Desalination 249 (2009) 217–223

Contents lists available at ScienceDirect

Desalination

journal homepage: www.elsevier.com/locate/desal

Removal of total dissolved solids, nitrates and ammonium ions from drinking water using charge-barrier capacitive deionisation

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ARTICLE INFO

Article history:
Accepted 13 December 2008
Available online 3 October 2009

Keywords:
Drinking water
Capacitive deionisation
Electrosorption
Desalination
Nitrates
Ammonium ions

ABSTRACT

A charge-barrier capacitive deionisation system was tested for electrochemical removal of Total Dissolved Solids (TDS), nitrates and ammonium ions. Several experiments were conducted with inorganic species spiked in tap water. The system efficiency was first evaluated using experimental statistical designs with different concentrations of NaCl (150 to 3000 mg/L). The raw water conductivity and the targeted residual TDS in treated water were the key process variables. Power consumption increased linearly as the difference between these two values increased. Water recovery rate and electrical consumption, which varied respectively from 63.9% to 95.8% and from 0.45 to 5.35 kWh/m^3, were adequately described by a simple linear regression model (R^2: 0.98 and 0.99, respectively). Additional experiments performed on nitrates (100 mg N–NO_3/L) and ammonium ions (1000 mg N–NH_4/L) showed high levels of removal. A rise in TDS concentration led to a decrease in their removal due to the competition for electrodes carbon adsorption sites. It was concluded from this study that this technology offers an innovative alternative for demineralising water. However, assays should be conducted in natural waters and in a steady-state manner to confirm data obtained and get long-term performance.

1. Introduction

Drinking water supply is a major concern in developed and developing countries. Over the next 25 years, the number of individuals impacted by severe water shortages is expected to increase fourfold [1]. Sea water or brackish water desalination is a reliable technique to supply fresh water but low-cost technologies providing high water recovery rates are needed. The concentrations of salts in sea water and brackish water are 35–50 g/L and 800–3200 mg/L respectively, but a reduction of Total Dissolved Solids (TDS) to 500 mg/L is required to obtain palatable water. Industrial processes (semiconductor manufacturing, nuclear power plants, and pharmaceutical industry) also involve strictly regulated water quality [2]. Therefore, several technologies have been applied for the removal of TDS from sea and brackish waters.

Multi-stage flash process (MSF) represents 43.5% of world production [3] but requires a significant amount of energy to vaporize the water. Ion exchange (IX), electrodialysis (ED) and reverse osmosis (RO) are currently the most common techniques for water softening and desalination. However, IX requires regeneration steps using various chemicals and is not practical for high TDS concentrations. ED uses high electric potential and is susceptible to hardness scaling and organic fouling, which can be limited by pre-treatment. RO is the most cost-effective method among membrane technologies for removing salts but it requires pre-treatments and generates a high volume of concentrate.

Capacitive deionisation (CDI) has been developed recently. It consists of the process of removing ions through their adsorption on the surface of two oppositely charged porous electrodes. This electrochemical process is conducted at low voltage (typically 0.8–1.5 V) without high-pressure pumps and acts as a "flow-through" capacitor [4,5]. Theoretical aspects to CDI and basic electrochemical principles have already been described elsewhere [6].

During the purification cycle, cations and anions from aqueous solutions are drawn towards the cathode and anode, respectively, upon application of a voltage. The capacitive system collects ions over time from the influent water and releases effluent of gradually increasing salinity due to the limited ion adsorption capacity of the

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doi:10.1016/j.desal.2008.12.048

electrodes. Therefore, the purified water results from a blend of waters having various conductivities between the start and the end of the purification cycle. When (i) the electrodes are saturated with ions or (ii) the effluent conductivity level rises above the required conductivity, the electrodes are regenerated by applying a reverse potential to allow the adsorbed ions to be released into a concentrated waste stream. The loading cycle is repeated following the regeneration and purge cycle. The efficiency of CDI mainly depends on the surface area and adsorption properties of electrodes. Despite the high electrical conductivity and chemical stability of conventional activated carbon materials, operational problems including binder degradation and low overall capacity were observed [7,8]. Consequently, activated carbon cloth (ACC), a woven product of activated carbon fiber, has been improved and proposed [2,9]. Introduction of titania on the surface of ACC enhanced electrosorption and decreased physical adsorption. Carbon aerogels have also been studied extensively because of their high surface area (400–100 m^2/g), their low resistivity (<40 mΩ cm) and a nano-size porous structure [6,7]. This process is patented CDT™ (Capacitive Deionization Technology™) and was first developed by Lawrence Livermore National Laboratories (Berkeley, USA) [10,11]. Its viability was recently tested on brackish groundwater having TDS concentration of 5000 mg/L [12], showing that further research would be required to improve the efficiency of the system for high levels of salinity.

The general purpose of this study was to determine the feasibility and performance of electrochemical removal of TDS, nitrates and ammonium ions by using proprietary charge-barrier CDI technology (DesEL Technology from *ENPAR Tech. Inc.*). Optimal operation conditions, salts removal rates and power consumption were determined for various influent TDS concentrations.

2. Objectives

The work described in this paper has been undertaken to validate the charge-barrier CDI technology by pursuing two specific objectives:

- Study the TDS removal from raw waters having different concentrations of NaCl. The system performance was evaluated using experimental statistical designs [13];
- Determine nitrates and ammonium ions removal and evaluate the influence of TDS (NaCl and sulfates) on their removal.

3. Materials and methods

3.1. Electrode material

The electrodes, manufactured using a proprietary process, are mainly composed of powdered activated carbon with an organic binder. The electrodes are 0.250 mm thick. Previous designs of CDI systems were limited to the treatment of low saline solutions (<3000 mg TDS/L). The DesEL technology employs the charge-barrier innovation consisting of ion selective layers, which prevent cross-contamination of the purified effluent. These layers are used to adsorb the ions selectively on the electrodes and are similar in composition to ED membranes. One charge-barrier CDI stack has a dimension of 298 mm diameter × 366 mm height. A schematic diagram of the charge-barrier CDI stack is shown in Fig. 1.

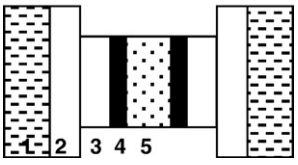

Fig. 1. Schematic of the charge-barrier CDI system: 1—Stack holder, 2—Current collector, 3—Electrode, 4—Charge-barrier, 5—Flow spacer.

3.2. The DesEL 9K pilot plant

The treatability tests were performed using a capacitive deionisation pilot unit (DesEL 9K, *ENPAR Tech. Inc., Ontario, CANADA*). It was composed of four electrochemical stacks each including 10 m^2 of electrode surface area (Fig. 2). The stacks were connected in parallel hydraulically and in series electrically. The DesEL 9K pilot system required a 220 V AC, 20 A, single-phase electrical supply. Internal volume of stacks was about 1.5 L for an approximate weight of 10 kg. Dimensions were 1.2(L) × 1.0(W) × 1.8(H) m. The operating potential was approximately DC 1.25 V per stack such that no electrolysis reactions occurred. The only pre-treatment required consisted of a 10 µm prefilter to avoid contamination of the charge-barrier CDI stack with particles.

The DesEL process was configured by specifying five parameters on the control panel through a Human Machine Interface (HMI):

- the adsorption (purification) time may range from 120 to 600 s;
- the desorption (regeneration) time ranges from 60 to 240 s;
- the purge time (s) is present at the end of the desorption time and should be long enough to purge out the concentrate, before the next treatment cycle;
- the conductivity of the treated water (Low Conductivity Set Point, µS/cm) is set to a value that depends on the required removal of inorganics from raw water and ranges from 0.01 to 1.0 mS/cm;
- the conductivity of the concentrated waste (High Conductivity Set Point, mS/cm) ensures that sufficient concentrate is removed from the stacks and may range from 1.0 to 20.0 mS/cm.

These parameters are interrelated and their values must be optimized to achieve a specific treatment objective [14].

3.3. System description

A process and instrumentation schematic is provided in Fig. 3. The system automatically cycled through the purification, regeneration and purge cycles. Cycle times, control valve operation and conductivity set points were controlled by a Programmable Logic Controller (PLC). During a purification cycle, aqueous solutions were pumped from an influent tank (total volume ≈ 280 L) through the stacks by a magnetic drive centrifugal pump (*Iwaki* model MD-70RZ). If the conductivity of the treated solution was less than the required treatment set point (Low Conductivity Set Point), the Pure Out valve opened and water was discharged in a 50 L carboy. If the conductivity rose above the set point, the Pure Recycle valve was opened (and Pure Out was closed) directing the water stream back through the stacks. In the regeneration cycle, the polarity of the stack was reversed to remove the ions from the electrodes. The purge step was used to flush the stack by using a given quantity of influent water to form a concentrated solution. If the conductivity was above the desired waste outlet limit (High Conductivity Set Point), the Purge Out valve was activated and the waste was sent to a reservoir. If the conductivity decreased below the waste outlet limit, the Purge Recycle valve was activated (Purge Out was closed) and the water stream was returned to the source tank. A new purification cycle started when the regeneration and purge cycles were completed.

In this study, the High Conductivity Set Point was specified at its minimal value (1.0 mS/cm). During the purge cycle, the whole concentrated stream (Purge Out and Purge Recycle) was thus directed through 10 L carboys. This allowed a constant influent water quality during one experiment. Proportions of clean and concentrate streams varied depending on the composition of the raw water and the desired composition of the treated water.

3.4. Experimental setup

Inorganic species (NaCl, $NaNO_3$, NH_4Cl) were spiked in prefiltered tap water (10 µm prefilter, *Labcor*, Canada) with a background TDS of

Fig. 2. Front view (left) and rear view (right) of the DesEL 9K pilot plant.

about 150 mg/L. No prefilter fouling was observed during the course of the study. All experiments were performed at room temperature (water temperature: 20 °C–22 °C). Two influent water tanks were used, which gave experiment durations of 1 h–1.5 h, depending on water quality and values of the five parameters. Purified water composite samples were collected in 50 L carboys during each purification cycle. Concentrated wastes were sampled in 10 L carboys following every regeneration–purge stage. TDS and conductivity were measured at the end of each cycle. Common physico-chemical analyses were performed on influent water and on a general sample for treated and purged water for the complete duration of the test. An experiment was considered complete when the system stopped *i.e.* when an alarm started indicating a low influent tank level. Therefore, the volume studied per experiment was about 280 L. The implementation of each test followed a strict procedure. Before each test, one purification–regeneration–purge cycle was done to ensure that electrodes had the same adsorption capacity as the previous experiments. Purified water conductivity and intensity data measured at the end of the cycles were used for this purpose.

The evolution of purified and purged water conductivity (mS/cm), time (s), flowrate (L/min), pressure (psi), voltage (V), intensity (A), influent water pH and the volume of purified water and concentrated stream were logged by a laptop computer using DataWorx PLC data logging software (*Automation Direct*). On-line flowrate, pH and conductivity (range: 0.0–10.0 mS/cm) values given by the pilot plant transmitters (*Burkert* model 8035, 8025 and 8225, respectively) were confirmed before starting the experiments. pH, total hardness and alkalinity analyses were performed according to standard methods

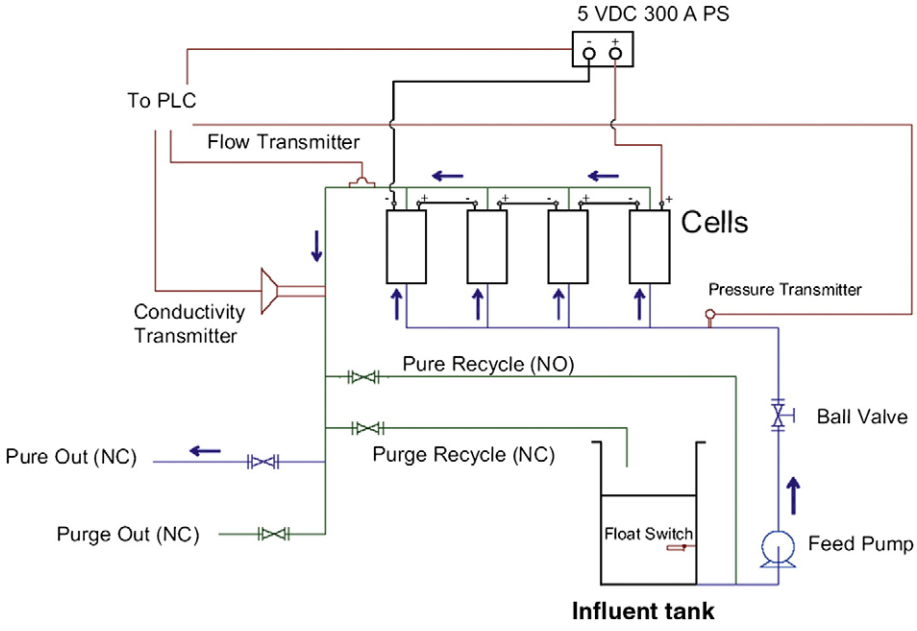

Fig. 3. Process and instrumentation schematic of the DesEL 9K pilot plant (*ENPAR Tech. Inc.*).

4500-H^+, 2340 C and 2320 B, respectively [15]. Conductivity was analysed by a conductivity meter CMD 83 (*Radiometer Copenhagen*). Ion selective electrodes were used to analyse nitrates (4500-D) and ammonium ions (4500-NH_3 D). Sulfates were measured by the turbidimetric method 4500-E (photometer *Milton Roy Spectronic 20D*).

3.5. Design of experiments

The experimental designs were conducted in batches using NaCl concentrations of 150, 1000 and 3000 mg/L in order to establish optimum operation conditions. This led to raw water conductivities varying from 0.51 to 5.68 mS/cm. A design of experiments approach allowed (i) to perform statistically designed experiments, (ii) to identify the key process variables and (iii) to predict the water recovery rate and the power consumption. The water recovery rate was calculated using Eq. (1):

$$Y_1 = \frac{V_t}{V_r} = \frac{V_t}{V_t + V_{purge}} \quad (1)$$

where Y_1 is the water recovery rate (%), V_r is the raw water volume (L), V_t is the treated water volume (L), and V_{purge} is the purged water volume (L).

Statistically designing experiments is useful when many input variables may influence the performance of the process. Moreover, the interaction among the parameters can be evaluated with limited number of experiments [16]. Input and output variables are called independent and dependant variables, respectively. Four general models are available in order to analyse the data obtained: linear terms, linear and quadratic terms, linear and interaction terms and a general model combining linear, quadratic and interaction terms. This last model would be described by the following equation where two independent variables are considered.

$$Y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_{12} x_1 x_2 + \beta_{11} x_1^2 + \beta_{22} x_2^2 \quad (2)$$

where β_0 is the interception coefficient, β_1 and β_2 are the linear coefficients, β_{12} is the interaction coefficient, β_{11} and β_{22} are the quadratic coefficients, x_1 and x_2 are the independent variables, and Y is the dependant variable. STATISTICA version 7.0 software was used for regression and graphical analysis of the obtained data.

Different designs were studied depending on the influent TDS concentrations. For a NaCl concentration of 1000 mg/L, a central composite design [13] was used (18 experiments). Independent variables (x_i) were the water flowrate (8–12 L/min), the purification time (300–500 s), the regeneration time (100–120 s) and the Low Conductivity Set Point (100–300 µS/cm). Five values were tested for each variable. For a NaCl concentration of 3000 mg/L, a 3^2 factorial design was considered (9 experiments). The water flowrate (8–12 L/min) and the Low Conductivity Set Point (550–1650 µS/cm) were chosen as independent variables with three values each. Specific additional experiments were also conducted on a 150 mg/L NaCl concentration. Low Conductivity Set Point values were set to reach TDS (conductivity) removal rates of 90–92%, 85–95% and 70–90% for 150, 1000 and 3000 mg/L TDS, respectively. Data obtained for these three TDS concentrations were combined in order to produce a general linear model including the raw water TDS concentration (from 150 mg/L to 3000 mg/L with a 150 mg/L TDS background concentration). Independent variables were the raw water conductivity, the regeneration, the purge and purification times as well as the water flowrate and the Low Conductivity Set Point. Additional assays were performed with drinking water spiked with nitrates (100 mg N–NO_3/L) and ammonium ions (1000 mg N–NH_4/L). The influence of TDS concentration (sulfates and NaCl) on the removal of the target compounds was explored.

4. Results and discussion

4.1. Operation of the DesEL 9K pilot plant

Two assays were performed to illustrate the typical operation of the DesEL 9K pilot plant depending on whether a recirculation was observed during the purification cycle. The values of the input variables are presented in Table 1. Conductivity removal was set to 90% and 80% for assays 1 and 2, respectively. Fig. 4 shows the conductivity changes for assay 1 composed of 6 treatment cycles (purification, regeneration and purge). Fig. 5 focuses on the first cycle. First, treated water conductivity decreased below raw water conductivity due to ion adsorption (400 s). Then, the reverse potential was applied and electrodes were regenerated (110 s). Finally, ions beforehand adsorbed were removed from the surface of the electrodes during the purge cycle (25 s). As the Low Conductivity Set Point was exceeded during the purification cycle, a recirculation was noticed and the conductivity fluctuated: the Pure Recycle valve was opened directing the water stream back through the stacks to reach the Low Conductivity Set Point again. The Pure Recycle valve was operated about 5 times in each purification cycle (Figs. 4 and 5). The duration of the purification cycle should be set so that the valves are actuated less than twice in a cycle [14]. During assay 2, no recirculation was noted because the Low Conductivity Set Point was never reached during each purification cycle (Fig. 6). The capacity of electrodes was not reached after 300 s of ionic adsorption and in this specific case, the adsorption time could have been increased. Intensity fluctuated depending on the saturation of electrodes: current intensity exponentially decreased (from a maximum of 300 A) through purification cycles since less ions were adsorbed on the electrodes with time. The use of ion-exchange membranes prevents ion adsorption on the electrodes during the regeneration step. This enhances the salt removal capabilities, contrary to primary CDI [17]. An additional advantage of the charge-barrier technology may be the prevention of precipitation of minerals concentrated into the electrodes.

4.2. Charge-barrier CDI performance

The treatability results of all experiments ($N = 27$) conducted on 1000 mg/L and 3000 mg/L TDS are presented in Table 2. The raw water TDS concentration varied from 940 to 1290 mg/L due to variations in tap water background TDS concentration. Conductivity removal varied from 80.9% to 94.3% depending on the operation conditions. On average, the treated water showed reductions in TDS of 90.3%, in hardness of 90.3% and in alkalinity of 84.4% for 1000 mg/L TDS. Removals were 81.7% and 76.2% for hardness and alkalinity, respectively, for experiments performed on 3000 mg/L TDS. In all the experiments, the conductivity in the treated water was close to or lower than the conductivity required (Low Conductivity Set Point). Moreover, studying the conductivity changes and the volume of the treated water composite samples showed that the steady-state conditions were reached after a few treatment cycles. The treatment

Table 1
Values of input variables.

	Assay 1	Assay 2
Date	2006-05-25	2006-08-01
Raw water conductivity (µS/cm)	1800	290
Purification time (s)	400	300
Regeneration time (s)	110	110
Purge time (s)	25	25
Total cycle time (s)	535	435
Flowrate (L/min)	10	10
Low Conductivity Set Point (µS/cm)	180	58

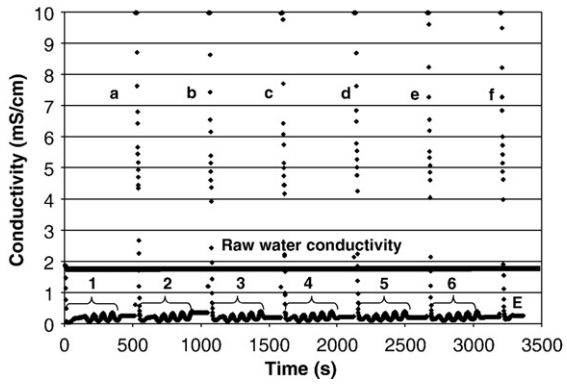

Fig. 4. Conductivity changes during assay 1. 1–6: Adsorption cycles; a–f: Regeneration–purge cycles; E: End of experiment.

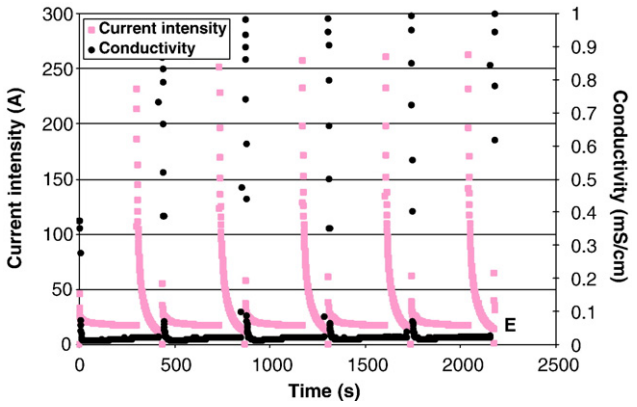

Fig. 6. Conductivity and current intensity fluctuations during assay 2. E: end of experiment.

efficiency remained constant over multiple cycles. For the 3000 mg/L TDS concentration, TDS removal of 70% was easily achieved. Conductivity in the treated water never rose above 1.07 mS/cm whereas the Low Conductivity Set Point was 1.65 mS/cm (Table 3). Conductivity in the treated water was closer to the set points for the two greater TDS removals required (80% and 90%). A higher flowrate yielded a higher conductivity in the treated water for identical Low Conductivity Set Point (1.10 and 1.65 mS/cm) and raw water quality. These results already described [17] showed that the TDS removal depends on the residence time of the solution on the electrodes. The salts removal increases when more time is available for mass transfer. However, no significant variations were observed in terms of water recovery rate and electrical consumption. Moreover, conductivity removal varied from 90.2% to 94.8% when testing a 150 mg/L NaCl concentration. A greater flowrate also increased the TDS removal from the electrodes during the purge cycle. Overall, purge time should be raised since the conductivity following regeneration–purge cycles was often greater than the raw water conductivity.

The DC power supply of the DesEL pilot plant was set to operate at a constant voltage output of 5.0 V, *i.e.* 1.25 V per stack. Previous studies conducted at 40–100 mL/min showed that the optimal DC voltage for ACC-based membrane CDI was 1.2 V in order to increase the salt removal and limit the energy consumption [17]. The greatest salt removal was measured at 1.2–1.3 V during experiments performed on NaCl solutions (from 4 to 5882 mg/L) at 15 mL/min [10]. CDI performance was also studied using 2 M NaCl solution [18]. The regeneration of the CDI unit (5 min) begun after the sorption phase (10 min). At a flowrate of 100 mL/min, the maximum salt removal (95%) was obtained at 1.4 V. The salt removal increased with the applied DC voltage but electrolysis was observed above 1.6 V. In this study, one experiment was performed using a DC voltage of 4.5 V (1.12 V per stack) instead of 5.0 V. The conductivity in the treated water was slightly higher at 4.5 V than the one at 5.0 V, with mean conductivities of 185 and 173 µS/cm, respectively, for seven treatment cycles.

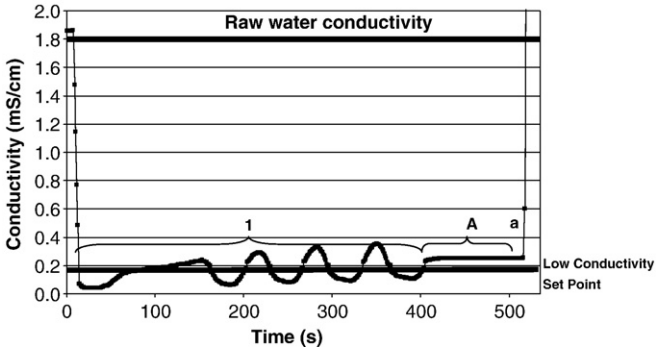

Fig. 5. Conductivity changes during the first treatment cycle of assay 1. 1: Adsorption cycle; A: Regeneration cycle; a: Purge cycle.

4.3. Regression models

The TDS removal was studied under different experimental conditions. The application of statistics offers an empirical relationship between the independent variables and the dependant variables. Models were chosen according to the correlation coefficient R^2, the lack of fit (p) criteria, the normal distribution of residues and the variance homogeneity. For the 1000 mg/L TDS concentration, water recovery rate and electrical consumption were described by quadratic and interaction terms (R^2: 0.99, $p = 0.40$) and linear terms (R^2: 0.68, $p = 0.16$), respectively. For the 3000 mg/L TDS concentration, water recovery rate and electrical consumption were described by linear and quadratic terms (R^2: 0.96 and 0.97, respectively). When combining performance data from all conditions (150, 1000 and 3000 mg/L), it was observed that the dependant variables (water recovery rate and power consumption) were described by a simple linear regression model (R^2: 0.98 and 0.99, respectively). The result of these models is represented by Eqs. (3) and (4) for water recovery rate (Y_1) and electrical consumption (Y_2), respectively:

$$Y_1 = 1.2 - 3.5 \times 10^{-2} X_1 + 9.9 \times 10^{-5} X_2 - 8.2 \times 10^{-3} X_3 + 8.4 \times 10^{-5} X_4 - 7.4 \times 10^{-3} X_5 + 9.2 \times 10^{-2} X_6 \quad (3)$$

$$Y_2 = -0.3 + 0.9 X_1 - 1.7 \times 10^{-3} X_2 + 4.3 \times 10^{-2} X_3 + 2.7 \times 10^{-4} X_4 - 5.5 \times 10^{-2} X_5 - 1.5 X_6 \quad (4)$$

where X_1 is the raw water conductivity (mS/cm), X_2 is the regeneration time (s), X_3 is the purge time (s), X_4 is the purification time (s), X_5 is the flowrate (L/min), and X_6 is the Low Conductivity Set Point (mS/cm).

In the analysis of variance (ANOVA) and for the tested conditions, it was found that the duration of the regeneration cycle had no impact on the water recovery rate whereas the duration of the purification,

Table 2
Minimum and maximum values of physico-chemical parameters.

Type of water	TDS (mg/L)	Conductivity (mS/cm)	pH	Total hardness (mg/L $CaCO_3$)	Total alkalinity (mg/L $CaCO_3$)
Raw	940–1290	1.72–2.04	7.70–8.02	110–130	79–88
Treated	60–160	0.11–0.29	6.62–7.14	8–16	7–21
Rejected	6980–12,620	11.22–17.50	7.72–8.37	1020–1520	655–1055
Raw	~3000	5.36–5.68	7.70–7.80	114–126	72–84
Treated	–	0.42–1.07	6.76–7.38	12–26	8–29
Rejected	–	13.80–18.10	7.55–8.19	500–1380	–

Table 3
Conductivity data for the 3000 mg/L TDS concentration.

Experiment	Flow (L/min)	Low Conductivity Set Point (mS/cm)	Conductivity (mS/cm)			Conductivity removal (%)	
			Raw water	Treated water	Rejected water	Expected	Measured
5	10.0	1.10	5.40	0.81	16.40	79.6	85.0
4	10.0	1.65	5.41	0.99	18.10	69.5	81.8
8	12.0	1.10	5.46	0.82	15.80	79.9	85.0
3	8.0	0.55	5.36	0.42	15.90	89.7	92.2
9	12.0	0.55	5.39	0.42	13.80	89.8	92.2
1	8.0	1.65	5.53	0.82	17.40	70.2	85.2
2	8.0	1.10	5.68	0.75	16.80	80.6	86.8
7	12.0	1.65	5.62	1.07	16.50	70.6	80.9
6	10.0	0.55	5.68	0.43	14.60	90.3	92.5

regeneration and purge cycles had little or no impact on the electrical consumption. From this study, the two key variables affecting performance were identified as the raw water conductivity ($p \leq 1.04 \times 10^{-8}$) and the targeted residual TDS in treated water ($p \leq 5.62 \times 10^{-10}$). Power consumption increased linearly as the difference between these two values increased (Fig. 7). Water recovery rate and electrical consumption varied respectively from 63.9% to 95.8% and from 0.45 to 5.35 kWh/m^3. Water flowrate had also a statistically significant impact ($p \leq 0.02$). For specific operation conditions previously described, the energy consumption value obtained was 2.0 kWh/m^3 [18]. Moreover, energy consumption increased exponentially with the applied current on CDT^{TM} electrodes [12].

From Fig. 8 where power consumption, Low Conductivity Set Point and raw water conductivity are presented in a *Distance Weighted Least Squares fitting*, it can be seen clearly that the electrical consumption has increased by increasing the raw water conductivity and by lowering the Low Conductivity Set Point. This figure shows that values of the input variables must be carefully chosen in order to find the optimal operation conditions. Performance of the process depends on the raw water quality and TDS removal needed. For example, a lower Conductivity Set Point requires shorter purification times for the same raw water conductivity because electrodes reach more rapidly the Set Point. The salts removal and energy consumption were normalized to gram of salts removed per gram of carbon and Wh per gram of salts removed, respectively (Table 4). These data confirmed that increasing raw water salts concentration improved electrical capacity of the carbon electrodes through reduction of the double layer thickness. The maximum loading capacity for the carbon cells is estimated at 3.0 mg/g of carbon. Previous studies showed that the maximum sorption capacity of carbon aerogel stacks was 7.0 mg TDS/g carbon aerogel with a minimum energy consumption of 0.21 Wh/g salts removed [12].

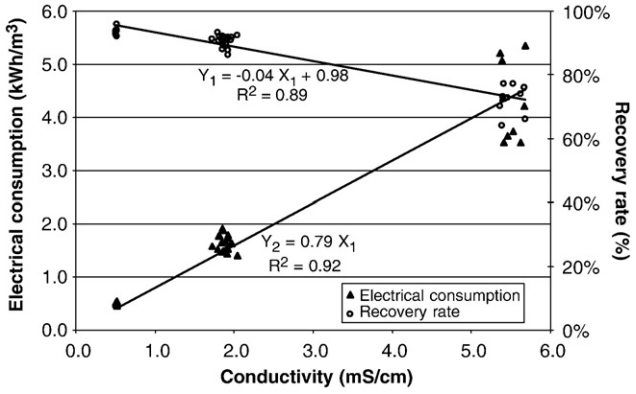

Fig. 7. Water recovery rate (Y_1) and electrical consumption (Y_2) for NaCl spiking experiments.

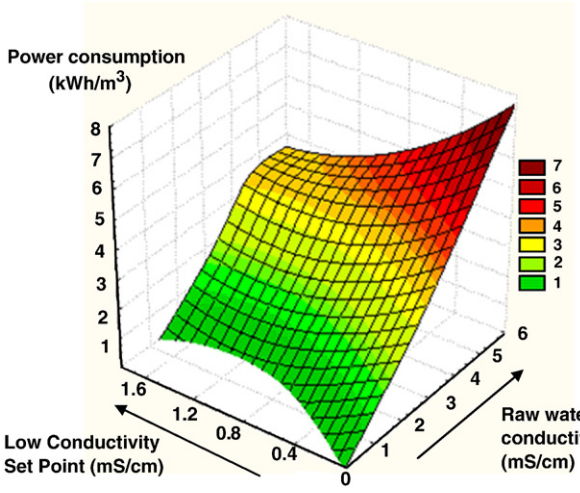

Fig. 8. Power consumption for various raw water conductivity and Low Conductivity Set Point.

4.4. Nitrates and ammonium ions removal

It was intended to use the charge-barrier CDI technology to treat waters polluted with high concentrations of nitrates and ammonium ions. Their presence in drinking water is toxic for human beings, especially nitrates, and elevated concentrations worldwide have increased focus on alternative removal processes [19,20]. Purification, regeneration and purge times as well as flowrate were 300 s, 110 s, 25 s and 10 L/min respectively for experiments conducted on nitrates. Conductivity removal was set to 90%. Three experiments were conducted on ammonium ions by using purification, regeneration and purge times of 150 s, 130–140 s and 40–50 s. The water flowrate was 8 L/min to limit the saturation of electrodes and promote mass transfer. Conductivity removal was set to 50%. The raw water conductivity varied from 0.45 mS/cm up to 2.51 mS/cm and from 7.2 up to 11.7 mS/cm for experiments performed on nitrates and ammonium ions, respectively. High levels of nitrates and ammonium ions removal were obtained (88.0% to 98.0% and 71.9% to 88.1%, respectively). Moreover, the TDS removal as measured by the conductivity removal (92.8–93.9% for experiments on nitrates and 61.9%–86.3% for experiments on ammonium ions) was greater than expected (90% and 50%, respectively). When studying nitrates removal, water recovery rates varied from 88.6% to 93.8% and electrical consumption ranged from 0.44 kWh/m^3 to 2.04 kWh/m^3. For ammonium ions, water recovery rates varied from 72.3% to 77.5% and electrical consumption ranged from 3.73 kWh/m^3 to 4.44 kWh/m^3. Those data are consistent with those obtained with similar raw water conductivity, as previously noted when NaCl was spiked in prefiltered tap water.

As expected, a rise in TDS concentration led to a decrease in nitrates and ammonium ions removal due to the competition for electrodes carbon adsorption sites. Nitrates removal decreased from 98.0% to 88.0% when adding 1000 mg/L NaCl while ammonium ions removal decreased from 88.1% to 71.9% when adding 2850 mg/L NaCl. This rise in TDS also generated a water recovery rate decrease and an electrical consumption increase, for the same input conditions. A

Table 4
Comparison of energy consumption (Wh/g salts) and sorption (mg/g carbon).

Raw water conductivity (mS/cm)	Energy consumption (Wh/g salts)	Sorption (mg/g carbon)
0.50–0.52	1.71 ± 0.09	0.40 ± 0.09
1.72–2.04	1.47 ± 0.12	1.15 ± 0.17
5.36–5.68	1.00 ± 0.10	1.95 ± 0.30

higher raw water conductivity would require shorter purification cycles as the saturation of electrodes is reached more rapidly. Moreover, the addition of sulfates had a minor impact since nitrates removal was 98%, 97.4% and 95.6% for raw waters containing sulfates concentrations of 0, 50 and 100 mg/L, respectively. Further work would be required to study the effects of ion properties on electrosorption capacities of charge-barrier CDI. Previous research with carbon aerogel-based CDI suggested the occurrence of ion selectivity based on ionic size [10]. The impact of ion charge and atomic weight was already studied [8]. Experiments were carried out using 0.005 M solutions at 1.4 V, 100 mL/min, ambient pH and a run time of 10 min. Data showed that the sorption of the divalent species was limited when multiple ions of varying valences were present.

IX, RO and ED are suitable water treatment processes to treat nitrate-laden water. Charge-barrier CDI exhibited an alternative for removing nitrates and ammonium ions from drinking water. The use of charge-barrier CDI did not require any chemical to regenerate the carbon electrodes, which avoided the formation of a secondary waste by-product. Concentrations of nitrates in treated water were reduced to less than 11.8 mg/L whereas the maximum concentration of nitrate-N allowed based on US EPA guidelines is 10 mg/L. The DesEL system is capable of removing nitrate-N to levels below this concentration in drinking water but for high raw water conductivities, the Low Conductivity Set Point should be decreased. Deterioration of the carbon electrodes performance was not observed and the process could be operated at various levels of conductivity removal and water recovery efficiencies without the electrolysis of capacitive carbon stacks. However, the use of several treatment stages could be necessary depending on the conductivity required in the treated water and the raw water conductivity. During experiments conducted on ammonium ions, the minimal concentration obtained in the treated water was 122.9 mg $N–NH_4$/L with one treatment stage.

Finally, the experimental design focused on the removal of various concentrations of TDS, nitrates and ammonium ions in an influent with low concentration (2.0–2.5 mg C/L) of Natural Organic Matter (NOM). It would be interesting to perform experiments with natural waters in order to verify the impact of higher NOM concentrations on ion selective layers and on the sorption capacity of electrodes. According to [8], the presence of NOM appeared to reduce the inorganic sorption capacity of the carbon aerogel material. An increase in the NOM concentration also produced a reduction in the adsorption capacity of bromide with Ag-doped carbon aerogels [21]. This may be due to the blocking of aerogel pores by adsorption of the organic matter. High-surface-area carbons, such as activated carbon, strongly adsorb organic material which may constitute nutrients supporting bacterial growth, resulting in biofouling [22].

5. Summary and conclusions

Charge-barrier capacitive deionisation was effective at removing TDS (80.9%–94.3%), nitrates (88%–98%) and ammonium ions (71.9%–88.1%) from water streams. Power consumption ranged between 0.45 and 5.35 kWh/m^3 by using a raw water TDS concentration between 150 and 3000 mg/L TDS. One of the main advantages is that no chemicals are required for the regeneration of the electrodes. Preliminary results demonstrated that this technology offers an innovative alternative for demineralising water up to a certain level of salinity. The statistical model developed to predict TDS removal is statistically highly significant but should be validated using other experimental conditions. Since experiments were conducted in spiked water, they may not represent a natural water matrix. Assays should be conducted in natural waters and in a steady-state manner (hundreds of treatment cycles) to confirm data obtained. From a research perspective, further work would also be required to understand and explore the long-term fouling of the electrodes. Longer time period testing would be necessary to fully answer this question. Chemicals may also be used for pre-treatment if raw waters contain high concentrations of NOM. Further work would be beneficial to explore the interaction between the electrically charged electrodes and the NOM present in some raw natural waters.

Acknowledgments

The writers would like to acknowledge the staff of the NSERC Chair on Drinking Water and CREDEAU, as well as Mélanie Bolduc and Denis Bouchard, for their support in the laboratory work. They would also like to thank Leonard Seed and Dr. Gene Shelp (*ENPAR Tech. Inc., Ontario*) for their technical support.

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