Desalting in Wastewater Reclamation Using Capacitive Deionization with Carbon Aerogel Electrodes

Jeffery H. Richardson
Joseph C. Farmer
David V. Fix
J. A. H. de Pruneda
Gregory V. Mack
John F. Poco
Jacquelyn K. Nielsen
Richard W. Pekala

This paper was prepared for submittal to American Desalting Association 1996 Biennial Conference & Exposition
Monterey, CA
August 4 - 7, 1996

July 1996

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED
DISCLAIMER

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.
DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.
Desalting in Wastewater Reclamation using Capacitive Deionization with Carbon Aerogel Electrodes


Chemistry and Materials Science Directorate, Lawrence Livermore National Laboratory, P. O. Box 808, Livermore, CA 94550

Abstract

Capacitive deionization with carbon aerogel electrodes is an efficient and economical new process for removing salt and impurities from water. Carbon aerogel is a material that enables the successful purification of water because of its high surface area, optimum pore size, and low electrical resistivity. The electrodes are maintained at a potential difference of about one volt; ions are removed from the water by the imposed electrostatic field and retained on the electrode surface until the polarity is reversed. The capacitive deionization of water with a stack of carbon aerogel electrodes has been successfully demonstrated. The overall process offers advantages when compared to conventional water-purification methods, requiring neither pumps, membranes, distillation columns, nor thermal heaters. Consequently, the overall process is both robust and energy efficient. The current state of technology development, commercialization, and potential applications of this process are reviewed. Particular attention and comparison with alternate technologies will be done for seawater, brackish water, and desalting in wastewater reclamation.

Introduction

Technologies for the desalting of water to produce potable water for domestic and agricultural use has been extensively reviewed [1, 2]. Principle approaches have been to separate either water from the solution (e.g., thermal distillation, reverse osmosis) or ions from the water (e.g., electrodialysis, ion exchange). High salt contents (up to 3.5% for
seawater) plus varying organic and solid particulate levels in water provide a continuing challenge to all separation processes from the standpoint of cost and efficiency. Frequently a separation technique has to used in conjunction with other techniques, and improvements in materials or energy sources enables the development of new technical solutions which then have to be evaluated on the basis of cost and efficiency. The development of aerogels has recently provided such an enabling impetus, resulting in new developments in the basic technology of capacitive deionization.

Capacitive deionization (CDI) involves the use of porous electrodes to remove dissolved ions through application of an electrostatic field. A process for the capacitive deionization of water with a stack of carbon aerogel electrodes has been developed at Lawrence Livermore National Laboratory. Aqueous solutions of soluble salts are passed through a stack of carbon aerogel electrodes, each having a very high specific surface area (400 to 1100 m²/g). After polarization, non-reducible and non-oxidizable ions are removed from the electrolyte by the imposed electric field and held in electric double layers formed at the surfaces of electrodes, as shown in Figure 1. As desired, the effluent from the cell is purified water. A variety of salts have been shown to be removed by CDI: NaCl and NaNO₃, [3], NH₄ClO₄, [4], hexavalent chromium in the form of HCrO₄⁻/CrO₇²⁻/Cr₂O₇⁻ [5].

This process is also capable of simultaneously removing a variety of other impurities. For example, dissolved heavy metals and suspended colloids can be removed by electrodeposition and electrophoresis, respectively. CDI has several potential advantages over other more conventional technologies. For example, ion exchange is now used as a means for removing anions and cations, including heavy metals and radioisotopes, from process and waste water in various industries. This process generates large volumes of corrosive secondary wastes that must be treated for disposal through regeneration processes. With CDI, unlike ion exchange, no acids, bases, or salt solutions are required for regeneration of the system. Regeneration is accomplished by electrically discharging the cell. Therefore, no secondary waste is generated. In contrast to thermal
processes such as evaporation, CDI is much more energy efficient. Since no membranes or high pressure pumps are required, CDI offers operational advantages over electrodialysis and reverse osmosis (RO).

**Experimental**

Conceptually, the CDI process is very simple. After application of a voltage between two adjacent carbon aerogel electrodes, cations and anions are drawn towards the cathode and anode, respectively, as illustrated in Figure 1. These ions are held in the electric double layers formed at the extensive surface of the carbon aerogel electrodes until the voltage is reduced. Double-sided electrodes are made by gluing two sheets of a porous carbon aerogel composite (CAC) to both sides of a titanium plate that serves as both a current collector and a structural support. CAC has an exceptionally high specific surface area of ~500 m²/g.

Neither the use of porous electrodes nor CDI represent new technology. Several publications and patents have appeared that discuss the use of porous electrodes for the recovery of heavy metals from aqueous solutions [6-8]. In these cases, metallic ions are electrodeposited on the surfaces of cathodes with relatively low specific surface areas.

The first studies on CDI appeared in the early 1960s describing flow-through capacitors with porous, activated-carbon electrodes for the desalination of brackish water [9]. Subsequent work led to the development of a comprehensive theoretical model for the capacitive charging of porous carbon electrodes [10]. Several years later, work on CDI was done in Israel and published in the 1980’s [11]. Though CDI was eventually abandoned for water treatment due to various problems, including the failure to demonstrate degradation-free electrode performance, preliminary cost studies did indicate that an efficient, low-cost desalination plant based upon this technology could be built if adequate durability of the electrodes could be achieved [10]. Since this work was conducted decades before the invention of carbon aerogel electrodes, such materials were not included in the study.
Several practical problems are encountered with these early CDI systems using activated carbon. For example, significant fractions of the carbon surface may be occluded in electrodes that use polymeric binders; hence, all the surface area is not available for interaction with the solution. Activated carbon appropriate for use in beds with low pressure drop also has a relatively low specific surface area. Process efficiency is lowered by the large potential drop that develops in thick electrodes and packed beds. Even though adjacent carbon particles may touch, intimate electrical contact may not exist. Consequently, the electrical resistance is high.

The development of aerogels serve as the enabling technology which makes this CDI system technically and economically attractive. The preparation of resorcinol-formaldehyde (RF) aerogels and their carbonized derivatives has been described previously [12, 13]. Carbon aerogels serve as ideal material for CDI electrodes. The electrical resistance of a carbon aerogel electrode is much lower than a comparable electrode made of activated carbon. Additionally, although other carbon materials may have higher BET surface areas, those materials have much of the surface area located inside pores having diameters less than 1 nm. It is very doubtful that this level of porosity contributes to electrochemical double layer formation since electrolyte penetration and double layer formation are questionable on this scale (i.e., in other carbon materials the electrochemically active area is only a fraction of the measured BET surface area).

An electrolytic double-layer capacitor for energy storage based on carbon aerogel has been developed by Lawrence Livermore National Laboratory [14]. The carbon aerogel electrodes used in this device had very high volumetric surface areas, ranging from 100 to 700 m²/cm³ and relatively low corresponding bulk densities, ranging from 0.3 to 1.0 g/cm³. These characteristics made it possible to construct a device with a very high energy density. The electrical continuity of the material permits stored energy to be released rapidly, resulting in a relatively high power density (>2 kW/kg).
CAC electrodes are assembled into stacks using a lower stainless steel header with a rubber gasket and threaded rods, the array of CAC electrodes, gaskets, and spacers, and an upper stainless steel header. Even electrodes serve as cathodes while odd electrodes serve as anodes. An electrode separation of 0.05 cm is maintained by cylindrical nylon spacers concentric with the threaded rods and a rubber compression seal. Since the orifices in each electrode alternate from one side of the stack to the other, the flow path through the stack is serpentine. A stack of 192 pairs of carbon aerogel electrodes has a total active surface area of approximately $10^9$ cm$^2$. Flow through the stack is generated by a programmable, magnetically-coupled, screw pump with a 304 stainless steel head. The pressure drop across a stack of 48 electrode pairs is only 0.35 kg/cm$^2$ (5 psi) at 1.7 L/min, whereas the drop across a stack of 192 electrode pairs is less than 0.98 kg/cm$^2$ (14 psi) at 1.5 L/min.

Electrical conductivity, pH, individual ion concentrations, and temperature are continuously monitored. The CDI system in the laboratory consists of two stacks of CAC electrodes in parallel. This system enables one stack to be regenerated while the other deionizes (i.e., potential-swing electrosorption). During potential-swing operation, a portion of the current produced during regeneration could be used for purification so the overall energy efficiency of the process is improved. A computerized data acquisition system logs important operating parameters such as voltage, current, conductivity, pH, and temperature. Figure 2 is a schematic diagram illustrating the overall assembly of the apparatus into the CDI system.

Solutions of NaCl, NaNO$_3$, and NH$_4$ClO$_4$ were used over a range of conductivities (typically 10 to 1000 $\mu$S cm$^{-1}$) at potentials of 0.6, 0.8, 1.0 and 1.2 V. Batch-mode experiments were done by continuously recycling electrolyte at a flow rate of 1.0 liter/min. Single-pass experiments without were done at a flow rate of 25 ml/min. Chromium removal was investigated using contaminated ground water at the LLNL Treatment Facility C. The TDS of the ground water used is about 530 ppm, with inlet total Cr content of about 35 ppb. A slip stream was taken to provide a feed rate of 100 ml/min.
Results and Discussion

Overall, tests demonstrated that CDI with carbon aerogel can effectively remove dissolved salts from water. Deionization was accomplished during charging, while regeneration was accomplished during discharge. The concentration and conductivity of a typical salt solutions was cycled up and down numerous times by charging and discharging the stack. The ability of the CAC electrodes to remove ions from water, i.e., the electrosorption capacity, had a strong dependence on cell voltage. The best results were achieved at 1.2 V, with relatively poor performance below 0.4 V. No severe irreversible degradation in performance was observed after cycling the stacks several months. Breakthrough was observed during single-pass experiments without recycle. Rejuvenation of aged electrodes can be almost completely recovered repeatedly by voltage reversal.

Typical results are illustrated with NaCl in Figure 3 for the CDI system operated in the recycle mode. Figure 4 illustrates a single-pass demonstration of CDI to remove NH₄ClO₄ at 100 µS cm⁻¹ at 1.2 V. For the number of electrode pairs present, the same level of removal was not achieved at 1000 µS cm⁻¹ at 1.2 V (Figure 5). However, as demonstrated with more dilute solutions, the addition of more electrode pairs does result in a continual decrease in the outlet conductivity. Qualitatively, the time to breakthrough increases proportionally with the number of electrode pairs. Under similar conditions, the capacity of the electrodes is anion limited, and comparison with Cl⁻ with ClO₄⁻ indicates that the CAC electrode capacity for large monovalent anions is less than for smaller anions. Higher electrode voltages result in greater deionization; a representative demonstration of this observation is given for NaN0₃ in Figure 6.

The loss of electrosorption capacity of carbon aerogel electrodes has been observed during prolonged operation [3,4]. Fortunately, such losses can be substantially recovered by reversal of the cell voltage. It is believed that
the voltage reversal drives chemically bound ions from the surface of the carbon aerogel by imposing a significant repulsive electrostatic force. Rejuvenation can be used to increase the electrosorption capacity of aged electrodes to levels approaching those achieved initially. The rejuvenation of 384 aged electrode pairs is illustrated by Fig. 7. In this case, such operation increased the removal of NH₄ClO₄ from 79% to 94%. It appears that such rejuvenation can be repeated numerous times with essentially the same desirable result.

CDI has been used to continuously remove trivalent and hexavalent chromium from raw, untreated ground water at 530 ppm TDS. Figure 8 shows a plot of the concentrations of both Cr(VI) and Cr(III) in the outlet stream during the first 28 h of operation. The Cr(VI) is believed to be in the form of HCrO₄⁻/CrO₄²⁻/Cr₂O₇²⁻, whereas the Cr(III) is believed to be in the form of Cr(OH)³⁺/Cr(OH)₂⁺/Cr(OH)₄⁻/CrO₂⁻ [15]. The possibility of forming non-ionic chromium hydroxide monomer, dimer, trimer, and tetramer is recognized. Essentially all of the chromium in the inlet stream was Cr(VI), because the total Cr measured by AAS was nearly the same as the Cr(VI) measured by colorimetry. Immediately following polarization at 0.9 V, the total concentration of chromium in the outlet stream dropped from 30-35 ppb to less than 10 ppb. The concentration then started to trend upward. The speciation of chromium in the outlet stream was approximately 30% Cr(III) and 70% Cr(VI). After operating the cells at 0.9 V for 8 h, the polarization was increased to 1.2 V. The additional polarization lowered the total concentration of chromium in the outlet stream from 15 to 8 ppb, while the concentration of Cr(VI) in the outlet dropped from 12 to 5 ppb. The concentration of Cr(VI) remained below 7 ppb during the 28 h shown in the figure, whereas the total concentration of chromium remained below 10 ppb. It is evident that in addition to removing Cr(VI) from the stream of water, Cr(VI) was reduced to Cr(III). Furthermore, the chromium removal continued long after saturation of the carbon aerogel with other ionic species, indicating a high degree of selectivity towards chromium.

The minimum energy requirements of the CDI process have been estimated [4]. The minimum theoretical work required by an isothermal
process to separate a 1000 ppm NH₄ClO₄ solution into a 1 ppm product stream and a 95,000 ppm concentrate stream is approximately 1.6 J mol⁻¹ (0.1 Wh gal⁻¹), assuming that the NH₄ClO₄ obeys the Debye-Hückel activity coefficient model. The minimum electrical energy required for charging a CDI cell with NH₄⁺ and ClO₄⁻ is 4.5 J mol⁻¹ (0.26 Wh gal⁻¹) at 0.6 V and 9.0 J mol⁻¹ (0.52 Wh gal⁻¹) at 1.2 V. These values correspond to QV/2 where Q is the stored electrical charge and V is the cell voltage. In real systems, ohmic losses and finite pressure drops lead to energy requirements above these limiting values. However, energy recovery by a second device operating in parallel can be used to substantially reduce the overall requirement, allowing CDI systems to more closely approach the theoretical minimum based on thermodynamics.

While a more detailed study should and is being done, it appears that in many cases CDI compares favorably with the energy requirements for other desalting technologies (e.g., reverse osmosis, thermal distillation). Additionally, the virtually infinite shelf life plus the robustness of carbon electrodes under service conditions suggest an operational advantage with respect to material durability for CDI; some of the CAC electrodes have been operated for nearly 2 years continuously with no significant degradation in performance. These potential attributes of CDI are being more closely evaluated. Additionally, systems are being assembled with 50-100 times the aerogel electrode surface area. It is intended that these systems will be applied to pilot- and field-scale evaluations of CDI.

References


Figure Captions

Figure 1. Schematic diagram illustrating the principal of capacitive deionization with carbon aerogel electrodes. Cations and anions are held in the electric double layers formed at the cathode and anode, respectively. The high specific surface area of the carbon aerogel enables the process to remove a significant amount of dissolved ions from the water passing between the electrodes.
Figure 2. Schematic diagram illustrating the overall assembly of the various components into the CDI system.

Figure 3. Deionization of a fixed volume of 100 µS cm⁻¹ NaCl solution. Complete recycle of 4.0 liters at a rate of 1.0 liter / min. The apparatus included 384 aged electrode pairs operated at a cell voltage of 1.2 V.

Figure 4. Single-pass experiment with 100 µS cm⁻¹ NH₄ClO₄ solution at a flow rate of 25 ml / min. The apparatus included 384 electrode pairs operated at a cell voltage of 1.2 V.

Figure 5. Single-pass experiment with 1000 µS cm⁻¹ NH₄ClO₄ solution at a flow rate of 25 ml / min. The apparatus included 384 electrode pairs operated at a cell voltage of 1.2 V.

Figure 6. Deionization of a fixed volume of 100 µS cm⁻¹ NaNO₃ solution. Complete recycle of 4.0 liters at a rate of 1.0 liter / min. The apparatus included 192 new electrode pairs operated at cell voltages ranging from 0.6 to 1.2 V.

Figure 7. Use of voltage reversal as a means of rejuvenating aged carbon aerogel electrodes. Deionization of a fixed volume of 100 µS cm⁻¹ NH₄ClO₄ solution. Complete recycle of 4.0 liters at a rate of 1.0 liter / min. The apparatus included 384 aged electrode pairs operated at a cell voltage of 1.2 V.

Figure 8. Selective removal of 35 ppb Cr(VI) from brackish LLNL ground water (530 ppm TDS).

Acknowledgments

This work was performed under the auspices of the U.S. Department of Energy, by Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.
A single cube of carbon aerogel, one inch on a side, has an effective surface area of more than twenty million square inches. This unusually high effective surface area makes it possible to adsorb large numbers of ions.
Figure 2
Figure 3
Figure 4
Figure 5
Figure 6
Figure 7
Figure 8