

Investigation of Saline and Brackish Waters Desalination by Carbon Aerogel Technology

M. R. Massoudinejad¹, E. Aghayani¹, K. Arman², F. Gohari¹ and H. Mohamadi^{1*}

¹Department of Environmental Health Engineering, School of Public Health, Shahid Beheshti University of Medical Sciences, Tehran, Iran.

²Department of Environmental Engineering, School of Agricultural Engineering, Payame Noor University, Tehran, Iran

Received: December 5 2013

Accepted: December 31 2013

ABSTRACT

The Capacitive Deionization Technology (CDI) with carbon aerogel is a new process to remove salt from saline and brackish waters. Carbon aerogel is type of organic carbon, which your unique porous structure is suitable for desalinating. Low potential for clogging, production low wastewater, electrostatic regeneration aerogels and consequently no need to be acid, including the benefits of this technology. In this regard, the first polymerization resorcinol compounds and formaldehyde in the air pressure and the pyrolysis compounds obtained, Will attempt to create carbon aerogel pages. By manufacturing device in the pilot-scale, the effect of different parameters includes the input of NaCl concentration, electric current, flow, distance between electrodes and pH, on NaCl absorption by aerogel carbon electrodes was investigated. Absorption rate by increasing flow and NaCl concentration in the input flow were increases more and increasing the distance between the electrodes, Flow and pH decrease the amount of absorption rate. Results in optimal conditions, Shows the absorption rate 1.43×10^{-4} moles of NaCl Per gram of was by carbon aerogel that suggests this method is appropriate and cost-effectiveness.

KEY WORDS; Saline water, Capacitive Deionization, Carbon Aerogel, Absorption, Desalination

1. INTRODUCTION

Our need for fresh water is ever increasing and the present fresh water resources can't satisfy our needs. At present, by ever-increasing population and cities development, water can't be accessible as the natural purified water with low expense and easily [2]. Today, using of drinking water for industrial and agricultural applications will face humans with water shortage crisis in the near future [1]. Simultaneous with population's increase and fresh water resources' decrease or drought ..., using of unusual water resources such as wastewater, salty water and sea water have been increased all over the world [3]. In the southern area and weather conditions, lack of permanent or semi- constant surface flows, a few flows can penetrate to the underground reservoirs [20].

In these areas, there are many barriers for using of the fresh water in the modern agriculture especially for species plants, do accessing.

Investment and exploitation's expenses for the present desalination method are very high, and so far there isn't any technology with about 65% recycles output for sea water. In other sides, the lowest expense of energy is linked to fossil fuels and then electricity which comes from thermal power plants, but these energy resources will diffuse pollutants such as NO_x, SO₂, volatile compounds (VOCs) and etc. in the process of desalination. Therefore, use of the new desalination methods with less energy expense is very important [2]. In our country (IRAN), for water desalination, several processes such as Multi-Stage Flash (MSF), Reverse Osmosis (RO) and Multi-Effect Distillation (MED) process types and from production capacity aspect; Ro, MSF and MED are placed in the first to the third ranks, respectively [10]. The problem of evaporation processes (MSF and MED), not only is high energy expense but is high precipitation and corrosion, which they can be controlled by an experienced operator group [4]. In RO and Electro Dialysis (ED) methods, very large expenses of investment in one side and their limitations for sea water desalination in other side have restricted their applications. Development in new water desalination methods for producing fresh water from salty waters and reducing its expenses and using of the nuclear energy is one of the main alternatives against the world water challenges in the 21st century [10]. Today, the membrane technologies and ion-exchange resin are the most widespread methods for water desalination [11]. Disadvantages of the membrane processes includes: complexity in the membrane processes, high volume of the produced salty wastewater during its exploitation, the membrane's high susceptibility, its blockage and its low flexibility against the water quality and temperature changes [22]. Disadvantages of ion-exchange resin include: 1) Using of hydrochloric acid (HCL) and sulfuric acid (H₂SO₄) for resin regeneration process. 2) Production of salty water in high volumes and 3) Necessity to wastewater injection discharges to the safety wells [9, 11]. There for, new desalination technologies, in addition to increasing more fresh water, should be able to overcome these limitations [22]. Using of Capacitive Deionization (CDI) technology with carbon aerogel electrodes is one of these methods. Carbon aerogel which is the most common material in CDI technology is an organic aerogel that is suitable for desalination due to its unique porous structure [18]. The first studies published on capacitive deionization appeared around 1966. Caudle et al. used porous flow-through electrodes made of activated carbon powder to desalinate water [5, 17]. Johnson et al. conducted similar studies of reversible electro sorption, or capacitive deionization, and published their work in 1970 [13, 14]. Their experimental program included verification of the theoretical basis for the process, parametric studies, and evaluation of a variety of candidate electrode materials. Johnson's work prompted Newman to develop a comprehensive theoretical model for the capacitive charging of porous carbon electrodes [12]. Capacitive Deionization (CDI) technology using carbon aerogel electrodes is a new process for saline and brackish waters desalination and has many advantages over other desalination's methods. The low

blockage and precipitation potential, easier usage conditions, low wastewater, aerogel electrostatic regeneration and having no need to acid and low energy consumption are these advantages^[8, 21]. Carbon aerogel is an ideal and suitable material for ions electrochemical adsorption due to its consolidated structure, high Electrical Conductivity (EC) (10-100siemens/cm) high specific surface (400–1200 m²/g), porousness size distribution and its controllability^[7, 23].

In this study, feasibility to make carbon aerogel in order to remove salinity generating factors from saline and brackish waters has been considered. Also, it aims to study the main bilateral and separate parameters' effect such as PH, the primal concentration of salinity factors and the electric current to increase removal efficiency.

2. MATERIALS AND METHODS

For saline and brackish waters desalination with carbon aerogel technology in experimental pilot scale, at first carbon aerogel electrodes should be made. To make carbon aerogel extensively, some phenol materials such as polyhydroxy-benzenes (preferably di- and trihydroxy benzene) which is better to be resorcinol (C₆H₄(OH)₂) (1, 3-dihydroxy benzene) should be mixed with one catechol (1,2-dihydroxybenzene) materials; hydroquinone, phloroglucinol and preferably formaldehyde (HCHO) in the presence of a basic catalyst for forming gel organizer polymer. In this research, carbon aerogel electrodes made by polymerization and pyrolysis of resorcinol and formaldehyde compounds mixture. Poly condensation of resorcinol with formaldehyde in alkaline conditions produces polymers which are connected to each other as a cluster and formed a network, so, reaction of sodium carbonate (Na₂CO₃) as a catalyst^[19]. These obtained mixtures which were gel and yellow colored, poured in 20 °C glass vials; because during reaction, gels should be avoided from oxygen. Glass vials were placed in the room temperature about 24h, in the temperature of 50 °C for 24h and in 90 °C for 24h^[16]. Some large capillaries may be created in gel which they are due to gaps or wrinkles by solvent evaporation. Therefore, solvent shouldn't be separated by evaporation method. In some cases, supercritical drying may be used by CO₂, but this method is very expensive and dangerous due to its high temperature and pressure. Solvent change is another aerogel drying method by acetone and cyclohexane (C₆H₁₂) which was used in this research. By using of gel drying method without evaporation, the main morphology of gel can be preserved. The color of aerogels in this stage in form light red to dark red. In the next stage which is pyrolysis, aerogel were carbonized and black carbonic foams with less density and 0.1 μm porous were made. X-Ray Diffract meter (XRD) method was used to determine specific surface, pores size and vents settlement model synthesized carbon aerogels. The next step was making of carbon aerogel electrodes. These electrodes were made by sticking carbon aerogel sheets or granules to both sides of titanium which it not only is an electrical conductor but a structural protector. Stick materials were made by mixing the flexible resins (epoxy CY 230) with graphite micro particles in order to increase specific conduction of conductivity amount with 1 to 10 ratios (graphite / epoxy). Researchers in some experiments used epoxy with 5% carbon particles or silver epoxy^[6]. This research used silver epoxy. A thin layer of silver epoxy was placed on titanium sheets, and then carbon aerogel granules were glued on them slowly.

Using this method, the saline factors removal process is very simple, so that after creating a current between two near carbon aerogel electrodes, their cations and anions were attracted to cathode and anode respectively.

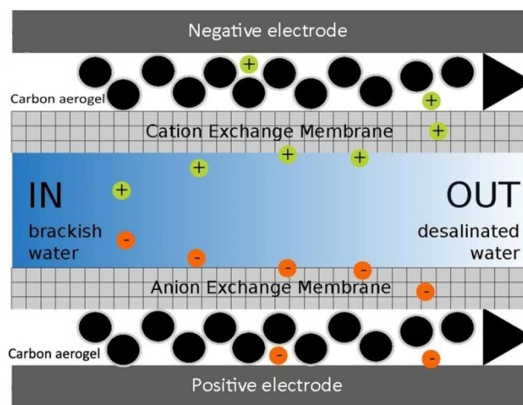


Fig. 1 Carbon Aerogel CDI Process

The basic principle of the capacitive deionization is illustrated in Fig. 1, that it is schematic diagram of this technology 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 carbon aerogel enables the process to remove a significant amount of dissolved ions from the water passing between the electrodes.

Totally, a collection of carbon aerogel sheets along with metal sheets were placed in a container which is called cell. When this cell was made, carbon aerogels were separated by glass or plastic which were un-conductive materials to prevent from direct connection between them. In this system, about the half of carbon aerogel sheets play as cathode and other half as anode. Synthetic samples of saline and brackish waters were passed through these electrodes spirally, and anions were attracted to anode and cations were attracted to cathode. The flow was batch type. The electrical conductivity of feeding storage was measured continually. Feeding storage electrical conductivity was measured continuously. Constant number showed that carbon aerogel electrodes were saturated. The maximal carbon aerogel absorption capacity was determined by mass balance of absorbed salt with amount of used aerogel, in cell. The effect of Concentration, pH, Current intensity, Flow rate and distance between each pair of carbon-aerogel sheets on electro sorption of CDI was examined using the pilot-scale testing unit treating synthetic sodium chloride solutions.

By different voltages and pHs and change in electrodes distance, effects of these parameters on system efficiency were considered in the different concentration of saline and brackish waters. The effect of each variable on removal efficiency was measured by changing one parameter and keeping other parameter as constant. Therefore, by comparing the salinity of the input and output waters and computing system's efficiency in all conditions, the best voltage and distance between the electrodes for accessing to high efficiency were determined. In practice, carbon aerogel regeneration was performed by revers current or interruption in current about 15-30 minutes, so this cycle was restarted.

3. RESULTS AND DISCUSSION

In this Study, carbon aerogel was used to make fresh water from saline waters and several effective parameters on this process were considered by one factor in time method, so, the best conditions for making fresh water and NaCl removal from were determined. The main and effective factors on capacitive deionization which were studied by carbon aerogel, include, input concentration, electric current, pH, flow and distance between electrodes.

In order to surface analysis and pores diameter measurement, T- plot, BJH (Barrett, Joyner) and BET (Brunauer, Emmett, Teller) methods were used. The carbon aerogel surface analysis results by BET method showed that the surface is $677.8 \text{ m}^2/\text{gr}$ and results of carbon aerogel surface analysis by BJH and T-plot methods showed that the pore's diameter is between 1-80 nm. The pores volume according to BJH method was 0.4 cc/gr . Figures have provided as follows:

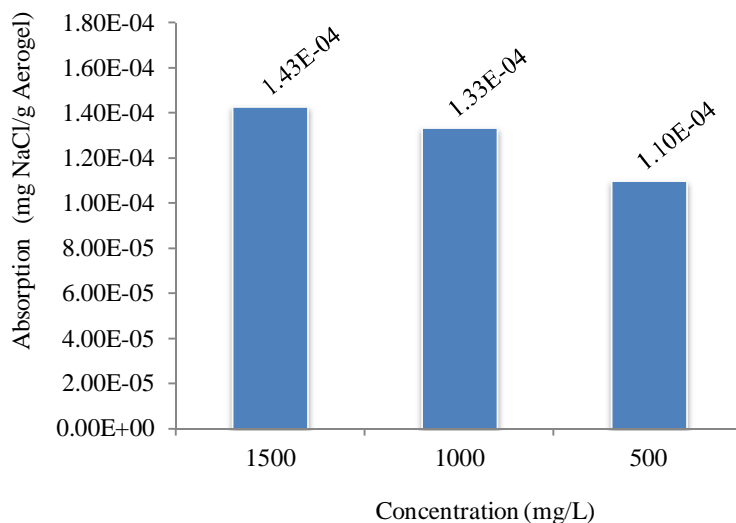


Fig. 2 Inlet NaCl concentration on the absorption capacity of carbon aerogel electrodes (D=0.5cm, Q=50ml/min, I=1.5Amp, pH=5.7)

The effect of inlet NaCl concentration on the absorption capacity of carbon aerogel electrodes illustrate in Fig. 2. This study showed that increasing electrolytes concentration could reduce electrical double layer thickness, and consequently, improve electrical capacity of the carbon aerogel.

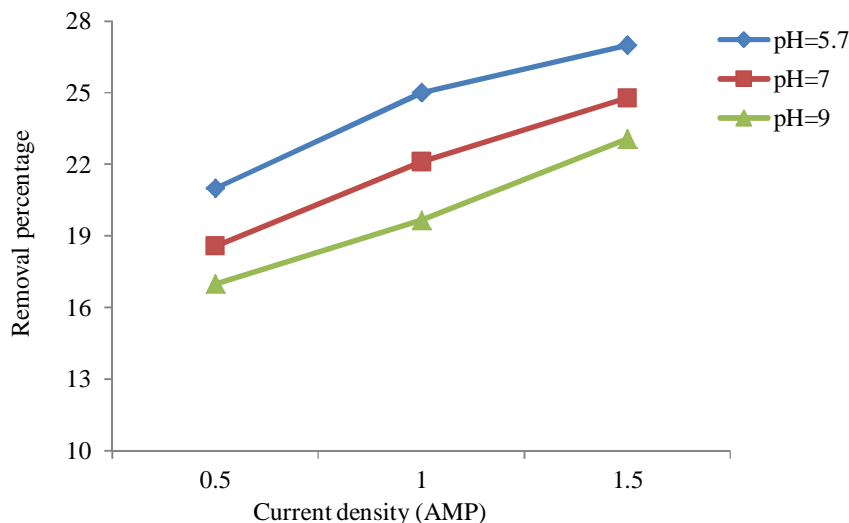


Fig. 3 Removal percentage of NaCl at different electric current and pH (Cs=500mg/L, D=0.5cm, Q=50ml/min)

Fig. 3 illustrates the effect of electric current and pH on the desalination efficiency at constant concentration, flow rate and distance between each pair of carbon-aerogel sheets. As is shown in Fig. 3, desalination efficiency increases as the current increases and pH decreases.

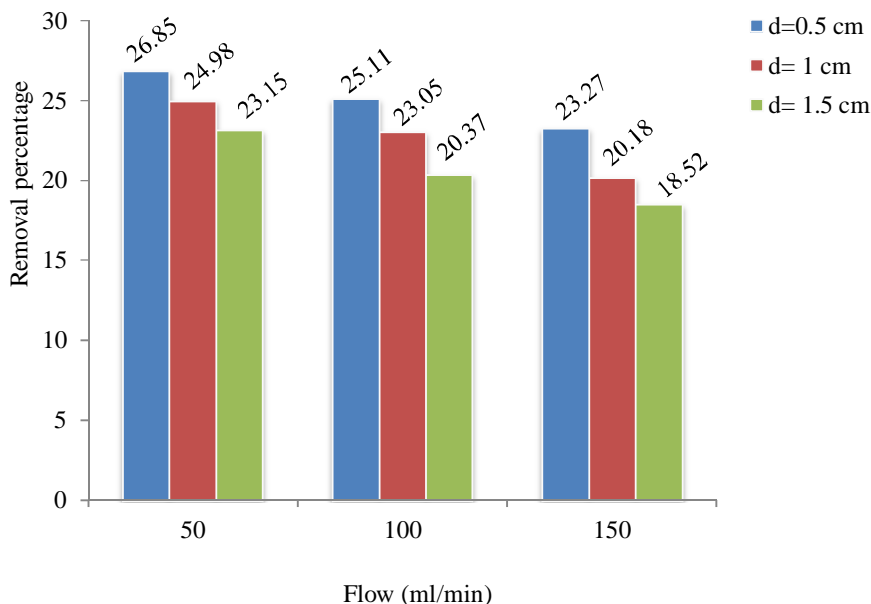


Fig. 4 Removal percentage of NaCl at different flows and distance between electrodes (Cs=500mg/L, pH=5.7, I=1.5Amp)

Fig. 4 shows the removal percentage of NaCl at different flows and distance between electrodes at constant concentration, pH and current intensity. Increasing in feed flow rate and distance between electrodes decreased the performance of electrodes electrosorption.

In this study, one of the modern methods for making fresh water was considered. The Capacitive Deionization Technology (CDI) to remove salt from saline and brackish waters is a new process in compared with other processes such as reverse osmosis (RO), electro dialyze (ED) and ion-exchange resin^[20]. Experiments in pilot scale showed that CDI by using of synthesized carbon aerogel electrodes in fresh air pressure conditions can remove NaCl from saline and brackish waters. In this present research, carbon aerogels which were synthesized in fresh air pressure conditions, were used to remove NaCl ions. As Figure 2 has shown, by increasing NaCl concentration, the amount of carbon aerogel electrode absorption increases, so that in the concentration of 1500mg/l, the amount of absorption was 1.43×10^{-4} mole of NaCl pergram of carbon aerogel. This amount is comparable with absorption amount in Jung et al. researches, in which the amount of absorption for capacitive deionization mono-cell system was 1.2×10^{-4} mole NaCl/gr Aerogel, and for multi-cell system was 2.1×10^{-4} mole NaCl/gr Aerogel^[15].

The relationship between NaCl concentration and its absorption by carbon aerogel electrodes in the level of significant $p \leq 0.01$ has Pearson correlation coefficient equal to ($r=0.81$), and this justify that by increasing salt (NaCl) concentration, the amount of absorption has increased. The ability of electrodes with carbon aerogel granules and their absorption capacity in order to remove ions from water is completely related to electric current. As figure 3 show, by increasing input electric current to system, NaCl removal efficiency is increased. Statistical analysis shows that there is a significant correlation between electric current and the amount of NaCl absorption for each gram of aerogel ($p \leq 0.01$). In other side, as Figure 4 has shown by decreasing the distance between electrodes, absorption efficiency is increasing due to more potential differences between electrodes and more electrical double layers formation. For flow, statistical analysis shows that there is a significant correlation between NaCl concentration and NaCl removal efficiency in $p \leq 0.01$. The best results were obtained in 50ml/min flow, and this show that in less flow, electrodes have more times for ion absorption. The relationship between flow and absorption efficiency is provided in figure 4. Because electrical absorption process is reversible, by reversing or cutting of the current, ions are released rapidly. Therefore, electrodes can be regenerated and be used more and more.

4. CONCLUSION

In this Study capacitive deionization technology (CDI) with carbon aerogels was used to make fresh water from saline waters and several effective parameters on this process were considered by one factor in time method, so the best conditions for NaCl removal from were determined. In this study carbon aerogels which were synthesized in fresh air pressure conditions, were used.

By increasing NaCl concentration the amount of carbon aerogel electrode absorption increases, so that in the concentration of 1500mg/l, the amount of absorption was 1.43×10^{-4} mol NaCl/gr carbon aerogel. The ability of electrodes with carbon aerogel and their absorption capacity in order to remove ions from water is completely related to electric current. By increasing input electric current to system, NaCl removal efficiency is increased. As expected, the best performance (salt removal) was achieved at 1.5 ampere. In other side, by decreasing the distance between electrodes, absorption efficiency is

increasing due to more potential differences between electrodes and more electrical double layers formation. For flow analysis shows that there is a significant correlation between NaCl concentration and NaCl removal efficiency. The best results were obtained in 50ml/min. According to the results obtained in this study, it appears that using of capacitive desalination technology (CDI) with Carbon Aerogel electrodes for NaCl removal from saline and brackish waters is a suitable method.

Acknowledgment

The authors declare that they have no conflicts of interest in the research.

REFERENCES

1. **Amidpur M, Zamen M, Sufari M. (2007).**Optimizing of energy consumption in HD solar desalination systems. *Sixth National Energy Congress*; Tehran, Iran.
2. **Arab F. (2005).** Desalination of water supply: past, Present and future. *Water and Environment Journal*.**64**:11-20.
3. **Benko KL, Drewes JE. (2008).**Produced water in the Western United States: geographical distribution, occurrence, and composition. *Environmental Engineering Science*.**25**(2):239-46.
4. **Binayi S. (2005).**Operating experience of desalination systems. *Water and Environment Journal*.**64**:29-32.
5. **Caudle, D. D., Tucker, J. H., Cooper, J. L., Arnold, B. B., Papastamataki,A. (1966).**Electrochemical Demineralization of Water with Carbon Electrodes. *Research Report, Oklahoma University Research Institute*. 205.
6. **Farmer J. (1996).**The use of carbon aerogel electrode for environmental cleanup. *USA: DTIC; Report No.:LLNL654*.
7. **Farmer JC, Fix DV, Mack GV, Pekala RW, Poco JF. (1996).**Capacitive Desalination of NaCl and NaNO₃ Solutions with Carbon Aerogel Electrodes. *Journal of the Electrochemical Society*.**143**:159-69.
8. **Farmer JC, Fix DV, Mack GV, Pekala RW, Poco JF. (1995).**Capacitive, desalination with carbon aerogel electrodes: Carbonate, sulfate, and phosphate: *Lawrence Livermore National Lab., CA (United States)*.
9. **Funston R, Ganesh R, Leong LYC, editors. (2002).** Evaluation of Technical and Economic Feasibility of Treating Oilfield Produced Water to Create a "New" Water Resource.
10. **Ghanadi M. (2005).**Urban and rural desalination systems in Iran and their Water quality. *Water and Environment Journal*.**64**:3- 10.
11. **IOGCC/ALL C. (2006).** A guide to practical management of produced water from on shore oil and gas operations in the United States. *A final report prepared for US Department of Energy. Tulsa, Oklahoma*.
12. **Johnson, A. M., (1973).**Electric Demineralizing Apparatus, U.S. Pat. No. 3,755,135.
13. **Johnson, A. M.; Venolia, A. W.; Newman, J., Wilbourne, R. G.; Wong, C. M.; Gillam, W. S., Johnson, S., Horowitz, R. H., (1970).**Electrosorb Process for Desalting Water, Office of Saline Water Research and Development Progress Report No. 516, U.S. Dept. Interior Pub. 200 056,31.
14. **Johnson, A. M., Venolia, A. W., Wilbourne, R. G., Newman, J., (1970).** The Electrosorb Process for Desalting Water, Marquardt Co., Van Nuys, CA, 36.
15. **Jung HH, Hwang SW, Hyun SH, Lee KH, Kim GT. (2007).**Capacitive desalination characteristics of nanostructured carbon aerogel electrodes synthesized via ambient drying desalination.**216**(1-3):377-85.
16. **Mayer ST, inventor. (1995).**Method of low pressure and/or evaporative drying of aerogel. *United State patentUS5420168*
17. **Murphy, G. W., Bloomfield, J. J., Smith, F. W., Neptune, W. E., Caudle, D.D. (1996).** Demineralization of Saline Water by Electrically-Induced Adsorption of Porous Carbon Electrodes, *Oklahoma University Research Institute*.
18. **Pekala R, Farmer J, Alviso C, Tran T, Mayer S, Miller J, et al. (1998).**Carbon aerogels for electrochemical applications. *Journal of non-crystalline solids*. **225**(1):74-80.
19. **Pekala RW, inventor. (1991).** Low density, resorcinol-formaldehyde aerogels. *United State patent US4997804*
20. **Taghavi M. (2005).**Water and water distribution in the Geshm of island. *Gheshm News Magazine*. 104.
21. **Xu P, Drewes JE, Heil D, Wang G. (2008).**Treatment of brackish produced water using carbon aerogel-based capacitive desalination technology. *Water research*.**42**:2605-17.
22. **Yang KL, Ying TY, Yiacoumi S, Tsouris C, Vittoratos ES. (2001).**Electrosorption of ions from aqueous solutions by carbon aerogel: An electrical double-layer model. *Langmuir*.**17**(6):1961-9.
23. **Ying TY, Yang KL, Yiacoumi S, Tsouris C. (2002).**Electrosorption of ions from aqueous solutions by nanostructured carbon aerogel. *Journal of colloid and interface science*.**250**(1):18-27.