



Nitrate removal from water using electrostatic regeneration of functionalized adsorbent

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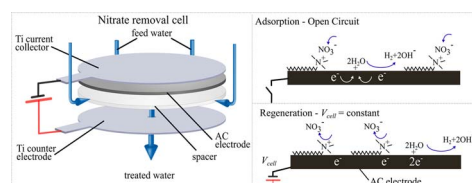
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GRAPHICAL ABSTRACT



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ABSTRACT

Nitrate is an important pollutant in drinking water worldwide, and a number of methods exist for its removal from water including ion exchange and reverse osmosis. However, these approaches suffer from a variety of disadvantages including requirements for supply and disposal of brine used for regeneration in ion exchange and low water recovery ratio for reverse osmosis. Here, we demonstrate the use of high surface area activated carbon electrodes functionalized with moieties having high affinity for adsorption of nitrate from aqueous solution, such as those used in ion exchange. Adsorption of surfactant molecules having a quaternary amine ionic group to the activated carbon surfaces provides functionalization of the surfaces without complex chemistries. The functionalized electrodes have adsorption capacities of about 80 mg NO₃⁻ per gram of activated carbon material. Unlike a traditional ion exchanger, the functionalized surfaces can be repeatedly regenerated by the application of an electrostatic potential which displaces the bound NO₃⁻ while leaving an excess of electronic charge on the electrode. The cell is completed by a counter electrode passing current via Faradaic reactions during regeneration. The proposed system is a hybrid form of capacitive deionization, wherein one electrode is strongly capacitive and the counter electrode is dominated by Faradaic reactions. Up to approximately 40% of the initial capacity of the electrode is accessible following electrical regeneration.

1. Introduction

Nitrate is a pollutant of major and rapidly increasing concern in drinking water worldwide. High nitrate levels in groundwater are associated with changes in the balance of the nitrogen cycle due to intensive agriculture. The growing use of fertilizers and worldwide

increase in agricultural intensity continue to increase the impact of this pollutant [1–3].

Nitrate itself is rather benign, but it has the potential for reduction to toxic nitrite in the human digestive system. Infants are considered highly sensitive to high nitrate levels, with significant risk of developing methemoglobinemia, a potentially fatal condition reducing the

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oxygen carrying capacity of the blood. Livestock are likewise at risk from poisoning from high nitrate levels. Nitrates in food and drinking water are also implicated in the generation of carcinogenic nitrosamines. [4–7]

Due to the often diffuse nature of nitrate contamination, the most compatible methods for nitrate treatment are commonly distributed, point-of-entry, or point-of-use systems [8]. One of the most popular methods of treatment for nitrate removal in distributed settings is ion exchange [9,10]. Ion exchange is a commonly applied technique to treat water with a range of ionic contaminants (e.g. nitrate, perchlorate, alkaline earth ions). In ion exchange, charged groups (e.g. cationic quaternary amines) attached to a resin are initially weakly bound to counter charged ions (e.g. Cl^-). When exposed to a solution containing ions with a higher chemical affinity (e.g. NO_3^-), these ions displace the lower affinity ions and are removed from the solution. Lower affinity ions are “exchanged” for higher affinity ions in solution based on the difference in their bound-to-free equilibrium constants. The relative affinities are influenced by the size, bonding, and electronic structure of the ions and surface groups [11].

Resins for nitrate removal often use standard anion exchange quaternary amine moieties such as trimethyl amine (type I) or dimethylethanol amine (type II) bound to divinylbenzene pendant groups of the polymer matrix [12–13]. These groups show somewhat higher affinity for nitrate versus chloride or bromide ions [11,13]. However, their affinity for sulfate ions is higher still, so their capacity for nitrate is reduced for feed solutions high in sulfate. Nitrate specific resins have been developed, which employ moieties such as triethyl- and tributylamine [9, 14].

Ion exchange is highly effective and widely applied for a variety of water treatment needs such as hardness and nitrate removal. However, the standard technique suffers from several drawbacks. When all lower affinity ions on the resin have been exchanged for higher affinity ions, the resin is exhausted and must be regenerated or replaced. When regenerated in place, a brine (e.g. NaCl) is applied to the resin bed at sufficient concentrations (e.g. 1 M) to drive the equilibrium toward the state with a majority of the active sites again occupied by weakly bound ions. The regeneration process thus requires significant quantities of concentrated brine, and this poses a number of problems in the implementation of ion exchange systems. The requirements for regular brine tank filling and material cost are significant impediments to application in point-of-use and point-of-entry systems.

Although point-of-entry systems are a key segment of treatment equipment, they have particular difficulty with disposal of brine during regeneration, as high levels of salinity are damaging to most inland plant life. Furthermore, such installations typically rely on septic systems for waste water disposal, which may be susceptible to clogging when exposed to highly saline waste streams due to the salting out of weakly soluble oily species [15]. Reverse osmosis systems are also effective for nitrate removal from drinking water [16–17]. However, they suffer from high costs and often from poor ratios of recovered to input water due to the low operating pressures generally applicable in point-of-entry and point-of-use systems and the need to minimize fouling [17–18]. Biological methods are highly effective for nitrate removal from waste water, but are not commonly deployed for drinking water currently [19–20]. A number of adsorbents are also capable of passive removal of nitrate from water [21]. Capacitive deionization (CDI) is an alternative method for removal of ionic contaminants from water [24–26]. CDI uses electrostatic interactions to adsorb ionic contaminants from solution onto high surface area electrodes leaving behind purified water which is flushed from the cell. The electrodes are then discharged to release the contaminants into a concentrated waste stream, which is flushed from the cell with additional feed water to complete the cycle. CDI cells can be used without ion selective membranes [24] or with such membranes in an effort to improve charge efficiency [27–28]. Further, CDI can be implemented such that ions are adsorbed due to the application of an applied potential difference to

electrodes (“traditional” CDI), or ions can be adsorbed without applied potentials by the action of chemical charges on electrode surfaces. In the latter case, ions are removed from the CDI cell by applying a potential—a process termed inverted CDI [29]. Inverted CDI uses native surface charges for the adsorption action, but the role of chemical affinity has not been well understood. Relevant to the current work, the application of CDI to trapping of nitrate has been limited to CDI cells operated in a “traditional mode” (i.e. nitrate ions trapped under applied fields) with carbon electrodes alone [30–32] as well as electrodes incorporating anionic selective membranes [33], including membranes with specific affinity for nitrate [34–37]. The latter cells use these membranes as a selective element. This is in contrast to the current work in which the selective (to nitrate) element is functionalized directly on the conductive carbon surface. Electrochemical oxidation and reduction has also been applied for the in-situ, transient formation of ionic surface groups with high affinity for ionic solutes on functionalized electrodes as in the electrically switched ion exchange method (ESIX) [38–40]. ESIX has been applied to the removal of nitrate using conductive polymer active electrodes [41–42]. Recently, asymmetric Faradaic cells using electrochemical redox-functionalization methods have been demonstrated with nanostructured polymer/carbon nanotube electrodes that are capable of efficient separation of ions from solution with high selectivity and suppression of parasitic side reactions such as water splitting [22–23].

In this study, we demonstrate a means of separation of nitrate from solution which overcomes major limitations of the existing methods. The method presented here can be generally described as a hybrid CDI approach. We implement an adsorbent that removes nitrate from solution with high affinity, and then regenerate this adsorbent electrostatically rather than through exposure to high concentration brine. The requirements for brine disposal are thus eliminated. We leverage the established nitrate affinity of trimethyl quaternary amines to drive nitrate removal from solution via adsorption onto functionalized high surface area activated carbon [43]. This adsorption is performed under no applied potential to the electrode. As in inverted CDI, we then remove the adsorbed ions by application of a potential to the conductive activated carbon substrate. In contrast to inverted CDI as commonly implemented, the cell is completed by a titanium electrode that passes current during regeneration of the active electrode via Faradaic reactions occurring in solution but not primarily involving the electrode material itself. (Although, aging of the electrode suggests the possibility of some secondary participation as discussed below.) A key element of this design is the prevention of re-adsorption of the expelled nitrate from the active electrode during regeneration.

2. Materials and methods

2.1. Electrode material

We used commercially available PACMM activated carbon material (Material Methods LLC., Irvine, CA) as the active porous carbon electrode. This material has been previously applied and characterized in CDI [44–49]. The electrode has a thickness of $\sim 300 \mu\text{m}$.

2.2. Surfactant treatment of electrode material

We functionalized the active electrode with trimethyl quaternary amine moieties by adsorption of the common cationic surfactant cetyltrimonium bromide (CTAB) on the surfaces of the activated carbon (Fig. 1b). CTAB has been shown to be adsorbed on activated carbon and dramatically increase its capacity to passively adsorb high affinity ions such as perchlorate, [50–53] as well as provide surface charges for CDI [54]. We soaked the activated carbon electrodes in aqueous solutions of 10 mM CTAB and 10 mM NaCl overnight with roughly 1.25 g of electrode material per liter of solution. The nonpolar alkane segment of the CTAB molecule adsorbs readily to the AC surface and leaves the

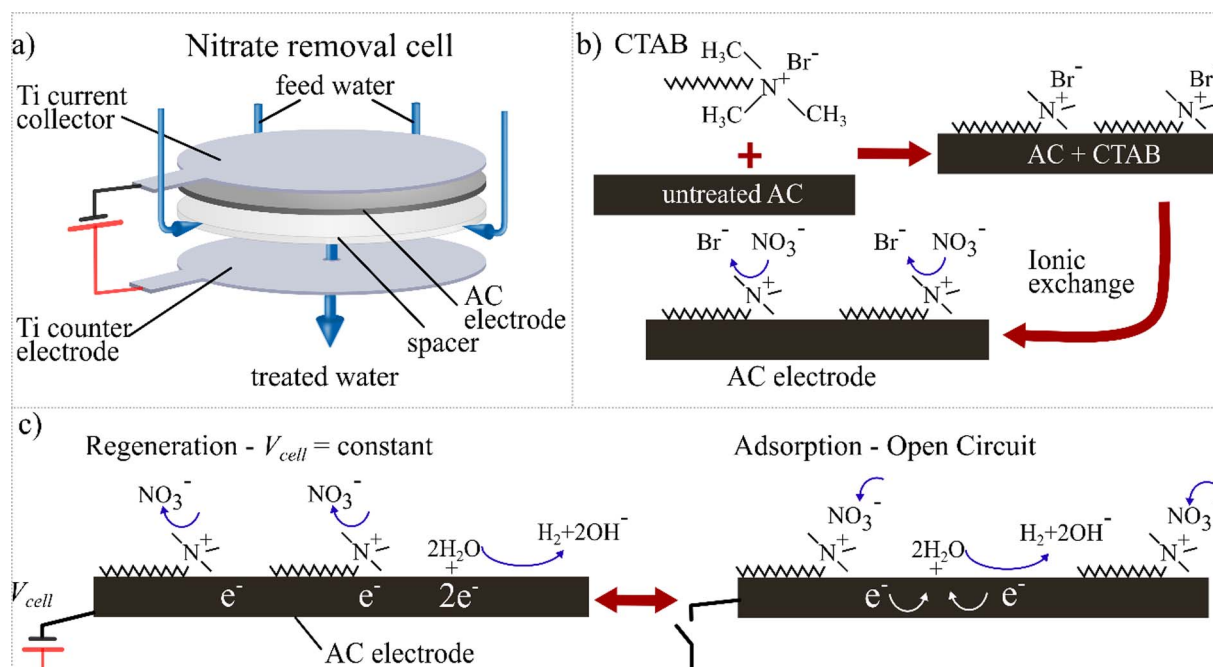


Fig. 1. a.) Schematic of radial flow-between nitrate treatment cell with CTAB functionalized AC electrode and titanium Faradaic counter electrode. Arrows represent flow paths. b) Schematic of CTAB treatment of AC and the initial ionic exchange process in which NO₃⁻ displaces Br⁻ due to the higher affinity of the quaternary amine functional group for the former. c) Schematic of the cyclical electrical regeneration and passive adsorption in functionalized electrode. Potential, V_{cell}, is applied to the electrode (left) which drives off nitrate, and simultaneously creates Faradaic reactions at the counter electrode as well as some smaller Faraday current at the AC electrode. Following regeneration, the AC electrode is electrically isolated (open circuit) and passive adsorption of nitrate occurs in the electrode along with the dissipation of the stored charge via Faradaic reactions on the active electrode.

quaternary amine head group exposed for later interaction with anions in solution.

2.2.1. Nitrate concentration measurement

We quantified nitrate concentration in solution via optical absorption using UV absorbance in a spectrophotometer (Agilent Cary 6000i UV/Vis/NIR) [55]. We measured optical absorption at either 205 nm or 225 nm depending on the presence of bromide ions in solution. The shorter wavelength provides somewhat higher sensitivity to the NO₃⁻ ion but suffers from significant absorption from Br⁻ as well. Therefore, we used 225 nm for NO₃⁻ concentration measurements for the initial exposure of the treated electrode to NO₃⁻ during which Br⁻ is expelled [56]. After the initial adsorption, we used adsorption at 205 nm for measurement of nitrate concentration. For the majority of measurements, we collected fractions of the effluent over 30 min intervals into separate samples contained in 15 mL conical plastic tubes using a fraction collector with an effluent flow rate of 0.43 mL/min (13 mL/sample). For short time response measurements, we flowed the effluent directly through the spectrophotometer cuvette for online measurement. Additional details of the nitrate measurement procedure are available in the [Supporting information](#) of this paper.

2.3. Cell design

Fig. 1a shows a schematic of the nitrate treatment cell. The cell uses a radial inflow geometry. Feed water is supplied to the outer periphery of the circular active and counter electrodes, and flows between the two electrodes toward the center of the cell through a woven plastic mesh spacer (300 μm thick). The treated water then exits the cell through a hole in the center of the counter electrode, which is formed from titanium (140 μm thick) and operates through Faradaic reactions at its surface. A titanium current collector (50 μm thick, Grade 2) also presses against the active electrode to form electrical contact. A peristaltic pump provides continuous flow of feed water to the cell, and treated effluent is either collected using a fraction collector for analysis or sent directly through a flow cuvette for UV adsorption measurement. The

active area of the cell is 3.5 cm in diameter, and the active electrode has a mass of 0.15 g.

2.4. Adsorption/regeneration cycle

Immediately following CTAB treatment, the active electrode acts as a traditional ion exchanger (**Fig. 1**b). However, in contrast to traditional regeneration methods using high concentration of low affinity ions, here we regenerate the active electrode by the application of a negative potential, relative to the counter electrode (**Fig. 1**c), which displaces the NO₃⁻ ions and leaves behind excess electrical charge in the electrode that balances the positive amine groups on the surface. Hydroxyl ions may also be generated by Faradaic reactions during regeneration and participate in ion exchange with NO₃⁻ ions. Following regeneration, the active electrode again acts as an adsorbent with no connection to the counter electrode. As nitrate ions are bound by the amine groups, electronic charge is dissipated from the electrode via Faradaic reactions at its surface. (See **Fig. 4** and discussion below).

3. Results and discussion

3.1. NO₃⁻ adsorption by functionalized activated carbon saturated with halide ions

Immediately following functionalization of the active electrode, the quaternary ammonium groups are saturated with a mixture of Br⁻ and Cl⁻ ions. When exposed to solutions containing ions with higher affinity, such as NO₃⁻, the higher affinity anions displace the surface bound ions of lower affinity (i.e. Br⁻ and Cl⁻) (as in a traditional ion exchange resin) (**Fig. 1**b). **Fig. 2** shows the time response of the effluent from the cell for an electrode with no applied potential which was freshly functionalized and exposed to an input stream containing 200 ppm NaNO₃ and with a flow rate of 2.9 mL/min/g-electrode (0.43 mL/min for the cell). Effluent NaNO₃ concentration dropped to 45 ppm for 1 h then slowly rose until it approached the input concentration after ~12 h. As shown in the inset of **Fig. 2**, the active

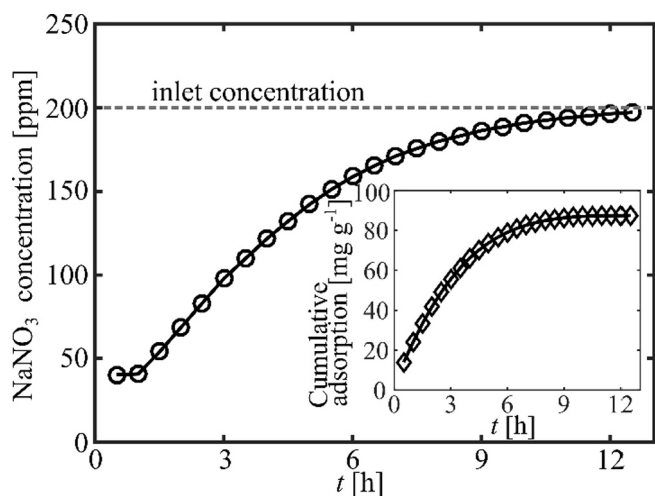


Fig. 2. Adsorption of NO_3^- by freshly CTAB treated AC electrode. (main) Effluent NaNO_3 concentration is shown versus time for 200 ppm NaNO_3 inlet concentration. Flow rate was 2.9 mL/min/g-electrode (0.43 mL/min for full cell). Symbols are experimental data points corresponding to times of collection for samples with volume 13 mL each. (inset) Cumulative adsorption on electrode vs. time in mass of NaNO_3 normalized by mass of electrode. Total adsorption is 83 mg NO_3^- /g-electrode.

electrode was saturated with NO_3^- by a cumulative adsorption of 83 mg NO_3^- /g-electrode. This value corresponds to the first adsorption of a freshly functionalized electrode. For comparison, commercial ion exchange resins show a capacity of up to ~ 150 mg NO_3^- /g. [9] PACMM material that has not been treated with CTAB shows a total NO_3^- capacity of less than 5 mg NO_3^- /g electrode. We separately investigated the nitrate affinity of CTAB-treated activated carbon in the presence of chloride anions, as detailed in Section 4 of the [Supporting information](#). The results of this experiment show a substantially higher affinity for NO_3^- compared to Cl^- .

3.2. Electrical regeneration of functionalized AC

In contrast with ion exchange resins, our functionalized activated carbon electrode can be electrically regenerated to restore adsorption activity. [Fig. 3](#) shows a series of selected regeneration and adsorption cycles (numbered) for the active electrode. (Cycles 6–9 are discussed later, and not shown in [Fig. 3](#).) The input stream was again maintained with a NaNO_3 concentration of 200 ppm and flow rate of 2.9 mL/min/g-electrode (0.43 mL/min for full cell). [Fig. 3a](#) shows the effluent concentration for regeneration using a constant cell voltage of -3 V applied to the active electrode with respect to the counter electrode for 4 h followed by adsorption at open circuit. Application of negative potential to the active electrode drives off bound NO_3^- anions. Current corresponding to the nitrate ion release (as well as Faradaic reactions on the active electrode) flows to the counter electrode. As the counter

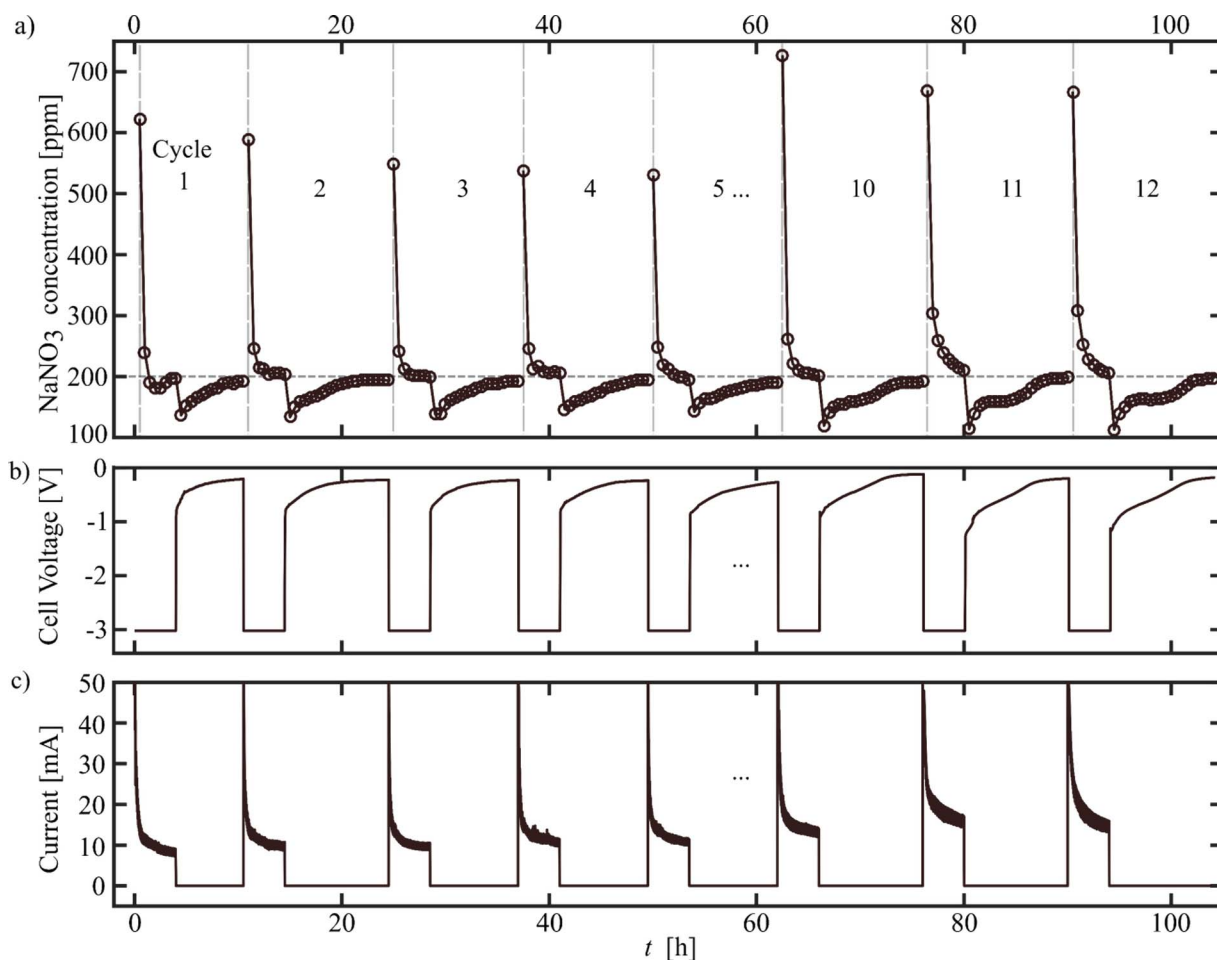


Fig. 3. Cyclic adsorption of nitrate using electrical regeneration. Time series showing a) Effluent NaNO_3 concentration vs. time for input concentration of 200 ppm NaNO_3 , b) cell voltage (active electrode potential with respect to counter electrode), and c) current versus time for fixed flow rate ($Q = 0.43$ mL/min). For cycles 1 through 5 and 10 through 12, we adsorbed at open circuit, while in cycles 6–7 (shown in SI) we adsorbed at short circuit. The time axis has been abridged to include only active cell times. The length of inactive time between each consecutive cycle are given in [Supporting information](#).

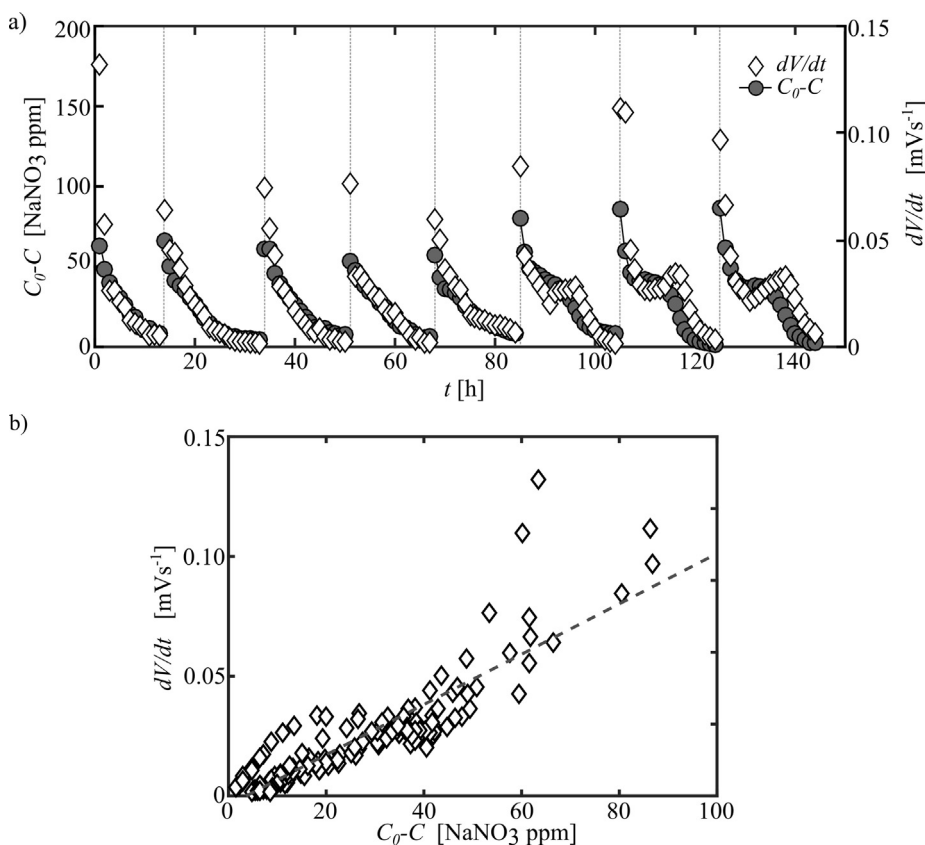


Fig. 4. a) Adsorption of NO_3^- (left ordinate) by electrically regenerated electrodes versus time (as deduced from effluent stream), and (right ordinate) time derivative of porous electrode voltage during the adsorption cycles versus time. Symbols indicate time of collection for samples with volume 13 mL. b) Correlation plot of nitrate removal versus time derivative of porous electrode voltage during the adsorption cycles at open circuit. Rate of adsorption correlates strongly with discharge of electrode (dV/dt) indicating anion adsorption is balanced by removal of electronic charge from electrode by Faradaic reactions.

electrode has minimal capacitance, Faradaic reactions at the counter electrode accommodate this current. The regeneration voltage of -3 V exceeds the electrolysis threshold for water. Therefore, we expect Faradaic reactions to occur on the active electrode, as well, in parallel with the expulsion of nitrate ions.

Following regeneration, the quaternary amine groups of the CTAB molecules are balanced (at least in part) by electronic charge in the electrode, as seen by the retention of a negative voltage on the active electrode with respect to the counter electrode. Fig. 3b and c show the voltage between the active and counter electrodes and the current leaving the active electrode, respectively, during each regeneration/adsorption cycle. The time axis in Fig. 3 indicates only total active time during cycles. Inactive time between cycles is excluded for clarity of presentation, but the active electrode is exposed to the input nitrate stream at 200 ppm concentration during this time as well.

During adsorption, NO_3^- ions are removed from solution and electronic charge is dissipated from the electrode (Fig. 1c). This results in a gradual decrease in the magnitude of cell potential during adsorption (Fig. 3b). The adsorption cycles shown in Fig. 3 occur with an open circuit between the active and counter electrodes. Consequently, the electronic charge in the electrode is dissipated by Faradaic reactions on the electrode itself (Fig. 1c). As discussed below, the observed capacity of the active electrode for nitrate adsorption following electrical regeneration is significantly lower than that of the freshly functionalized electrode (e.g. $\sim 40\%$ of initial capacity). A possible mechanism for this difference is the loss of cetrimonium ions (CTA^+) from the electrode, as the non-polar tail group is expected to be relatively weakly bound to the electrode surface. However, the negative potential applied to the active electrode with respect to the counter electrode acts to retain the CTA^+ ions.

Fig. 4 shows the correspondence of nitrate removal from solution and electronic charge dissipation from the electrode. Fig. 4a gives time series for nitrate removal rate (represented by the difference in input and effluent NaNO_3 concentration at fixed flow rate) and charge

dissipation rate of the capacitive electrode (calculated as the time rate of change of potential for the capacitive electrode) during adsorption for each of the cycles shown in Fig. 3. Adsorption for these cycles occurs at open circuit, so no current flows through the external circuit and the titanium counter electrode essentially acts as a reference electrode. Fig. 4b shows the correlation between nitrate removal rate (as measured in effluent) and electrode potential discharge rate. The strong correlation between electronic discharge of the electrode and nitrate removal suggests that electrons are the dominant species balancing the positive amine groups on the electrode surface following regeneration. However, OH^- ions generated by Faradaic reactions during regeneration may also be present and participate in later ion exchange reactions with NO_3^- ions.

Cycles 6–7 (see Supporting Information, Figure S1) were conducted using a short circuit between the active and counter electrodes. Effluent concentration in these cycles shows similar behavior to that seen in Fig. 3a, indicating dominance of Faradaic reactions on the active electrode.

Table 1 gives the cumulative NaNO_3 adsorption and expulsion for each cycle as well as the maximum and minimum effluent concentrations averaged over 30 min during regeneration and adsorption, respectively. The cumulative mass of NaNO_3 released during regeneration per mass of electrode material is 33 mg/g during the first two cycles, but falls with additional cycles. Comparison of the regenerated quantity of NaNO_3 with the charge transferred to the active electrode during regeneration (Fig. 3c) indicates that a large majority (e.g. $> 95\%$) of the cell current during regeneration corresponds to Faradaic reactions on the active electrode. The cumulative adsorbed mass measured per cycle is consistently below the released mass, averaging ~ 20 mg/g for the first 7 cycles. We hypothesize that this difference is due to additional adsorption that occurs while the cell is offline, and perhaps, chemical changes in the active or counter electrodes. Evaporation during collection or errors in flowrate may also contribute.

We noted dramatic reductions in effluent nitrate concentration

Table 1

Cumulative adsorbed and expelled NaNO_3 per unit mass of electrode, as well as maximum and minimum NaNO_3 concentration for each cycle from Fig. 3a. Input concentration was 200 ppm NaNO_3 and flow rate was 0.43 mL/min.

Cycle	Adsorption, [mg g ⁻¹]	min. C, ppm	Regeneration, [mg g ⁻¹]	max. C, ppm
1	17.1	136	32.5	623
2	20.0	133	32.7	588
3	21.6	138	28.4	548
4	20.1	146	30.3	538
5	20.7	142	28.2	530
6	22.1	141	28.2	509
7	18.6	144	23.2	465
10	34.4	119	42.1	727
11	35.8	113	47.8	669
12	37.6	113	44.9	667

during purge for cycles 8 and 9, and minimal adsorption capacity after purge. Following cycle 9, we replaced the counter electrode with a fresh titanium sheet but retained the previously used active electrode. This replacement resulted in a significant improvement in both regeneration and adsorption performance, as seen from Fig. 3a. After counter electrode replacement, the cumulative NaNO_3 mass released during regeneration rises to ~ 45 mg/g, and the cumulative adsorption increases to ~ 36 mg/g. The transient response of effluent concentration and cell voltage also show a notable difference following replacement of the counter electrode, displaying a plateau in effluent concentration and an inflection point in electrode potential discharge rate. The mechanisms for these differences in regeneration and adsorption behavior associated with changes in the counter electrode are not clear. Titanium is commonly used as an anode in electrochemical systems due to the extreme corrosion resistance imparted by the surface oxide coating [57]. We tested the possibility of excessive oxidation on the surface by polishing both the titanium current collector and counter electrode with abrasive, but observed no effect. We hypothesize that improved contact between the active electrode material and current collector following reassembly of the cell may contribute to the behavior observed. We also believe that impurities in the electrode may play a role in the Faradaic reactions occurring in solution at the counter electrode during purge, and these impurities may leach from the electrode during operation, reducing its effectiveness as they are depleted. A more robust electrode material such as platinum or platinized titanium may offer superior durability. As we describe below, we hope, as part of future work, to replace the Faradaic electrode in our cell with a porous capacitive counter electrode to minimize Faradaic currents and improve power efficiency.

The adsorption capacity accessible through electrical regeneration was consistently lower than for the initially treated electrode. Fig. 5a compares the adsorption behavior for the active electrode immediately after CTAB treatment and for the cyclically operating electrode with multiple electrical regenerations. The comparisons show that only a fraction of the initial adsorbance capacity was accessible during normal operation with electrical regeneration. For cycles 1–5 only about 24% of the initial capacity was available. After replacement of the counter electrode (cycles 10–12), about 43% of the capacity was repeatedly accessible.

3.3. Possible NO_2^- generation

The significant voltages applied during regeneration provide the potential for electrochemical reduction of NO_3^- to NO_2^- . We tested for the presence of nitrite ions in the cell effluent during regeneration with a range of cell voltages from -1 to -8 V. Using a colorimetric test (LaMotte Insta-TEST 2996 Nitrate/Nitrite test strips, LaMotte Co., Chestertown, MA), with a detection limit of ~ 1.5 ppm NO_2^- , we detected no nitrite production in the effluent for regeneration voltage

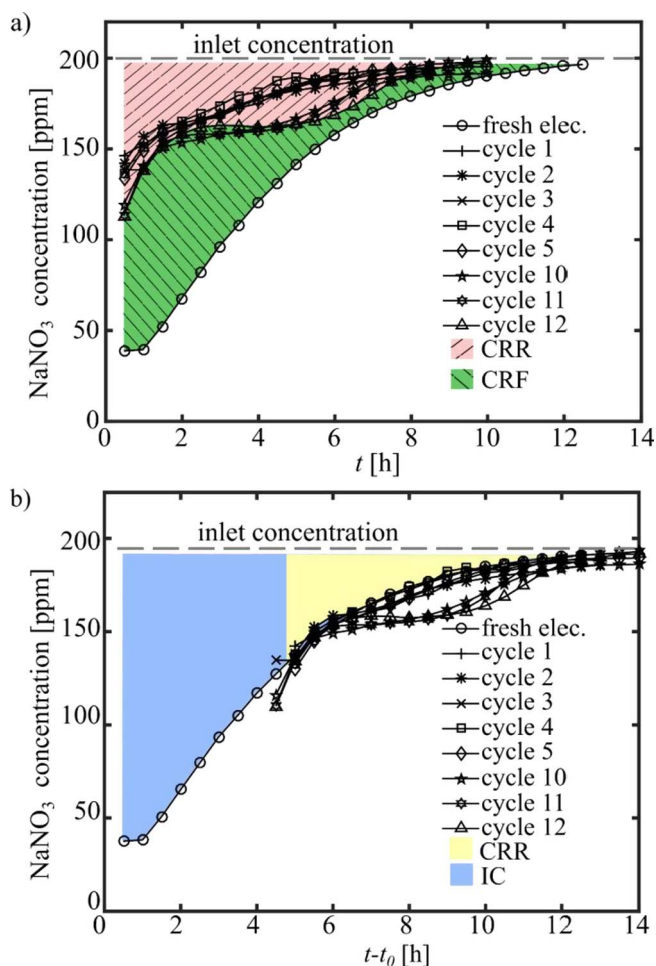


Fig. 5. a) Adsorption behavior for AC electrode following electrical regeneration in comparison with fresh CTAB treatment. Series show effluent NaNO_3 concentration vs. time for 200 ppm NaNO_3 inlet concentration. Hatched areas represent maximum cumulative NO_3^- removal following electrical regeneration (CRR, cumulative removal with electrical regeneration) and initially treated electrode (CRF, cumulative removal fresh electrode). b) Effluent NaNO_3 concentration vs. time with time axis for each series shifted such that electrode saturation times (i.e. time where effluent concentration equals inlet concentration) are coincident. Time shift shows that adsorption rate is strongly correlated to degree of electrode saturation. Area CRR is representative of adsorption following electrical regeneration. Left area corresponds to inaccessible capacitance, IC, for NO_3^- adsorption possibly due to electrical limitations. Symbols indicate time of collection for samples with volume 13 mL. Flow rate is 0.43 mL/min.

magnitudes below 4 V. At cell voltages more negative than -4 V, nitrite is produced in the effluent stream.

3.4. NO_3^- adsorption following electrical regeneration

The plots of Fig. 5 show how the rate of nitrate removal depends strongly on the degree of nitrate saturation in the active electrode. To highlight this dependence, we show in Fig. 5b the effluent concentrations following electrical regeneration shifted along the time axis (by ~ 4.5 h). This enables a more direct comparison between the adsorption capacity of regenerated electrode versus the later stages of adsorption for the freshly treated electrode. Interestingly, the electrode displays similar relationships between the rate of nitrate removal and remaining available adsorption capacity following electrical regeneration and initial treatment.

Fig. 6 shows measurements of nitrate removal rate following electrical regeneration at -5 V as a function of time for three different flow rates. Increased flow rate offers increased removal rate, although the increase in removal rate is not directly proportional to flow rate. Fig. 6b

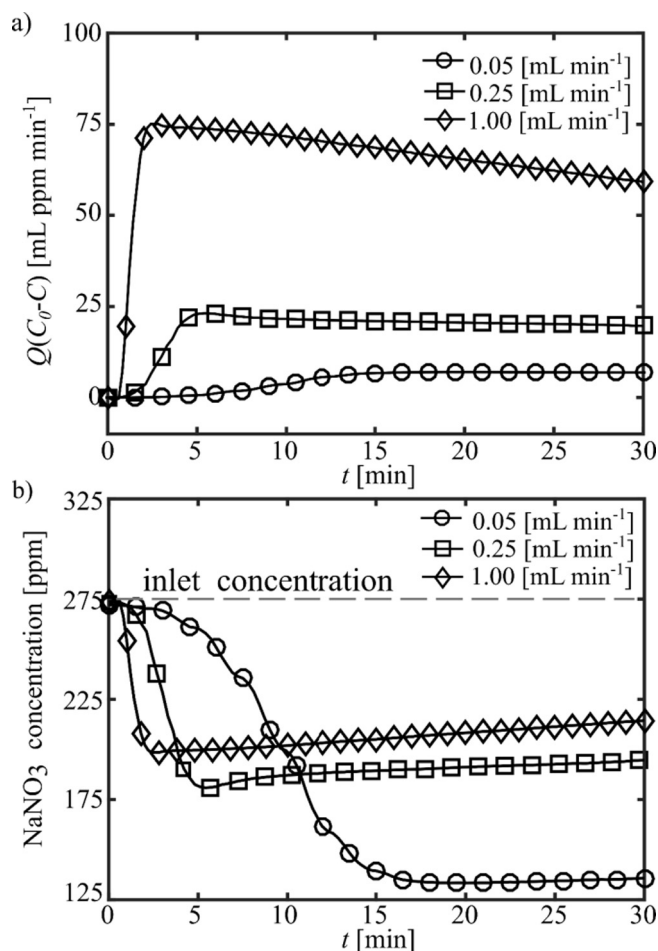


Fig. 6. Coupling between adsorption rate and flow rate. a) Adsorption rate of NaNO_3 versus time, and b) NaNO_3 concentration versus time for electrically regenerated AC electrode for various flow rates at a fixed input concentration of 275 ppm NaNO_3 . Here, electrode was regenerated at -5 V before each adsorption. Strong flow rate dependence of adsorption rate suggests a mass transport limitation.

shows the trade-off between the increased removal rate of nitrate and the increased nitrate concentration of the effluent, as the cell's removal rate cannot keep up with the demands of increased flow rate. We hypothesize that the trends of Fig. 6a and b are due to a complex coupling between mass transport limitations, adsorption rate kinetics, and the finite capacity of the cell. For example, we hypothesize that the rate of diffusion is strongly influenced by the near electrode surface concentrations of nitrate, which result from a coupling between streamwise advection and transverse diffusion of nitrate. We hope to further explore these coupled effects in a future study.

4. Conclusions

We have shown a nitrate removal cell which uses functionalized groups on a high surface area electrode for both passive adsorption of nitrate, and electrical, on-demand regeneration of the adsorber using no regeneration chemicals whatsoever. The electrically regenerated passive adsorber is activated carbon with groups having high affinity for nitrate consisting of quaternary amines (CTAB). We show a capacity of ~ 80 mg NaNO_3/g activated carbon which is comparable to that available from ion exchange resins. The bulk electrical conductivity of the activated carbon substrate allows the application of an electrical potential to expel adsorbed nitrate ions and regenerate the ion exchange groups without application of high concentration brine. The electrode retains about 43% of the initial capacity following electrical regeneration, and the electrode can be repeatedly regenerated. The ability to

electrically regenerate an active electrode provides potential advantages in terms of reduced maintenance and waste disposal needs. The most important limitation of the current cell is our use here of a Faradaic counter electrode employing water electrolysis. This Faradaic counter electrode is convenient for demonstration but leads to higher regeneration voltages and larger energy consumption during regeneration due to the high potential required to drive electrolysis. However, faradaic electrodes have been demonstrated in asymmetric redox cells for electrochemical separation that suppress water splitting and allow lower potential swings during cycling. [22] In future systems, we will pursue the use of capacitive counter electrodes employing functionalization with opposing surface charges to prevent adsorption of nitrate during regeneration. Such an approach falls within the scope of inverted CDI operation, but takes advantage of the specific chemical affinity of the surface functionalization for high selectivity of ions removed from solution.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cej.2017.10.161>.

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