

ELECTROCHEMICAL DESALINATION OF NaCl SOLUTIONS BY ELECTROSORPTION ON NANO-POROUS CARBON AEROGEL ELECTRODES

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ABSTRACT

The objective of this study is to elucidate the efficiency of electrosorption on desalination of aqueous NaCl solution using nano-structured carbon aerogel electrodes. The experiments were performed in an electrosorption cell consisting of a pair of carbon aerogel sheets separated by a 0.5cm spacer. The electrosorption performance is investigated with different applied voltages and solution concentrations. It increases with increasing applied voltage, higher concentration gradient and less double-layer overlapping effect. Under the experimental conditions at the optimum applied voltage of 1.2 Volt and initial NaCl concentration 100 - 1000 mg l⁻¹, the electrosorption capacity was found to be 5.20 - 14.22 mg NaCl/g carbon aerogel. Na⁺ and Cl⁻ ions are electro-absorbed at the electrical double layer without electron transfer redox reactions at anode and cathode. The good electrosorption performance of carbon aerogel electrodes might be attributed to their high specific area, high electrical conductivity, chemical inertness and optimal pore size distribution for the passage and easy movement of ions during electrosorption and electrodesorption. The process is reversible, as the electrode charge/discharge procedure can be repeated innumerable times without any significant loss of salt sorption capacity in all cycles.

Keywords: Electrochemical desalination; electrosorption - electrodesorption; carbon aerogel electrodes

1. Introduction

Electrodeionization is the removal of ions and ionizable species from water or organic liquids. It uses electrically active media and an electrical potential to cause ion transport and may be operated continuously or batch wise. Continuous processes, such as electrodialysis (ED) (Abou-Shaby *et al.*, 2011; DiMachio *et al.*, 1998; Willauer *et al.*, 2011; Zhang *et al.*, 2011), and filled cell electrodialysis or otherwise called continuous electrodeionization (CEDI) (Arar *et al.*, 2013; Lu *et al.*, 2011) comprise alternating permselective cation exchange membranes and anion exchange membranes. Under the influence of the electric field only cations and only anions, respectively are allowed to permeate their mass, while simultaneously co-ions are retained. In this way diluate and concentrate compartments are created and deionization occurs. Electrostatic shielding electrodialysis (ESED) uses ionic current sinks instead of ion exchange membranes to create the necessary diluate and concentrate compartments (Dermentzis, 2010; Dermentzis *et al.*, 2012).

Batch electrodeionization processes such as capacitive deionization (CDI) or otherwise called electrosorption (Cohen *et al.*, 2011; Demirer *et al.*, 2013; Jung *et al.*, 2007; Zhang *et al.*, 2011) and membrane capacitive deionization (Biesheuvel & van der Val, 2010; Lee *et al.*, 2011) are collection / discharge processes which rely on the formation of double-layer supercapacitor at the solution/electrode interface. When an electric field is applied between two electrodes, ions in the solution are forced to move towards to the opposite charged electrodes, resulting in purification of the treated solution. CDI dates back to the mid-1960s and early 1970s when porous electrodes made of activated carbon powder were used in a flow-through capacitor for water desalination (Oren, 2008). CDI is the most economic and energy efficient method of water deionization. It needs porous nano-sized electrodes with very large specific area, such as carbon aerogels (Gabelich *et al.*, 2002), carbon nanotubes and nanofibres (Wang *et al.*, 2006), or activated nano-structured carbon cloths (Ahn *et al.*, 2007) to increase the salt sorption capacity. The costly high specific area electrodes and the fact that the process could not be turned to a continuous one remain the main drawbacks of this technology.

Carbon aerogel electrodes exhibit an excellent electrosorption performance due to their high specific area, high electrical conductivity, chemical inertness and optimal pore size distribution. Therefore, these electrodes have proved to be unique materials for electrochemical removal of salt from brackish or seawater (Cohen *et al.*, 2011; Gabelich *et al.*, 2002; Jung *et al.*, 2007). Furthermore, these electrodes have been tested for removal of other charged contaminants from industrial wastewater, such as heavy metal ions (Rana *et al.*, 2004; Yiaccoumi *et al.*, 2000) and ionic or ionizable organics (Wu *et al.*, 2008).

The contribution of the present research is: a) to present the fundamental aspect of the electrosorption/electrodesorption process; b) to provide a critical review of the advantages and limitations of capacitive deionization; and c) to elucidate the efficiency of capacitive deionization on desalination of aqueous NaCl solutions using nano-structured carbon aerogel electrodes. All operating parameters affecting the electrosorption performance, such as applied voltage, solution concentration and solution pH are examined and the electrosorption capacity of NaCl on carbon aerogel electrodes is investigated.

2. Materials and methods

2.1 Electrochemical cell

All experiments were carried out in a 100 ml rectangular laboratory glass vessel with dimensions 10 cm in length, 10 cm in height and 1 cm in width. Two sheets of carbon aerogel electrodes (Marketch Int. USA) with dimensions 8 cm in height and 8 cm in width each were used as anode and cathode. The electrodes were placed vertically parallel to each other at a distance of 0.5 cm between them. The solution volume was 30 ml. A saturated calomel electrode (SCE) was used as a reference electrode. Proper provisions were made in the lid of the glass vessel for fixing the anode, the cathode and the bridge of the reference electrode.

The carbon aerogel electrodes were used as received. Their main properties, as supplied by the manufacturer, are listed in Table 1.

Table 1. Main characteristics of carbon aerogel electrodes

Parameter	Value
Surface area	600 m ² g ⁻¹
Average pore size	75 - 80 nm
Density	0.4 - 0.5 g cm ⁻³
Capacitance	28 - 30 F g ⁻¹
Resistivity	0.01 - 0.04 Ωcm

2.2 Apparatus

A DC power supply (Agilent E3612A, USA) was used for measuring the electrode potential and current. The experiments were conducted at room temperature. The NaCl concentrations were determined by measuring the electrical conductivity of the treated NaCl solution. A linear relationship existing between NaCl concentration and conductivity via a calibration curve was made prior to electrosorption experiments, which is depicted in *Figure 1*. The values of conductivity in $\mu\text{S cm}^{-1}$ are about twice higher than those of concentration in mg l^{-1} .

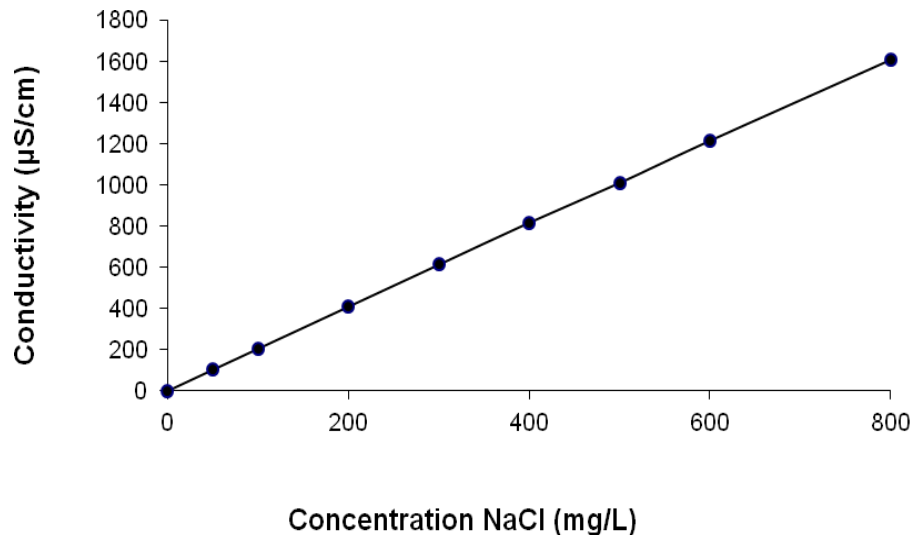


Figure 1. Conductivity versus concentration of dilute NaCl solutions.

Conductivity was measured by means of a conductometer (WTW). pH and temperature were determined using a pH-meter (Hanna) connected to a combined electrode comprising a temperature sensor.

The salt electrosorption capacity (q) defined as the quantity of NaCl electro-absorbed per unit mass of carbon aerogel was determined using Equation (1):

$$q = \frac{(C_0 - C) V}{m} \quad (1)$$

where

C_0 and C are the solution concentrations of NaCl at the beginning and at any time (mg l^{-1}), respectively, V is the solution volume (l) and m is the mass of carbon aerogel electrode (g).

3. Results and discussion

The main factors affecting the electrosorptive deionization are the applied potential and the initial solution concentration, i.e. initial NaCl concentration.

3.1 Effect of applied potential

To study the effect of applied potential (voltage) on NaCl removal experiments were carried out under varying voltages of 0, 0.6 and 1.2 V at fixed NaCl concentration of 100 mg l^{-1} , neutral pH = 7 and 30 min time run. The results are shown in Figure 2. The initial conductivity of $205 \mu\text{S cm}^{-1}$ of the treated NaCl solution decreased to 194, 130 and $38 \mu\text{S cm}^{-1}$ at the corresponding applied voltage of 0.0, 0.6 and 1.2 V, respectively.

Higher removal efficiency for NaCl was achieved at higher voltages. This is a presumable phenomenon as increased voltage increases the flow velocity of electrons and the electrostatic attraction of ions by the opposite charged electrodes.

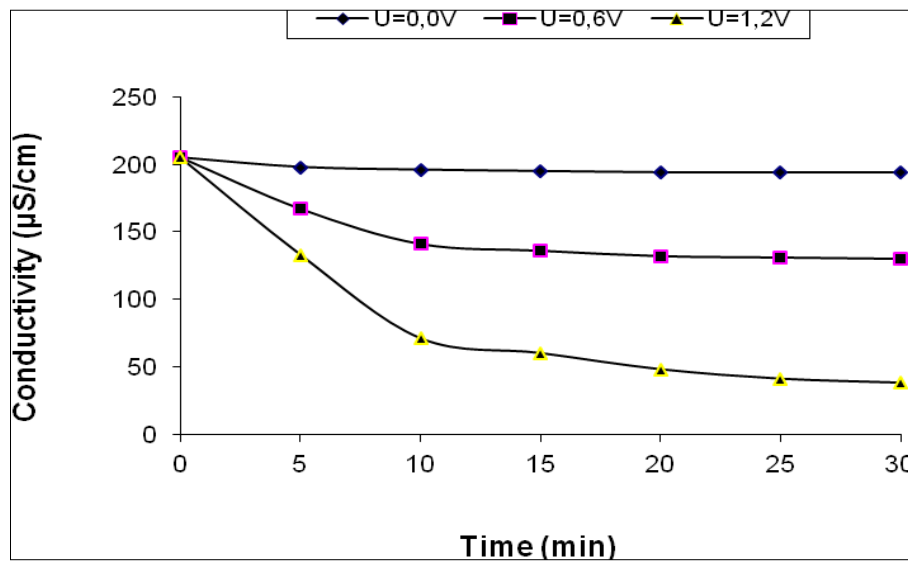


Figure 2. Conductivity variation versus time at various applied voltages.

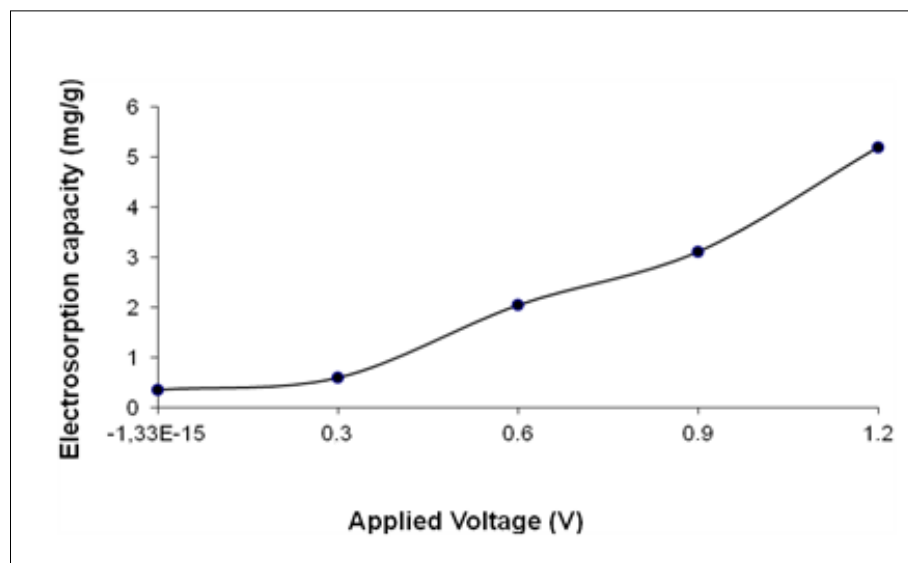


Figure 3. Electrosorption capacity of NaCl on carbon aerogel versus applied voltage.

The observed pH drop from 7 to 5.65 during the open-circuit adsorption of NaCl at 0.0 V provides evidence for ion exchange phenomena between Na^+ and H^+ ions, which take place on the carbon aerogel surface. During the electrosorption process at 0.6 and 1.2 V, pH increases only slightly, namely to 6.37 and 6.88, respectively.

At voltages higher than the electrochemical decomposition potential of water (1.23 V) higher removal efficiency of NaCl could be achieved. However, partially water electrolysis to hydrogen and oxygen gas due to H^+ and OH^- ion discharge at the cathode and anode, respectively, could be observed. For this reason the electrodes were polarized at voltages not higher than 1.2 V.

The salt electrosorption capacity calculated from Equation 1, amounts to 0.35, 0.59, 2.04, 3.11 and 5.20 mg l⁻¹ NaCl per g carbon aerogel for the applied voltages of 0.0, 0.3, 0.6, 0.9 and 1.2 V, respectively (Figure 3).

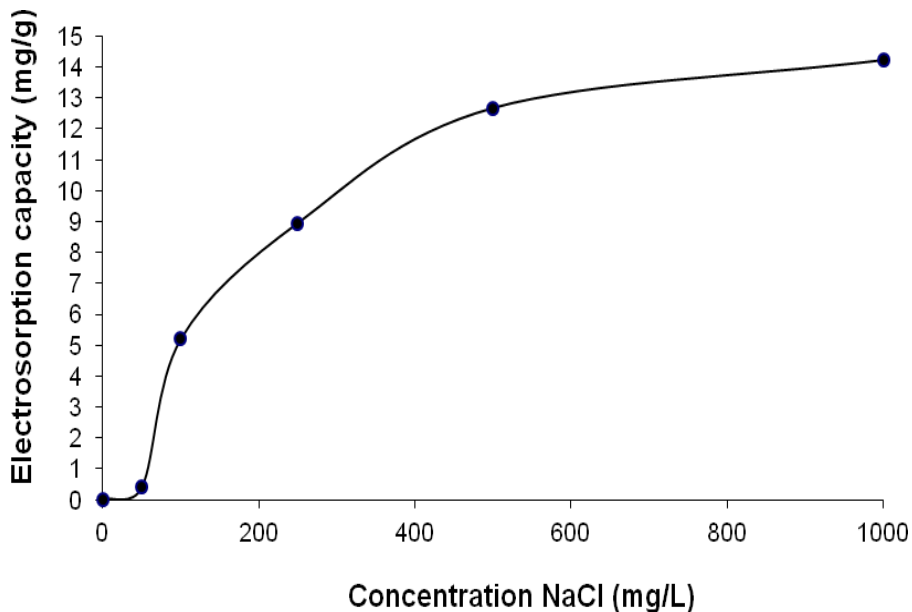


Figure 4. Electrosorption capacity of NaCl on carbon aerogel versus NaCl initial concentration

3.2 Electrodesorption and electrode regeneration

The electrodesorption process helps to regenerate the electrodes and recover the adsorbed NaCl from the electrodes. Regeneration of electrodes can be accomplished by two modes, namely discharging the cell at 0.0 V or reversing the cell polarity at an opposite charge. In the first mode a considerable amount of the electrical energy stored in the capacitor can easily be recovered during the regeneration step. In this way, capacitive deionization is an electrochemical means of saving electrical energy and delivering clean water (Anderson *et al.*, 2010). In the second mode of reverse polarization the regeneration effectiveness and the electrode reactivation are increased.

The charged carbon aerogel electrodes were short-circuited and depolarized to 0.0 V. The absorbed Na⁺ and Cl⁻ ions were released from the cathode and the anode, respectively, and the solution conductivity rapidly reached its initial value. Almost 100 % of NaCl could be recovered by the electrodesorption/regeneration step. The electrosorption/electrodesorption procedure is a rapid and reversible process, which can be repeated innumerable times without any significant loss of salt sorption capacity in all cycles, as known from electrochemical double layer supercapacitors (Kötz & Carlen, 2000). Ions are electrostatically held on the electric double layer during polarization and released from it during depolarization of the electrodes. In practice, no undesirable ion discharge through faradaic electron transfer redox reactions take place at the electrode/solution interface.

The good electrosorption/electrodesorption performance of carbon aerogel electrodes might be attributed to their high specific area, high electrical conductivity, chemical inertness and optimal pore size distribution for the passage and easy movement of ions during the electrosorption and electrodesorption steps.

4. Conclusions

In this work, the performance of capacitive deionization for desalination of dilute aqueous NaCl solutions using carbon aerogel electrodes was investigated. Carbon aerogel electrodes with the high specific area, optimal pore size distribution and high electrical conductivity are unique electrode

materials for double layer capacitors and electrosorption of ions. The deionization mechanism relies on electrostatic interactions between charged electrodes and ions and formation of electric double layer on the carbon aerogel surface. The low applied potential ensures non faradaic capacitive currents without electron transfer redox reactions at the electrode/solution interface and furthermore, low electrical energy consumption, most of which can also be recovered in the electrode regeneration step. Charge and discharge of the electrodes can be repeated boundlessly without any significant loss of the salt sorption capacity. It was found that the electrosorption capacity increased by increasing the applied voltage due to stronger electrostatic attraction. Voltages higher than the electrochemical decomposition potential of water (1.23 V) should not be applied in order to avoid the undesirable hydrogen and oxygen gas evolution at the cathode and the anode respectively. The electrosorption capacity increased sharply by increasing the initial NaCl concentration in the range 0-500 mg l⁻¹, due to higher concentration gradient, reaching the value of 12.67 mg NaCl per g of carbon aerogel. Furthermore, it increased only slightly to 14.22 mg l⁻¹ at 1000 mg l⁻¹ NaCl. It can be concluded that capacitive deionization is potentially attractive for desalination of low salinity brackish and surface waters.

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