Removal of Nitrate by Asymmetric Capacitive Deionization

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Abstract

Contamination of groundwater with nitrates is a major concern, especially for areas relying on this as a drinking water source. In this work, a capacitive deionization (CDI) system equipped with carbon electrodes coated with different metal oxides was studied to determine its ability to reduce nitrate concentrations. Results performed in a three-electrode cell were used as a proof of concept and demonstrated that coated electrodes had higher nitrate removal than that of uncoated electrodes, likely because of a reduction in hydrophobicity and an increase in surface area provided by the metal oxides. Moreover, tests using different electrolytes (NaNO_3 and $\text{Ca}(\text{NO}_3)_2$) revealed similar nitrate removal values, although different electrosorption patterns were observed for Na^+ and Ca^{2+} . Furthermore, an operational mode based on a multistep approach showed that nitrates could be removed below regulatory limits while reducing the volume of waste brine. A larger, eight-cell flow CDI reactor was also tested. The results from this reactor showed that the cell potential, as well as the ion being removed from a multicomponent solution (Ca^{2+} , Na^+ , Cl^- , NO_3^-) influence electrosorption kinetics. Different adsorption mechanisms based on ion charge/size/electrode affinity are discussed, possibly leading to a methodology for preferentially removing certain ions by CDI technology.

Keywords: Nitrate removal; capacitive deionization; asymmetric CDI; ion selective removal; oxide-coated electrodes.

1. Introduction

Groundwater, considered the most extracted resource on Earth [1], provides between 25% to 40% of the world's drinking water [2]. Contamination by certain ions such as fluoride [3], perchlorate [4] or nitrate [3] is a threat to the availability of affordable potable water. In particular, nitrate represents one of the most serious problems due to its intensive application as a fertilizer and its high water solubility [5, 6]. Considering its low adsorption affinity in different kinds of soils, nitrate also appears highly likely to leach into groundwater wells and reservoirs [7]. Its adverse health effects include its reduction into nitrite, which subsequently reduces hemoglobin to methemoglobin and alters the oxygen transport capacity within blood cells ('blue baby' syndrome) [6], as well as its potential link with several kinds of cancer due to its ability to form nitrosamines [5, 8, 9] when ingested in high concentrations. Moreover, from an environmental standpoint, the presence of nitrate in water bodies such as rivers or lakes may lead to eutrophication. Such increase in the algae population depletes dissolved oxygen in water, increasing the risk of death in certain aquatic organisms [6]. Based on these considerations, organizations such as the World Health Organization (WHO) or the Environmental Protection Agency (U.S. EPA) have set a maximum concentration limit (MCL) for nitrate in drinking water of 10 mg L⁻¹ nitrogen-basis (45 mg L⁻¹ of nitrate) [3, 5, 10]. Therefore, contaminated groundwater wells used as the primary source of drinking water require treatment to achieve minimum health standards.

Current technologies for nitrate removal are typically divided into biological processes and physico-chemical treatments. Biological denitrification, a popular alternative in municipal wastewater treatment, has the advantage of being low cost, but the disadvantages of needing large-scale installation, having slow ion removal kinetics and a high sensitivity to pH, temperature and the presence of other toxic compounds [6, 11]. As for physical-chemical processes, ion exchange (IX) is the most widely employed treatment and frequently employed in wells, since it is cost effective for small-scale applications, as well as simple to operate and

monitor [6]. Nevertheless, IX requires the introduction of external NaCl to exchange ions in a 1:1 basis with nitrate, which may affect water quality in areas with already high nitrate concentrations. Membrane-based technologies such as reverse osmosis (RO), nanofiltration (NF) or electrodialysis (ED) have also been shown to effectively remove nitrate ions [12, 13]. However, the high energy demand required to provide either high pressures or voltages, along with the reduction of ion removal efficiency when treating brackish waters (2000-5000 mg L⁻¹ in salt concentration), may limit the use of these technologies [3, 6, 14].

Capacitive Deionization (CDI) is an emerging water desalination technology that is based on the electrosorption of ions on porous electrodes by applying low potentials (typically below 1.5 V) [15-17]. The low voltages used in this process along with the possibility of retrieving part of the energy employed during the sorption of ions [18, 19] may lead to lower energy consumption [20]. Furthermore, no additional chemicals are required in the CDI process and high water recoveries can be obtained [21]. To date, CDI applications have been largely focused on brackish water desalination [17, 22-24], but recent research has shown its applicability for removing ions such as nitrate [14], sulfate [25, 26], fluoride [3], as well as sodium and chloride. CDI has also been suggested for the selective removal of nitrate [3, 27] using either nitrate-selective composite carbon electrodes or by controlling the applied current [14, 28]. While these studies have shown that CDI may be a new means of removing nitrate from groundwater, aspects such as ion removal mechanisms/patterns or the occurrence of faradaic reactions have not been thoroughly addressed.

In this work, low surface area carbons coated with different metal oxides (SiO₂ on the cathode and Al₂O₃ on the anode) were employed in an asymmetric CDI cell configuration for removing nitrate ions. The choice of metal oxides was based on differences in their zeta potentials (surface charges) in an aqueous environment, where the SiO₂ particles will be negative above pH 3 and the Al₂O₃ positive below pH 9. The different surface charge of the oxides, when no external potentials are applied to the electrodes, should reduce the co-ion desorption during the adsorption

step and minimize the counter-ion electrosorption (crossover) during electrode regeneration (i.e., ion desorption) [29]. Additional benefits of using oxide-coated electrode composites in CDI have also been mentioned [29-33] and include: (1) the large surface site densities of oxide composite electrodes [29, 30], (2) the reduction of hydrophobicity of the carbon substrate [29, 34] that leads to improved ion transport and adsorption kinetics [35], and (3) an increase in the charge efficiency due to the asymmetric natural surface potential associated with these oxides [33, 36-38]

Initial experiments described in this study were based on a three-electrode cell configuration using nitrate-based salts (NaNO_3 or $\text{Ca}(\text{NO}_3)_2$). These small-scale tests were conducted as a “proof of concept” to evaluate the net effect of the metal oxide coatings on nitrate removal, and to assess the ability of the coated electrode composites to reduce water nitrate concentrations below regulatory limits. Next, the system was scaled up from the single cell (electrode area $\approx 25 \text{ cm}^2$) to an eight-cell flow CDI reactor (electrode area $\approx 1814 \text{ cm}^2$) and the results from this much larger system presented. Finally, multicomponent electrolyte experiments (Na^+ , Ca^{2+} , Cl^- and NO_3^-) were performed to observe if any synergistic, antagonistic or even ion selective processes occur in this process.

2. Materials and Methods

2.1 Materials

Low surface area carbon fiber (CF) sheet electrodes ($2 \text{ m}^2 \text{ g}^{-1}$ in BET area) employed in this study were previously described elsewhere [30, 32]. For these experiments, the CF sheets were either uncoated (for baseline comparisons) or coated with a nano-porous thin film of either SiO_2 or $\gamma\text{-Al}_2\text{O}_3$ as previously described [30, 32]. Briefly, the coating process consisted of three steps: (1) CF sheets were heated at 350°C for 2.5 hours in air; (2) CF sheets were immersed in SiO_2 or $\gamma\text{-AlOOH}$ sols; (3) CF sheets coated with oxides were fired at 350°C for 2.5 hours to

sinter the particles to the CF sheets. The resulting content of metal oxide deposited on the CF sheets (by wt% of the entire electrode) was between 3.8-6.7 % for the SiO₂ composites (composites = CF sheet + metal oxide) and 3.2-3.8 % for the γ -Al₂O₃ composites. BET surface areas of the SiO₂ and γ -Al₂O₃ composite electrodes were 26-35 m² g⁻¹ and 18-19 m² g⁻¹ respectively.

2.2 Methods

2.2.1 Small CDI Three Electrode Cell

Initial experiments were conducted in a batch reactor using a three-electrode electrochemical cell (Fig 1). Two electrodes (5.08 cm x 5.08 cm) were separated by 2 pieces of a non-conductive open mesh (0.1 mm thick) and employed as the working and counter electrodes, while a saturated calomel electrode (SCE) was used as the reference electrode. Experiments were performed by placing either two uncoated CF sheets ('symmetric' configuration), or a SiO₂-coated sheet as the working electrode and an γ -Al₂O₃-coated sheet as the counter electrode ('asymmetric' configuration).

Electrosorption experiments were performed by immersing the electrodes in a vessel filled with 40 ml of electrolyte solution, stirred with a magnetic stir bar. A constant potential of -1.5 V was then applied between the WE (cathode during removal) and the reference electrode for 20 min using a potentiostat (Princeton Applied Research, VMP2). In the regeneration phase (desorption of ions from the electrode), the potential was switched to +0.7 V for 20 min. Experiments were repeated three times using different electrode pairs (previously conditioned), with the exception of 6 meq L⁻¹ and the multistep experiments that were repeated twice showing in all cases good repeatability.

Samples were withdrawn from the solution at 5 min intervals and analyzed by ion chromatography (Dionex ICS-2100, Column: Dionex Ion Pac® AS9-HC 4 x 25 mm Analytical). The pH of the electrolyte was measured before starting the CDI experiment and at the end of the

removal and regeneration phases. Electrolyte solutions employed in this part of the study, NaNO_3 , $\text{Ca}(\text{NO}_3)_2$ and CaCl_2 (Fisher Scientific), were prepared in 18.2 M Ω high-purity water. For data analysis, ion concentrations are expressed as mmol L⁻¹ or mEq L⁻¹ (mEq L⁻¹ = mmol L⁻¹ x 2 for Ca^{2+} and mmol L⁻¹ x 1 for Na^+ , NO_3^- and Cl^-).

Fig. 1. Schematic of the CDI cell employed in the small-scale CDI experiments.

2.2.2 Scaling-Up the Process – CDI Flow Reactor

A scaled-up process (Fig. 2) was conducted by upgrading from the three-electrode electrochemical cell with a fixed cell volume described above (40 ml of solution, two electrodes with geometric areas of $\approx 25 \text{ cm}^2$ each) to a CDI reactor outfitted with 8 flow cells electrically and hydraulically connected in parallel. The reactor held $\approx 520 \text{ ml}$ of water and had sixteen

electrodes each having an area of $\approx 116.5 \text{ cm}^2$. The electric potential was applied between the SiO_2 (cathodes, i.e. those negatively charged during the removal step) and Al_2O_3 coated (anodes, i.e. those positively charged during the removal step) electrodes instead of applying the voltage between the SiO_2 coated electrode (working electrode) and the SCE (reference electrode). CDI experiments described in this section were performed using a CDI system described in detail in previous publications [25, 26]. Briefly, the CDI reactor was outfitted with 8 cells each of them having two oxide coated carbon electrodes (116.5 cm^2 each) separated by a non-conductive Teflon mesh and hydraulically sealed with rubber gaskets. Batch experiments were performed by pumping 720 ml of electrolyte solution from a cylinder (45 ml min^{-1} constant flow rate) through the CDI system using an Omega FPUDX 1703A metering pump while conductivity and pH were measured inline by Omega probes (CDE-1201-conductivity and PHE-7357-10-pH) located in the inlet and the outlet of the reactor. A power supply (GW Instek GPD-3303S) was employed to apply the potential difference between the electrodes and the electric currents were measured using an Agilent 34405A multimeter electrically connected in series to the CDI unit. After passing through the system, samples were withdrawn at different times and ion concentrations determined by ion chromatography. It should also be noted that before performing the nitrate experiments described in this paper, the electrodes in the reactor were conditioned by performing 15 batch CDI experiments (removal/regeneration cycles) prior to the nitrates experiments. High purity water was flushed through the CDI system for 30 min after each one of the experiments as part of the cleaning step.

**Proof of Concept
Three Electrode Cell**

**2 Carbon Electrodes
1 Reference Electrode**

**Volume: 40 mL
Electrode Area : 25 cm²
Total Electrode Area: 50 cm²**

**Proof of Scale-Up
CDI Flow Reactor**

16 Carbon Electrodes

**Volume: 520 mL
Electrode Area : 117 cm²
Total Electrode Area: 1864 cm²**

Fig. 2. Scaled-up process from a fixed volume three-electrode cell to an eight-cell (each cell composed of two electrodes) CDI flow reactor.

2.2.3 Electrode Charging Properties – Zeta Potential Measurements

To investigate the charging properties of the metal oxide composite electrodes when different electrolytes were used in the electrosorption experiments, zeta potential measurements (Malvern Zetasizer 3000HSA) of the powdered SiO₂ and γ -Al₂O₃ xerogels were performed. Powdered γ -Al₂O₃ xerogel was used as surrogate materials for the composite electrodes. Measurements were taken at different pH values in electrolyte solutions (NaNO₃, NaCl and Na₂SO₄) with the same ionic strength $I = 0.01 \text{ mol L}^{-1}$.

3. Results & Discussion

3.1. “Proof of Concept”: Small-Scale Experiments

3.1.1 Effect of the Metal Oxide Coatings on Nitrate Removal

CDI experiments were performed in a 1.6 mmol L^{-1} NaNO₃ solution with the coated composite electrodes and the uncoated carbon electrodes to test the effect of the metal oxide

coatings on NO_3^- removal. As shown in Fig. 3, when both electrodes were left uncoated, only 12% of the initial NO_3^- concentration and 5% of the Na^+ was removed during the 20-min removal period. However, when the coated electrodes were submitted to the same testing, a significant increase in ion removal was observed. After 15 min of removal, 50% of the NO_3^- and 56% of the Na^+ was removed.

The above results agree well with previous experiments conducted using CaCl_2 solutions and a similar experimental approach [29, 32]. Those studies showed that the enhancement of the specific surface area and specific capacitance achieved by the coatings had a direct influence on the electrosorption of ions [29, 30]. However, these previous studies also showed asymmetric ion removal in terms of the charge equivalents of Ca^{2+} and Cl^- removed; specifically, more mEq L^{-1} of Ca^{2+} were removed than Cl^- . This removal was accompanied by a large pH drop or increase in H^+ concentration (one of the main species responsible for maintaining the requirement of electrical neutrality in solution). In addition, the authors also observed faradaic reactions such as the oxidation of chloride to chlorate at the same applied potential (-1.5V vs. SCE) [29, 32]. In contrast to these previous CDI studies, the pH values measured in this study using NaNO_3 did not reveal a large pH drop (pH before removal step (≈ 5.3) and after (≈ 5.0)) or asymmetric ion removal.

Fig. 3. Removal (0 to 20 min) and regeneration (20 to 40 min) of a CDI cell composed of two uncoated carbon electrodes in comparison with a CDI cell outfitted with a SiO_2 coated carbon as the negative electrode and $\gamma\text{-Al}_2\text{O}_3$ coated carbon as the positive during removal.

3.1.2 Influence of the Cation on Nitrate Removal

In order to investigate whether the cation species in solution influence the adsorption of nitrates on the opposite electrode, experiments were performed with a $1.6 \text{ mmol L}^{-1} \text{ Ca(NO}_3)_2$ solution and compared with the results obtained using a NaNO_3 solution. The ion concentration profile over time (Fig. 4A) showed very similar nitrate removal trends using these different salts; the maximum amount of nitrate removed was 0.017 ± 0.03 and $0.015 \pm 0.03 \text{ mEq g}^{-1}$ for NaNO_3 and $\text{Ca(NO}_3)_2$ respectively. However, the removal kinetics of Ca^{2+} and Na^+ (Fig. 4B) appeared quite different. Sodium adsorption was fast at the beginning of the experiment and leveled off after approximately 10 minutes. In addition, the shape of the Na^+ kinetic curve appeared similar to that observed for nitrate removal. On the other hand, the Ca^{2+} ions were slowly adsorbed at the beginning of the test (first 5 min), but then were continually removed in a nearly linear fashion for the remainder of the experiment.

Fig. 4. Time profiles of nitrate (A) and cation (B) concentrations during electrosorption experiments when either $\text{Ca(NO}_3)_2$ or NaNO_3 were employed as electrolytes in the CDI experiments.

Different hypothesis could be used to explain this behavior. First, it appears that monovalent ions with smaller hydrated radius (Na^+ : 358 pm, NO_3^- : 335 pm) [39] were adsorbed faster than Ca^{2+} whose hydrated radius is larger (412 pm) [39]. Thus, a higher monovalent ion

adsorption was observed at the beginning of the experiment while divalent ions were preferentially adsorbed at longer times of operation. Zhao et al. [40] also reported slower removal kinetics for the divalent ion (Ca^{2+}) than that of the monovalent (Na^+) in CDI experiments using multicomponent electrolytes. These authors suggested a time dependence on ion selectivity in the electrical double layer (EDL) based on transport resistance of ions outside the EDL and the ion adsorption capacity of the EDL which in turn depends on the applied voltage during the experiment.

A second hypothesis that could explain this behavior might be related to the different ion removal mechanism for NO_3^- , Ca^{2+} and Na^+ . This hypothesis is based on previous work where the electrophoretic mobility of SiO_2 particles suspended in NaCl and CaCl_2 solutions at different pH values was studied [32]. In this work, Ca^{2+} ions were found to show a certain affinity for SiO_2 particles, seemingly indicative of specific adsorption noted by a shift in the isoelectric pH (pH_{iep}). On the other hand, this behavior was not observed in the presence of sodium ions. These observations suggest that two different processes may remove Ca^{2+} ions: electroadsorption in the EDL and specific adsorption on the SiO_2 coating. In contrast, these findings also imply that Na^+ ions are only removed by electroadsorption in the EDL. In this manuscript, the zeta potential of Al_2O_3 particles suspended in NaCl , NaNO_3 and Na_2SO_4 was measured to detect shifts in the pH_{iep} , indicative of specific adsorption of NO_3^- ions. The results, displayed in Fig. 5, show that the pH_{iep} of the Al_2O_3 particles is around 9 for NaCl and NaNO_3 , meaning these particles will have positive surface charges at pH values below ~ 9 . However, the figure also shows that sulfate ions reduce the pH_{iep} of the Al_2O_3 , which is indicative of specific adsorption of sulfate on the Al_2O_3 particles. The differences in behavior between chloride and nitrate from that of sulfates reveals that one would not expect to observe any specific adsorption of the Cl^- or the NO_3^- ions on the Al_2O_3 particles. This implies that the only ion removal mechanism for Na^+ and NO_3^- seems to be that of electro-adsorption in the EDL. Based on this analysis, one might suggest that the lack of specific adsorption of monovalent ions on the metal oxide could influence the kinetics of this

electroadsorption process (i.e. – specific adsorption should not play a role in the removal kinetics of monovalent ions such as NO_3^- and Cl^- in the CDI process, but may with anions such as SO_4^{2-}).

Fig. 5. Electrophoretic mobility curves for $\gamma\text{-Al}_2\text{O}_3$ particles in different electrolytes (NaCl, Na_2SO_4 and NaNO_3).

3.1.3 Influence of Nitrate Concentrations and a Comparison to other Anions – Asymmetric Removal

An additional consequence of the different ion adsorption profiles observed for Ca^{2+} and NO_3^- ions (Fig. 4) was the asymmetric ion removal with respect to charge. The experiment performed using $\text{Ca}(\text{NO}_3)_2$ showed the occurrence of asymmetric removal during the entire duration of the experiment (after 20 min, Ca^{2+} : 0.020 mEq g^{-1} > NO_3^- : 0.014 mEq g^{-1}), in contrast to the experiment performed with NaNO_3 (Na^+ : $0.013 \text{ mEq g}^{-1} \approx \text{NO}_3^-$: 0.015 mEq g^{-1}). Moreover, pH measurements taken at the beginning and at the end of the removal phase showed that while the pH had a slight decrease in the case of the experiments performed with NaNO_3 (from 5.4 to 5.1), a significant pH decay (from 5.8 to 3.8) was observed when $\text{Ca}(\text{NO}_3)_2$ was used as the electrolyte. Since the same potential was applied irrespective of the cations tested, the pH drop appeared, in this case, to be associated with asymmetric removal rather than the occurrence of faradaic reactions such as water electrolysis, carbon oxidation and oxygen or proton reduction reactions [25, 41, 42].

In order to study the effect of the initial electrolyte concentration on asymmetric removal, a further experiment using $\text{Ca}(\text{NO}_3)_2$ at a higher concentration ($6 \text{ mEq} \cdot \text{L}^{-1}$) was performed. Results of this experiment, displayed in Fig. 6A, clearly indicate that asymmetric removal (with respect to charge of the ionic species Ca^{2+} vs. NO_3^-) is occurring; particularly, when the electrolyte concentration is increased. Thus, Ca^{2+} removal obtained after 20 min was much higher (0.079 mEq g^{-1}) than the NO_3 removal (0.041 mEq g^{-1}). For comparison purposes, a supplementary experiment was performed using a different anion (CaCl_2 , 6 mEq L^{-1}). Results displayed in (Fig. 6B) confirmed the asymmetric ion removal characterized by a higher adsorption of Ca^{2+} than Cl^- . In addition to this similarity, electrosorption experiments conducted with $\text{Ca}(\text{NO}_3)_2$ and CaCl_2 were in both cases accompanied by a decrease in pH values (from 5.2 to 2.9). The findings regarding CaCl_2 were explained in previous studies [29, 32] and likely based on the occurrence of chloride oxidation to chlorates, the specific adsorption of the Ca^{2+} ions onto the oxide phase (SiO_2) of the composite electrode and the oxidation of the carbon electrode. Conversely, while Ca^{2+} sorption appears driven by EDL electro-sorption and specific adsorption in both the CaCl_2 and $\text{Ca}(\text{NO}_3)_2$ systems, no evidence of parasitic reactions involving NO_3^- ions, determined by the absence of any new nitrogen compounds in the ion chromatographs, were observed in the experiments discussed in this study. Therefore, it appears that the higher removal of Ca^{2+} over NO_3^- ions seems to be a major contributor to the pH decrease along with other faradaic reactions such as carbon oxidation, and oxygen reduction that might occur during the experiment.

Fig. 6. Electrosorption experiments performed using $\text{Ca}(\text{NO}_3)_2$ (A) and CaCl_2 (B) electrolyte.

3.1.4 Single Step vs Multistep Nitrate Removal with Capacitive Deionization

With the goal of reducing nitrate concentrations from 100 mg L^{-1} (1.6 mEq L^{-1} of NO_3^-) to values below the WHO-advised level of 45 mg L^{-1} as NO_3^- (0.7 mEq L^{-1} of NO_3^-), an alternative method of operation was explored. Based on the results displayed in Fig. 4, where the nitrate removal appeared to level off after approximately 10 min of operation, a multistep operational mode was studied. In the multistep mode after 10 minutes of removal, the electrode pair was manually lifted from the “feed” solution ($100 \text{ mg L}^{-1} \text{ NO}_3^-$; $1.6 \text{ mEq L}^{-1} \text{ NaNO}_3$), and brought into contact with another solution (namely “brine”) contained in another vessel. Initially, the brine solution had half the salt concentration of the feed solution. After 5 min of regenerating the electrode pair by (applying $+0.7 \text{ V}$ vs. SCE), the pair was moved back into the initial solution. A new removal period using the same conditions as in the first removal step was conducted for 5 more minutes. This process was repeated two more times for a total of three 5 min immersions for the removal phase, i.e. - 25 minutes of total removal time (10+5+5+5 minutes). A similar operational method previously described as “electrodes in motion” was successfully tested using carbon coated wires as CDI electrodes [16]. The idea behind this operational mode was to simulate the CDI process under more realistic (real-world) operational parameters, where the treated solution and the brine solution are replaced depending on whether the CDI system is in the removal or regeneration phase.

Fig. 7 shows the nitrate concentration profiles of single and multiple cycle experiments. This graph illustrates the increase in nitrate removal from 50 to 61 % upon multiple immersions. In this way, a nitrate concentration of 39 mg L^{-1} (0.6 mEq L^{-1} of NO_3^-), which is below the health advisory limit (45 mg L^{-1}), was achieved. Fig. 7 also shows that by extending the number of cycles ($n = 4$) the nitrate concentration could be reduced down to 32 mg L^{-1} (0.5 mEq L^{-1} of NO_3^-) translating into 68 % nitrate removal. A further analysis of the nitrate removal rate per cycle

indicates that the first cycle showed faster ion removal ($4.20 \text{ mg L}^{-1} \text{ min}^{-1}$) than consecutive cycles, where the removal rate substantially decreased ($1.37, 2.33$ and $1.50 \text{ mg L}^{-1} \text{ min}^{-1}$). A plausible reason for this finding could be related to incomplete salt desorption during the electrode regeneration phase thus leading to a reduction in the nitrate removal rate in subsequent removal cycles. Moreover, the reduction of ion conductivity in the solution at lower nitrate concentrations might also lead to slower removal rates due to the increase in ionic resistance of the solution. The mass balance calculation using nitrate data support this hypothesis indicating that the amount of nitrate adsorbed during removal was not fully desorbed during the regeneration phase (data not shown). Based on this, the progressive electrode saturation suffered cycle by cycle led to the ion electrosorption capacity reduction. The authors suggest that longer electrode regeneration periods might help solve this issue. Despite this, when examining Fig. 7, an increase in nitrate concentration in the brine solution with successive cycling is observed. This result seems to indicate the ability to concentrate a brine solution, and this could have an important impact on reducing the cost of brine disposal. Lastly, it should be noted that pH measurements taken at the end of each removal step ($\text{pH}_0 = 6.7$; $\text{pH}_{10} = 5.97$; $\text{pH}_{15} = 5.90$; $\text{pH}_{20} = 5.99$; $\text{pH}_{25} = 5.92$) supports the results obtained in previous experiments performed with NaNO_3 electrolyte where no significant pH changes were observed.

Fig. 7. Different operational modes for nitrate removal using a three-electrode CDI cell.

3.2.1. Flow Cell Reactor Performance: Influence of Applied Voltage on Nitrate Removal

The above sections display the “proof of concept” that the metal oxide coated electrodes can successfully decrease nitrate concentration below regulatory limits and that coatings greatly improve the ion removal capabilities of the electrode. However, the above tests were performed in a small bench scale reactor, treating only 40 ml of solution. In this section, we examine the ability of a flow cell CDI reactor that has over 37x the electrode area (50 cm^2 vs. 1864 cm^2) of the small scale reactor and will treat 18x the volume of water (40 ml vs. 720 ml). With this in mind, a group of batch experiments in which the applied cell voltage between the electrodes was increased from 1.0 to 1.5 V for 150 min and flow rate was kept at 45 ml min^{-1} were performed by recirculating $\approx 720 \text{ ml}$ of a $1.9 \text{ mEq L}^{-1} \text{ Ca(NO}_3)_2$ ($120 \text{ mg} \cdot \text{L}^{-1}$ as NO_3^-) electrolyte solution throughout the reactor. Fig. 8 shows that the application of a higher cell voltage resulted in increasing nitrate removal from 44 % (1.0 V) to 56 % (1.5 V). Hence, the initial nitrate concentration, $\approx 120 \text{ mg L}^{-1}$ ($1.9 \text{ mEq L}^{-1} \text{ NO}_3^-$) was reduced to a value of $\approx 54 \text{ mg L}^{-1}$ ($0.9 \text{ mEq L}^{-1} \text{ NO}_3^-$) when the highest voltage was applied. This value is fairly close to the limit specified in the aforementioned regulation (45 mg L^{-1} as NO_3^-).

Fig. 8. Effect of Cell Voltage on Nitrate Removal

As was the case for the small cell, the occurrence of asymmetric removal was also studied in the experiments performed with the flow reactor. However, in the case of the flow reactor experiments, the effect of the cell voltage was evaluated for a longer period of time (240 min). Fig. 9 shows the influence of the cell voltage on the ion concentration versus time profiles

along with the changes in pH. Results displayed in Fig. 9A-C once again demonstrate that NO_3^- removal seemed faster than Ca^{2+} adsorption for the initial 90 min of all the experiments, regardless of cell voltage. Nevertheless, results also showed that while the nitrate removal kinetics appeared to slow down and level off after 180 min of the experiment, Ca^{2+} electrosorption continued beyond that point. After applying 1.0 V for 4 hours (Fig 9A) calcium and nitrate removal equilibrated to fairly symmetric values (NO_3^- : 48 %; Ca^{2+} : 47 %, in mEq L^{-1}). However, when the cell voltage was increased from 1.0 to 1.2 V the above equilibrium was reached just after 90 min and even faster when the applied cell voltage was 1.5 V. In addition, removal of calcium was higher than for nitrate ions with increased potential; after 4 hours, the results showed the following removal ratios at 1.2 V: NO_3^- : 50 %; Ca^{2+} : 61 % in mEq L^{-1} , whereas for 1.5 V these values were NO_3^- : 56 %; Ca^{2+} : 66 % in mEq L^{-1} .

The first conclusion that might be extracted from these experiments is that higher voltages not only speed up ion removal kinetics of both ions but also reduce the time where the calcium adsorption started to be greater than nitrate removal (Fig 9B and 9C). This result confirms that time dependence of ion removal could be tuned by using cell voltage. Moreover, the results indicate that the occurrence of a time dependent ion removal not only appears when the electrolyte contains cations with different charges (such as Na^+ and Ca^{2+}) [40], but also when the electrolyte contains differently charged anions and cations.

The analysis of the pH curves leads one to conclude that for all of the selected cell voltages, ion removal was followed by a decrease in pH. Thus, pH decreased from values between 6.9-7.5, to 4.9 (1.0 V), 4.7 (1.2 V) and 4.5 (1.2V) after 240 min. This pH decrease, in the same way as ion removal, seemed to be time dependent, showing that longer times of operation, in all cases, lead to lower values of pH. In the previous section, the observed pH drop was associated with the compensation of the solution ion balance displaced by the higher removal of Ca^{2+} over NO_3^- ions. The pH-time profiles displayed in Fig. 9A-C supports this hypothesis since the application of higher cell voltages speeds up calcium removal over that of nitrate leading to

more drastic decreases in pH. In addition, carbon oxidation reactions might be also occurring at high voltages contributing to the solution acidification as well. The occurrence of this kind of faradaic reactions could be justified by the increase of the current density values observed in the transient part of the curves when the applied cell voltage was boosted (Fig. 9D). Choi studies about the CDI performance at constant current [42] determined that while pH effluent decreases slowly at the beginning of the experiment at low current densities, deeper pH changes were observed when the CDI experiments were performed at higher current densities.

Fig. 9. Effect of cell voltage on the symmetry of ion removal: 1.0 V (A), 1.2 V (B), 1.5 V (C) and current density (D).

3.2.2. Multicomponent Electrolyte Experiments

To investigate the electrosorption of nitrate in an experiment more closely tied to real world scenarios, additional experiments were performed with the CDI reactor using a

multicomponent electrolyte. A CDI batch experiment was conducted using a 2 mEq L⁻¹ Na⁺, Ca²⁺, Cl⁻, NO₃⁻ solution and applying 1.5 V as a cell voltage. Results reported in Fig. 10 appear to support the hypotheses suggested by single salt experiments. Nitrate removal was initially faster than calcium, but after 60 minutes nitrate removal leveled off while calcium removal continued. After 180 min, Ca²⁺ removal (33 %) was higher than NO₃⁻ removal (26 %).

Calcium and sodium time profiles were consistent with observations of time-dependent cation selectivity reported by Zhao et al. [40] in CDI experiments with chloride salts. In this work, those findings were also found to be true in an electrolyte solution with two anions. Hence, the difference in removal kinetics between Ca²⁺ and Na⁺ should be taken into account when developing/operating a CDI water softening system. In terms of anion selectivity, these results showed that nitrate and chloride removal were quite similar albeit that the nitrate electrosorption was slightly slower than that of chloride.

As a final consideration, pH measurements revealed an acidification of the solution from 7.8 to 5.4. At the beginning of this experiment, a minor drop of pH from 7.8 to 7.0 was observed. However, the major decay occurred after 60 min coincident with the point where the concentration of the monovalent ions leveled off while the calcium removal continued. Fig. 10 shows that pH values then decreased from 7.0 (60 min) to 5.4 (180 min). This result indicates that a decrease in pH values would be expected when longer times of operation are employed, as long as calcium removal continues. Hence, evaluating the impact of pH changes on electrode performance in the presence of other ions such as carbonates that might buffer the solution, is an important factor that should be considered when testing the use of CDI as a water softening or nitrate removal system in real world scenarios.

Fig. 10. Ion removal in a multi-component salt experiment.

Conclusions

In this work, carbon electrodes coated with SiO_2 or Al_2O_3 showed a higher nitrate removal capacity than uncoated symmetric carbon electrodes. The improvement was likely associated with the metal oxides ability to provide faster ion transport through the carbon electrode due to a reduction in hydrophobicity, an increase in specific surface area and an increase in the number of adsorption sites. It was also determined, by performing CDI experiments using nitrate coupled with either Na^+ or Ca^{2+} , that while nitrate removal values were similar in both cases, sodium and calcium followed different electrosorption patterns. Particularly, sodium removal followed the nitrate electrosorption pattern while calcium removal was much slower at the beginning of the experiments. Time dependent ion selectivity in the EDL was noted as a plausible explanation for this finding. Moreover, the affinity of Ca^{2+} ions for SiO_2 particles indicates that besides electrosorption in the double layer, specific adsorption of calcium on the silica-coated electrode likely occurs. An important consequence of the time dependency removal was the asymmetric removal observed in the case of $\text{Ca}(\text{NO}_3)_2$ experiments and the subsequent pH acidification of the solution.

In addition to two step cycling (removal and regeneration) experiments, multi-step experiments showed the potential for the composite electrodes tested to reduce nitrate concentrations below the limits stipulated by the WHO. Furthermore, the regeneration of the electrodes using this mode of operation produced more concentrated waste brines that may have a positive impact on the reduction of brine wastes and process costs.

Finally, an eight-cell flow CDI reactor capable of treating a larger volume of water was successfully tested. Different cell voltage tests with the CDI reactor showed that the time dependence of ion removal could be tuned using applied potentials. Moreover, multicomponent experiments showed the occurrence of time dependent ion removal does not only appear when the electrolyte contains cations with different charges (Ca^{2+} Na^{+} and only Cl^{-} as anion) but also when the electrolyte contains different anions (Cl^{-} and NO_3^{-}). This conclusion may lead to the possibility of selectively removing certain ions.

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Proof of Concept

Three Electrode Cell

Nitrate Removal

Proof of Scale-Up

CDI Flow Reactor