

Acidified Activated Charcoal for Deionized Water through Capacitive Deionization Technology

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Abstract: Capacitive deionization (CDI) is a second-generation desalination process used to desalinate brackish water. It is an inexpensive and environmentally friendly method. A study was performed to examine the suitability of using acidified activated charcoal in CDI technology for the production of clean water. CDI electrochemical measurements of acidified activated charcoal revealed a high specific capacitance of 191.7 Fg^{-1} at 1 M compared to 160 Fg^{-1} at 0.1 M indicating an active potential for ion electrosorption at higher concentrations. The results of symmetries CDI cells prove that it is possible to significantly enhance the electrosorption performance of acidified activated charcoal during electrochemical desorption at 1.8 V (4.1 mg/g) using $100 \mu\text{S cm}^{-1}$.

Keywords: Desalination; Activated Charcoal; Capacitive deionization; Electrosorption.

1 Introduction

Capacitive deionization (CDI) is a promising technology for desalinating water by selecting unwanted dissolved salt ions. Comparatively to other technologies such as ion exchange resins [1], this type of desalination is low-cost and does not emit harmful chemicals into the environment. A CDI consists of two electrodes stacked up against each other and separated by a spacer to prevent short circuits. In this process, a direct current of less than 2 volts is used in an electrochemical mechanism, which reduces the amount of energy required compared to standard reverse osmosis. EDLCs are double-layer electrode capacitors (adsorption/desorption processes based on a dual-layer electrode design). Electrochemical cells produce EDLC when the oppositely charged electrodes are approached by an electric current. The ions in the solution repel the oppositely charged electrodes because of this electrochemical interaction [2-4]. In other words, the cations transfer to the cathode surface while the ions transfer to the anode surface. Inverting or removing the applied voltage between the two electrodes causes the adsorbed ions to leave the electrode surfaces toward the waste stream [3]. The electrode material is considered the main key to CDI performance. To achieve good desalination performance, certain properties of the electrode materials must be present, such as high specific surface area, electrical conductivity, stability, and good wettability [5,6]. Carbon materials are considered the most

important materials used in CDI due to their aforementioned properties [7-9]. Water was treated with activated charcoal to remove salt ions. The electrochemical properties of the activated charcoal electrode have been studied at different salt concentrations (0.1, 0.5, and 1 M NaCl). In addition, the activated charcoal electrode in the CDI cell was investigated at different salt concentrations (100, 200, and 300 $\mu\text{S/cm}$) and a potential of 0.8 V.

2 Materials and Methods

2.1 Materials

Charcoal activated Pharma Grade (acid wash, LOBACHeme) was used in this study. Polyvinylidene fluoride (PVDF), sodium chloride (NaCl), and dimethylformamide (DMF) were purchased from Sigma-Aldrich.

2.2 Electrochemical Characteristics of the Fabricated Nano Composites

The electrochemical study was investigated used conventional 3E cells. The CV analyses were conducted in a potential window range from -400 to 600 mV and different concentrations (0.1, 0.5, and 1M) of NaCl aqueous solutions. AC, Pt rode, and Ag/AgCl (3M KCl) electrodes were applied as working, counter, and reference electrodes, respectively. A frequency response analyzer (FRA) was exploited to

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accomplish EIS. The amplitude of the alternating voltage was 5 mV with a frequency range of 0.01-10 kHz. The specific capacitance (C_s , F/G) were calculated used the following equation:

$$C_s = \frac{\int I dV}{2 \nu m \Delta V} \quad (1)$$

Where C_s is the specific capacitance (Fg^{-1}), I is the response current (A), V is the potential (V), ν is the potential scan rate (V/s), and m is the mass of the electro-active materials in the electrode (g).

2.3 Electro sorptive Capacity Measurement

90 wt.% activated charcoal, 10 wt.% PVDF as a binder and DMF drops were mixed and sonicated for 10 min to form a homogenous paste. The homogenous paste was coated on two titanium sheets ($10 \times 10 \text{ cm}^2$). The cationic membrane electrode and the anionic membrane electrode were dried at 100°C for 24 h to remove the solvent. They were separated by a nylon cloth spacer. The stainless-steel current collector plates were connected to the DC power supply. An aqueous NaCl solution with an initial concentration of $\sim 48 \text{ mg/L}$ was pumped into the lab self-made CDI at a flow rate of 10 mL/min by a peristaltic pump. The CDI performance was determined at 0.8 V. Conductive meter was used to measure the change in the conductivity between influent and effluent aqueous NaCl solution (Hanna Instruments, HI-2300). The calibration curve was plotted to evaluate the concentration of the NaCl aqueous solution. Then the electrode electro sorption capacity (Sc , mg g^{-1}) was determined using the following equation:

$$Sc = \frac{(C_0 - C)V}{m} \quad (2)$$

Where V (L) is the total volume of NaCl solution, and m (g) is the total mass of the working electrodes.

3 Results and Discussions

The Scanning Electron Microscope (SEM) image of the pristine activated charcoal (Figure 1A and B) showed a rock-like shape with an irregular and heterogeneous surface morphology. Figure 2A exhibits the X-Ray Diffraction (XRD) analysis of activated charcoal. As shown in Figure 2, AC revealed two broad peaks positioned at 2θ values of 24.3° and 43.1° , which are in agreement with the (002) and (100) crystal planes of graphite, respectively (JCPDS card no. 41-1487). The broad diffraction peaks revealed a disordered amorphous structure of the activated charcoal. Raman spectroscopy is a tool to obtain structural information about the molecular vibration or rotational energy of the material. Furthermore, it is commonly used to describe the structural features of carbonaceous materials and oxide materials that display lattice disorder [10]. The Raman spectra of pristine activated charcoal are shown in figure 2B. Two spectrum peaks appeared at 1350 and 1595 cm^{-1} , which are denoted to the D-band and G-band, respectively [10].

These peaks are typically found in the spectra of carbon materials.

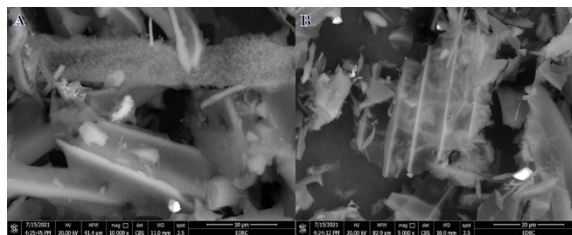


Fig. 1: SEM images of activated charcoal.

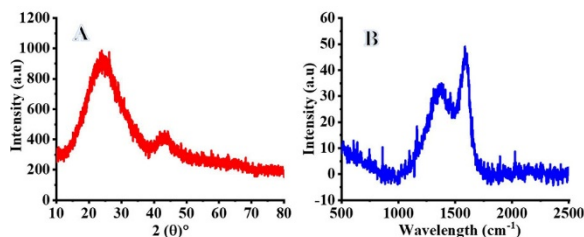


Fig. 2: XRD patterns of pristine activated charcoal (A) and Raman spectra of pristine activated charcoal (B).

3.1 Electrochemical Performance

CV tests are an effective tool to evaluate the CDI electro sorption performance and specific capacitance of the fabricated electrode for adsorption/desorption capacity. All CVs were measured in a potential window from -0.4 to 0.6 V vs. Ag/AgCl reference electrode. Figure 3A, C, and E show CV profiles of activated charcoal electrodes at different sweep rates in the presence of different concentrations (0.1, 0.5, and 1 M) of NaCl aqueous solution. As displayed in the figures, rectangular shape CV curves have a good symmetry in the current-potential window without faradic peaks at lower and higher scan rates were obtained. Therefore, the anions are more smitten on the surface of the activated charcoal electrode with formed an excellent EDL due to the columbic interaction. Furthermore, it was observed that the increase in current density of the activated charcoal, which demonstrates the fast and perfect reversible electro sorption charge-discharge process. It is also observed the high capacitance and good electrochemical performance; suggesting the high electro sorption capacity even in hard saturation. The electrochemical behavior of the electrodes is demonstrating low resistance, high capacitance, and excellent electrochemical performance of activated charcoal. The CV measurements for electrode material was studied at different scan rates ((10, 25, 50, 75, 100, 150, and 200) mVs^{-1}) and potential window range -0.4 to 0.6 V in the presence of different NaCl concentrations (0.1, 0.5, and 1M) (Figure 3A, C, and E), the same CV shapes have been obtained. The specific capacitance (C_s , Fg^{-1}) is considered an important phenomenon to evaluate the CDI character. As shown in Figures 3B, D, and F, the values for all

concentrations were determined from the integration area of CV cycles using equation (1) and plotted versus scan rates (Figure 3B, D, and F). As seen in the figure, the value of specific capacitance is increased with an increase in the salt concentration.

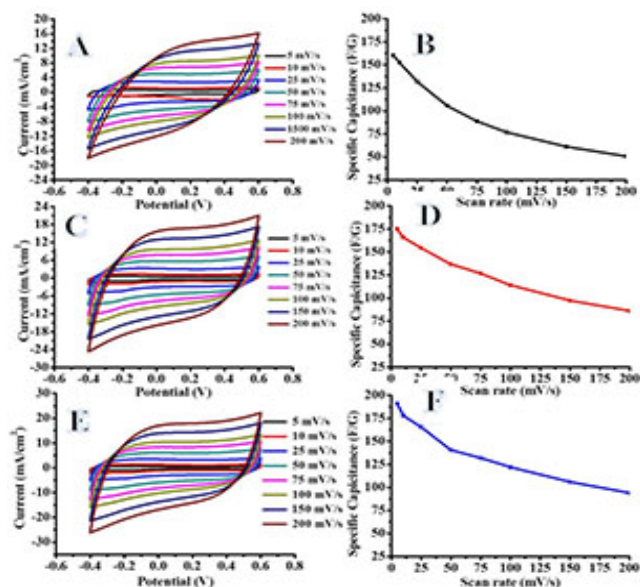


Fig. 3: CV profiles of the activated charcoal electrode at different scan rates in 0.1M (A), 0.5M (C), and 1M (E) and C_s for the activated charcoal.

EIS measurements are a tool to determine the performance of electrode materials in respect to the electrolyte solution and the electrode material charge transfer behavior at the electrode/electrolyte interface. Figure 4A display the Nyquist plots of the activated charcoal electrode in 1 M NaCl aqueous solution in the frequency range from 0.01 to 10 kHz with an AC perturbation of 5 mV. Generally, a defined semicircle appears in the high-frequency region for electrode materials. As we have known, a semicircle is closely related to the electron-transfer process, the electrical conductivity of the electrodes, and the solution interface. As seen from Nyquist plots, the activated charcoal electrode has appeared the electrode material possess inclined line in the high-frequency section alternate a semicircle shape, which indicates a dramatic reduction in the polarization resistance. Furthermore, the vertical line is continuous in the low-frequency section because of their typical double-layered capacitive behavior, demonstrating the great capacitive behavior of the electrode materials, which suggested the fast electrolyte ions diffusion into pores of electrode materials [11,12]. The equivalent series resistance (ESR) was calculated from the intersection of EIS curves at the Z_{real} axis in the high-frequency section, which expressed the sum of the ionic resistance of NaCl aqueous solution, the intrinsic resistance of the electrode materials, and the contact resistance at the interface of active material/current collectors [13-15]. Lifetime and cost are the main factors that influence the commercialization of CDI electrodes.

Therefore, the regeneration of the introduced activated charcoal composite electrode material was studied at 1, 1.4, and 1.8 V in 1 M NaCl aqueous solution via charge-discharge test (Figure 4B). The plots reflected good reversibility and high electrochemical stability at both electrodes. The conductivity values returned to their start values during the desorption process, indicating the complete desorption of the adsorbed ions to the electrolyte after the voltage release.

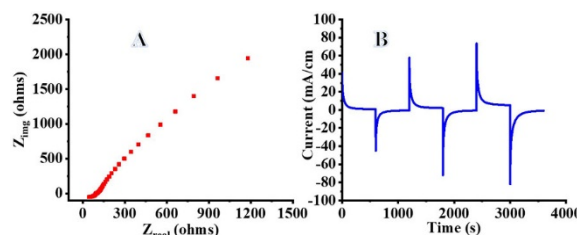


Fig. 4: Nyquist plot (A) and Chrono charge-discharge potentiostatic of activated charcoal electrode material in 1.0 M NaCl solution at different potential 1, 1.4, and 1.8V (B).

3.2 CDI cell Performance

Batch mode CDI cells have been used to evaluate the desalination performance of the as-fabricated electrodes in $\sim 100 \mu\text{S cm}^{-1}$ NaCl solution at different potentials (1, 1.4, and 1.8 V) with a flow rate of 10 mL min^{-1} . As observed in Figure 5A, when the voltage is applied between the two symmetrical electrodes, it was observed that the initial conductivity of the saline solution of activated charcoal electrode materials rapidly decreases, demonstrating the fast salt ions adsorption on the surface of the charged electrodes with

the applied voltage. This process is stogy decrease until reaching salt ions adsorption equilibrium, suggesting the salt ions were highly accumulated on the surface of electrodes during the CDI cell operation, as the surface became electrosorption saturation. The CDI performance of activated charcoal was tested at different applied potentials (1, 1.4, and 1.8 V; Figure 5A) in $100 \mu\text{S cm}^{-1}$ of NaCl solution. The conductivity of the saline solution decreased with the increase in voltage. Accordingly, the obtained results are plotted in Figure 5B. The activated charcoal electrode indicates the significant salt adsorption amount (3 mg g^{-1}) at 1 V, (3.6 mg g^{-1}) at 1.4 V, and (4.1 mg g^{-1}) at 1.8 V. Good electrical conductivity and electrochemical behavior of activated charcoal enhancement a large number of ions transport towards electrodes, thus, a significant salt ions adsorption capacity.

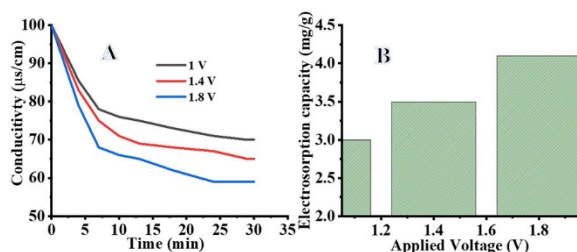


Fig. 5: (A) Effect of applied potential in the CDI cell performance for the activated charcoal electrode material in the presence of NaCl aqueous solution ($100 \mu\text{S cm}^{-1}$) and (B) Electrosorption capacity at applied potential.

4 Conclusions

In this study, a simple acidified activated charcoal powder was applied for water desalination used CDI technology. Electrochemical measurements of acidified activated charcoal revealed that highest specific capacitance of 191.7 Fg^{-1} at 1M compared to 160 Fg^{-1} at 0.1 M indicating the high capacitive for ion electrosorption at a higher concentration. Symmetric CDI cell reveals high electrosorption performance 4.1 mg g^{-1} at 1.8 V used $100 \mu\text{S cm}^{-1}$ of NaCl solution. This study confirms the possibility to enhance the electrosorption performance of a cheaply available acidified activated charcoal.

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