



Developing a CDI Desalination System on a Laboratory Scale Using Active Carbon Electrodes

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ABSTRACT

Capacitive deionization (CDI) is an emerging energy efficient, low-pressure and low-cost intensive desalination process that has recently attracted experts' attention. The process is to explain that ions (cations and anions) can be separated by a pure electrostatic force imposed by a small bias potential. Even at a rather low voltage of 1.2 V, desalinated water can be produced. The process can be well operational by a professional cell design. Although various processes have been manufactured before, in this study, membrane was removed and a new unit was designed and manufactured (Using CFD Simulation). In this case, the combination of activated carbon powder (with an effective surface area of 2600 m² per gram), carbon black, and polyvinyl alcohol with a ratio of 35/35/30 coated on carbon paper as electrode materials was considered for tests. The weight was 1.41 grams for each material, and the thickness was 0.44 mm. CDI system was tested, and the results of charge-discharge cycles, cyclic voltammetry, and impedance spectroscopy were evaluated. It can be implied that there is no need for a strong pump and, also, pressure drop can be reduced due to such a noticeable space between two electrodes. Preliminary experimental results showed high specific capacitance (2.1 Farad) and ultra-high salt adsorption capacity, compared with similar cases.

1. INTRODUCTION

1.1. Importance of desalination

Water is the basis of life on the planet. Water is a major component of the environment and an essential element for the existence of human life. Therefore, water resources are attributed a special significance among natural resources. The Earth has about 1.4 billion cubic kilometers of water, which is equivalent to 70 % of the planet's surface. Oceans constitute about 97.5 % of the total amount of water on the planet that is saline water, and the rest of 2.5 % water amount is freshwater. In freshwater content, 79 % is frozen in poles and glaciers and 20 % in groundwater moisture, which is not readily available for human use. In addition, given the small amount of groundwater, only about 0.5 % of the total amount of water on Earth is suitable for living on the earth (Fig. 1) [1].

The total water consumption in Iran in 2004 in all agricultural, urban, and industrial sections was estimated to be 93.3 Km³. This amount includes 40.0 Km³ of surface water, 53.1 Km³ of groundwater, and 0.2 Km³ of freshwater (Figure 2). Due to the aforementioned limitations, salty waters and their desalination into fresh water have received greater attention recently.

As defined by the World Water Organization, all processes associated with the removal of water-soluble salt and the supply of drinking water from saline water with a total concentration of 3.5 % or 35,000 mg/l (or Brackish Water with a total concentration of 20,000 to 30,000 mg/l) are assumed to be desalination processes. Desalination is a serious solution to the problem of dehydration in warm and dry areas.

More than 59.9 million cubic meters of desalted water are produced daily in 14451 sites around the world. Most countries in the Middle East and the Gulf region (such as the United Arab Emirates, Kuwait, and particularly Saudi Arabia) are the leading countries in this area due to limited sources of freshwater and access to affordable energy [3].

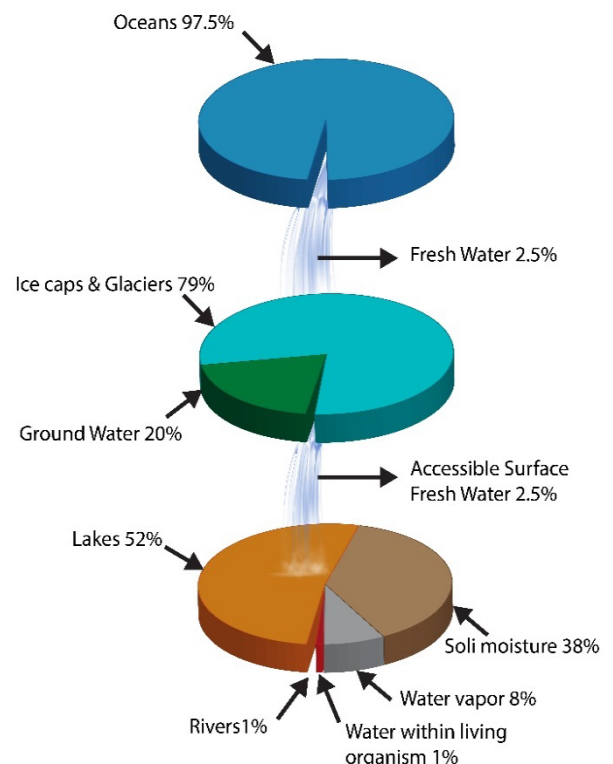


Figure 1. Distribution of water resources in the world.

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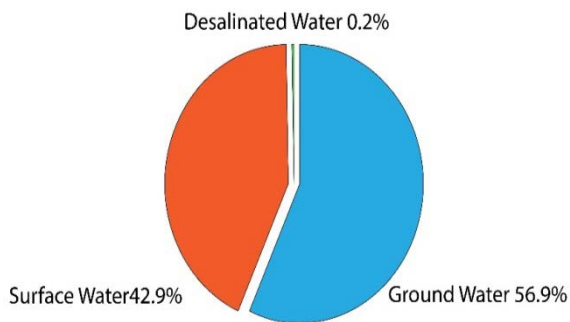


Figure 2. Share of water resources in Iran 2004 [2].

1.2. Desalination techniques

Techniques of desalinating saline water are different in the world, and the capacity of freshwater and energy consumed in each of the methods is different. From a theoretical point of view, all desalination processes require a minimum amount of energy to be able to provide fresh water. There have been some instances of inefficiency when energy was going to be transferred from one place to another or converted from one state to another. Low efficiency of this process at this stage leads to an increase in energy consumption, which itself increases the cost of desalination. Nowadays, different methods such as reverse osmosis, multi-stage distillation, and thermal evaporation methods are used as the main processes for desalinating saline water. In the membrane processes, the impurities are separated by compressive force. One of the most important issues associated with these technologies is the cost, making the process inefficient due to financial constraints at times. The costs of these processes include initial investment costs, startup costs, and maintenance costs of the system over the lifetime of the machine (Figure 3) [4,5].

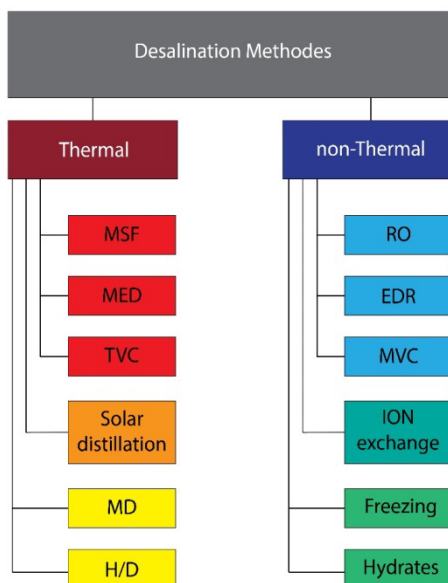


Figure 3. Classification of water desalination methods based on the consumed energy type [6].

The possibility of developing new water desalination processes, reducing investment costs, and using renewable energies has become one of the most promising options to address the global challenges of the twenty-first century. Indeed, the selection and development of a desalting process are more efficient and cost-effective than that of existing

methods. Hence, the choice of the best water desalination method to reduce the costs and provide adequate water is inevitable. The proposed method in this paper is a novel Capacitive Deionization-based solution to overcome the weaknesses and problems encountered in other methods. In addition, the study of no-membrane design to increase energy efficiency and economic justification is the most important goal.

2. RESEARCH AND METHOD

2.1. What is capacitive deionization?

Capacitive Deionization (CDI) is a new solution that requires less energy to start up due to its low fluid pressure and no-membrane contact. Therefore, it requires low maintenance costs (Figure 4). The cycle of this system generally involves two stages of charge (ion absorption) and discharge (ion emission). In the first instance, the electrostatic force is supplied to the electrode plates about one volt supplied by an external source. Electrodes that are deposited on carbon-based materials are like a ready-to-charge capacitor; when charged with saline water from the plates, sodium ions are adsorbed onto one plate and the negative ions of chlorine are charged on the other plate [7,8].

The first difference between this method and most others is that the former dissolves water-soluble salt, while all previous forms of the entire saltwater solution have become separated. In addition, at first glance, it appears that the biggest problem in membrane methods is the collapse of pressure in water membrane; of note, their lifetime is not considered. Now that water is desalinated, the capacitor is in full charge. By disconnecting the electrostatic current and disposing of the capacitor, sodium and chloride ions are separated from the electrodes and can be collected.

In addition, what is noteworthy is a 220-volt electrical current that drains the capacitor when it is discharged. This power supply can be stored and used to supply pump energy. The energy saver will then be energized. Of course, the amount of energy lost in the path for various reasons, such as friction, heat, etc., is inevitable; however, this energy dissipation and the initial drive force of the device by the input power supply, like a portable solar cell, are simply compensated, thus yielding high energy efficiency for CDI [9].

As mentioned, CDI works by using a pair of porous carbon electrodes that store ions after applying electrical voltage. These electrodes can be assembled into columns of several pairs. The ions are absorbed through a channel between the two electrodes through the flow of water and placed in the pores inside the carbon material. This process is based on the formation of a double electric layer inside the CDI unit. The formation of a double electric layer is the basis of the storage of capacitive energy and the mechanism through which monovalent ions are absorbed and selectively separated from the gross solution [10].

2.2. Electrical double layer, basement theory of CDI

An electric double layer is a concept that was realized in the early nineteenth century and has since developed in various fields of physics and chemistry and recently in a wide range of electrical appliances in the form of capacitors and batteries. Typically, solid particles produce a surface charge when

contacted with an aqueous electrolyte solution. The need for electrical neutralization causes load distribution in the surrounding space of particles (by ion distribution), neutralized by a layer of opposing charge ions. That is, it absorbs a positive charge level of negative ions (and vice versa) and collects total load to zero; in other words, a double electric layer around particles is created [11].

Understanding the theory of dual electric layers and its foundation leads to a better development of the electrode-forming materials and, as a result, increases the efficiency of water desalinations by using the concept of capacitance. A double electric layer has a complex engineering with distinct sections, and various models have been proposed to explain its formation (Figure 5) [12].

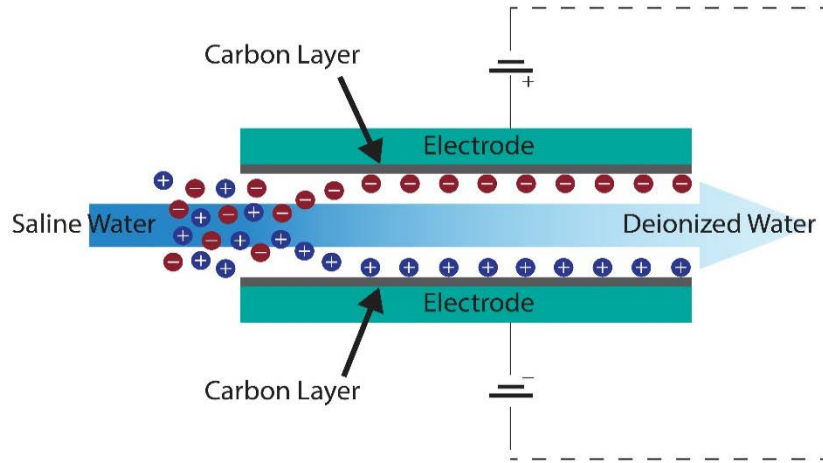


Figure 4. Rechargeable capacitor.

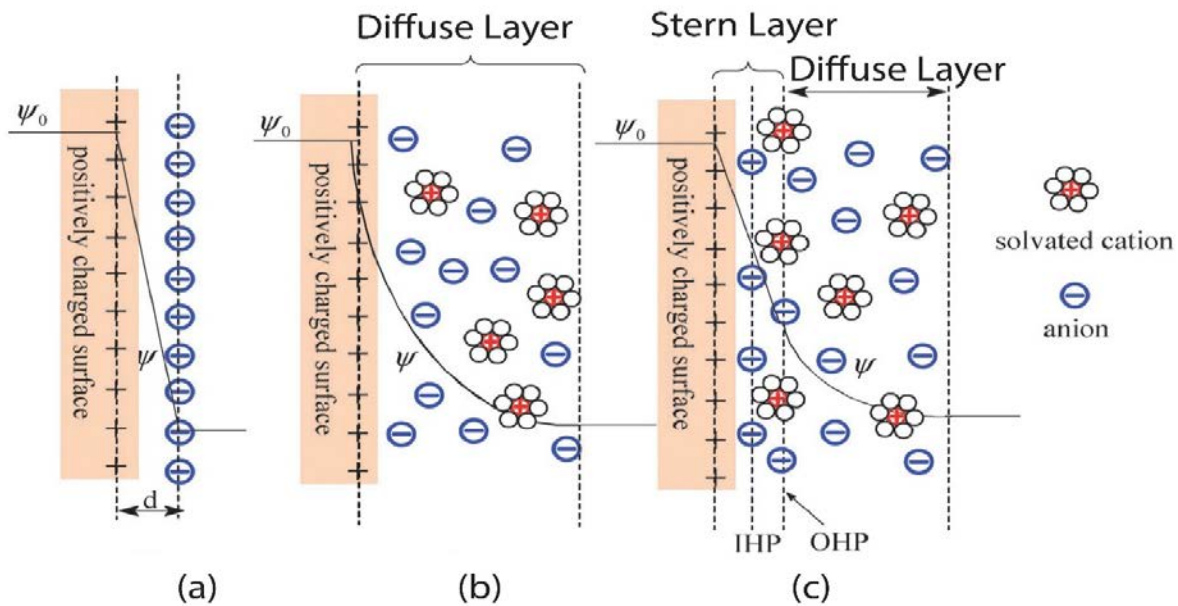


Figure 5. Schematic diagram of a double electric layer modeling from the anode surface. (A) Helmholtz model, (B) Chapman's Orb Model, (C) Stern model. Duplicate electrical layer thickness. Ψ_0 and Ψ , the electrode surface potential, and the electrode potential on the electrolyte unit [12].

By considering the capacitive capacity in the stern layer as C_s and the capacitive capacity in the diffusion layer as C_d , the total capacitive capacity, C_T , is defined as follows:

$$\frac{1}{C_T} = \frac{1}{C_s} + \frac{1}{C_d} \quad (1)$$

Capacitor capacitance C (in terms of F/g for each electrode) is as follows:

$$C = \frac{\epsilon_r \epsilon_0}{d} A \quad (2)$$

where ϵ_r (a dimensionless constant) is known as a dielectric constant, ϵ_0 is the vacuum coefficient of vacuum, A is the accessible surface of the electrode for the electrolyte ions, and

d is the effective thickness of the double electric layer. The pseudo capacitance of the super capacitors due to the regenerative process is not observed in capacitor diodes, because the potentials imposed by the electrochemical characteristics of the electrolyte are less than 1.24 volts. The electrodes are then discharged by a short circuit or current direction change [13-15].

3. DESIGN AND MANUFACTURING

3.1. laboratory scale of CDI setup

A laboratory setup kit for conducting CDI involves water reservoirs, pumps, capacitor deionization, power supply, and electrical conductivity meter (Figure 6) [13].

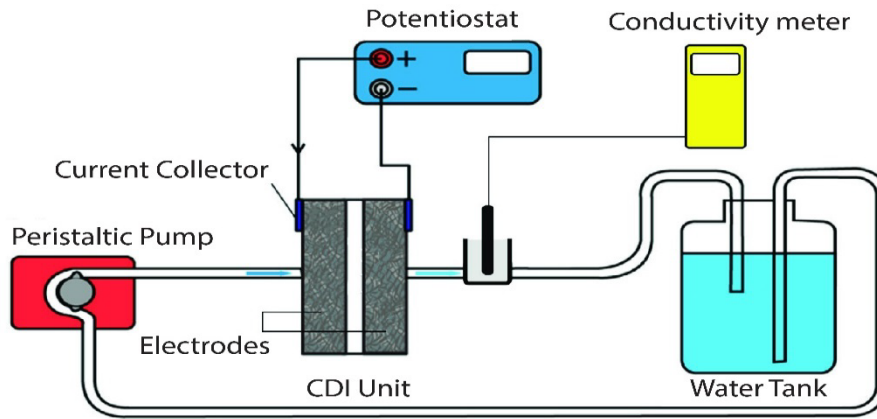


Figure 6. Schematic image of a lab designed diode capacitor designed.

The central core of the setup is the desalination unit. The CDI consists of two electrodes of carbon with a 1.62 mm separation distance (Figure 7).

The operational procedure is that, at first, saltwater is drained by a pump from the reservoir and sent to the inside of

the CDI. Inside the unit over the passage of water through the two electrodes, separation and desalination are performed by applying the voltage; then, the outlet water is sent to a small reservoir to measure its electrical conductivity. Then, water in the hose is sent to the outlet tank.

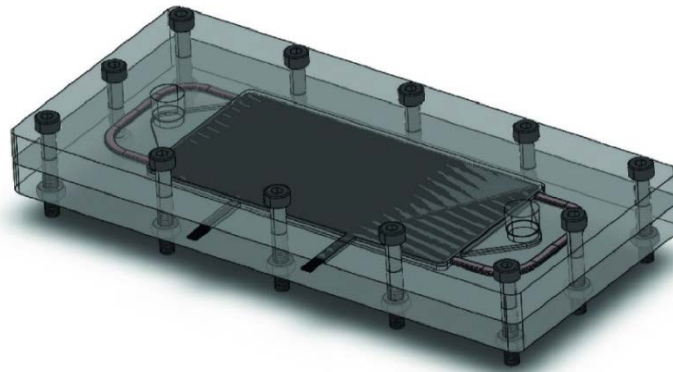


Figure 7. CDI unit design in SOLIDWORKS software.

3.2. Active carbon, carbon black, and commercial material to test the design of unit

Carbon-based materials are the most well-known and most used materials for making porous carbon electrodes with high effective surface and electrical conductivity for use in CDI. The electrodes used in this project were active carbon. Of course, this does not mean that these electrodes are entirely composed of this material. A combination of activated carbon powder, carbon black, and polyvinyl alcohol with a 35/35/30 diluted electrode material is tested in this project. Activated carbon (Merck CAS No. 7440-44-0) as a very high effective surface (3500-1000 m²/g) increases the absorption capacity of the salt and the capacity of the capacitor. Soot carbon also strengthens the electrical conductivity of the electrode; in addition, if it sits on the electrode surface more uniformly, a more even current distribution and a longer life for the electrode can be considered. In addition, there is a need for a material to provide the strength and bonding of powders to each other and to the connector surface. For this purpose, polyvinyl alcohol was used as powder. Finally, a pair of electrodes (2 electrodes separately) is characterized by 10 cm length and 5cm width (Figure 8).

4. EXPERIMENT AND RESULTS

4.1. Computational fluid dynamics simulation

Fluid flow through the cell can be examined through fluid dynamic calculations. The purpose of this simulation is to reduce polarization and estimate the probable dead areas before construction and starting the experiments. The calculation of the results of solving the governing equations for the flow requires a precise selection of the boundary and initial conditions. In this project, the equations are solved based on Newman boundary conditions. Therefore, to study the flow regime, by using the speed and the cross-sectional area (the largest cross-section causing instability), Reynolds number was calculated to be 2.23, which is much smaller than 2000, indicating that the flow is laminar.

$$Re = \frac{\rho V D}{\mu} \quad (3)$$

In a CDI, it is very important that the inlet fluid flows in the gap between the two electrodes evenly without any flow overlap so that the maximum surface contact with the electrodes occurs and, thus, the overall desalination efficiency increases [16]. This is the reason why the velocity analysis was carried out. If the incoming edges, which do not have contact with the electrode, are completely ignored, the dead regions become clearly visible in the quadrilateral of the CDI; these regions are reliant on the structural nature of the whole square (rectangular) and are about 9 % of the total area in the simulation of this condition (Figure 9).

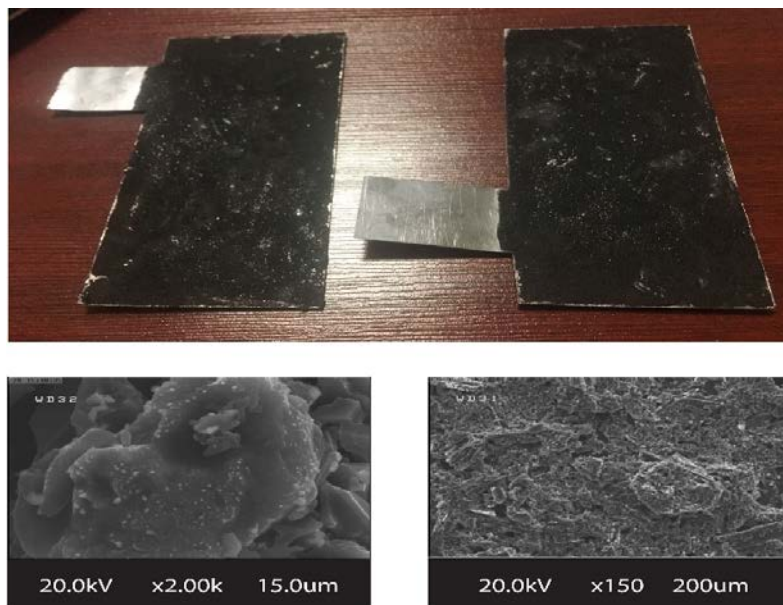


Figure 8. Electrodes used and scanning electron microscopes.

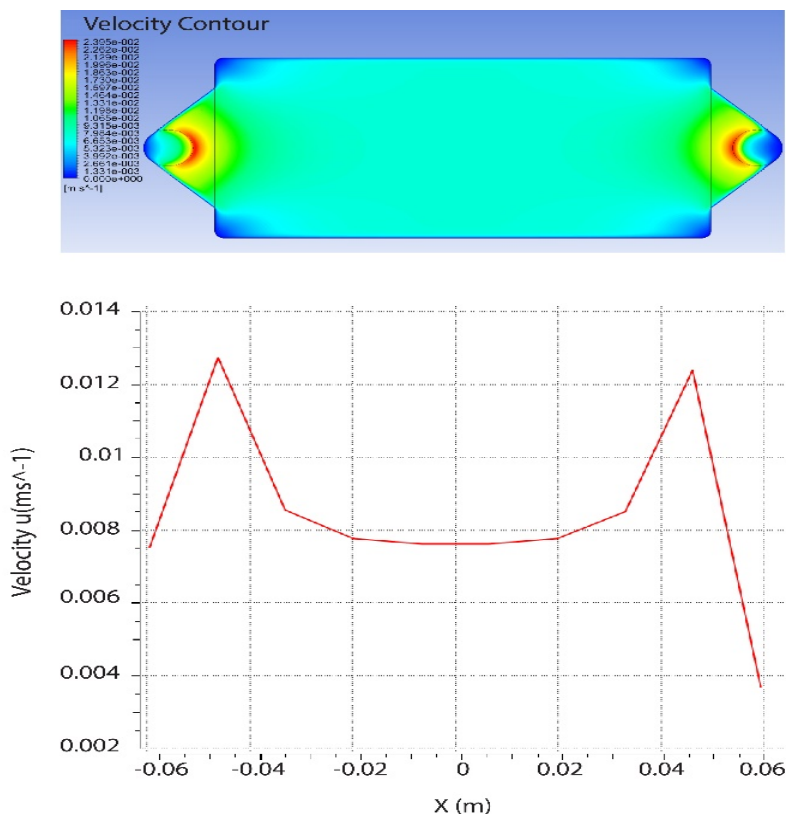


Figure 9. Simulation of velocity vectors within a capacitor diodes unit.

4.2. CV curve plot

The cycle voltammetry curve may provide information on the amount of chemical reactions and the quantitative characteristics of the reactions; however, its qualitative information is more important for understanding the capacitance drainage mechanism. In this project, as most of research studies, 1 molar saline water was used, and the potential range was considered to be $\Delta V=1$ and between -1 and 1 volt due to the water degradation potential (1.24 V) [17]. In the positive range, the charge is monitored and, in the negative interval (the reverse voltage), we will see the

discharge. In addition, these experiments were carried out at voltage rates of 100 mV/s, 50 mV/s, 10 mV/s, and 5 mV/s. The standard concentration of cyclic voltammetry experiments in CDI is usually considered to be 1 mole (Figure 10).

As can be seen, as the applied voltage increases, the consumption current also increases. A rectangular graph is seen at low rates and is furthered by increasing the voltage applied. The reason for this can be related to the characteristic resistance of the electrodes and the polarization effects. The ohmic resistance of ions in electrodes can affect the formation of a double electric layer. The voltammetry graph of the recorded cycle is very smooth and without any disorder such

as the maximum and minimum points, peaks, and noise, suggesting that the absorption mechanism is based solely on the formation of a double electric layer and no chemical reaction (Faraday) has been performed in the desalination

process. Thus, the capacity of the capacitor is determined by the calculation method, which is considered in NOVA software by default (Table 1).

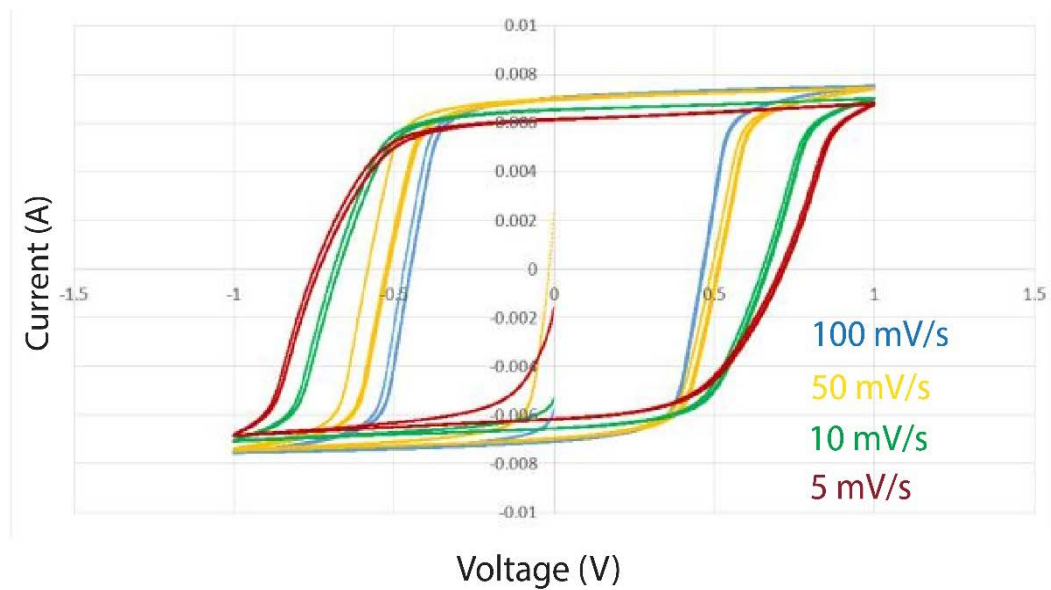


Figure 10. Voltammetry cyclic diagram at different voltage rates (Obtained using Autolab potentiostat/NOVA software).

Table 1. Calculation of capacitor capacity using a voltammetry cyclic curve.

Capacitance (F/g)	Voltage rate (V/S)
0.08	0.1
0.16	0.05
0.78	0.01
1.49	0.005

4.2. Nyquist plot

To measure impedance in the CDI, we do the same as it works for super capacitors in an open circuit. Of note, potentially, there is no current between the cathode and the anode. Impedance is calculated at an intermittent potential in the range of 5 to 10 millivolts in a limited frequency range. This frequency range should be selected in accordance with the capacitance and surface strength of the capacitor. The typical frequency range is considered to evaluate the CDI EIS between 0.1-100 Hz.

Impedance consists of a real part and a fictional part defined as follows:

$$Z = Z' + jZ'' \quad (4)$$

In fact, its true part can be called resistive, and the imaginary part of it is represented by a capacitor in an electric circuit. The result of the electrochemical impedance spectroscopy is known as the Nyquist chart. The Nyquist chart shows the relation between Z' and Z'' . For an ideal capacitor, the graph is a completely vertical (perpendicular to Z') line and shows no resistance in the set. Conversely, for the ideal resistor, the graph is a completely horizontal (perpendicular to Z'') line, and shows that there are no capacitor and reservoir in the set. The electrochemical impedance spectroscopy in this

project was carried out by implementing 10 frequencies in the frequency range of 0.01 Hz to 100 Hz with a range of 0.01. The Nyquist diagram shows that the electrical circuit equivalent to the tested CDI is the combination of resistors and capacitors (Figure 11).

The capacitance of a capacitor in CDI (i.e., the CDI is the total number of fasteners, electrodes, and electrolytes between them, because each of them has their resistor and capacitance in their structure and nature) is based on the imaginary part of the impedance and is expressed as follows:

$$C = \frac{-1}{\omega Z'' m} = \frac{-1}{2\pi f Z'' m} \quad (5)$$

It is difficult and partially impossible to find a specific boundary and accurate calculation to determine the share of resistors and capacitors through the Nyquist chart. Therefore, a constant phase element is used to analyze it. The stationary phase element is used in equivalent circuit modeling and the fitting of electrochemical impedance spectroscopy data. A stationary phase element is a component of an equivalent electrical circuit, modeling the behavior of a double electric layer.

$$CPE = \frac{1}{Y_{CPE}} = \frac{1}{Q_0 (\omega i)^n} \quad (6)$$

where Q is a constant independent of the frequency and electrode specification. The power n has an interval of -1 to $+1$, at which $n=-1$ represents the net inductance, $n=0$ is the pure resistance, and $n=+1$ represents a pure capacitor.

The binding plates are carbon-based and have slight absorbance; however, since they are completely carbon-coated, they are in practice a resistive part and can be ignored

in their capacitive capacities. In this way, the equivalent circuit is obtained as follows (Figure 12).

As can be seen, the resistance of one of the connecting plates is $875.49 \text{ m}\Omega$ and the other is $920.29 \text{ m}\Omega$. Regarding the constant phase element, $n=0.472$. That is, the resistivity of the capacitive diodes is 5.6% more than their capacitive property.

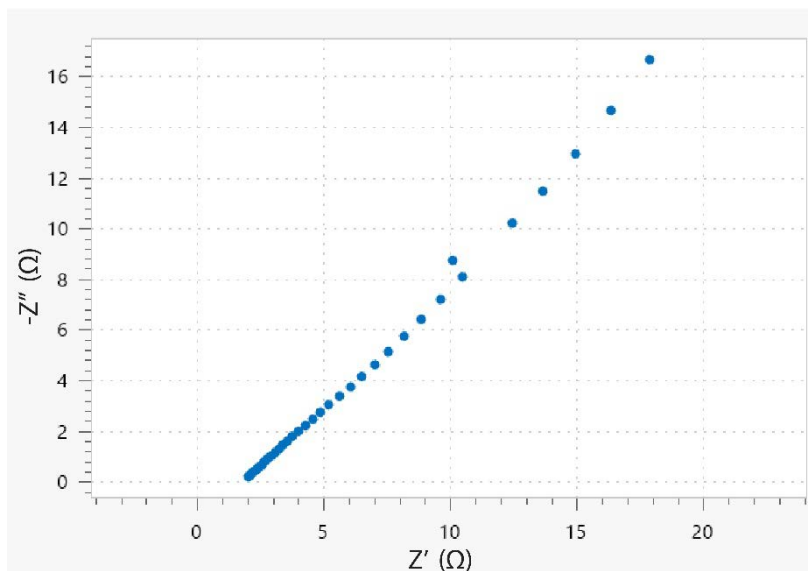


Figure 11. Nyquist chart (Obtained using Autolab potentiostat/NOVA software).

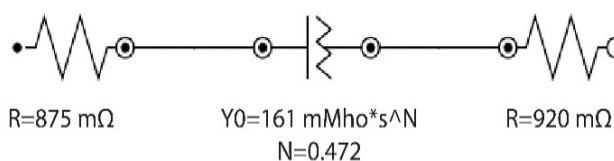


Figure 12. Equivalent circuit of CDI.

5. CONCLUSIONS

This study investigated CDI as an efficient technique of desalination process in case of removed membrane. The process was run based on the fact that ions were separated by a pure electrostatic potential at a low voltage of 1.2 V . This direct current with low voltage can easily be produced using a small solar panel. Cations and anions move to the electrostatic double layers inside their opposite charged electrodes. The novelty of the present work is that, in this study, membrane was removed and a unit was designed and manufactured. In addition to the manufacturing, Activated carbon was used as the electrode material and the CDI system was evaluated in charge-discharge cycles, cyclic voltammetry, and impedance spectroscopy. Experimental results showed high specific capacitance and ultra-high salt adsorption capacity, compared with similar cases.

6. ACKNOWLEDGEMENT

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