

# **Report for 2005TX198B: Carbon Aerogel Electrodes: Adsorption-Desorption and Regeneration Study for Purification of Water**

## Publications

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Report Follows

# *Carbon Aerogel Electrodes: Adsorption-Desorption and Regeneration Study for Purification of Water*

**Sanjay Tewari**

## **Abstract**

Carbon has been used traditionally in many forms, to name a few charcoal; powder; activated pellets; carbon cloth; for water treatment but there have been various problems associated with their use. Carbon aerogel (CA) is comparatively new form. It has large surface area because of its ultra-micro-porous structure; it also has high conductivity which is suitable for capacitive de-ionization (CDI) technology. CA electrodes were used in CDI for metal ions, bacteria, and some organic pollutants removal. The problem is once these electrodes are used and saturated they lose their capacity for removing ions and they need to be replaced. CA is expensive and replacement of CA electrodes increases the cost of water treatment for this reason they need to be regenerated. Regeneration studies by various researchers so far involves equal or more amount of clean water than the amount of water treated by it. In addition to this cost estimation for this process has not been done extensively. This study investigates various methods to regenerate CA electrodes to reduce the amount of water involved. To predict desorption behavior in a better manner a model is to be prepared.

## **1.0 Introduction & Background**

### **Carbon Aerogels**

Carbon has been used in different forms to treat water electrochemically. Some carbon forms used are high area carbon-cloth<sup>1</sup> or carbon-felt electrodes<sup>2-4</sup> and recently carbon aerogels (CAs).<sup>5-12</sup> “Under most conditions, pollutant impurities are present at low concentrations so that the electrochemical processes are diffusion-controlled”.<sup>2</sup> This diffusion limited mass-transport can be enhanced by using high-area, porous electrodes at which 2-dimensional electrochemistry start acting like “quasi-3-dimensional behavior” due to the large distributed area.<sup>2</sup>

Ayranci and Conway (2001)<sup>3</sup> successfully used high surface area carbon-felt electrodes for water purification. They studied inorganic, sulfur-containing anions and concluded that adsorptive effectiveness was related to factors such as charge, size and shape of ions that play important role in their hydration behavior. They also observed that polarization of carbon-felt surfaces caused an increase in the rate of adsorption of the ions. It was also found that reversing the polarization for sufficiently long periods of time caused an initial desorption of ions due to discharging of the electrode, followed by the re-adsorption of oppositely charged ions.

A successful attempt was made, showing that electro-adsorbing carbon electrodes may be multi-staged in a column of two porous electrodes that can desalinate water to a concentration ratio greater than 100 between product and waste.<sup>13</sup> The process was based on *electrochemical parametric pumping*, a method developed in conjunction with multi-staging electro-adsorption.<sup>9</sup> This concept of electro-sorption of charged species was

generalized to include particulate matter such as colloids and bacteria. It was thus shown that *E. coli* bacteria<sup>14</sup>, which carry a negative charge; such that porous carbon electrodes can partially retain the organisms (alive) upon potential reversal.

Recent research has shown that carbon aero-gels can be used effectively for the demineralization of wastewater of low-to-moderate ionic strength. Electro-sorption has been used for different kinds of water purification processes like heavy metal ion removal and desalination of dilute solutions.

## CA Preparation and Properties

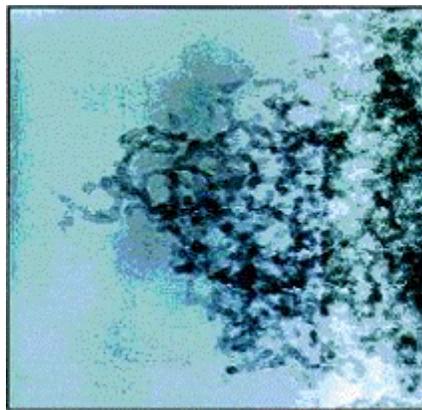
CAs represent a new class of nanoporous materials. They have ultrafine cell/pore size ( $<100$  nm), high surface area ( $> 400$  m<sup>2</sup>/g), and a solid matrix composed of interconnected colloidal-like particles, platelets, or fibers, synthesized from resorcinol-formaldehyde (RF), phenol-resorcinol-formaldehyde, phenolic-furfural, melamine-formaldehyde, polyurethanes and polyureas.<sup>15-20</sup> These organic aerogels can be transformed in the forms of monoliths, powders, micro spheres, or thin film composites, if pyrolyzed in an inert atmosphere.<sup>5, 21, 22</sup>

Fricke and Tillotson (1997)<sup>23</sup> discussed production, characterization, and applications of carbon aero-gels in detail. Li and Guo (2000)<sup>24</sup> carried out some experiments for the preparation of low-density carbon aero-gels from cresol/formaldehyde mixtures and in their experiments, a cresol mixture is first used to poly-condense with formaldehyde (F) catalyzed by NaOH for the preparation of the organic aero-gels. Li and Guo (2000)<sup>24</sup> concluded that a cresol mixture could be used as a raw material to prepare low-density monolithic, crack-free aero-gels and carbon aero-gels. Density is an important index to judge aero-gel quality. The lower the carbon aero-gel density, the lower the electrical resistivity, hence the preparation of super-low-density aero-gel is important in understanding the physical transport mechanism within these materials. Li *et al.* (2002)<sup>25</sup> attempted to make lower cost aero-gels by using cresol. A mixture of cresol ( $C_m$ ), resorcinol and formaldehyde has been used as an alternative economic route to the classical resorcinol-formaldehyde synthesis. The porous structure of the mixed carbon aero-gels ( $C_m$ RF) is similar to that of RF carbon aero-gels.

The idea behind electro-sorption is to force ions or ionic species towards oppositely charged electrodes with the help of an electric field. Under this kind of environment charged ions are held in the strong field on the electrodes, and once the electric field is removed the ions are quickly released. Obviously in these systems electrodes of high electrical conductivity and high surface area form electrical double layers near their surfaces is required. Electrical double layer is formed in the solutions when a charged surfaces comes in contact to liquid solutions having charged ions in it and ions of opposite charge get attracted to this charged surface and they make a layer at the surface of contact. Granular activated carbon (GAC) has been used for electrodes<sup>26-28</sup> however there were some problems associated with GAC used as an electrode in electro-sorption such as applying GAC as a uniform coating where some kind of glue is needed. This glue reduces the efficiency and is not able to hold GAC to the surface adequately. Carbon aero-gel monolithic, high-surface area and high-electrical conductivity material<sup>10</sup> has been found to have excellent characteristics for electro-sorption.<sup>5-11</sup>

The thermal properties of carbon aero-gels do not play much of a role in water treatment processes but heat/temperature treatment during their formation plays an important role in determining the structure of the carbon aero-gels. It is known that the porosity of the carbon, measured by adsorptive methods, decreases with increasing heat treatment temperature (Marsh and Wynne-Jones).<sup>29</sup> Much work has been carried out to understand the thermal properties of carbon aero-gels. Bock *et al.* (1995)<sup>30</sup>, Gross and Fricke (1995)<sup>31</sup>, and Hanzawa *et al.* (2002)<sup>32</sup> discussed the thermal behavior of carbon aero-gels during its preparation.

Reichenauer *et al.* (1998)<sup>33</sup> and Saliger *et al.* (2000)<sup>34</sup> conducted investigations concerning the micro-porosity of carbon aero-gels. Reichenauer *et al.* (1998)<sup>33</sup> concluded that higher pyrolysis temperatures trigger formation and growth of ‘encapsulated’ micro-pores like those present in glassy carbon. Saliger *et al.* (2000)<sup>34</sup> observed in their experiments that a large amount of micro-porosity that is hidden in carbon aero-gels could be made accessible by activation methods without loss of monolithicity. Tamon *et al.* (1998)<sup>35</sup> studied the meso-porous structure of organic and carbon aero-gels and concluded that meso-pore radius of the RF can be controlled in the range of 2.5-9.2 nm by changing the mole ratio of resorcinol to  $\text{Na}_2\text{CO}_3$  used as catalyst and the ratio of the of resorcinol to distilled water used as diluent. Shrinkage also plays a role in the control of the meso-pore radius. The pyrolysis temperature is also significant, as it increases, the meso-pore volume becomes small but the peak radius of pore size distribution is maintained. It was also noticed that with the increase in the pyrolysis temperature, ethane adsorption becomes larger than ethylene adsorption on the aero-gels. The carbon aero-gels prepared by pyrolysis at 1000 °C have the same adsorption characteristics of ethane and ethylene as activated carbons do.



**Fig. 1** Carbon aero-gel microstructure: transmission electron micrograph at 500, 000 X magnification.<sup>11</sup>

## CA and electrochemical applications

Carbon aerogels were the first electrically conductive aerogels. Their high electrical conductivity, high surface area and ultra-fine (nanometer) pore size make them an ideal choice for electrodes in super-capacitors and capacitive de-ionization (CDI) processes<sup>23</sup>. Wang *et al.* (2001)<sup>36</sup> studied the morphological effects on the electrical and electrochemical properties of carbon aerogels. Suitability of carbon aerogels for super-capacitors was explored by Fisher *et al.* (1997)<sup>37</sup>, Saliger *et al.* (1998)<sup>38</sup>, and Pekala *et al.* (1998)<sup>9</sup>. A super-capacitor is used for energy storage using voltage-induced separation of charge at the electrolyte/solid interface. CDI uses a similar principle as super-capacitors where a voltage is applied to the carbon electrodes acting as cathode and anode, which removes ionic impurities from a flowing aqueous stream. Jayson *et al.* (1987)<sup>4</sup> investigated electro-sorption of mercury (II) acetate onto activated charcoal cloth from aqueous solutions using shaking and flow through techniques. The flow-through method gave lower adsorption results due to a decrease in concentration gradient and the limitation of film diffusion. Jayson *et al.* applied the electrical potential to activated carbon cloth and demonstrated an increase in the uptake of the mercury (II). Total capacity of electro-sorption depends mainly upon two factors; the first is the electrical double layer capacity due to the electrostatic attraction force between the ions and electrode. This is affected chiefly by the concentration of the ions in solution and the applied voltage. The other factor is the pseudo-capacity due to faradic reactions, which depend on the chemical characteristics of the solute and the functional groups on the electrode surface<sup>12</sup>. Yang *et al.* (2001)<sup>10</sup> proposed a model to understand the electro-sorption mechanisms on the carbon aerogels from a microscopic view in order to describe total ion capacity. This model predicts electro-sorption of ions from aqueous solutions by carbon aerogel electrodes. Because of the porous nature of the electrodes, the total capacity of the systems was obtained by summing the contributions of the individual pores. When a pore has a width smaller than a specific value (cutoff pore width), it does not contribute to the total capacity because of the electrical double-layer overlapping effect and this effect greatly reduces the electro-sorption capacity for electrodes with significant numbers of micro-pores. The cutoff pore width was found to decrease with increasing ion solution concentration and applied voltage. Traditional approaches consider that the total surface area of the material is available for the electro-sorption, while Ying *et al.* (2001)<sup>10</sup> showed that pore size distribution of the material should also be considered. Therefore, integrating the capacity in each pore over the pore size distribution rather than using the total surface area should calculate total capacity.

Flow through electrode model: From past research<sup>39-43</sup> it has been shown that flow-through porous electrodes can remove heavy metals from dilute streams, and direct comparison with other electrode systems (fluidized bed electrodes and parallel plate electrodes) show that flow-through porous electrodes can perform better. Trainham and Newman (1977)<sup>44</sup> emphasized that more sophisticated models are required to help design better flow-through porous electrodes so that they can compete with other processes (e.g., foam fractionation, ion exchange, precipitation, and cementation). Trainham and Newman developed a one-dimensional model for flow-through porous electrodes operating above and below the limiting current of a metal deposition reaction. The model assumes that there is one primary reactant species in an excess of supporting electrolyte, and that a simultaneous side reaction may occur. Ohmic mass-transfer and heterogeneous

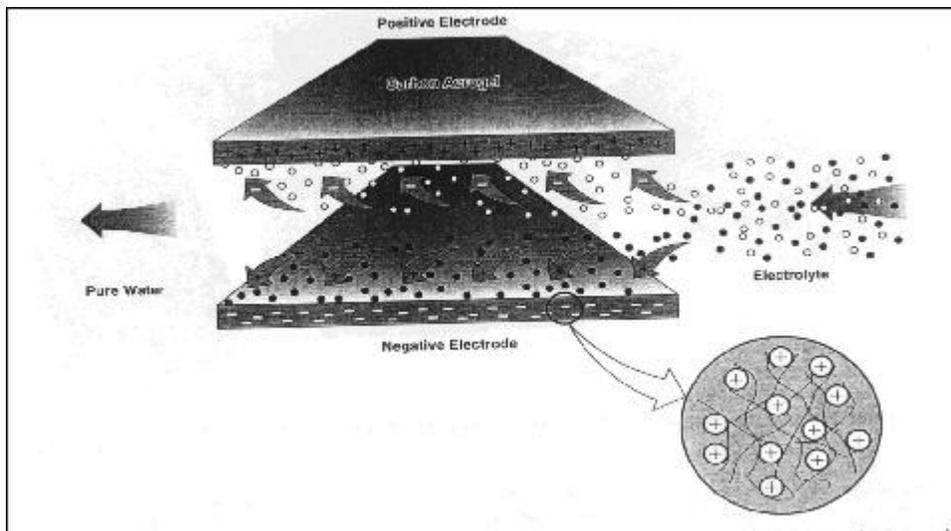
kinetic limitations were considered to predict a non-uniform reaction rate. According to Trainham and Newman (1977)<sup>44</sup>, the metal-ion removal from dilute streams using a flow-through porous electrode with parallel current and fluid can be described with the following restrictions:

- (i) The model is one dimensional;
- (ii) The porous cathode is of length  $L$  and has an isotropic porosity  $\epsilon$  and specific surface area 'a' which remains constant in time;
- (iii) The hydrodynamics are characterized by superficial velocity  $v$  and an average mass-transfer coefficient  $k_m$ , where axial diffusion and dispersion account for deviations from plug flow;
- (iv) There is one reactant species in excess supportive electrolyte;
- (v) A simultaneous side reaction may occur which is characterized by its rate at half-wave potential of the primary reaction. Also if the side reaction involves generation of a gas, it is assumed that the gas will remain in the solution so that the velocity profile will not be disturbed;
- (vi) The conductivity of the matrix and pore solution phases is uniform.

Assumptions i-iii simplify the calculation procedure, and are necessary due to the lack of a better description of the complex porous geometry. The validity of the assumptions iv-vi rests on a small reactant concentration. As a consequence of assumptions iv and v, the current efficiency should be high, which further simplifies the model by removing the need to follow any reactant species concentration, which participates in the side reaction. This approach emphasizes the salient features of the interaction between an unwanted side reaction and metal deposition reaction.” Analysis and numerical solutions have been carried out in related publications. Trainham and Newman observed satisfactory agreement between model predictions and experimental data on over-all reactor performance and deposit distributions.

### **Capacitive de-ionization technology**

CDI is the process of removing ions using capacitive adsorption. Ions are adsorbed onto the surface of the porous electrodes by applying electric field, producing de-ionized water as discussed before. However, the efficiency of CDI strongly depends upon the surface properties of the electrodes such as surface area and surface chemistry<sup>45,9</sup>. A number of publications and patents have appeared showing the use of porous electrodes for recovery of heavy metals from aqueous solutions<sup>27, 43, 44, 46-48</sup>. In these studies electro-sorption of metallic ions were observed on cathodes with relatively low surface areas.

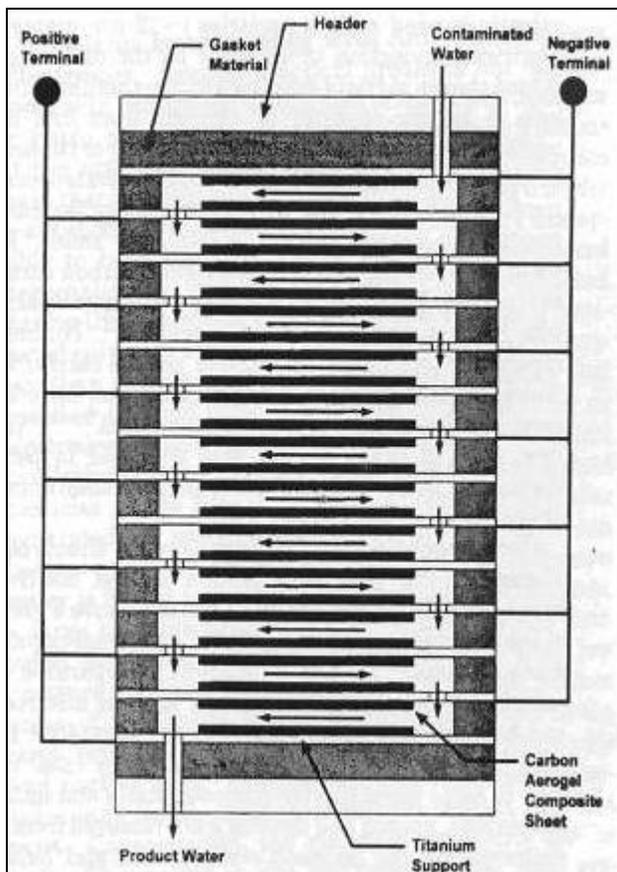


**Fig. 2** Schematic diagram illustrating the principle of capacitive deionization with carbon aero-gel electrodes. Cations and anions are held in the electric double layers formed at the cathode and anode, respectively. The high specific surface area of carbon aero-gel enables the process to remove a significant amount of dissolved ions from the water passing between the electrodes.<sup>6</sup>

The earliest studies on CDI were conducted at the University of Oklahoma in the early 1960's<sup>26</sup>. Johnson and Newman (1971)<sup>49</sup> conceived upon a comprehensive theoretical model for the capacitive charging of porous carbon electrodes, this analysis is still generally applicable to all CDI systems. Activated carbon was difficult to hold and form into thin conductive sheets for use as electrodes. Inert polymeric binders were used to hold the GAC particles together in thin sheets and this inert material was not helpful in the electro-sorption process. Durability of the electrodes was the main problem found in the research of Johnson and Newman. Between 1978 and 1983 CDI studies were conducted using carbon aerogels<sup>50, 13</sup>. Two separated electrodes were used in the form of a column and were able to reduce the concentration of NaCl and NaNO<sub>3</sub> by a factor of (1/100). Carbon aero-gels have been used successfully and efficiently for capacitive deionization of NaCl and NaNO<sub>3</sub> solutions<sup>5</sup>, NH<sub>4</sub>ClO<sub>4</sub> solutions<sup>6</sup>, electro-sorption of chromium ions as a means of treating ground water<sup>7</sup>, electro-sorption of inorganic salts from aqueous solution<sup>51</sup> and treating low-level radioactive waste and remediating contaminated ground water<sup>8</sup>. The basic principle of the capacitive de-ionization is illustrated in Fig. 2. A voltage is applied to the carbon aero-gel electrodes, acting as cathode and anode, removing ionic impurities from a flowing aqueous stream, as the ions tend to move to oppositely charged electrodes.

Farmer *et al.* (1996)<sup>5</sup> carried out experiments on NaCl and NaNO<sub>3</sub> solutions. The solutions were passed through stacks of carbon, high specific surface area (400 to 1100 m<sup>2</sup>/g), aero-gel electrodes as shown in Fig. 3. After electrode polarization, non-reducible and non-oxidizable ions were removed from the electrolyte by the imposed electric fields and held in the electric double layers formed at the surfaces of the electrodes. Experiments were conducted over a broad range of solution conductivity and cell voltage.

Conductivities ranged from 10 to 1000  $\mu\text{S}/\text{cm}$ , and voltage levels were 0.0, 0.4, 0.6, 0.7, 0.8, 1.0, and 1.2 V. Four liters of electrolyte was recycled continuously in batch mode experiments at a flow rate of 1.0 liter/min. Single-pass experiments were conducted pumping 20 liters of electrolyte through the electrode stack at a flow of 25 ml/min and there was no recycle of electrolyte. The ability of the electrodes to remove ions from water had a strong dependence on cell voltage. 1.2 V gave best results and at 0.4 V performance was relatively poor. 95% of the salt in a 100  $\mu\text{S}/\text{cm}$  feed stream was removed until saturation of the carbon aero-gel electrodes was reached. After operating for months a loss of 6 to 8 % of electrode capacity was observed. Rejuvenation of aged electrodes was done by voltage reversal. It was concluded that voltage reversal drives chemically bound ions from the surface of the carbon aero-gel by imposing significant repulsive electrostatic force. Rejuvenation was used to increase the electro-sorption capacity of aged electrodes back to initial levels (approximately 80% to above 95%).



**Fig. 3** Schematic representation of an electrochemical cell similar to that used for experiments with 12 double-sided electrodes<sup>7</sup>

Farmer *et al.* (1996)<sup>6</sup> treated  $\text{NH}_4\text{ClO}_4$  solutions following same procedure as described above in their  $\text{NaCl}$  and  $\text{NaNO}_3$  experiments. The best salt removal voltage was found to

be 1.2 V. For the single-pass experiments, 384 electrodes pairs were used in the system. 95% of the salt in a 100  $\mu\text{S}/\text{cm}$  feed stream was removed until saturation of the carbon aero-gel electrodes was reached. The capacity of the carbon aero-gel anode to electro-sorb ( $\text{ClO}_4^-$ ) was found to be small, compared to the capacity of these electrodes to electro-sorb  $\text{Cl}^-$  ions. This was also true in case of  $\text{NO}_3^-$  ions. This would indicate some preference for smaller size ions in the aero-gel system.

Framer *et al.* (1997)<sup>7</sup> examined the treatment of groundwater, contaminated with Cr (VI). During a feasibility study, it was observed that the level of hexavalent chromium in the groundwater could be lowered from 35 to 2 ppb, which is well below the acceptable level of 11 ppb. A field test was also carried out successfully, in which three stacks of 48 double-sided carbon aero-gel electrodes were polarized at 1.2 V and used to continuously remove Cr (VI) and Cr (III) from raw untreated ground water. It was seen that electro-sorption of chromium was favored over other anions at the part per million level. The selectivity of chromium ions over these other ions was great; chromium was removed in the presence of 530 ppm of TDS.

Gabelich *et al.* (2002)<sup>11</sup> carried out extensive studies on the removal of various cations and anions by carbon aero-gels. Gabelich *et al.* determined that the effects of ion charge, ion size, and ion mass on electro-sorption capacity were the main variables from several series of experiments containing one or more representative ions of the varying properties.  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Rb}^+$  cations and  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$  anions were selected as they can be found in natural water and are readily available as reagents. Experiments were carried out with 0.005 M solutions in a single-pass manner using CDI stacks as discussed before. The run time for these tests was 10 min at 1.4 V. No poisoning, scaling, or electrode degradation under these operating conditions was observed, even after 36 experiments. Percent removal for sodium and potassium were high as compared to calcium and magnesium, and a similar pattern was observed in the case of anions also. Percent removal of chloride was highest and removal of nitrates and  $\text{SiO}_2$  was very low, while removal of sulfate was satisfactory.

### **Regeneration of CA electrodes**

As stated elsewhere in this proposal, the regeneration process of saturated CA electrodes can occur via several methods. The basic technique is to simply back wash the cell with clean water. However backwashing normally requires equal or more water for regeneration than the clean water produced, so additional techniques in combination of backwash are required.

Gabelich *et al.* (2000)<sup>11</sup> applied short circuiting of the electrodes while recycling back the original test water. The regeneration was carried out for approximately 20 min. After each experiment the CDI unit was flushed with deionized water. Information about the amount of water required for regeneration was not given.

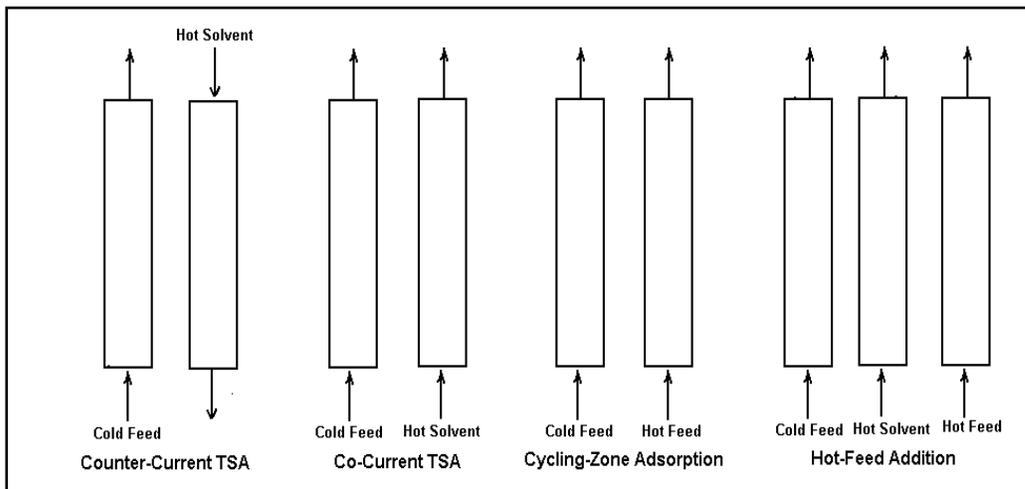
Farmer *et al.* (1996)<sup>5</sup> also short circuited the electrodes so that accumulated charge can be discharged and so can attracted ions and thus regeneration process but the regeneration period was 32 min. However they failed to mention the water required for this step. Farmer *et al.* carried out another experiment<sup>6</sup>, this time with  $\text{NH}_4\text{ClO}_4$  solutions where

regeneration was complete after 30 min. However they again did not mention the quantity of water used in the regeneration process.

Ryoo and Seo (2003)<sup>1</sup> improved capacitive deionization function of activated carbon cloth (ACC) by titania modification. Ryoo and Seo (2003)<sup>1</sup>, in their experiments with ACC electrodes, noticed decrease in concentration of electrolyte (NaCl) due to adsorption either physically or electrically. ACC is composed of activated carbon fiber thus has large surface area and many charging sites, ions are adsorbed on it, this is physical adsorption, apply electrical field to ACC and more ions are adsorbed, it is now electric potential adsorption. Ions adsorbed during electric potential adsorption are easily desorbed when either electric field is taken off or electrodes are discharged. Ryoo and Seo (2003)<sup>1</sup> found that a large electric potential is effective for regeneration step while large physical adsorption reduces the efficiency of regeneration process.

Ayranci and Conway (2001)<sup>3</sup> did system evaluation for water purification using adsorption and electrosorption at high-area carbon-felt electrodes and discovered that partial desorption was achieved by discharging the electrodes. They suggested flushing the system by hot water, as desorption is expected to increase with temperature.

Natrajan and Wankat (2003)<sup>52</sup> carried out experiments for concentrating dilute solutions using adsorption on activated carbon followed by partial thermal regeneration. After studying existing processes (as shown in the figure 4) for adsorption and desorption; they proposed a new process “Hot-Feed Addition” (HFA), a combination of the principles of co-current Thermal-Swing Adsorption (TSA) and Cycling Zone Adsorption (CZA). HFA is a co-current process, which cycles between cold feed, hot solvent and hot feed. TSA, CZA and HFA are illustrated in the figure below. The possibility of the successful use of HFA is to be explored in the regeneration of the CA electrodes.



**Fig. 4** Adsorption processes as discussed by Natrajan and Wankat (2003)<sup>52</sup>

Koresh and Soffer(1977)<sup>28</sup> studied double layer capacitance of ultramicroporous carbon electrodes and concluded that the “mobility of ions into ultra-micro-pores of carbon electrodes is several orders of magnitude smaller than in the free solution outside the pores”.

Kramer *et al.* (2005)<sup>53</sup> conducted an evaluation of carbon aerogel aquacell of Capacitive Deionization Technology Systems, Inc., for desalination using capacitive deionization and concluded that successful regeneration can be carried out for low TDS values but the amount of water used for regeneration was more than the amount of clean water produced. Deterioration of CA was also noticed during experiments in the cells prepared by CDT, Inc. It was also concluded that due to short circuiting of water flow utilization of total CA was not achieved.

Carbon aero-gels can be very useful in the purification of water, as there is very little loss of the aero-gel material during regeneration. There is no large power requirement for operating CDI units. Carbon aero-gels are better candidates for electrodes when compared to loosely bound activated carbons.

Basic information for studying electro-sorption of metals and other impurities are available and can be used in experiments for complex systems and to explore the possibility of using this system for wastewater of higher strength. Systems should have ionic selectivity, depending upon the size, charge, and complexation of the ions being separated. Initial parametric studies have not provided sufficient data to establish the performance of the electrodes over extended periods of times.

However, it must be noted that very little work, if any, has been documented on the regeneration of the aero-gels and the proper methods of operation in order to maximize the quantity of clean water produced. Model of regeneration behavior of carbon aero-gel electrodes is not available and is one of the objectives of this proposal. Further, none of the literature mentioned any cost estimates for the CDI technology. The focus of this study is going to be regeneration of saturated carbon aero-gel electrodes with minimal use of water. This study also focuses on modeling of this regeneration behavior.

## **2.0 Research Objectives**

The goal of this study is to obtain fundamental information about the desorption behavior of adsorbed metal ions on CA electrodes and determine suitable conditions for efficient regeneration of CA electrodes.

### **Objective 1 - Establish effect of concentration gradient on desorption**

Concentration gradient is to be increased by increasing flow velocity of flush water and by sonication under flow and non flow conditions. This will favor diffusion from CA surface and thus desorption. Effect of flow rate of water on desorption will help determine optimal flow rate conditions for efficient regeneration. This will also be studied in combination of some other test conditions such as HFA, shorting of electrodes and by reversing polarity of the electrodes to explore the cumulative effects on desorption.

## **Objective 2 - Study effect of physical size of ions on desorption**

As explained earlier if ions are to get out of pores their individual size becomes important. Small ions will be desorbed from these micro pores easily as compared to larger ions. Results from this study would establish desorption behavior of CA as a function of physical ion size. This will help understand the suitability of CDT in the treatment of water with various ions.

## **Objective 3 - Examine the effect of multivalent and monovalent ions on desorption**

Effect of individual charge of ions will be examined during regeneration of CA electrodes.

## **Objective 4 - Study effect of pore size of CA electrodes on desorption**

Since ions get adsorbed on numerous charging sites on the surface and in micropores of CA, during regeneration process these trapped ions are needed to be freed. Small pore size and greater large surface area means pores have small opening while having comparatively large surface area and this would create problem during desorption as ions will not be able to get out that easily. The larger the pore size will favor more desorption. How variation in ion size and type affect desorption process will be studied and this will help to elucidate desorption as a diffusion limited process.

## **Objective 5 – Effect of CA thickness on adsorption and desorption**

CA thickness is to be varied and effect of variation of thickness would be studied on desorption process.

## **Objective 6 - Examine the thermal effect on desorption of ion from CA electrodes**

General thermal properties of desorption indicate rise in temperature increases desorption and this property would be used here to enhance the regeneration of CA electrodes. Behavior of CA is to be examined in HFA process. Effect of temperature of feed water on desorption would be the outcome of this phase.

## **Objective 7 - Modeling the desorption behavior of CA**

Based on results of all experiments for desorption of CA, modeling of desorption will be the final step. In this step existing models will be unified and/or modified to represent this study as a surface-pore-diffusion model.

## **3.0 Materials/Methodology**

### **Chemicals**

All chemicals will be analytical grade and used without further purification. Solutions will be prepared with deionized (17.8 MΩ-cm) water. Plastic volumetric flasks and vessels will be cleaned with 1 % HNO<sub>3</sub> or 1 % HCl and rinsed several times with

deionized (DI) water before use. All tubing and pumps will be cleaned with DI water. Gabelich *et al.*<sup>11</sup> carried out their studies using certified ACS-grade potassium chloride, potassium bromide, rubidium chloride, rubidium bromide magnesium sulfate, magnesium bromide, sodium nitrate and potassium nitrate, this study will use the same chemicals for the desorption studies. In addition to these chemicals, sodium chloride will also be used.

### **Adsorption on CA**

CA sheets will be immersed in water with varying TDS for saturation at different periods of time so that ions are adsorbed on CA surface this is physical adsorption and then adsorption would be carried out applying some potential across electrodes, this will help in electrical field adsorption as explained by Ryoo and Seo (2003)<sup>1</sup>. Effect of structural properties of CA and chemical properties of the ions will not be studied as it is well documented<sup>5-9, 12-14</sup>, desorption process would be the next step and is the focus of this study.

### **Desorption Process**

The desorption process will be studied for the effect of charge, effect of mass and effect of radius of ions along with flow rate across electrodes and voltage applied to CA electrodes. CA pyrolyzed at two different temperatures and of two different densities would be used for the evaluation of the effect of CA structural properties on desorption process. Effect of structural properties on desorption process will be evaluated. A combination of the different thickness and density will be used for this purpose. This will give an opportunity to evaluate the effect of variation of pore size of CA on the desorption process.

### **Analytical Methods**

The main parameter would be conductivity of the water and it would be monitored constantly using a Corning conductivity meter coupled to a computer using serial port connection and data acquisition software (TAL technologies Inc.). Samples would be taken at regular time intervals and would be analyzed for ion content. Atomic adsorption spectroscopy (method 3500) would be used for cations and ion chromatography (method 4500) would be used for anions.

## **4.0 Results and Conclusions**

Experiments are still being carried out and once the study is completed, results will be shared with Texas A&M University and Texas Water Research Institute.

### **Acknowledgements**

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