

ASYMMETRIC CAPACITIVE DEIONIZATION (CDI), AN EMERGING TECHNOLOGY FOR WATER TREATMENT IN SMALL COMMUNITIES

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Abstract

Capacitive deionization (CDI) is one of the emerging water technologies attracting interest in recent years (Anderson *et al*, 2010). CDI may represent a unique opportunity for small communities, who lack both water and energy as this process provides the unique opportunity to purify water while at the same time storing energy. In the process of removing ions energy is stored in pores of the electrical double layer capacitor. A new CDI system was developed by the ECTP of University of Wisconsin using nanooxides carbon coated electrodes. This system represents an asymmetric CDI process. Application of asymmetric CDI to water softening and nitrate removal is explored in this paper. Laboratory scale experiments were performed treating, initially, several synthetic solutions having different ionic concentrations. In addition, the system was tried in a real water scenario. The influence of ionic concentration and composition on the removal process was studied both in terms of kinetics and equilibrium adsorption isotherms. Around 70–75% of Ca^{2+} was removed when 1mM and 2.5mM CaCl_2 solution were treated. Therefore, at higher concentrations, our electrodes were able to remove higher amounts of Ca^{2+} . Initial tests conducted in treating natural waters samples resulted in 68% of Ca^{2+} removal after 60 min of treatment. Furthermore, the Mg^{2+} and Sr^{2+} removal rates obtained were 57% and 71%, respectively. Lastly, a 55% nitrate removal was accomplished during the real water test pointing out that this asymmetric CDI system has the potential of solving water pollution issues related to nitrates.

Keywords: Capacitive Deionization (CDI), Electrosorption, coated carbon electrodes, asymmetric electrodes, water softening.

Introduction

The problems associated with water scarcity, drought and water pollution are expected to increase in the coming decades. Small communities are especially exposed to these problems, and even regions currently considered having adequate water resources. In an attempt to address these problems related to both water quality as well as water quantity, recent research has focused on emerging water

technologies such as forward osmosis, biomimetic systems or capacitive deionization (CDI). In this paper we address the later of these processes namely CDI.

CDI works by removing ions present in water by applying a constant voltage between two electrodes immersed into solution. When removal is complete, the electrodes are regenerated by reversing the voltage. During regeneration, the ions that were deposited on the electrodes undergo a desorption process and are returned to the solution as a brackish wastewater. Most current CDI or electro-adsorption systems typically employ conducting high surface area carbon electrodes in a variety of forms. These can be carbon aerogels, carbon cloths, composite electrodes or more contemporary carbon nanotubes and nanofibers or graphene. These new materials have increased the areas to which the CDI process may be applied: water softening, nitrate removal, removing heavy metals in industrial waste streams, brackish water desalination, and reverse osmosis brine recovery.

A new CDI system was developed by the Environmental Chemistry and Technology Program of University of Wisconsin using nanooxides carbon coated electrodes (Leonard et al., 2008). A similar idea was also explored by Ryoo and Seo, (2003). However, these authors did not employ two different coated electrodes (e.g. nanoporous silicon dioxide and alumina) in order to remove ions from water. Recently, studies performed by Avraham *et al.*, (2010) developed a model, which supported the idea that, asymmetric CDI technology can achieve higher charge efficiencies than symmetric CDI cells.

As has been mentioned above, most of the recent CDI studies have focused on new materials (especially various porous carbon electrodes). However, few studies have been devoted to addressing another important issue; the water and energy link. In the CDI process it is possible to store energy while treating water! The electrochemical double layer of the electrodes employed in capacitive deionization could makes this paradigm shift in water treatment possible. Anderson *et al*, (2010) showed the theoretical capacity of this technology to compete with more established technologies as Reverse Osmosis (RO) or Electrodialysis (ED). All of these advantages along with the fact that no requirement for chemical addition makes CDI a promising technology that could be employed in small communities. Renewable energies such as solar could be coupled with CDI systems could be an interesting alternative to present desalination technologies (García-Rodríguez, 2003).

Methods

Deionization experiments were performed in a batch reactor using 2" (5.08 cm) x 2" (5.08 cm) electrodes immersed in 40 ml of CaCl₂ solution (1mM and 2.5 mM). All experiments employed the classic three-electrode electrochemical configuration (Fig 1), with a SiO₂-coated electrode as the working electrode, an Al₂O₃-coated

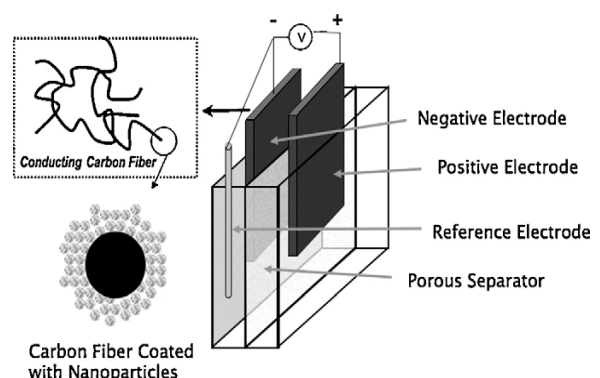


Figure 1. Laboratory scale experiments performance. Leonard, et al., (2009). *Electrochemical Acta*, 54: 5286.

electrode as the counter electrode, a porous fabric nylon separator between the two electrodes, and a saturated calomel electrode (SCE) serving as the reference electrode (Leonard et al., 2009). All voltages are referenced to the SCE. For 20 min, a constant voltage of -1.5 V was applied using a potentiostat. During this time, cations migrate to the electrode whose surface is charged negatively while the positive counter electrode attracts anions. After 20 minutes, the potential was switched to 0.9 V. In this fashion, the ions are firstly removed from solution but then re-deposited as a waste solution. Samples were withdrawn from the CaCl_2 solution at 5 minutes intervals. In contrast with other studies where only conductivity has been employed to measure changes in ionic composition, results reported here are coming from the use of inductively coupled plasma.

Results and Discussion

Laboratory scale experiments were performed using different concentrations (1mM and 2.5mM) of CaCl_2 solutions and different pairs of electrodes. In the first case (1mM), 70% Ca^{2+} and 60% Cl^- removal was accomplished. In the second case (2.5mM) 70% Ca^{2+} and 55% Cl^- was removed (Fig 2). Therefore, the asymmetric CDI system was able to maintain good removal rates even when the ion concentration was increased 2.5 times. Regeneration capacity was also tested. After 20 min, a quite similar regeneration rate was observed, 65% for 1mM and 60% for 2.5mM .

Kinetics parameters, E_{Rem} ($\text{mg}/\text{min m}^2$) and R_{Rem} (mg/m^2), were calculated as a tool to scale the CDI process to real world scenarios. Increases in ion concentration resulted in a consequent rise in the rate of removal from $35\text{ mg}/\text{min m}^2$ to $74\text{ mg}/\text{min m}^2$. Real water testing (120 ppm Ca^{2+}) was conducted as initial experiment to compare our laboratory results with actual waters obtained in the field. After 60 min of removal, almost 70% Ca^{2+} was removed. This translates into a rate of removal of $32\text{ mg}/\text{min}$ per square meter of electrode. Not only was Ca^{2+} monitored, but also Mg^{2+} and Mn^{2+} as well, reaching 57% and 65% removal respectively. Lastly, we conducted a test of the system in its ability to remove nitrates in real water samples. Results showed a 55% of removal after 60 min. Durability test were also conducted. Over the time frame of all of these tests we could not detect any changes in removal rates nor degradation of the carbon electrodes.

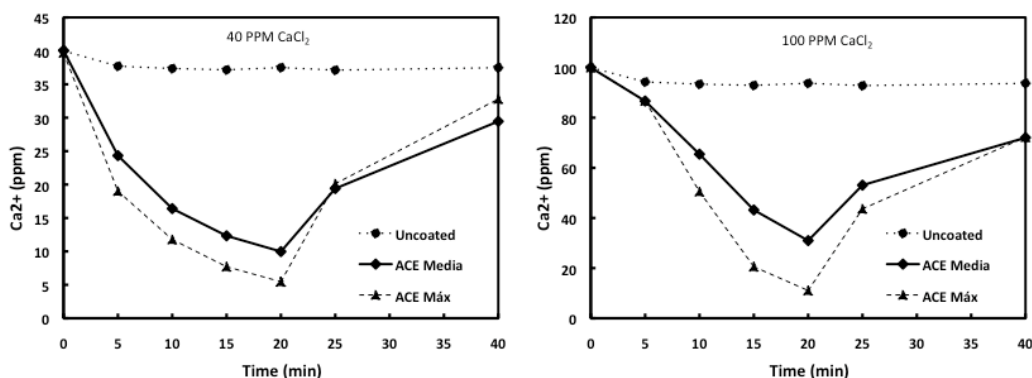


Figure 2. Comparison 1mM and 2.5mM CaCl_2 solution test.

Conclusions

We believe that asymmetric CDI technologies may have the potential of helping to deliver potable water in small communities. Since energy is stored for reuse in the CDI process, it should be more efficient and could be readily coupled to renewable energy systems. Our carbon electrodes coated with two different types of nanoporous oxides managed to maintain removal rates even when the concentration of solution to be treated increased by a factor of 2.5. Laboratory tests showed the capacity of this system to accomplish fairly impressive ion removal (specially Ca^{2+}) not only in synthetic solutions but also in real water samples. Results confirm the high removal trend of the divalent ions, as reported in previous research (Welgemoed *et al.*, 2005; Xu *et al.*, 2008).

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