CHARACTERIZATION OF ION TRANSPORT AND -SORPTION IN A CARBON BASED POROUS ELECTRODE FOR DESALINATION PURPOSES

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ABSTRACT

New and more efficient water desalination technologies have been a topic of incipient research over the past few decades. Although much of the attention and efforts have focused on the improvement of membrane-based desalination methods such as reverse osmosis, the development of new high-surface area carbon-based-electrode materials have brought substantial interest towards capacitive deionization (CDI), a novel technique that uses electric fields to separate the ionic species from the water. Part of the new interest on CDI is its ability to store and return a fraction of the energy used in the desalination process. This characteristic is not common to other electric-field-based desalination methods such as electro-deionization (EDI) and electro-dialysis reversal (EDR) where none of the input energy is recoverable. This paper presents work conducted to analyze the energy recovery, thermodynamic efficiency, and ionic adsorption/desorption rates in a CDI cell using different salt concentration solutions and various flow-rates. Voltage and electrical current measurements are conducted during the desalination and porous electrode regeneration processes and used to evaluate the percentage of energy recovery. Salinity measurements of the inflow and outflow stream concentrations using conductivity probes, alongside the current measurements, are used to calculate ion adsorption/desorption efficiencies. Correlation of these measurements with an analytical species transport model provides information about the net ionic adsorption/desorption rates in non-saturated-carbon-electrode scenarios. The results show a strong dependence of the net electrical energy requirements with the number of carbon electrodes regeneration cycles. Finally, a non-dimensional number that compares the convective and electro-kinetic transport times is presented. The energy requirements and adsorption/desorption rates analyses conducted for this water-desalination process could be extended to other ion-adsorption applications such as the re-process of spent nuclear fuels in a near future.

1. INTRODUCTION

With the current population of the planet soaring to approximately seven billion, there has never been a more appropriate time to consider the state of the world’s natural resources. In particular
clean water resources have become more strained as the population increases \[1,2\]; in fact, the continents with the largest populations, Asia and Africa, have some of the fewest drinking water resources per person \[2\]. Attention has consequently focused on converting abundant sea water resources into potable water through various methods \[2-5\].

The existing desalination processes could be grouped according to the method it uses to separate the dissolved ions: membrane based, thermally based, electrically based, or a combination of any of the previous. The first category purifies water using one or various membranes and includes reverse osmosis (RO) and membrane electro dialysis \[2,6,7\]. Thermally based methods change the phase of the fluid and include multistage flash distillation (MSF), multi-effect distillation (MED), and mechanical vapor compression \[2\]. Last, electrically based methods use an electric potential and include electro dialysis (which also makes use of membranes) and capacitive deionization (CDI) \[2-4\]. Of all these methods, reverse osmosis and multistage flash distillation are currently the most popular. Table 1 compares the energy required per m\(^3\) of desalinated water by CDI and other methods.

<table>
<thead>
<tr>
<th>Technology</th>
<th>Energy Required [kWh/m(^3)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>RO</td>
<td>2.9 – 3.7</td>
</tr>
<tr>
<td>MSF</td>
<td>4</td>
</tr>
<tr>
<td>MED</td>
<td>5</td>
</tr>
<tr>
<td>CDI</td>
<td>1.1 - 2.0</td>
</tr>
</tbody>
</table>

Table 1 Comparison of the energy per m\(^3\) required by CDI and the other most popular water desalination methods \[2,8\]

 Capacitive deionization is a relatively novel desalination technique where an electric field is applied to separate ions from a solution stream by adsorbing them onto a high surface area material \[2,4\]. This electrically based desalination method consists of two sub-processes shown in the schematics of Figure 1: desalination and regeneration. The uniqueness of CDI as a desalination method relies on its capability to recover part of the input energy through the system regeneration.

During the desalination process, the electric potential provided by a power supply generates an electric field across the electrodes that pull the ions from the solution to the corresponding electrode depending on their polarities. The resulting output solution had lower ionic concentration. The net movement of charged particles creates a electric current that decreases as the porous electrodes are saturated. When the capacity of the storage medium is reached and no more ions can be collected, there would be no variation between ionic concentration of the inlet and outlet solution until the system is regenerated.

Although the regeneration of the CDI system could be performed by short-circuiting the electrodes \[9\], some authors suggest the inversion of their polarity and use of selective membranes to speed up this process \[3\]. The regeneration by short-circuiting the electrodes creates an electric current through the discharge of stored ions resulting in a recovery of part of the energy stored during ion absorption. Because of its capability to partially recover the input energy, a CDI system would require a significantly lower energy input (about 2 kWh/m\(^3\) for a 70% concentration reduction) \[2\].

Although the concept of capacitive deionization dates back to the late 1960s and early 1970s, it was not until the development of high surface porous materials in the 1990s that capacitive
deionization became an attractive technology [2-4]. The use of electrodes made of high surface area conductive materials increases the system capacitance to adsorb and retain electric charge [10]. Therefore, evaluating and measuring the adsorption capability of various materials such as carbon aerogel and carbon nanotubes plays an important role in evaluating the performance of a CDI system. Various authors [2, 10, 11] have suggested determining the electrode’s capacitance using electrochemical analysis techniques and assuming that both the desalination and regeneration processes are non-faradic. On the other hand, Zhao et al. [12] determined the effective surface area and electrode capacitance from measurement of the equilibrium salt adsorption and electrode charge. Furthermore, various authors have used the charge efficiency (ratio of the amount of salt absorbed to the charge on the electrode) of the desalination process as a whole to evaluate the adsorption of ions [12], but haven’t looked at how it varies with time within each desalination process.

A key point in determining the practicality of the CDI process is evaluating how efficiently the system is able to purify an input solution. The present paper aims to evaluate variations on the energetic performance of a CDI system when the desalination and regeneration processes are alternated before steady concentrations are reached as in experiments conducted by Anderson et al. [2], and Welgemoed and Schutte [3]. Also, low concentration solutions and flow-rates were employed to analyze the ionic adsorption process.

2. METHODOLOGY

2.1 Experiment set-up

Desalination experiments were conducted at the Multiscale Thermal-Fluids Laboratory at the University of Texas at Austin. The set-up for a typical test includes a Harvard Apparatus PHD 2000 syringe pump to pump the solution at a constant flow rate; an eDAQ Flow-Thru Conductivity Electrode ET908 and a Vernier conductivity probe to measure the conductivity of the solution at the exit of the cell; an Agilent E3647A power supply; an Omega® FLR-1601A flow meter; an Omega® PX429-10WDDU5V differential pressure transducer to evaluate the pressure drop along the CDI cell; a 30.1 ohm electric resistor to short circuit the CDI cell during its regeneration; and a custom CDI cell. Figure 2 shows the actual experimental setup and a schematic.

A schematic of the CDI cell is shown in Figure 3. The cell contains two metal electrodes made of titanium foil, two high surface area carbon foam sheets from Marketch Technologies with a nominal surface area of 600 m²/g and dimensions 2.3 x 25.4 cm, and a polymer mesh divider of 2 mm thickness.

2.2 General experiment procedure

The two typical processes (desalination and regeneration) were evaluated for this paper using the system described before. During both operations, the salt solution contained in multiple syringes was impulsed through the cell by the PHD 2000 syringe pump.
pump at a constant flow-rate monitored by the FLR-1601A flow meter. Before starting a desalination process, the conductivity readings were checked and were constant to assure that variations in this parameter correspond to the adsorption of ions within the cell. During the desalination, a constant electric potential difference of 1.0 V was applied between the two cell electrodes. As ions were absorbed into the carbon sheet, their concentration, and thus the conductivity of the solution, decreased. This change was measured by the eDAQ Flow-Thru probe located at the exit of the CDI cell. Besides conductivity, the current supplied to the system was also recorded by the Agilent E3647A power supply to calculate the energy used and ions displaced from this process.

To start the regeneration of the system, the cell was disconnected from the power supply and grounded using the electric resistor. Due to the removal of the electric field within the cell, the coins were repelled from the electrodes to the solution stream. The increase in salinity of the solution was again measured at the exit of the cell. Different to desalination, the voltage across the electrodes varied as the carbon sheets are regenerated. During regeneration, the voltage across the electrodes was measured by a National Instruments USB 6008 DAQ and was used with the known electrical resistance to calculate the energy recovered by the system.

2.3 Transient and steady tests

Two types of CDI tests were conducted for this paper: steady and transient. The difference between these tests is the duration of the desalination and regeneration processes. During a steady test, desalination continues until the carbon sheet is completely saturated and reaches a steady state. This saturation point is noted when the conductivity of the outlet increases back to the initial value. Once the desalination was complete, a regeneration process began and continued until the solution conductivity decreased back to the initial value.

During a transient test, the transition from desalination to regeneration is not made at the saturation point; instead occurs when the salinity of the outlet solution reaches a minimum. The regeneration occurs until the salinity reaches a maximum. The time it takes for the first cycle to reach the new transition points were measured and used to run the following cycles. In the amount of time necessary to complete one steady test, 15 to 20 transient tests could be completed. Figure 4a and 4b shows an example of conductivity and current data from a transient test.
2.4 Energy and efficiency analysis

To measure how well the carbon sheet is performing as flow rate, initial concentration, and type of test changes, the energy recovery and the adsorption efficiency were calculated. The energy recovery is the ratio of energy generated during regeneration to the energy used during desalination; it is calculated using Equations 1 and Equation 2 where \( V_{\text{desal}} \) is the voltage applied to the CDI cell [V] and \( I \) is the electrical current [A] measured by the power supply during the desalination, \( R [\Omega] \) is the resistor used to short-circuit the cell and \( V_{\text{regen}} \) is the voltage measured by the DAQ [V] during the regeneration process.

\[
E_{\text{desat}} = \int V_{\text{desal}} * I(t) \, dt 
\]  
\( (1) \)

\[
E_{\text{regen}} = \int V_{\text{regen}}(t)^2 \, dt / R 
\]  
\( (2) \)

The adsorption efficiency, defined as the ratio of the number of ions adsorbed to the number of electrons displaced, was calculated from Equations 3 to 4 where \( N_A \) is the Avogadro’s number, \( \sigma_o \) and \( \sigma \) are the inlet and outlet solution conductivities [S/m] respectively, \( F \) is the Faraday’s constant [Coulomb/mol], and \( v^{Cl^-} \) and \( v^{Na^+} \) are the chloride and sodium ion mobility [m²/Vs] respectively.

\[
\text{ions ads} = \frac{N_A Q \int_{\Omega}^{} (\sigma_o - \sigma) \, d\tau}{F (v^{Cl^-} + v^{Na^+})} 
\]  
\( (3) \)

\[
elect. \, \text{displ.} = \frac{\int I \, d\tau}{1.6 \times 10^{-19}} 
\]  
\( (4) \)

2.5 Simplified analytical models of steady state tests

Analysis of data from the steady test results led research in the direction of two simplified analytical mass transfer models to find a relationship between flow rate and the ratio of minimum and initial conductivities. Some initial assumptions used in analyzing the conductivity output curve draw a parallel with mass transfer theories. Namely, by assuming steady adsorption processes that do not exceed the saturation limit of the porous carbon sheet, the CDI cell was modeled as an internal flow problem, with either a constant salt concentration boundary condition or a constant adsorption rate.

Analysis of a 1D adsorption process with constant salt concentration boundary condition is described in Figure 5, Equation 5 and Equation 6, where \( C_{\text{bulk}} \) is the bulk ion concentration of the fluid within the cell and is defined by Equation 7: \( W [\text{m}] \) is the channel width, \( C [\text{moles/m}^3] \) is the ionic concentration, \( H [\text{m}] \) is the height of the cell (thickness of the polymer spacer), \( Q [\text{m}^3/\text{s}] \) is the solution flow rate, and, \( M_{\text{in}}, M_{\text{out}} \) and \( M_{\text{abs}} \) [mol/m²s] are the inlet, outlet and adsorbed ionic molar fluxes respectively, and \( V_{\text{electric}} \) is the velocity of the ion toward the electrode(y direction). In this model, the adsorption rate was modeled as the product of the bulk concentration and the electro-kinetic velocity.

\[
\frac{dC_{\text{bulk}}(x)}{dx} + \frac{V_{\text{electric}} W x}{Q} C_{\text{bulk}}(x) \]  
\( (5) \)

\[
C_{\text{bulk}}(x = 0) = C_0 
\]  
\( (6) \)

\[
C_{\text{bulk}} = \frac{W \int C(y) u(y) \, dy}{Q} 
\]  
\( (7) \)

\[
M_{\text{abs}} = C_{\text{bulk}} V_{\text{electric}} 
\]  
\( (8) \)

\[
M_{\text{in}} = C_{\text{bulk}} Q W H 
\]  
\( (9) \)
The solution of this model (Equation 10) shows an exponential decrease of the concentration ratio \( \frac{C}{C_0} \) along the cell.

\[
\frac{C_{\text{exit}}}{C_0} = \exp\left(\frac{-WL}{Q}V_{\text{Electric}}\right)
\]  

(10)

For a constant adsorption rate the profile of salt adsorption along the cell would be linear. Kinematic arguments will be used next to help describing this model. Figure 6 portrays the movement of individual ions flowing through the CDI cell at in three different cases as the solution flow rate increases. In the first case, an ion is absorbed into the aerogel with plenty of time; in this case we would expect to read a concentration of zero salt ions at the exit. In the second case, the ion reaches the aerogel at the very end of the cell, just barely being absorbed; in this case we would still expect a concentration reading of zero salt ions at the exit. In the third case it is impossible for the cell to adsorb all of the ions in the solution. Instead the conductivity would decrease to a percentage of the initial value depending on the flow rate. This percentage would be proportional to the distance \( b \) (distance from the bottom of the cell to the ion that reaches the end of the cell and gets adsorbed) as shown in Equation 11.

\[
\frac{b}{H} = \frac{C_{\text{exit}}}{C_0}
\]  

(11)

Therefore substituting values yields

\[
\frac{C_{\text{min}}}{C_{\text{initial}}} = \frac{V_{\text{Electric}}WL}{Q}
\]  

(13)

3. RESULTS AND DISCUSSION

3.1 Transient tests

The energy recovery percentage of a transient type test increased with the number of cycles performed. Figure 4 shows the results for the transient test of a solution containing 0.2 mg/mL of NaCl at a flow rate of 40 mL/min. The energy recovery associated with this solution at three different flow rates are shown in Figure 7. The results show an increase in energy recovery with respect to cycle number similarly to the experiments using an electrochemical parametric pumping system by Oren [4]. As seen in Figure 4a, with each additional cycle the amount of ions adsorbed that remain at the electrode surface increases because the CDI cell is not fully regenerated. This increment in the amount of non-expelled ions might augment the energy recovery with cycle number because of a combination of two important factors. First, with each additional cycle fewer ions are able to be absorbed before saturating the electrode meaning there is less power input. Second, during regeneration a larger number of NaCl ions are rinsed and therefore larger amounts of energy are recovered due to a more saturated electrode and the repulsion forces between ions of the same polarity. Table 2 shows the input and recovered energies for the cycles 5 to 8 of the experiment at 40 mL/min.

Figure 6: Ion movement in CDI cell. The paths 1, 2 and 3 correspond to the ionic adsorptions when the convective time is smaller, equal, and larger than the electro kinetic time respectively.

Distance \( b \) can be obtained from a kinematic analysis of the ions by equating the time it takes to navigate the length of the cell and the time it takes for the ion to be adsorbed (travel a distance \( b \) at a velocity \( V_{\text{Electric}} \) as shown in Equation 12 where \( Q \) is the solution flow rate [m\(^3\)/s] and \( V_{\text{Electric}} \) is the constant adsorption velocity [m/s]. From this kinematic description, it can be seen that the ionic adsorption will be uniformly distributed along the electrodes along the cell for the paths 2 and 3 in Figure 6.
Figure 7: Energy recovery based on cycle

Table 2: Input and recovered energies of during the cycles 5 to 8 of a transient CDI experiment with a solution of 0.2 mg/ml and 40 mL/min

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Energy in [J]</th>
<th>Energy out [J]</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>3.79</td>
<td>0.23</td>
</tr>
<tr>
<td>6</td>
<td>3.67</td>
<td>0.27</td>
</tr>
<tr>
<td>7</td>
<td>3.59</td>
<td>0.29</td>
</tr>
</tbody>
</table>

3.2 Steady Tests

The longer term steady tests are used exclusively to analyze the adsorption process and provide an overview of time until carbon aerogel saturation, extent of concentration decrease, and adsorption efficiency variation during a desalination process. The total change in conductivity throughout the experiment serves to provide a measure of the percent desalination achieved. Flow rate and solution concentration served as testing parameters.

Figure 8a: Constant flow rate steady tests for varying salt concentrations. The flow rate was 0.5 mL/min and the voltage applied was 1V.

While holding the flow rate and increasing the salinity of the solution, the percentage of desalination appears to be constant as shown in Figure 8a. On the other hand, when the flow rate was adjusted for a constant salt concentration, it seems that percent desalination is inversely related to the flow rate as shown in Figure 8b as predicted by the models in Equation 6 and 9.

3.3 Adsorption efficiency

Figure 10 shows the variation in conductivity and adsorption efficiency calculated using Equation 12 and 13. As long as the aerogel is not near saturation, the conductivity of the outlet stream stays constant at its minimum. When the saturation limit of the aerogel is almost reached, less salt will be absorbed and the output concentration will increase back to the initial concentration value as shown in the figure below. The analysis of the adsorption efficiency as it varies with time shows that
it would reach a maximum value near the moment where the minimum conductivity is measured. This type of analysis could be used to determine the instant when to start the regeneration of the CDI cell in a transient operation mode. The low adsorption efficiencies calculated may be explained by the small amount of ions dissolved. Also, the plateau of the adsorption efficiency and conductivity would be expected to be shorter as higher concentrations and flow rates are employed.

3.4 Analytical models

Low flow rate tests at salt concentrations of 0.025 and 0.05 mg/ml were conducted to validate the models presented in this paper. The results are shown in Figure 9 where \( \frac{C_{\text{min}}}{C_0} \) is the ratio of the minimum reached to the initial concentrations. In order to compare these results to the models presented in Equation 6 and 9, the exponential and linear fitting curves were obtained and the \( V_{\text{elec}} \) were approximated from the coefficients of \( \frac{1}{Q} \) as \( 2 \times 10^{-7} \) and \( 5.1 \times 10^{-6} \) [m/s] for the constant concentration (Equation 6) and constant adsorption rate (Equation 9) models respectively.

The velocity \( V_{\text{elec}} \) could also be estimated by balancing the electric force with the Stokes’ drag of a spherical ionic particle as shown in Equation 14 where \( q \) is the electric charge of the ionic particle [Coulomb], \( R \) is the radius of the particle [m], and \( \mu \) is the viscosity of the solvent [N/m·s]. Assuming that Na⁺ and Cl⁻ ions are spheres of radius \( R = 9 \times 10^{-11} \) [m], the electric velocity would be calculated as \( 4.29 \times 10^{-5} \) [m/s], one or two orders of magnitude larger than the values obtained from the models. However, it should be remembered that this dynamic estimation doesn’t take into account potential decrease in \( V_{\text{elec}} \) caused by the porosity of the electrode and the presence of other co-ions near the surface of the aerogel that could lower the effective electric field an adsorbing ion feels.

\[
V_{\text{elec}} = \frac{qV}{6\pi H \mu R} \quad (14)
\]

Figure 9a: Constant concentration steady tests

Figure 9b: Constant concentration steady tests

Figure 10: Characteristic curve for steady desalination process
4. CONCLUSIONS

Steady and transient tests were conducted in a laboratory scale capacitive deionization system. The results show that in a transient operation, the percentage of energy recovery would increase with the number of cycle. This increment could be caused by the incomplete regeneration of the system.

Experimental data suggest that the percentage of salt adsorbed during a desalination process of low concentration solutions, the maximum percentage of salt that the carbon sheets are able to draw out of the solution is directly related to the residence time of the solution in the cell, but does not vary with the inlet solution concentration. However, both, the energy and adsorption efficiencies would vary as the salinity of the inlet solution change.

Two analytical models have been presented to study as a first approximation, the adsorption rate of solutions with very low ionic concentration. Although a constant adsorption model seems to estimate more accurately the adsorption velocity, a constant concentration model presents a better correlation to the data obtained. Further experiments at more flow rates are needed to validate one or the other. Also, larger variations in the concentration should be explored to evaluate the suitability of these models at brackish water concentrations.

Finally, analysis of the adsorption efficiency during a long desalination process suggests the existence of a region where the ratio of ions adsorbed to charge displac is at a maximum. Further analysis of this peak of adsorption efficiency would allow for operations of CDI systems in a transient mode with a better use of energy.

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