Short Communication

Adsorption and capacitive regeneration of nitrate using inverted capacitive deionization with surfactant functionalized carbon electrodes

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ABSTRACT

Nitrate is a pollutant present in groundwater worldwide. Several techniques are available to remove nitrate from water, but they are difficult to automate in remote settings or require chemicals for treatment for regeneration. Here, we demonstrate the use of two surfactant-treated high surface area porous electrodes for passive adsorption of nitrate followed by electrical regeneration. In order to generate the surface charge driving adsorption, we functionalized the active electrode (cathode) and capacitive counter electrode (anode) with cationic trimethyl quaternary amine groups have been shown to have a

1. Introduction

Nitrate (NO3⁻) is a contaminant of growing concern that affects water quality globally. Intensification of agricultural activities has led to a growth in the use of fertilizers, which are increasing nitrate levels in groundwater and disturbing the balance in the nitrogen cycle [1,2]. Nitrate indirectly produces health hazards by reduction to toxic nitrite in the human digestive system. Moreover, infants are susceptible to developing methemoglobinemia when exposed to high levels of nitrate [3–6].

Nitrate contamination in groundwater is often diffusely spread over large areas, making point-of-entry or point-of-use systems the most compatible methods for nitrate treatment [7]. Ion exchange is a popular method of treatment in such settings [8,9]. In this method, resins are functionalized with charged groups weakly bound to relatively low affinity ions (e.g. Cl⁻). Upon exposure to a solution with higher affinity ions (e.g. NO3⁻), these exchange with the lower affinity ions and are removed from the solution. For example, resins functionalized with trimethyl quaternary amine groups have been shown to have affinity for nitrate [10,11]. Reverse osmosis systems are also effective for nitrate removal from drinking water [12,13]; however, they suffer from high costs and poor water use efficiency [14]. Biological methods are effectively applied for nitrate removal from waste water but not commonly for drinking water [15,16].

Capacitive deionization (CDI) is another method to remove toxic ions from water [17–19]. CDI typically uses a potential to electrostatically adsorb/discharge ions onto/from high surface area electrodes [20]. The product of CDI is purified water during adsorption and a waste stream with high concentration of contaminants during discharge. CDI cells can be used with ion selective membranes to improve charge efficiency [21–23], or without membranes in flow-between or flow-through electrode configurations [20,24,25]. In “traditional” CDI, ions are adsorbed upon application of an external voltage (around 1 V). However, it is possible to adsorb ions onto the electrodes without external voltage by the action of chemical charges on the electrode surfaces. In this operational mode, application of a potential regenerates the CDI cell (ion expulsion) in a process named inverted CDI (i-CDI) [26–29]. Nitrate removal has been demonstrated using traditional CDI (adsorption of nitrate under an applied voltage) with carbon electrodes alone [30,31] or with ion selective membranes [32–34].
In a previous work [35], we took advantage of well-established nitrate affinity of trimethyl quaternary amines for nitrate sequestration [10,11]. To this end, we fabricated a cell with activated carbon (AC) electrodes functionalized with cetrimonium bromide (CTAB) cationic surfactant. The cell consisted of 3.5 cm diameter 300 µm thick CTAB-treated carbon electrode and a second, Faradaic electrode comprised of a single 50 µm thick titanium sheet. A solution of 200 ppm NaNO₃ at 0.43 ml min⁻¹ flow rate was fed to the cell. We showed that surface charge generated by CTAB leads to nitrate adsorption in the active electrode without applied potential (~ 80 mg NaNO₃ per g of activated carbon). We then regenerated the adsorbed ions by application of 3 V potential to the functionalized electrode. Unlike the current i-CDI cell, the circuit associated with regeneration of the active electrode of that preliminary cell was completed via Faradaic reactions on the titanium electrode.

Fig. 1 shows our current cell which uses two (capacitive) porous electrodes. Relative to our previous work, we replaced the inert titanium electrode with a surfactant-functionalized capacitive counter electrode. Similar to our previous work, we functionalized the active/adsorbing electrode using CTAB. CTAB imparts a positively charged surface for adsorption of nitrate [36]. We functionalized the capacitive counter electrode (also activated carbon) with a sodium dodecyl benzene sulphonate (SDBS) anionic surfactant. The latter treatment creates a negative surface charge to passively adsorb cations at short circuit (Fig. 1b). Throughout this paper, we refer to these active and counter porous electrodes as CTA-AC and DBS-AC, respectively.

During adsorption, NO₃⁻ and counter ions (Na⁺ ions here) are adsorbed to their respective electrodes, while electrons migrate from CTA-AC to DBS-AC. As in i-CDI, we remove the adsorbed ions by application of an external voltage to the electrodes (Fig. 1a). The resulting electric field drives electrons from DBS-AC to CTA-AC, repelling Na⁺ and NO₃⁻ ions. We here demonstrate successful nitrate removal (up to more than 10 mg sodium nitrate per g of both electrodes) with our i-CDI system. Relative to our preliminary work [35], this work shows we can replace the Faradaic titanium counter electrode with an SDBS-treated capacitive counter electrode to create a complete i-CDI cell. As we shall see, the current design increases the energy efficiency of nitrate removal (measure by energy-normalized adsorbed salt (ENAS) metric) by 1 to 2 orders of magnitude for a similar average salt adsorption rate (ASAR).

2. Materials and methods

2.1. Surfactant treatment of electrode material and capacitive counter electrode

Commercially available activated carbon electrodes (Material Methods LLC., PACMM™ 203, Irvine, CA) were used as the active porous carbon electrode and capacitive counter electrode. We functionalized the active electrode (cathode) with trimethyl quaternary amine moieties by adsorption of CTAB surfactant. To this end, we soaked 0.15 g of pristine activated carbon electrode in 500 mL aqueous solution of 10 mM CTAB and 10 mM NaCl overnight and then rinsed thoroughly with deionized (DI) water and dried. We performed a similar functionalization on the capacitive counter electrode with SDBS surfactant. We soaked 0.15 g of pristine activated carbon electrode in 500 mL aqueous solution of 10 mM SDBS and 10 mM NaCl overnight, rinsed with DI water, and dried. We refer to active and counter porous electrodes as CTA-AC and DBS-AC, respectively.

We measured electrical resistance of the electrodes with four-point probe method (Keithley 2400, Cleveland, OH). Upon surface treatment, resistance of uncompressed CTA-AC and DBS-AC electrodes increased respectively about 70% and 20% (from 7.4 Ω cm for untreated carbon to values of 12.5 and to 8.9 Ω cm, respectively). We also experimentally investigated the nitrate affinity of CTAB-treated activated carbon in presence of chloride anions, and describe this in more detail in Section S-1 of the SI.
2.2. Experimental setup

The general experimental setup is described in detail by Palko et al. [35] and the specific implementation in this work is summarized here. It consisted of a radial inflow geometry desalination cell [37], a reservoir with 200 ppm (~2.35 mM) sodium nitrate (NaNO$_3$) solution, a source meter (Keithley 2400, Cleveland, OH), a peristaltic pump (Ismatec IPC-4, Wertheim, Germany), and a flow-through conductivity meter (eDAQ, Denistone East, Australia). The cell consisted of a pair of ~300 μm thick electrodes (one CTA-AC and one DBS-AC) stacked between two 50 μm thick titanium sheet current collectors. A 300 μm thick woven plastic mesh (McMaster-Carr, Los Angeles, CA) was used as spacer between the electrodes. The electrodes had 3.5 cm outer diameter with 0.3 g total dry mass. We used 0.45 mL min$^{-1}$ flow rate and measured effluent conductivity with the conductivity meter. Upon surfactant treatment, we used our desalination cell with CTA-AC and DBS-AC electrodes for cyclic nitrate removal. To explore the relationship between applied potential and regeneration capacity of nitrate, we operated the cell at constant voltage (rather than constant current) and with pure sodium nitrate solution. Hence, we applied 0 V for adsorption (short circuit adsorption) and 0.2–1.4 V (with 0.2 V increments) for the regeneration step. Duration of adsorption and regeneration steps was 2 h each.

3. Results and discussion

3.1. Adsorption and electrical regeneration of functionalized activated carbon

Fig. 2 shows measured effluent concentration of NaNO$_3$ and external current for selected cycles with short circuit (at 0 V) adsorption and 0.2, 0.4, 0.6, 0.8, 1, and 1.2 V regeneration steps. Inflow stream was 200 ppm NaNO$_3$ solution at 0.45 mL min$^{-1}$ flow rate. The effluent concentration and electric current for cycles with increasing and decreasing order of regeneration voltages show very similar behavior (see Fig. 2). Upon application of voltage to the cell (negative voltage to CTA-AC and positive voltage to DBS-AC), the surfactant-bound Na$^+$ and NO$_3^−$ ions are repelled from their respective electrodes. High effluent concentration in regeneration is indicative of this repulsion. Results show an apparent increase in concentration baseline for voltages higher than ~1 V. We attribute this shift mainly to effluent pH fluctuations due to Faradaic reactions [38]. Subsequent to the regeneration, upon short circuit in the adsorption step, electrons in CTA-AC electrode (active electrode) discharge into DBS-AC electrode and the electric current is reversed. Migration of electrons from CTA-AC to DBS-AC is balanced with adsorption of NO$_3^−$ and Na$^+$ ions from flow stream into CTA-AC and DBS-AC, respectively. These fluxes lower the measured effluent concentration during the adsorption step. Note that in contrast to our preliminary work, [35] the regeneration step here is primarily capacitive (and not Faradaic) at voltages lower than about 1 V. This improves overall energy efficiency for nitrate removal (see Section 3.2), as Faradaic reactions here are insignificant compared to the previous use of a 3 V regeneration with a titanium Faradaic counter electrode (see [35] for more details).

3.2. Treatment of counter electrode is crucial for nitrate regeneration

We performed a set of experiments to demonstrate that treatment of the counter electrode with SDBS is crucial for effective regeneration of nitrate ions in our capacitive system. To this end, we built and operated a comparison cell consisting of one CTA-AC electrode (as active electrode) and one untreated porous AC electrode (as counter electrode). Fig. 3 shows schematics of these two types of cells (i.e. the current cell with CTA-AC and DBS-AC electrodes; and the comparison cell with one CTA-AC electrode and an untreated AC electrode) during adsorption and short circuit regeneration. For simplicity of presentation, counterions (Na$^+$) are not shown here. Figure S2 of the SI shows measured effluent concentration and electric current under 0.8 V and 0 V external voltages for this comparison cell. The comparison cell exhibits negligible ion adsorption. For example, we estimate the comparison cell adsorbs only about 0.1 mg g$^{-1}$ (mass of sodium nitrate removed per dry mass of both electrodes). By comparison, as we will describe in next Section, the i-CDI cell with both electrodes functionalized adsorbs about 6 mg g$^{-1}$ under the same conditions. We hypothesize that this behavior is due to electrostatic adsorption of nitrate ions at the untreated counter electrode during regeneration. In the absence of negatively charged dodecyl benzene sulphonate (DBS) surfactant, and during regeneration step, nitrate ions expelled from active (negative, CTA-AC) electrode, likely adsorb into the counter (positive) electrode. We also hypothesize that, for the i-CDI cell with both electrodes treated, the negatively charged DBS surfactant electrostatically shields nitrate ions from adsorbing to the counter electrode. This aids in rejection of nitrate ions from entering the untreated counter electrode.

Fig. 2. Measured (a) effluent concentration (area under peaks is proportional to amount of nitrate adsorbed) and (b) electrical current for selected cycles of nitrate regeneration (at 0.2, 0.4, 0.6, 0.8, 1, and 1.2 V) and adsorption (at short-circuit). The applied voltage during the regeneration step electrostatically repels NO$_3^−$ and Na$^+$ ions from the CTA-AC and DBS-AC functionalized electrodes, respectively. Results show an increase in effluent concentration baseline for >1 V. This shift can be attributed mainly to effluent pH fluctuations due to Faradaic reactions. The subsequent short circuit discharges electrons from CTA-AC to DBS-AC (current is reversed). The result is uptake of NO$_3^−$ and Na$^+$ ions from solution into CTA-AC and DBS-AC electrodes during adsorption, and a subsequent electrostatic regeneration of adsorption capability.
nitrate from the system in regeneration; and increases net adsorption of nitrate in the entire cycle.

3.3. Nitrate removal performance for cell with both electrodes functionalized

We here present salt adsorption and energy performance of our i-CDI cell. To this end, we applied 0 V for adsorption and 0.2–1.4 V (with 0.2 V increments) for the regeneration step, as mentioned in the Experimental setup section (see Section 2.2). The durations of adsorption and regeneration step were each 2 h (i.e. recovery ratio of 50%) and both were performed at the same 0.45 mL min\(^{-1}\) flow rate. Data of Fig. 2 was obtained from the same experiments which led to salt and energy calculations below (Figs. 4 and 5).

Fig. 4a shows experimental measurements of salt removal capacity of our cell as a function of regeneration voltage. The salt removal capacity is defined as mass of sodium nitrate removed (desorbed) in adsorption (regeneration) step per dry mass of both electrodes. Results show a linear increase in adsorption capacity (in absolute value) with regeneration voltage. Circles and diamonds respectively correspond to 2 h adsorption and 2 h regeneration step. The enhancement in adsorption with voltage is clear and suggests that higher regeneration voltages electrostatically repel more of the adsorbed ions; this in turn leaves more positively charged sites on CTA-AC electrode for the subsequent regeneration step.
nitrate adsorption step. Results show up to around 10 mg g\(^{-1}\) sodium nitrate adsorption which corresponds to about 30% average concentration reduction.

Fig. 4b shows transferred electronic charge (in units of Coulombs) during adsorption and regeneration steps as a function of regeneration voltage. While adsorption capacity is similar (in magnitude) for adsorption and regeneration steps, the transferred charge is higher in regeneration step, mainly due to higher Faradaic reactions. This suggests that charge efficiency (defined as salt removed or regenerated (in units of Coulombs) divided by transferred charge) is greater for adsorption compared to regeneration. Fig. 4c summarizes calculated charge efficiency for data shown in Figs. 4a and 4b. The charge efficiency for adsorption step (at 0 V) is 0.8–0.9 range and tends to increase with regeneration voltage (voltage applied at previous regeneration step). However, it decreases with voltage in regeneration step (diamond markers). This is expected because, as Fig. 4b suggests, Faradaic reactions are considerably higher in regeneration compared to adsorption. Solid lines here are to guide the eye.

We summarize our experimental study of the coupling between removal rate and energy efficiency in Fig. 5. Nitrate removal rate (in the adsorption step) can be quantified by average salt adsorption rate (ASAR) calculated as \(m_A/Q \cdot m_{kycle} \int (c_{\text{in}}-c_{\text{out}}) \, dt\), where \(m_A\) is salt molecular weight, \(Q\) is flow rate, \(m_{kycle}\) is dry mass of both electrodes, \(kycle\) is total cycle time, and \(c_{\text{in}}\) and \(c_{\text{out}}\) are inlet and outlet concentrations, and the integration is performed over the duration of the adsorption cycle [22,37]. The energy efficiency of the cycle is quantified by energy-normalized adsorbed salt (ENAS) calculated as \((m_A/Q \cdot E) \int (c_{\text{in}}-c_{\text{out}}) \, dt\), where \(E\) is overall energy consumption in a cycle [37]. Note that \(E\) here is the energy consumption during the regeneration step (the short-circuit adsorption step does not recover energy). Markers in Fig. 5a each correspond to a single cycle (regeneration and adsorption). Circles show measured ASAR and ENAS for the experiments discussed in Section 2.2 and the arrow shows direction of increase of regeneration voltage. Diamond markers are data for preliminary experiments reported in Palko et al. [35] with titanium Faradaic counter electrode, applying open circuit adsorption and 3 V regeneration. Results show 1–2 orders of magnitude higher ENAS, indicating considerably more energy efficient nitrate removal with the capacitive cell (compared to the Faradaic cell). We estimate that the energy consumption is at most 0.07 kW h m\(^{-3}\) (energy per volume of purified water) at 1.4 V regeneration voltage with ~30% salt removal. Figs. 5b and 5c respectively show ASAR and ENAS (for the same experiments as in Fig. 5a) as functions of regeneration voltage. The two metrics have opposite trends: the adsorption rate increases almost linearly with regeneration voltage, while energy efficiency drops with voltage. This shows a clear tradeoff between desalination rate and energy efficiency of our cell; a concept observed in traditional CDI as well [37].

4. Conclusions

We presented a CDI cell with surface functionalized electrodes for nitrate removal which was operated under passive (at 0 V) adsorption followed by electrical regeneration. We functionalized the active electrodes with CTAB, a quaternary ammonium cationic surfactant, and we functionalized the capacitive counter electrode with SDS anionic surfactant to enhance its cation adsorption capacity. The ability to electrically regenerate an active electrode provides potential advantages in terms of reduced maintenance costs and waste disposal needs. We showed that the adsorption capacity of the cell is linearly proportional to voltage applied during the previous regeneration step. We attribute this behavior to increased access to adsorption sites at higher regeneration voltages. We showed that replacing a Faradaic counter electrode by a capacitive counter electrode increases energy performance (ENAS) 1–2 orders of magnitude for the same adsorption rate (ASAR). Functionalized i-CDI systems have significant potential for high efficiency ionic pollutant removal with automated electrical regeneration and reduced waste disposal requirements.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.seppur.2017.11.027.

References

Supplementary Information for

Adsorption and capacitive regeneration of nitrate using inverted capacitive deionization with surfactant functionalized carbon electrodes

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Abstract
This document contains supplementary information and figures demonstrating (1) nitrate affinity (vs. chloride ions) of cetrimonium bromide (CTAB), and (2) adsorption performance of a CDI cell with CTAB-treated active electrode and untreated counter electrode.

S-1. Nitrate affinity of CTAB-treated carbon electrode
As mentioned in the main text, resins functionalized with trimethyl quaternary amine groups show affinity toward nitrate ions.[1,2] Additionally, CTAB (a quaternary ammonium surfactant) is known to adsorb onto activated carbon surface, and in turn, passively (in the absence of voltage) adsorb ions such as perchlorate.[3–5] We here demonstrate preferential adsorption of selected anions to CTAB-treated carbon electrode. To this end, we fabricated an i-CDI cell with CTAB-treated and SDBS-treated electrodes, each with dry mass of 0.41 g. We operated this i-CDI cell at 1 V for 5 h (regeneration step) followed by 0 V for another 5 h (adsorption step) under 0.73 ml min⁻¹ constant flowrate. Feed solution was 2 mM NaCl and 2 mM NaNO₃. Effluent solution was collected over 15 min intervals into separate containers, and concentration of chloride and nitrate ions was measured by ion chromatography (DIONEX DX 500, DIONEX, CA, USA) at Stanford ICP-MS/TIMS Facility. Figure S1 shows chloride and nitrate adsorption capacity of our i-CDI cell over adsorption step (in units of moles of anion adsorbed per gram of CTAB-treated electrode). Results show about 25 and 120 µmol g⁻¹ (equivalent to 0.9 and 7.4 mg g⁻¹) adsorption capacity for chloride and nitrate ions, respectively. Figure S1 thus clearly shows nitrate affinity of CTAB-treated electrode.

Figure S1. Preferential nitrate adsorption to an i-CDI cell with CTAB-treated and SDBS-treated electrodes. We operated the cell at 1 V regeneration and 0 V adsorption steps for 5 h each. Results show chloride and nitrate adsorption capacity of i-CDI cell in units of moles of anion per mass of CATB-treated electrode.

S-2. CDI cell with CTAB-treated active electrode and untreated counter electrode
In addition to i-CDI cell presented in the main text, we also built a cell consisting of one CTAB-treated electrode (as active electrode) and one untreated porous carbon electrode (as the counter electrode). Cell geometry and electrodes mass were approximately the same as those of the i-CDI cell in the main text. Figure S2 shows measured effluent concentration and electric current upon application of 0.8 V and 0 V external voltages. Interestingly, results show negligible salt adsorption for this comparison case versus to the results in Figure 2 of the main text. We observe this negligible adsorption despite the fact that the magnitude of electric current is comparable to that of our i-CDI cell with CTAB-treated and DBS-treated electrodes. We attribute this negligible salt adsorption to simultaneous expulsion and adsorption of

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nitrate ions from the electrodes. For example, when 0.8 V is applied to the cell, nitrate is expelled from CTA-AC active electrode and is simultaneously electrostatically adsorbed to the untreated, porous counter electrode. The reverse occurs for 0 V applied (short circuit between electrodes). This behavior is in contrast to our i-CDI cell with both CTA-AC and DBS-AC electrodes. For the latter cell, the negatively charged surfactant ion on the DBS-AC electrode surface likely electrostatically shields nitrate from re-adsorption to the electrode. This comparison experiment here is presented here to highlight the importance of treating both electrodes of the i-CDI cell.

References