. S. Gaikwad and C. Balomajumder, Simultaneous electrosorptive removal of chromium(VI) and fluoride ions by capacitive deionization (CDI): Multicomponent isotherm modeling and kinetic study, *Separation and Purification Technology*, 2017, **186**, 272–281.
- 29 J. Pan, Y. Zheng, J. Ding, C. Gao, B. Van der Bruggen and J. Shen, Fluoride Removal from Water by Membrane Capacitive Deionization with a Monovalent Anion Selective Membrane, *Ind. Eng. Chem. Res.*, 2018, **57**, 7048–7053.

- 30 W. Tang, P. Kovalsky, B. Cao, D. He and T. D. Waite, Fluoride Removal from Brackish Groundwaters by Constant Current Capacitive Deionization (CDI), *Environ. Sci. Technol.*, 2016, **50**, 10570–10579.
- 31 P. Wu, L. Xia, M. Dai, L. Lin and S. Song, Electrosorption of fluoride on TiO₂-loaded activated carbon in water, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2016, **502**, 66–73.
- 32 J. C. Farmer, S. M. Bahowick, J. E. Harrar, D. V. Fix, R. E. Martinelli, A. K. Vu and K. L. Carroll, Electrosorption of Chromium Ions on Carbon Aerogel Electrodes as a Means of Remediating Ground Water, *Energy Fuels*, 1997, **11**, 337–347.
- 33 W. Zhang, M. Mossad, J. S. Yazdi and L. Zou, A statistical experimental investigation on arsenic removal using capacitive deionization, *Desalination and Water Treatment*, 2016, **57**, 3254–3260.
- 34 C.-S. Fan, S.-C. Tseng, K.-C. Li and C.-H. Hou, Electro-removal of arsenic(III) and arsenic(V) from aqueous solutions by capacitive deionization, *Journal of Hazardous Materials*, 2016, **312**, 208–215.
- 35 C. Zhan, M. R. Cerón, S. A. Hawks, M. Otani, B. C. Wood, T. A. Pham, M. Stadermann and P. G. Campbell, Specific ion effects at graphitic interfaces, *Nat Commun*, 2019, **10**, 1–8.
- 36 R. Zhao, M. van Soestbergen, H. H. M. Rijnaarts, A. van der Wal, M. Z. Bazant and P. M. Biesheuvel, Time-dependent ion selectivity in capacitive charging of porous electrodes, *Journal of Colloid and Interface Science*, 2012, **384**, 38–44.
- 37 S.-J. Seo, H. Jeon, J. K. Lee, G.-Y. Kim, D. Park, H. Nojima, J. Lee and S.-H. Moon, Investigation on removal of hardness ions by capacitive deionization (CDI) for water softening applications, *Water Research*, 2010, **44**, 2267–2275.
- 38 J. Choi, H. Lee and S. Hong, Capacitive deionization (CDI) integrated with monovalent cation selective membrane for producing divalent cation-rich solution, *Desalination*, 2016, **400**, 38–46.
- 39 X. Zhang, K. Zuo, X. Zhang, C. Zhang and P. Liang, Selective ion separation by capacitive deionization (CDI) based technologies: a state-of-the-art review, *Environmental Science: Water Research & Technology*, , DOI:10.1039/C9EW00835G.
- 40 K. Zuo, J. Kim, A. Jain, T. Wang, R. Verduzco, M. Long and Q. Li, Novel Composite Electrodes for Selective Removal of Sulfate by the Capacitive Deionization Process, *Environ. Sci. Technol.*, 2018, **52**, 9486–9494.
- 41 D. I. Oyarzun, A. Hemmatifar, J. W. Palko, M. Stadermann and J. G. Santiago, Adsorption and capacitive regeneration of nitrate using inverted capacitive deionization with surfactant functionalized carbon electrodes, *Separation and Purification Technology*, 2018, **194**, 410–415.
- 42 O. Pastushok, F. Zhao, D. L. Ramasamy and M. Sillanpää, Nitrate removal and recovery by capacitive deionization (CDI), *Chemical Engineering Journal*, 2019, **375**, 121943.
- 43 Y.-J. Kim, J.-H. Kim and J.-H. Choi, Selective removal of nitrate ions by controlling the applied current in membrane capacitive deionization (MCDI), *Journal of Membrane Science*, 2013, **429**, 52–57.
- 44 Y.-J. Kim and J.-H. Choi, Selective removal of nitrate ion using a novel composite carbon electrode in capacitive deionization, *Water Research*, 2012, **46**, 6033–6039.

- 45 J.-H. Yeo and J.-H. Choi, Enhancement of nitrate removal from a solution of mixed nitrate, chloride and sulfate ions using a nitrate-selective carbon electrode, *Desalination*, 2013, **320**, 10–16.
- 46 W. Xing, J. Liang, W. Tang, G. Zeng, X. Wang, X. Li, L. Jiang, Y. Luo, X. Li, N. Tang and M. Huang, Perchlorate removal from brackish water by capacitive deionization: Experimental and theoretical investigations, *Chemical Engineering Journal*, 2019, **361**, 209–218.
- 47 J. J. Lado, R. E. Pérez-Roa, J. J. Wouters, M. I. Tejedor-Tejedor, C. Federspill, J. M. Ortiz and M. A. Anderson, Removal of nitrate by asymmetric capacitive deionization, *Separation and Purification Technology*, 2017, **183**, 145–152.
- 48 V. M. Palakkal, J. E. Rubio, Y. J. Lin and C. G. Arges, Low-Resistant Ion-Exchange Membranes for Energy Efficient Membrane Capacitive Deionization, *ACS Sustainable Chem. Eng.*, 2018, **6**, 13778–13786.
- 49 United States Patent and Trademark Office, 20130284601, 2013.
- 50 A. P. Straub, S. Lin and M. Elimelech, Module-Scale Analysis of Pressure Retarded Osmosis: Performance Limitations and Implications for Full-Scale Operation, *Environ. Sci. Technol.*, 2014, **48**, 12435–12444.
- 51 R. K. McGovern, A. M. Weiner, L. Sun, C. G. Chambers, S. M. Zubair and J. H. Lienhard V, On the cost of electrodialysis for the desalination of high salinity feeds, *Applied Energy*, 2014, **136**, 649–661.
- 52 Z. Li, M. S. Pan, L. Su, P.-C. Tsai, A. F. Badel, J. M. Valle, S. L. Eiler, K. Xiang, F. R. Brushett and Y.-M. Chiang, Air-Breathing Aqueous Sulfur Flow Battery for Ultralow-Cost Long-Duration Electrical Storage, *Joule*, 2017, **1**, 306–327.
- 53 A. Omosebi, X. Gao, N. Holubowitch, Z. Li, J. Landon and K. Liu, Anion Exchange Membrane Capacitive Deionization Cells, *J. Electrochem. Soc.*, 2017, **164**, E242–E247.
- 54 L. Weinstein and R. Dash, Capacitive Deionization: Challenges and Opportunities, *Desalin. Water Reuse*, 2013, **23**, 34–37.
- 55 V. Viswanathan, A. Crawford, D. Stephenson, S. Kim, W. Wang, B. Li, G. Coffey, E. Thomsen, G. Graff, P. Balducci, M. Kintner-Meyer and V. Sprenkle, Cost and performance model for redox flow batteries, *Journal of Power Sources*, 2014, **247**, 1040–1051.
- 56 P. Qian, H. Zhang, J. Chen, Y. Wen, Q. Luo, Z. Liu, D. You and B. Yi, A novel electrode-bipolar plate assembly for vanadium redox flow battery applications, *Journal of Power Sources*, 2008, **175**, 613–620.
- 57 S. Yan, S. O. Salley and K. Y. Simon Ng, Simultaneous transesterification and esterification of unrefined or waste oils over ZnO-La₂O₃ catalysts, *Applied Catalysis A: General*, 2009, **353**, 203–212.
- 58 R. M. Darling, K. G. Gallagher, J. A. Kowalski, S. Ha and F. R. Brushett, Pathways to low-cost electrochemical energy storage: a comparison of aqueous and nonaqueous flow batteries, *Energy Environ. Sci.*, 2014, **7**, 3459–3477.
- 59 D. L. Wood, J. Li and C. Daniel, Prospects for reducing the processing cost of lithium ion batteries, *Journal of Power Sources*, 2015, **275**, 234–242.
- 60 V. B. Jensen, J. L. Darby, C. Seidel and C. Gorman, *Drinking Water Treatment for Nitrate.*, Center for Watershed Sciences, University of California, Davis., 2012.

- 61 A. Ramachandran, D. I. Oyarzun, S. A. Hawks, P. G. Campbell, M. Stadermann and J. G. Santiago, Comments on “Comparison of energy consumption in desalination by capacitive deionization and reverse osmosis”, *Desalination*, 2019, **461**, 30–36.
- 62 X. Shang, R. D. Cusick and K. C. Smith, A Combined Modeling and Experimental Study Assessing the Impact of Fluid Pulsation on Charge and Energy Efficiency in Capacitive Deionization, *J. Electrochem. Soc.*, 2017, **164**, E536–E547.
- 63 A. Hemmatifar, J. W. Palko, M. Stadermann and J. G. Santiago, Energy breakdown in capacitive deionization, *Water Research*, 2016, **104**, 303–311.
- 64 M. Kim, M. del Cerro, S. Hand and R. D. Cusick, Enhancing capacitive deionization performance with charged structural polysaccharide electrode binders, *Water Research*, 2019, **148**, 388–397.
- 65 J. E. Dykstra, K. J. Keesman, P. M. Biesheuvel and A. van der Wal, Theory of pH changes in water desalination by capacitive deionization, *Water Research*, 2017, **119**, 178–186.
- 66 W. Tang, D. He, C. Zhang, P. Kovalsky and T. D. Waite, Comparison of Faradaic reactions in capacitive deionization (CDI) and membrane capacitive deionization (MCDI) water treatment processes, *Water Research*, 2017, **120**, 229–237.
- 67 W. J. Conlon, F. A. Blandon and J. Moody, Cost comparison of treatment alternatives for the removal of nitrates and DBCP from Southern California groundwater, *Desalination*, 1995, **103**, 89–100.
- 68 T. M. Mubita, J. E. Dykstra, P. M. Biesheuvel, A. van der Wal and S. Porada, Selective adsorption of nitrate over chloride in microporous carbons, *Water Research*, 2019, **164**, 114885.
- 69 D. Moreno and M. C. Hatzell, Constant chemical potential cycles for capacitive deionization, *Phys. Chem. Chem. Phys.*, , DOI:10.1039/C9CP05032A.
- 70 S. Schlumpberger, N. B. Lu, M. E. Suss and M. Z. Bazant, Scalable and Continuous Water Deionization by Shock Electrodialysis, *Environ. Sci. Technol. Lett.*, 2015, **2**, 367–372.
- 71 K. M. Conforti and M. Z. Bazant, Continuous ion-selective separations by shock electrodialysis, *AIChE Journal*, 2020, **66**, e16751.
- 72 A. King, D. Boyle, V. B. Jensen, G. Fogg and T. Harter, *Groundwater Remediation and Management for Nitrate*, Center for Watershed Sciences, University of California, Davis., 2012.
- 73 X. Gao, A. Omosebi, J. Landon and K. Liu, Surface charge enhanced carbon electrodes for stable and efficient capacitive deionization using inverted adsorption–desorption behavior, *Energy & Environmental Science*, 2015, **8**, 897–909.
- 74 X. Gao, A. Omosebi, J. Landon and K. Liu, Dependence of the Capacitive Deionization Performance on Potential of Zero Charge Shifting of Carbon Xerogel Electrodes during Long-Term Operation, *J. Electrochem. Soc.*, 2014, **161**, E159–E166.
- 75 P. M. Biesheuvel and A. van der Wal, Membrane capacitive deionization, *Journal of Membrane Science*, 2010, **346**, 256–262.
- 76 C. Zhang, D. He, J. Ma, W. Tang and T. D. Waite, Faradaic reactions in capacitive deionization (CDI) - problems and possibilities: A review, *Water Research*, 2018, **128**, 314–330.

- 77 A. Siekierka, B. Tomaszewska and M. Bryjak, Lithium capturing from geothermal water by hybrid capacitive deionization, *Desalination*, 2018, **436**, 8–14.
- 78 T. Ryu, J. C. Ryu, J. Shin, D. H. Lee, Y. H. Kim and K.-S. Chung, Recovery of Lithium by an Electrostatic Field-Assisted Desorption Process, *Ind. Eng. Chem. Res.*, 2013, **52**, 13738–13742.
- 79 D.-H. Lee, T. Ryu, J. Shin, J. C. Ryu, K.-S. Chung and Y. H. Kim, Selective lithium recovery from aqueous solution using a modified membrane capacitive deionization system, *Hydrometallurgy*, 2017, **173**, 283–288.
- 80 S. Kim, J. Lee, J. S. Kang, K. Jo, S. Kim, Y.-E. Sung and J. Yoon, Lithium recovery from brine using a λ -MnO₂/activated carbon hybrid supercapacitor system, *Chemosphere*, 2015, **125**, 50–56.
- 81 S. Kim, H. Yoon, D. Shin, J. Lee and J. Yoon, Electrochemical selective ion separation in capacitive deionization with sodium manganese oxide, *Journal of Colloid and Interface Science*, 2017, **506**, 644–648.
- 82 X. Su, J. Hübner, M. J. Kauke, L. Dalbosco, J. Thomas, C. C. Gonzalez, E. Zhu, M. Franzreb, T. F. Jamison and T. A. Hatton, Redox Interfaces for Electrochemically Controlled Protein–Surface Interactions: Bioseparations and Heterogeneous Enzyme Catalysis, *Chem. Mater.*, 2017, **29**, 5702–5712.
- 83 X. Su, H. J. Kulik, T. F. Jamison and T. A. Hatton, Anion-Selective Redox Electrodes: Electrochemically Mediated Separation with Heterogeneous Organometallic Interfaces, *Advanced Functional Materials*, 2016, **26**, 3394–3404.

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