

# INSTITUTE OF ENVIRONMENTAL SCIENCES & ENGINEERING



## Treatment of Inland Brackish Water using Capacitive Deionization

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### FYP Report

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## **Treatment of Inland Brackish Water using Capacitive Deionization**

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## **DEDICATION**

We would like to dedicate this research work to the poor and needy people of southern Punjab who are facing problems related to water quality and hygiene. They are drinking brackish ground water and therefore experience severe health problems.

## **ACKNOWLEDGEMENTS**

We would like to extend special thanks to WaterAid for all of its academic and financial support during this project. We would also like to express gratitude to the Associate Professor Dr. Sher Jamal Khan for his funding assistance and guidance during the whole period. Likewise, We would like to thank Dr. Yousuf Jamal for all of his support throughout the project. We are also grateful to Dr. Fouzia Malik (RCMS,NUST) and Dr. Arshad Hussain (H.o.D Chemical Engineering SCME,NUST) for conducting Cyclic Voltammetry and SEM analysis for our project. We would like to thank Dr. Ishtiaq Qazi (Associate Dean, IESE, NUST) and Dr. Zahir ud Din Khan (H.o.D Environmental Engineering, IESE, NUST) for assisting with building and maintaining the equipment and finally our friend Fawad Ahmed (MS Environmental Engineering) for his collegiate support throughout the year.

## **Abstract**

Desalination of brackish water using Capacitive Deionization (CDI) is studied in this research work to meet the Pakistan national drinking water quality standards (NDWQS) of <1000 mg/L total dissolved solids (TDS). CDI is based on the concept of electro-sorption. An electro-potential difference is applied across the two oppositely charged surface electrodes. System optimization was performed on parameters like absorbent selection, applied voltage, surface regeneration, and retention time of water in contact with carbon electrodes. A parallel flow of water is adjusted against electrodes in a batch and continuous flow arrangement. DC voltage source is used to provide electric potential to the graphite current collectors coated with activated carbon, and water flow between the electrodes is maintained with a peristaltic pump, TDS and conductivity is measured with a conductivity meter at specific intervals.

An increase in salts removal on carbon electrodes from brackish water is observed with an applied voltage from 1.4 to 1.8v. Increase in residence time has also shown a remarkable removal of salts up to drinking water limits. All carbon electrodes in continuous and batch arrangement have shown regeneration up to 90%. The CDI system is consistent in achieving acceptable drinking water limits of <1000 mg/L total dissolved solids (TDS) over the test period of three months. Output of this research has the potential of providing safe drinking water in remote areas of Pakistan where groundwater has high salinity.

**Keywords:** Desalination, Capacitive Deionization, Electro-sorption, Process Optimization, Regeneration

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## List of Abbreviations

CDI	Capacitive Deionization
AC	Activated Carbon
TDS	Total Dissolved Solids
TSS	Total Suspended Solids
DI	De-ionized
DC	Direct Current
WHO	World Health Organization
ppm	parts per million
ppt	parts per trillion
EPA	Environmental Protection Agency
NDWQS	National Drinking Water Quality Standards
CV	Cyclic Voltammetry
C.V	Co-Variance
SD	Standard Deviation



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# 1. Introduction

## 1.1 Background

Approximately 800 million people living on the earth do not have access to safe drinking water.<sup>1</sup> Moreover, almost one-quarter of people on the earth live in areas where the ground water is being depleted faster than it can be replaced (Gleeson, 2012). Although over 70% of the surface of the earth is covered with water, access to clean water remains a critical issue worldwide (Gleick, 1996). Providing for clean water in a safe, inexpensive and energy-efficient manner is amongst the most important technological challenges facing humanity the coming decades (Shannon, 2008), (Semiat, 2008), (Schiermeier, 2008). With the increasing demand on the declining world natural freshwater resources, alternative water supply options are being sought after (Ayoub, et al., 2014). It is estimated that in the next 20 years the average per capita supply of clean water will decrease by one-third (United Nations report). Desalination is one option for producing potable water from brackish water and seawater in many parts of the world, but most water desalination technologies are energy and capital intensive (Shannon, 2008). Extensive large-scale desalination will therefore serve as the main source of artificial freshwater supply, with the treatment of desalinated predicted to increase up to 100 million m<sup>3</sup> per day in 20 years (Fritzmam, 2007).

Water scarcity has been one of the most serious social, economic and environmental issues throughout the globe and its importance is quite clear by the fact that per capita water availability has reduced in many parts of the world. In WANA (West Asia and North Africa) region per capita water availability has fallen from 3600 m<sup>3</sup>/y in 1960 to 1000 m<sup>3</sup>/y in 2000, which is almost a 75% decrease (Jauad El Kharraz, 2012). The decrease in per capita water availability is due to increase in water demand, which is attributed to increase in population growth, industrial development, unsustainable water usage and several such reasons. The

increasing trend of reduction in water resources forced the world to find solution to this issue. Few of those solutions were water and waste water treatment, reduction in water usage, sustainable life style, rain water harvesting etc. One of the most applicable solution that was found to combat this issue was the treatment of saline water for drinking purpose also known as desalination.

As our planet comprise 70% of oceans. Thus desalinating water and making it available economically for drinking purposes should be the approach to cope with the problem. Various technologies have been adopted worldwide for desalination which include Reverse Osmosis, Solar Distillation, Multi-Stage Effect Distillation, Capacitive Deionization etc. Desalination technologies are categorized into three major types based on the principle of removal of salts from the water.

## **1.2 Desalination Technologies**

### **1.2.1 Membrane Technologies**

A membrane is a semi permeable material that allows tiny particles to pass through it but prevents the flow of larger particles. These membranes are used for desalination purposes as it allows only water to pass through it. Membrane based desalination include:

- Reverse Osmosis (RO)
- Ultrafiltration,
- Microfiltration

RO is the most commonly used membrane technology but its use is limited to developed areas as it requires high operation and maintenance cost. For brine to be treated through RO, the solution is passed through a membrane by applying pressure which retains the salt ions and allows the water molecules to pass freely.

Reverse Osmosis (RO) is the most common technology. It is a physical process that uses the osmosis phenomenon, i.e., the osmotic pressure difference between the saltwater and the pure water to remove salts from water. In this process, a pressure greater than the osmotic pressure is applied on saltwater to reverse the flow, which results in pure water passing through the synthetic membrane pores separated from the salt. A concentrated salt solution is retained for disposal (AWWA, 1999). RO however has quite high maintenance cost due to membrane clogging and a high energy cost for pumping water to the membrane.

### **1.2.2 Thermal Technologies**

These techniques desalinate water utilizing heat energy. The salt water is heated and the vapors are condensed to obtain pure water. These techniques are not used on large scale because of its higher operation costs. It is further divided into following categories:

- Multi-Effect Distillation (MED)
- Vapor Compression (VC)
- Multi-Stage Flash Distillation (MSFD)

The most commonly used thermal technology is MSF. In this technique, the desalinating plant has different stages which operate at different pressures. The pressure successively decreases in different stages. At start, water is heated at high pressure then is allowed to enter the other chamber where pressure is less than first one. Releasing the pressure causes water to escape from brine solution and thus collected and condensed.

### 1.2.3 Electro-sorption Technology

In this technology two electrodes are placed opposite to one another, and a voltage difference is applied, diffuse polarization layers develop on both the electrodes. Taken together, the two polarization layers contain an excess of salt ions over the ion concentration in bulk solution, and thus effectively part of the ions in the solution phase is removed. The removal of ions according to this principle from an (aqueous) stream flowing along the electrodes is called capacitive deionization (CDI) or electro sorption desalination (Arnolde, 1961), (Murphy, 1967), (Johnson, 1971), (Soffer, 1972). Capacitive Deionization is an easy to apply technology especially for developing countries where there is a problem of trained technical staff and energy shortage.

### 1.3 Problem Statement

Drinking saline water causes several health impacts which include: high blood pressure, edema, stomach cancer, neurological damage etc. CDI prototype was designed and performed for the treatment of brackish groundwater of Muzaffargarh. Several samples were collected from different sites. TDS was found to be in the range of 1200 ppm to 3000 ppm. The project was sponsored by an international NGO, WaterAid, this NGO works for providing proper sanitation and adequate supply of clean drinking water in under developed parts of the world. One of the projects that WaterAid is doing now-a-days is the desalination of brackish ground water in Southern Punjab.

Table 1 : Field Data of Wells Sampled

Site 1 ( Basti Mullah Walli)	Well 1 : TDS 1030 mg/L
	Well 2 : TDS 1200 mg/L
Site 2 ( Gharib-Abad Wandher)	Well 1 : TDS 2460 mg/L
Site 3 ( Basti Naeem-Abad)	Well 1 : TDS 3130 mg/L

## **1.4 Objectives**

The objective of the project was to design a lab-scale desalination unit having the potential to reduce the TDS (salinity) of drinking water as per NDWQS and WHO limits. The current drinking water standards of WHO require that the TDS concentration should be less than 1000 ppm (WHO, 2013). The Drinking Water Quality Standards set by EPA also requires that the drinking water should have TDS less than 1000 ppm (mg/L). The final objective was to design the lab-scale plant which can then be scaled up to pilot scale plant.

## **1.5 Capacitive Deionization**

Capacitive Deionization (CDI) has emerged over the years as a robust, energy efficient, and cost effective technology for desalination of water with a low or moderate salt content (Anderson, 2010). The energy efficiency of CDI for water with a salt concentration below approximately 10 g/L is due to the fact that the salt ions, which are the solute in the solvent (water), are removed from the mixture. Instead, other methods extract the solvent phase, water, from the salt solution. Furthermore, energy released during electrode regeneration (ion release, or electrode discharge) can be utilized to charge a neighboring cell operating in the ion electrosorption step, and in this way energy recovery is possible (Porada, 2013).

## 2. Literature Review

Approximately 97 % of the water available on planet earth comprises of sea water. It means that humans are left with only 3 % of the water for regular usage. To overcome this shortage, the sea water must be brought in use which is possible through desalination technologies. Around the globe, various desalination technologies are used each of which has its own pros and cons. Welgemoed has summarised the commonly used desalination technologies and their applications and the operating principles.

Table 2 : Desalination Technologies

Technology	Typical application	Operating Principle
<b>Thermal Processes</b>		
Multistage Flash Evaporation	Sea water desalination	Thermal evaporation
Multiple Effect Distillation with Mechanical Vapor Recompression	Sea water Desalination	Thermal evaporation with improved energy efficiency
Multiple Effect Distillation with Thermal Vapor Recompression	Sea water desalination	Thermal evaporation. More efficient than direct distillation but less efficient than MVR
<b>Membrane Processes</b>		
Reverse Osmosis	Sea water and brackish water desalination	Pressure driven and diffusion controlled membrane process. Removes particles down to 0.0001 microns
Nanofiltration	Industrial process/wastewater	Pressure driven and diffusion



	and potable water treatment	controlled. Removes particles down to 0.001 microns
Ultrafiltration	Industrial process/wastewater and potable water treatment	Pressure driven but does not remove ions. Removal is based on sieving upto 0.01 microns
Microfiltration	Industrial process/wastewater and potable water treatment	Pressure driven but does not remove ions. Removal is based on sieving upto 0.1 microns
Electrodialysis	Primary brackish water desalination	Charge driven membrane process that remove ions but not turbidity
<b>Ion Exchange Processes</b>		
Anion/Cation Exchange	Boiler feed water and water softening	Anions and Cations in a source water are exchanged for more desirable and less troublesome ions
Electro deionization	Ultra pure water production	Charge driven ion exchange process

Source: (Welgemoed, 2005)

Among all these technologies, Capacitive Deionization (CDI) is one such technology which achieves the objective of desalinating brackish water with very little energy usage. This process offers dramatic advantages in terms of both waste minimization and reduced

processing costs. The reject brine resulting from the regeneration step can be used in Salinity Gradient Solar Ponds to utilize the energy from solar radiation.

Therefore it has been studied as a low-polluting, energy-efficient, cost-effective alternative to the common desalination technologies, such as ion exchange, reverse osmosis, electro-dialysis and evaporation, which have a high energy demand (Zou, et al., 2008) where all ion exchange processes cannot be regenerated effectively thus decreasing the process efficiency.

Unlike ion exchange, no acids, bases, or salt solutions are required for regeneration of the surface of the electrodes in CDI, thereby substantially reducing the amount of secondary waste. For regeneration, simple tap water can be used. Compared with thermal processes, such as evaporation, electro-sorption consumes less energy to achieve similar results (Zou, Morris and Qi, 2008).

A CDI system simply consists of pair of oppositely charged electrodes, a D.C power source and a pump. Salt water passes between the electrodes and the ions are attracted towards them. The material adsorbed on the electrode surface is of extreme importance as it plays a very effective role in removal of ions. Porous carbons, in particular activated carbons, are used in a wide range of applications related to their adsorption capabilities due to the high surface areas, different pore size distribution and variable surface chemical composition that they can possess(Villar, et al., 2011).

The adsorption of ions on a carbon surface is classified as physical adsorption and electro-sorption: physical adsorption occurs due to the interaction between polar groups of the carbon surface and ions, and electro-sorption is due to the attraction between the charged electrode surface and ions. Ion removal by CDI is based on electro-sorption, but physical adsorption lowers CDI efficiency by holding ions on the surface during the regenerating step. Therefore,

a decrease in physical adsorption with an increase in electro-sorption is a promising way to enhance CDI performance (Ryoo, et al., 2003).

Different surface materials used in CDI are carbon cloth, carbon aerogel, activated carbon, activated carbon modified with titania and activated carbon modified with potassium hydroxide. All these materials have variable adsorption capacity and thus give different results when put into test. Besides, the surface area of electrodes is also an important parameter. The more surface area the more physical adsorption in terms of grams of salt adsorbed per unit of electrode weight (Villar, et al., 2010).

Recently, several researchers have found that nano-porous carbon electrodes, fabricated by mixing activated carbon powder in a polymer solution on the current collector can be considered as desirable candidates for electro-sorption of ions. It is noted that the deionization efficiency of carbon electrodes depends on surface properties (i.e., surface functional groups and surface polarity) of the material itself. Additionally, the deionization efficiency of activated carbon electrodes can be improved by surface modification via chemicals (i.e., KOH or HNO<sub>3</sub> solution) and metal oxide nanoparticles (i.e., TiO<sub>2</sub>) to increase the functional groups and surface density of hydrophilic group, respectively (Hou, et al., 2012).

As the technique charges and discharges a series of electrochemical capacitors in a cycle, the theoretical efficiency of the process should be high, especially for feed solutions with lower salt concentration such as brackish water. As the concentration in the feed water increases, the energy required for adsorption also increase due to the finite adsorption capacity of electrodes. That is why CDI focuses on treatment of brackish water rather than sea water which has very high TDS concentration as compared to brackish water (Fellman, et al., 2010).

Capacitive Desalination has the potential to be utilized in a variety of different water treatment applications, such as the purification of brackish well water, high organic and inorganic water, waste water purification, seawater desalination, treatment of nuclear and aqueous wastes, treatment of boiler water in nuclear and fossil power plants, production of high-purity water for semiconductor processing and removal of salt from water for agricultural irrigation. Since the energy requirements are relatively low compared to existing conventional water technology; it has become a possible water treatment alternative in remote areas where accessibility and energy resources are limited or low (Traylor, 2005).

Capacitive Deionization Technology (CDT) has a number of potential advantages over other desalination techniques like membrane processes and thermal distillation (Welgemoed, 2005).

- Less energy is needed for desalination because high-pressure pumps are not required. Due to low amounts of energy required, it is possible to make use of renewable energy sources like solar/wind power technology to power remote desalination units. It can also be used in communities where electric power is not easily accessible.
- The carbon electrodes can withstand much higher temperatures than membrane technology and is thus efficient for applications like boiler condensate polishing and fuel cell water deionizing systems.
- As there is no need of membranes and high-pressure pumps, the operation and maintenance cost is much lower than other technologies.
- Volume of brine that needs to be disposed of is less than that for membrane processes.

Besides all these advantages, CDT also has some disadvantages:

- As the technology is new compared to other desalination processes, no long term data is available for industrial size systems.

- It can only be used for low feed concentrations like brackish groundwater.

### 3. Materials and Methods

#### 3.1 Materials

Activated carbon was provided by Acros Organics (New Jersey, USA), Polyvinylidene Difluoride (PVDF) by International Laboratory (USA), Ethanol by RCI Labscan, N-N Dimethyl Acetate by MERCK (Germany), The synthetic feed solution was prepared by mixing 2000 mg of sodium chloride (NaCl) in 1 liter of deionized water. The synthetic feed solution used in the research for carrying experiments has Total Dissolved Solids (TDS) of 2000 mg/L and conductivity of 3.14 ms/cm

#### 3.2 Electrode Preparation

##### 3.2.1 Activated Carbon Electrode

Powdered Activated Carbon was mixed with PVDF 12 wt % of AC, which acted as a binder. N-N dimethyl was added (V/W) in a 2.2 ratio 1 to AC which was used as the solvent to prepare the slurry which usually was 2.2 ml of solvent for 1 gram of AC. Slurry prepared was stirred at 600 rpm for 2 hours to homogenize the binder and solvent in the whole mass. Then this slurry was applied on the graphite sheet which was then placed in oven at 120 °C for 3 hours.

#### 3.3 Experimental Setup for optimization

Graphite sheet of 1 mm thickness having dimensions of 8x5 in were prepared using activated carbon slurry. Electrodes were placed face to face having a space of 2 mm in between. The active surface area of electrodes was 40 in<sup>2</sup> after the fabrication of unit and this unit is

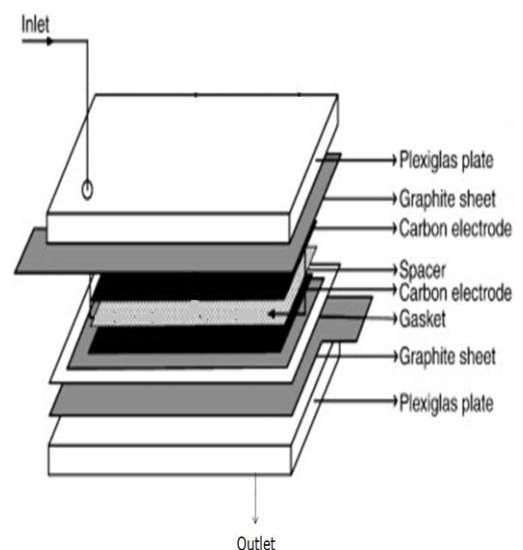


Figure 1: CDI cell design

placed in an acrylic plastic casing to keep the unit intact.

### **3.4 Lab Scale Setup (Parallel)**

Three pairs of electrodes were prepared. These were kept in an acrylic case in parallel configuration. The saline water flowed in from the top at one end and out from the top at the other end. There is a clearance of 0.5 inch at the bottom that facilitates the water to rise from the bottom and up in between the electrodes. This results in adsorption as the water comes into contact with the surface of the electrodes. The copper shim was used as the current collector. The electrodes were tested in batch and continuous flow systems. The regeneration was also carried out in continuous and batch flow systems. The effect of current on regeneration was also studied. The electrodes were tested at three different voltages and the effect of retention time was also examined.

#### **3.4.1 Electrodes size**

The electrodes were fabricated with the slurry stated above. The current collector was graphite sheet of 1mm thickness. The size of one electrode was 8 inch by 5 inch. The thickness of the electrode was kept as 8 mm. The electrodes tested were the ones which had a coating of powdered activated carbon only.

#### **3.4.2 Electrodes arrangement**

A total of 6 electrodes (3 pairs) were fabricated. The size of each electrode was as mentioned in 3.4.1. The electrodes were all arranged in parallel and placed in a box of dimensions 2 inch wide by 8 inch long by 7.5 inch high. The spacing between two electrodes was fixed to 2 mm. at the bottom of the box, a clearance of 1 inch was left in height for the water to fill the box and rise from the bottom. At the top, a clearance of 0.5 inch was left so that the treated water could be collected.

### **3.4.3 CDI Prototype Cell Casing**

The cell's dimensions were 2 inch wide by 8 inch long by 7.5 inch high. The electrodes were placed such that the 3 pairs could be arranged in parallel. The CDI prototype was made of plastic casing. The voltage is provided using a DC power supply. The connections are made at the top of the electrodes. To provide the electrical connections copper wires were used and they were attached to the top of the electrodes. The electrodes were packed in a way that the water only flows from the bottom to the top and the sideways flow is stopped by packing the electrodes to the sides of the cell.

### **3.5 Working**

A brine solution of 2000 ppm was used for experimentation. The volume of water enters from one end of the cell. It fills the bottom and then rises and fills each compartment of the electrode's pair in a parallel fashion. The flow is stopped once the complete cell is filled. The water is then given a retention time from 30 minutes to 3 hours to check the result of retention time. Three different voltages are used to check the results at different retention times. The voltages used are 1.4V, 1.6V and 1.8V. As the water rises, the adsorption takes place. The tank is filled to the top and the flow is stopped. The water is given retention time and this allows for in depth adsorption. After the retention time the water is collected from the top of the cell. The readings are taken for different voltages and different retention times. The flow rate is kept constant at 50 ml/min throughout all runs. This is the batch flow system. Once the retention time and voltage were optimized they were used to check the adsorption in continuous flow system.



### 3.5.1 Desalination/Deionization Step

A gap of 2mm was provided between two pair of electrodes for smooth water flow. A potential difference of 1.4, 1.6 and 1.8 volts was applied turn by turn across the electrodes to study the effect of different voltages on removal efficiency. The NaCl solution with the initial concentration of 2000 mg/L was pumped into the tested CDI cell at a constant flow rate of 50 mL/min using a peristaltic pump (BT100-1L, Longer pump,China). The TDS of the effluent was measured at different retention times.

When saline feed water was pumped through the CDI Cell, voltage applied across the electrodes guided the ions towards the oppositely charged electrodes. Positively charged ions were attached to negatively charged electrode and vice-versa.

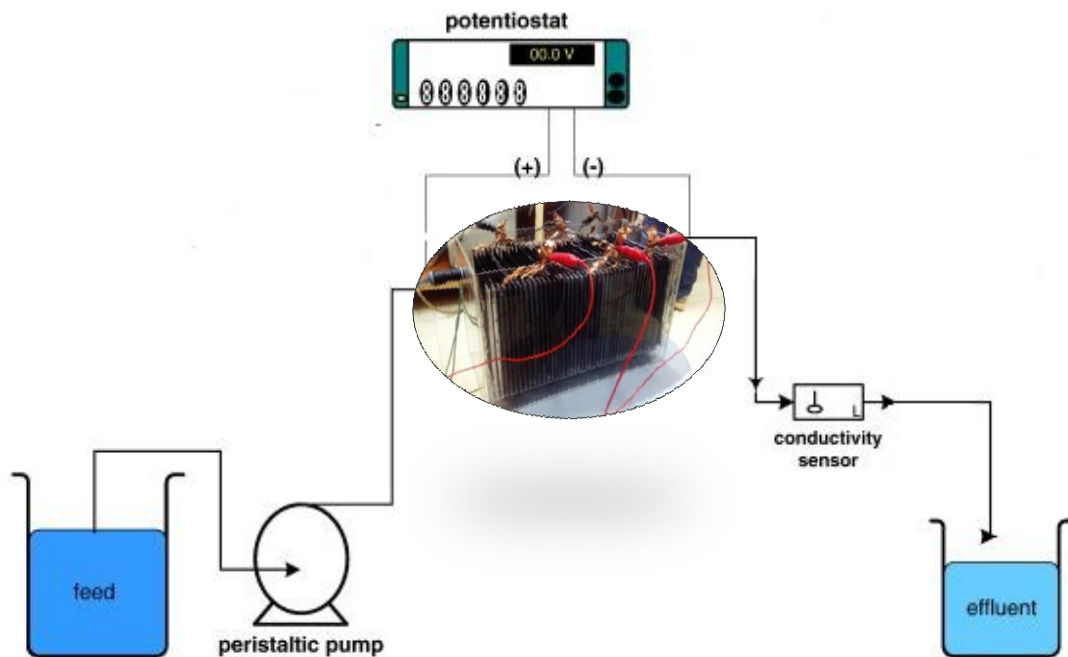


Figure 2: CDI schematic

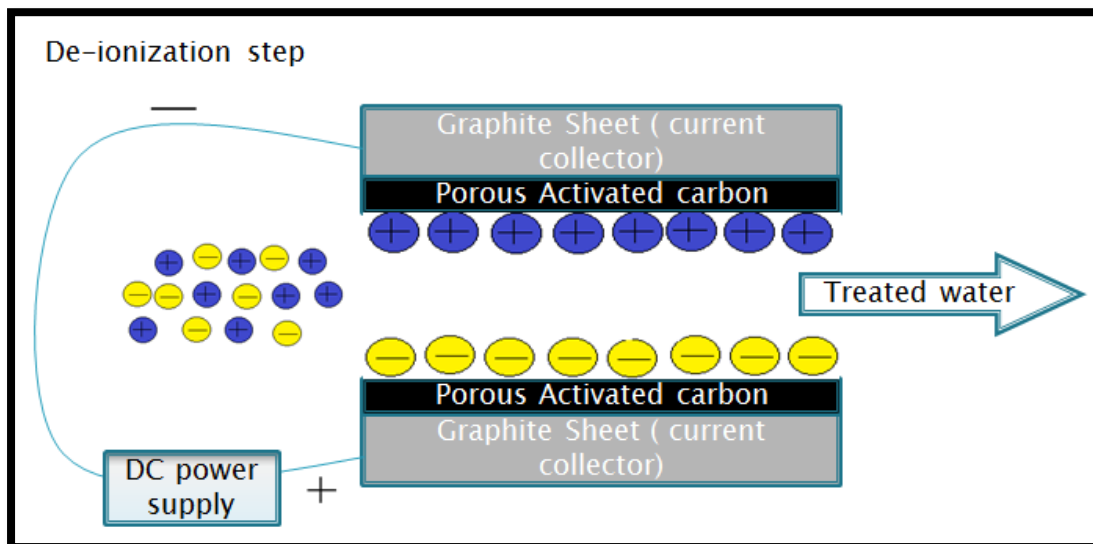


Figure 3: De-ionization process

During the operation of CDI cell after a certain time there was no significant removal of ions which indicated that the electrode's surface was saturated with the ions and it was time to regenerate them.

### 3.5.2 Regeneration Step

Regeneration was done by reversing the voltage across the electrode and then flushing the electrodes with tap water. The regeneration was carried out by reversing the electric charge and by removing the electric charge altogether. Once optimised the electrodes were then regenerated in batch and in continuous flow systems. The tap water was used for regeneration purposes as it yielded almost similar results to distilled water.

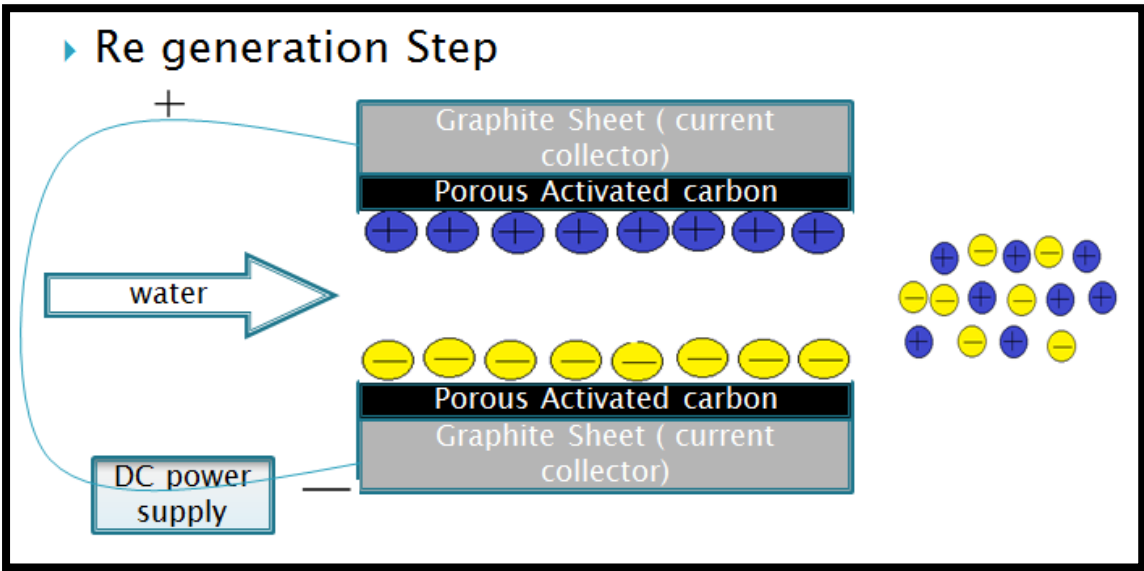


Figure 4: Regeneration process

## 4. Results and Discussions

### 4.1 Experimental Results

Experimental results consisted of different stages like adsorption in continuous and batch system and similarly regeneration in continuous and batch system. Additionally different voltage values are also checked and finally optimized.

#### 4.1.1 Adsorption in Batch flow system at different voltages

Adsorption step was carried out at different voltages like 1.4, 1.6 and 1.8 volts. Results of adsorption at different voltages gave different results which are listed in table 4. The adsorption step was carried out by running a synthetic solution of Sodium Chloride of 2000 ppm concentration. All experiments were triplicated and the effluent TDS at varying retention times was measured. The experiments were first carried out in a batch system and the values of voltage provided to the electrodes and the retention time were optimized. The experiment was then carried out in continuous flow with the optimized values for voltage and retention time. The experiment data is shown below.

Table 3 : Adsorption in batch system

Time (min)	TDS (ppm)		
	1.8 V	1.6 V	1.4 V
0	2000	2000	2033
30	1453	1610	1447
60	1292	1290	1283
120	1022	966	1074
180	871	840	925
240	827	861	880
300	1220	1150	1320

From table 4, it can be seen that 1.8V and 1.6V gave better results as compared to 1.4V.

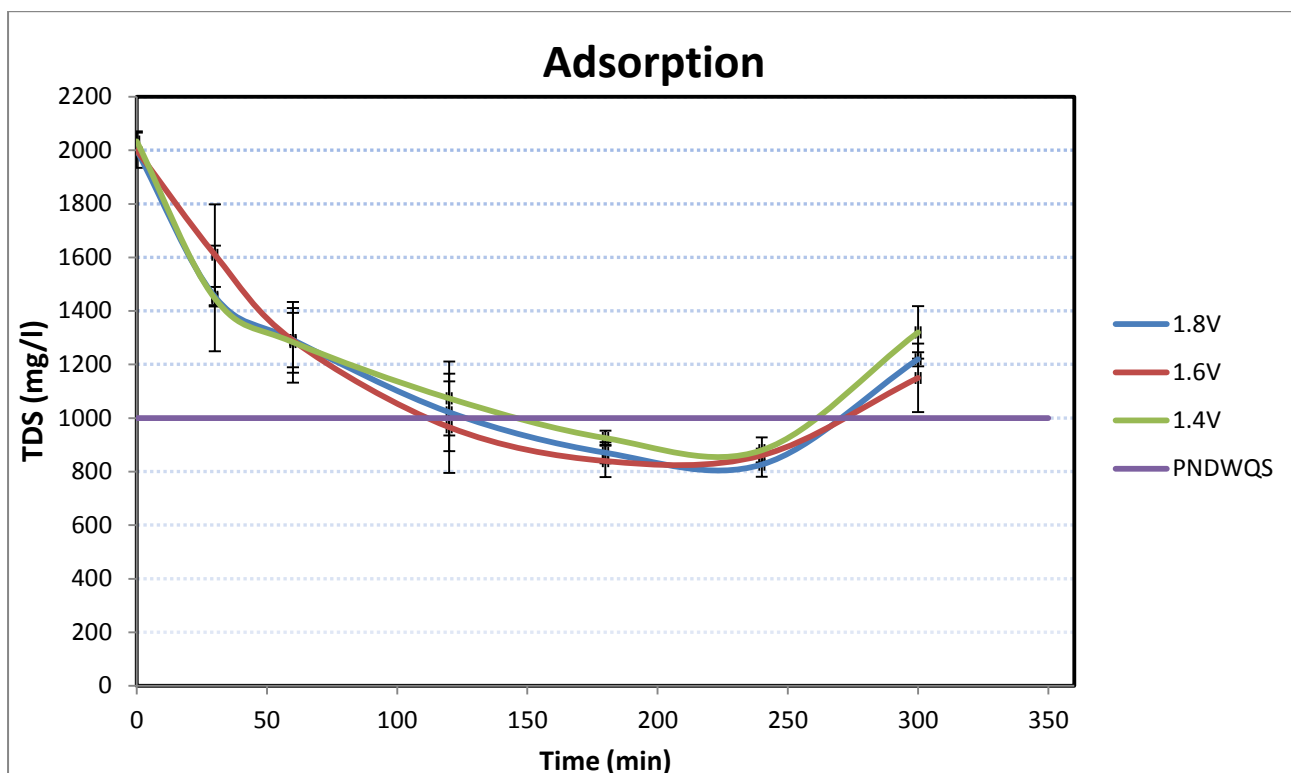


Figure 5: Adsorption in batch

The experiments results show that as the voltage is increased from 1.4V to 1.8V the TDS removal of the system is more effective. The effluent TDS falls below the Pakistan National Drinking Water Quality Standards (PNDWQS) of 1000 ppm after a retention time of 2 hours. At higher voltages this is achieved earlier as compared to the lower voltages. The effluent's TDS remains below the PNDWQS for almost 2.5 hours (150 min). This again varies for different voltages. The higher voltages have a greater time span where the TDS is below 1000 ppm and the lower voltages have a shorter time span. The lowest value of effluent TDS was observed to be 827 ppm at a voltage of 1.8V and a retention time of 4 hours. After a certain time of operation the effluent's TDS starts increasing, this is due to the surface of electrodes being saturated with salts and indicates the need of Regeneration (Desorption).

#### 4.5.2 Adsorption results at optimized voltage and Retention time for continuous system

The voltage was optimized at 1.8V from the results of the batch system. The value of retention time was also optimized from the results of the batch system and it was found to be 3 hours. The TDS of the effluent however did fall below the PNDWQS at 2 hours and so the continuous system was run at a flow rate of 8 ml/min to ensure a retention time of 2 hours. The table 4 below shows the results of the continuous system.

Table 4 : Adsorption in continuous system

Adsorption						
Time (min)	TDS (ppm)			Mean	SD	C.V (%)
	Run 1 (16/5/14)	Run 2 (23/5/14)	Run 3 (5/6/14)			
0	2050	2050	1990	2030	34.64	1.71
120	803	560	900	754	175.15	23.22
150	847	784	958	863	88.10	10.21
180	921	814	945	893	69.74	7.81
210	1210	871	1250	1110	208.23	18.75

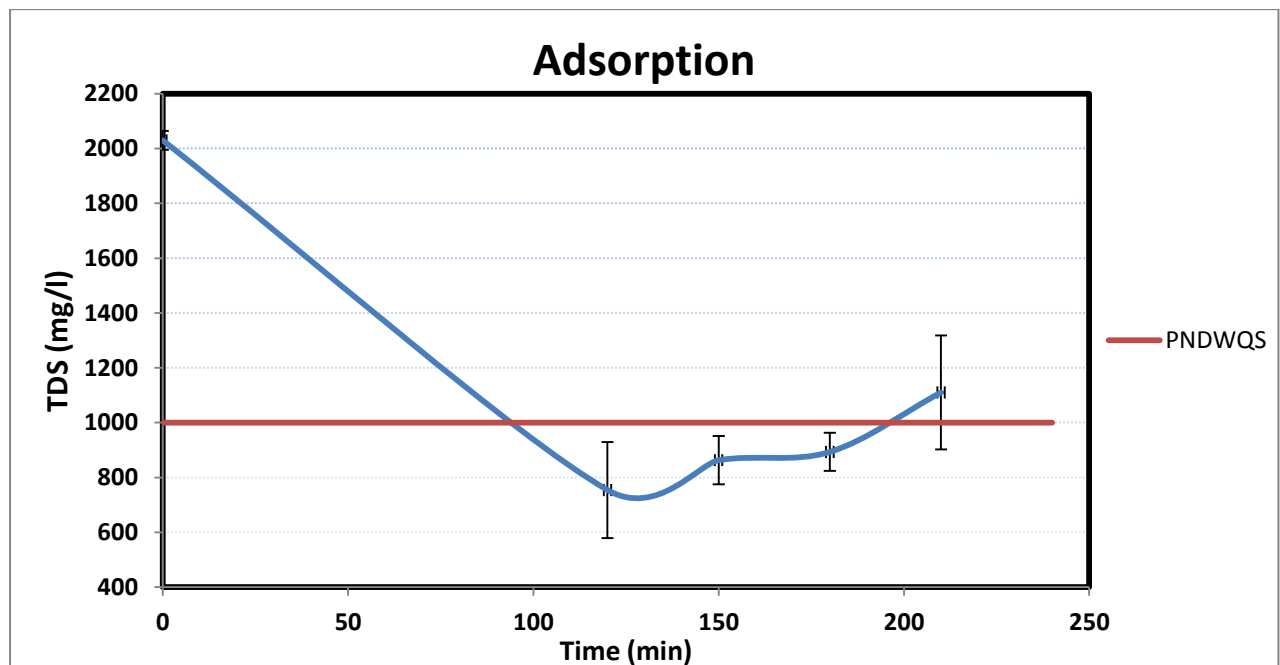


Figure 6: Adsorption in continuous system

It can be seen from the figure 6 that the effluent TDS falls below 1000 ppm after 90 minutes of flow. The lowest effluent TDS observed was 754 ppm after 2 hours of operation from the start. The effluent TDS remains below 1000 ppm for 1.5 hours (90 min) after which the electrodes' surface gets saturated due to the adsorption of salt ions on the surface and the effluent TDS starts increasing.

#### 4.5.3 Electrodes performance over time

The experiments were carried over a time period of 3 months. The electrodes were regenerated after their surface was saturated with the adsorbed salts. So during the complete research the electrodes were regenerated and used for adsorption repeatedly. The electrodes performance over the entire research period is shown in the table and figure below. Every subsequent reading is after regenerating the electrode.

Table 5 : Electrode performance during Adsorption

Time (days)	Influent (ppm)	Effluent (ppm)	PNDWQS (ppm)
0	2000	800	1000
1	1930	805	1000
10	1990	912	1000
20	2010	820	1000
30	2010	825	1000
40	2050	825	1000
50	2060	910	1000
60	2000	846	1000
70	2060	855	1000
80	2050	650	1000
90	1990	720	1000

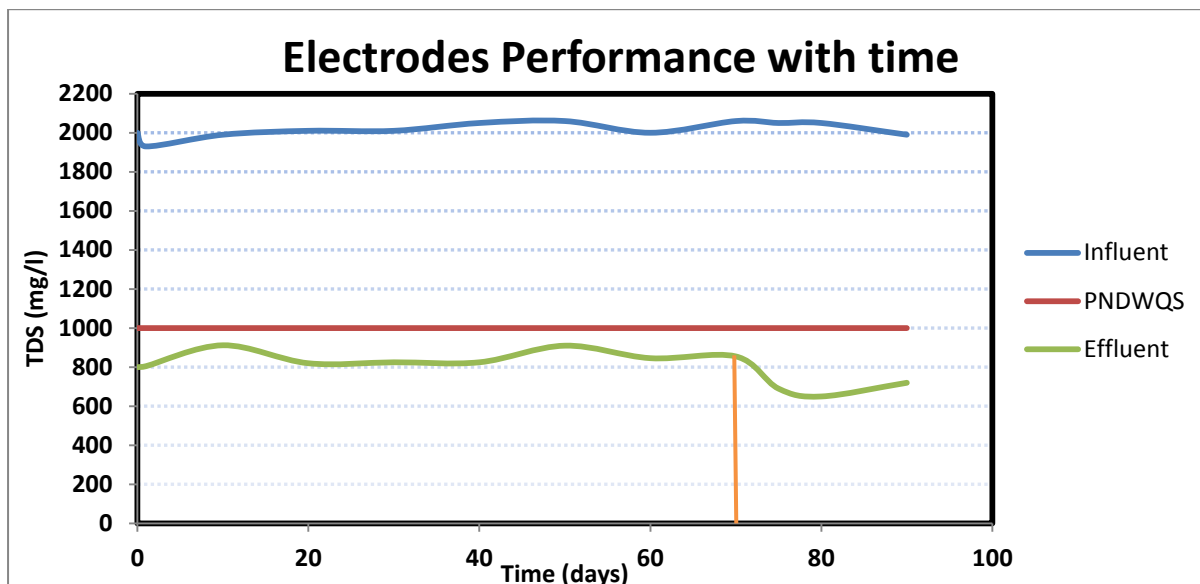


Figure 7: Electrode performance during Adsorption

The electrodes yielded almost similar results over the entire research period. The effluent TDS remained below 1000 ppm and the undulations in the Effluent line in the graph in figure 7 is because of the effect of different voltages. The electrodes were first tested for adsorption in a batch system for 70 days and then in a continuous flow system for the last 20 days.

### Regeneration

Once the electrodes were saturated i.e. they had adsorbed the salt ions to their full capacity, the surface becomes blocked and cannot adsorb any further salts from the solution. This necessitates regeneration. Various methods can be implied for regeneration. The most common is to remove or reverse the electric charge and pass clean, relatively less saline water through the electrodes to wash away the adsorbed salts. In this project we checked the effect of electric current on the regeneration of electrodes and also regenerated the setup using batch and continuous flow streams. Tap water or distilled water can be used for the washing purpose or a proportion of the treated water can also serve the purpose. In this research tap water was used for regeneration.



#### 4.5.6 Regeneration in Batch with electric Current reversal

The current carrying leads were reversed on the electrodes and then voltage was initially supplied for a short period of 10 to 15 seconds. The tank was filled with tap water simultaneously. The opposite charge now results on the electrode and the adsorbed ions are repelled from the electrodes into the water making it saline. The water was given some time so that the ions which weren't repelled could also be removed by physical desorption. The table 6 and figure 8 below show the effect of current on regeneration.

Table 6 : Regeneration with current reversal

Time (min)	TDS (mg/l)
0	0
12	460
60	1550
120	1900
180	2050

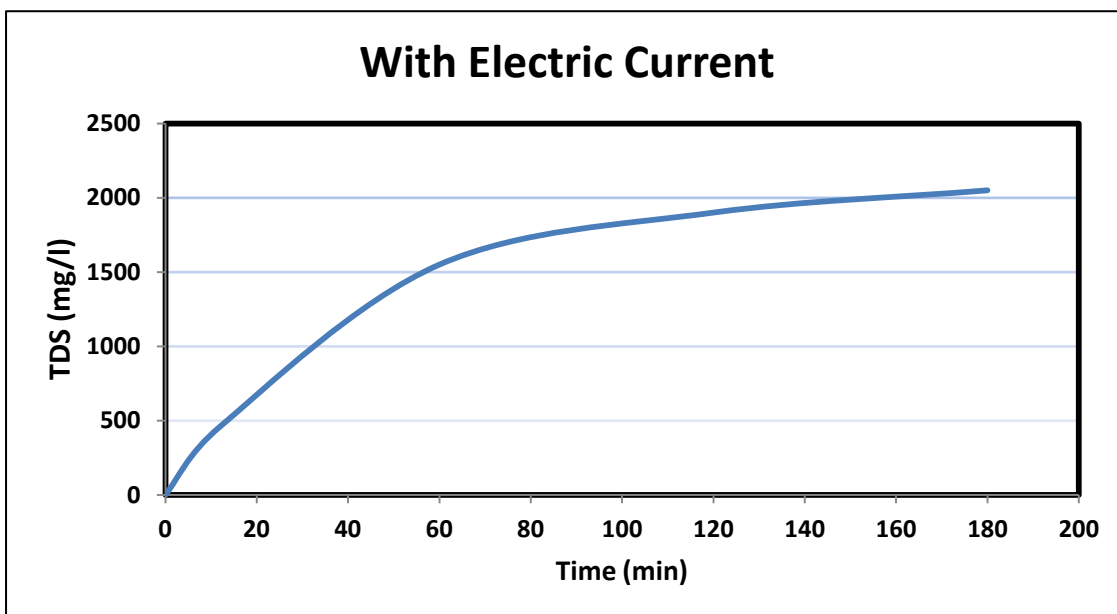


Figure 8: Regeneration with Electric Current Reversal

The initial reversal of the voltage resulted in a rapid release of salts into the solution. The salts adsorbed at the surface are easier to remove and take less amount of time. Most of the surface adsorbed salts were removed in the initial 90 minutes. After this the slope of the figure decreases which indicates that now the deeper adsorbed ions are being removed. At retention time of 2 to 3 hours the electrodes can be regenerated to their initial stage and almost all the salts are removed.

#### **4.5.4 Regeneration in Batch without Electric Current**

The current can totally be switched off and the regeneration can be done purely by the water. The force of attraction that holds together the ions on to the electrodes is mainly due to the electric charge. Once that is switched off the force weakens and as water flows through the electrodes it can flush away the salts with ease. Again saturated electrodes were regenerated and tap water was used for the regeneration. The table 7 and the figure 9 below show the results.

Table 7 : Regeneration in Batch without Electric Current

<b>Time (min)</b>	<b>TDS (mg/l)</b>
0	0
12	348
60	1491
120	1828
180	1938

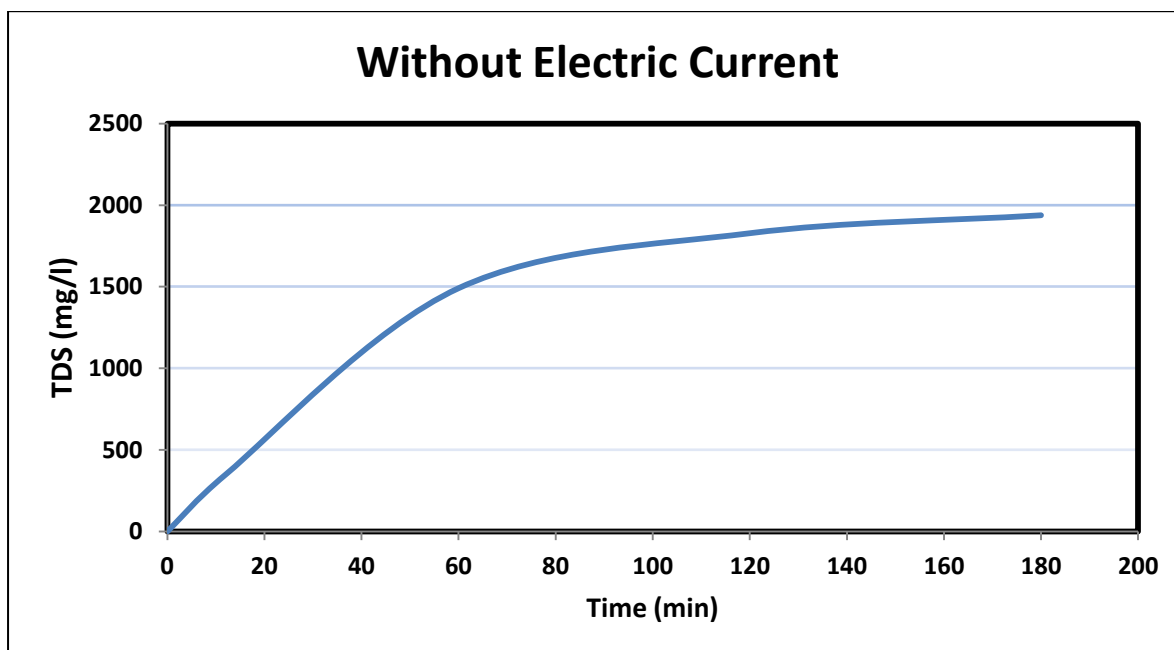


Figure 9: Regeneration in Batch without Electric Current

The results indicate that most of the desorption occurs in the initial 100 minutes and then the slope of the figure starts decreasing and a flat curve is observed. The overall slope of the figure is less as compared to the regeneration done using electric current but after a retention time of 3 hours most of the salts are removed from the electrodes' surface and as compared to the desorption carried out by using electric current it differs by 112 ppm.

#### 4.5.5 Regeneration in continuous System without current reversal

The electrodes can also be regenerated by using a continuous flow of water having a low salt content. The water used again was tap water for this purpose. It was passed through the electrodes with a flow rate of 100 ml/min and no current was used for desorption which had earlier been optimized in the batch studies. The results are shown in the table 8 and figure 10 below.

Table 8 : Regeneration in continuous w/o current

Time (min)	TDS (mg/L)
0	26
8	325
18	494
28	550
38	624
48	742
90	917

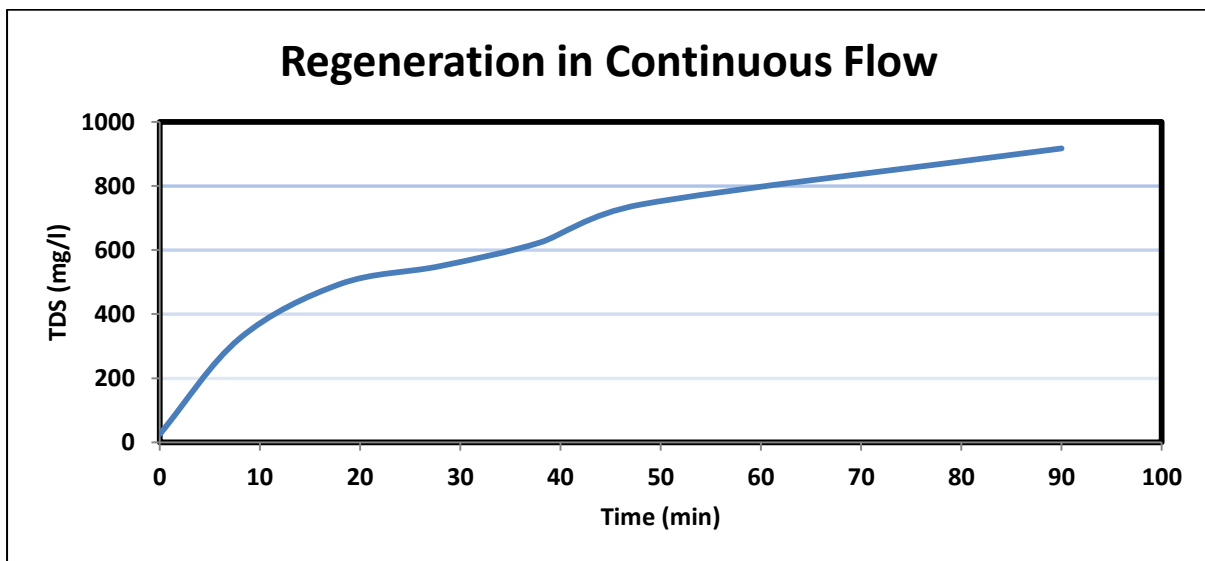


Figure 10: Regeneration in continuous w/o current

This method of regeneration also removes the adsorbed salts from the electrodes. The removal of salts is slow as compared to the batch system and requires greater time. The slope of the figure after the initial descent doesn't vary much and so the salts are still being removed at a constant rate. The experiment was carried out for 90 minutes and the electrodes still were not regenerated to their initial state even though 9000 ml of water had been used up in the experiment. The retention time plays a vital role in the desorption of the salts from the surface. The more the retention time provided the more is the removal of salts. So in a continuous system as the retention time is less so the removal of salts is also less as compared to the batch system.

## 4.6 Energy Dispersive X-ray Spectroscopy (EDS)

This was carried out to find out the relative proportions of elements in the electrodes. The electrodes made were of porous activated carbon, PVDF for binder material and NN-dimethyl acetamide was used as the solvent. Relative proportions of all these were found in the EDS analysis.

EDS makes use of the X-ray spectrum emitted by a solid sample bombarded with a focused beam of electrons to obtain a localized chemical analysis. All elements from atomic number 4 (Be) to 92 (U) can be detected in principle. Qualitative analysis involves the identification of the lines in the spectrum and is fairly straightforward owing to the simplicity of X-ray spectra. Quantitative analysis (determination of the concentrations of the elements present) entails measuring line intensities for each element in the sample and for the same elements in calibration Standards of known composition.

Since the electron probe analyses only to a shallow depth, specimens should be well polished so that surface roughness does not affect the results. Sample preparation is essentially as for reflected light microscopy, with the provision that only vacuum compatible materials must be used. Opaque samples may be embedded in epoxy resin blocks. For transmitted light viewing, polished thin sections on glass slides are prepared.

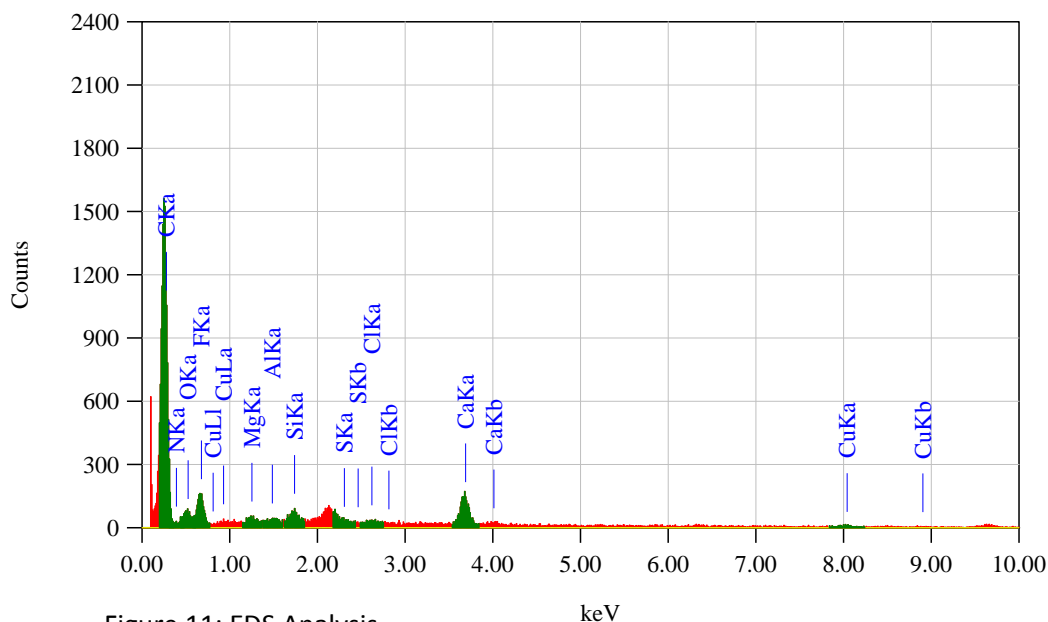


Figure 11: EDS Analysis

keV

From figure 11 it is evident that the most number of counts were obtained for Carbon (C). This is due to the fact that all electrodes had the coating of activated carbon which consists mainly of Carbon. Carbon concentration results were obtained by using the x-ray radiation of energy of about 0.3 keV energy. Slight concentrations of other elements like nitrogen, oxygen, Fluorine, copper, magnesium, Aluminum, Silicon, Sulfur, Chlorine and Calcium can also be reported from the figure 11. Range of energy of X-ray radiation used was from 0 -10 keV.

Table 9 : EDS Analysis Results

Element	(keV)	Mass%	Error%	Atom%	Compound	Mass%	Cation	K
C K	0.277	29.87	0.28	35.60				25.4340
N K*	0.392	47.39	3.64	48.45				60.2748
O K*	0.525	6.81	3.93	6.10				2.4437
F K	0.677	10.26	1.84	7.74				2.7448
Mg K*	1.253	0.41	0.68	0.24				0.3792
Al K*	1.486	0.25	0.60	0.13				0.2852
Si K*	1.739	0.59	0.57	0.30				0.8083
S K*	2.307	0.03	0.45	0.02				0.0623
Cl K*	2.621	0.14	0.50	0.06				0.2493
Ca K	3.690	3.12	0.80	1.11				5.7588
Cu K*	8.040	1.12	3.95	0.25				1.5597
<b>Total</b>		<b>100.00</b>		<b>100.00</b>				

From the data in table 9 above obtained through the EDS analysis of activated Carbon electrode shows that greatest mass fraction obtained for the elements was for nitrogen (N) that was 48.45% of the total mass. There are several reason for higher nitrogen mass fraction, one reason is that NN-dimethyl was used as a solvent to make the activated carbon slurry that

was coated on the graphite sheet, as NN-dimethyl is composed of nitrogen that caused an increase in Nitrogen mass fraction. Another reason for higher nitrogen content is that activated carbon surface is composed of different sizes of pores. From SEM analysis of the electrodes, the pore size range observed was from 24 to 41nm. These pores also accumulate a little bit of air molecules, as the 78% fraction of air is Nitrogen so this factor also causes an increase in nitrogen concentration.

The second highest mass fraction obtained for an element was for carbon that was around 30%. This was due to composition of activated carbon which is almost 99% carbon. The third highest mass fraction was for fluorine that was around 10%, this mass fraction of fluorine is attributed to the presence of Poly Vinyl Di-flouride which is used as a binder in making the activated carbon slurry. Oxygen mass fraction was mainly due to the presence of air molecules in the pores present on the surface of activated carbon electrode. Minor fractions obtained for other elements were due to presence of some impurities in the chemicals used for making the activated carbon slurry.

#### **4.7 Cyclic Voltammetry (CV)**

The cyclic voltammetry was performed to find the double layer characteristics of the electrodes. The electrodes during adsorption exhibit a double layer phenomenon and this can be studied and confirmed using CV. Cyclic voltammetry is the most widely used technique for acquiring qualitative information about electrochemical reactions. It offers a rapid location of redox potentials of the electro active species. In order to measure the capacitance of each electrode, cyclic voltammetry (CV) consists of three electrodes cell system and was performed using the AutoLab PGSTAT 30 (Eco Chemie, Netherland) with a three electrode cell at room temperature. The working electrode was a platinum wire attached to a small piece of carbon material; the counter electrode was a large piece of carbon material clipped to another platinum wire; and the reference electrode was an Ag/AgCl electrode. The carbon

electrode as a working electrode was immersed in the feed solution for CV measurement. An Ag/ AgCl, saturated KCl electrode and Pt/Ti plate was used as a reference and counter electrode, respectively. The potential was swept between -1 and 1 V with scan rates between 1 and 100 mV/s. The sweep range was from 100 kHz to 10 mHz with an amplitude of 5 mV.

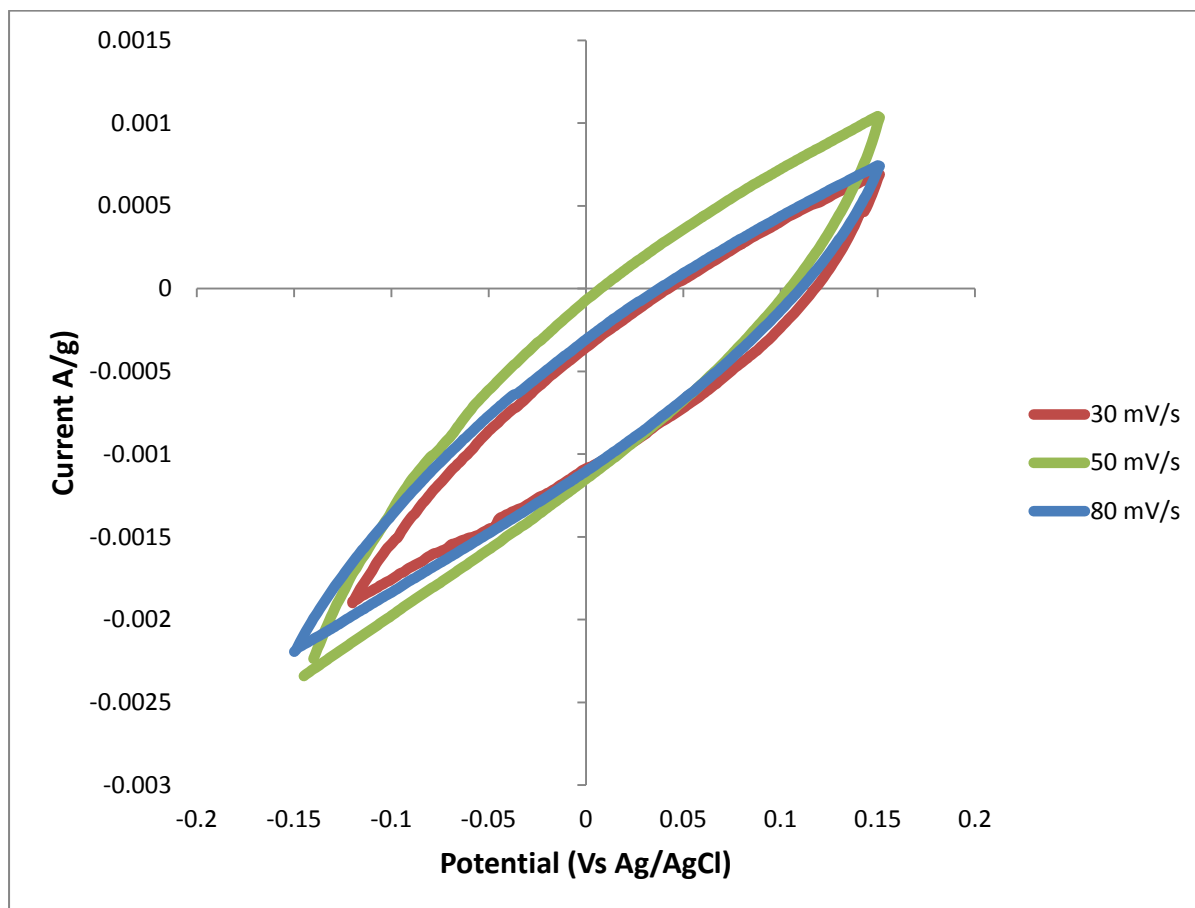


Figure 12: Cyclic Voltammetry

The cyclic voltammogram of smaller strip of electrodes at three different scan rates (5, 20, 50 mV/s) are shown in Figure 12 above. The CV shows that the electroadsorption and electrode desorption peaks have similar shape. This suggests that electrodes can form electrical double layer under charge potential, when the charge potential reversed, the formed electrical double layer gradually diminished. CV tests also showed the absence of any major faradic



charge transfer, indicating the fact that ions were removed from the NaCl solution by formed electrical double layer rather than the electrochemical reactions (Chen, 2011)

#### 4.8 Scanning Electron Microscopy

Scanning Electron Microscopes (SEM) are used for inspecting topographies of materials with a magnification range that encompasses that of optical microscopy and extends it to the nanoscale.

We conducted SEM through Low Vacuum Scanning Electron Microscope (JSM-6490LA) for A.C electrodes to find out the size of the pores that are present within these electrodes.

Given below are various SEM images obtained. The whitish color indicates binder material while black color with porous geometry indicates presence of activated carbon. Moreover, the electrodes were

studied under different resolution power which is mentioned on individual image and the size range of each image is also mentioned.



Figure 13: Low Vacuum Scanning Electron Microscope

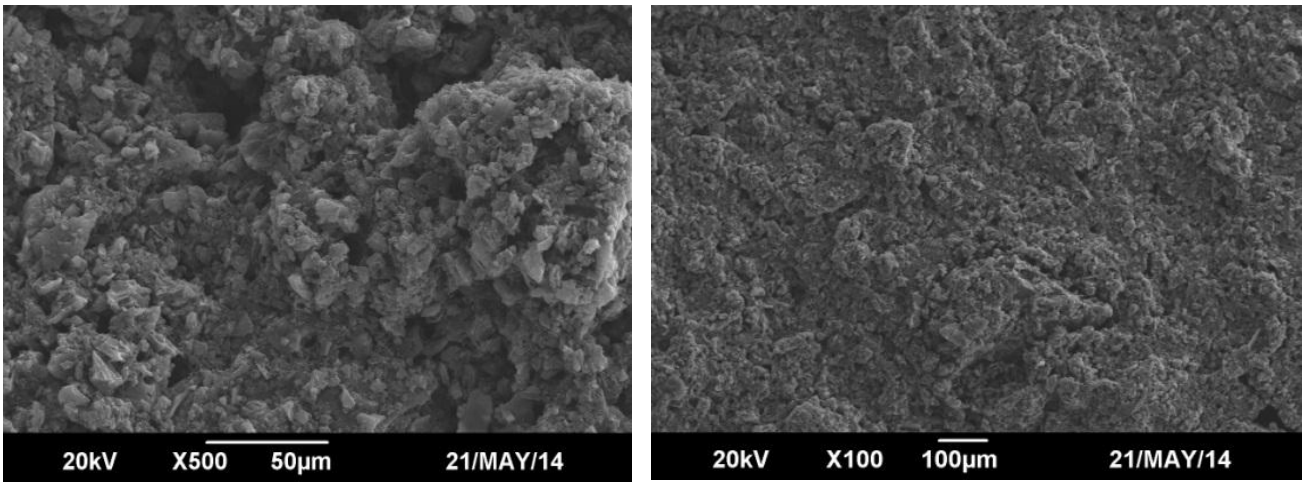


Figure 14: SEM images

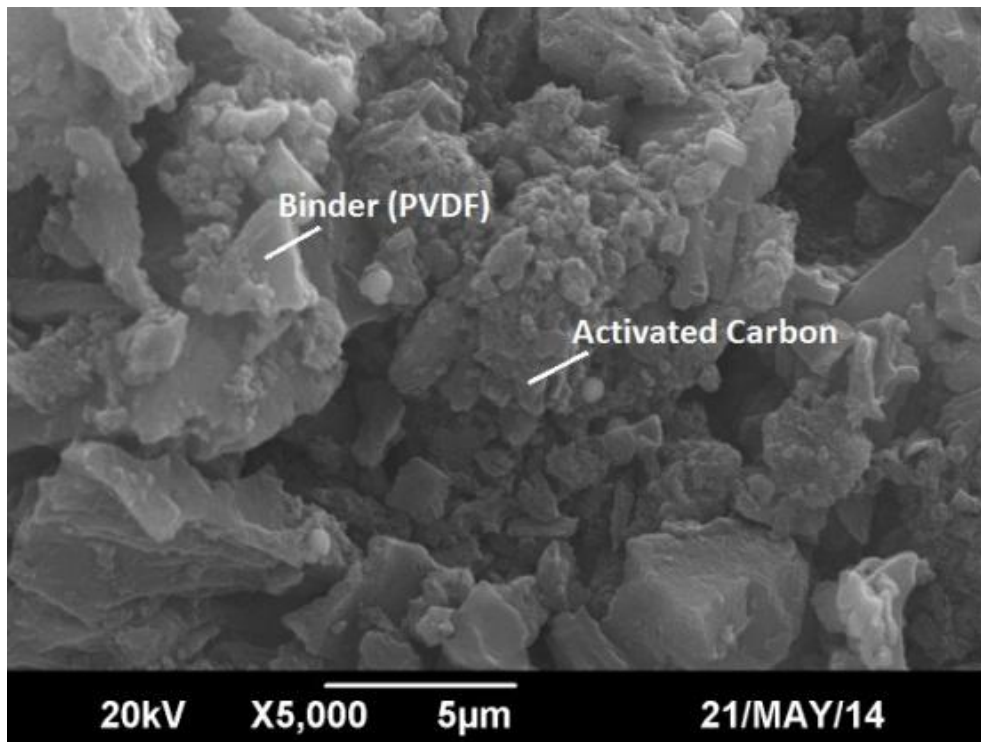


Figure 15 SEM at 5000X resolution

The resolution power of the above image is 5000X and shows surface characteristics accurately upto 5 microns.

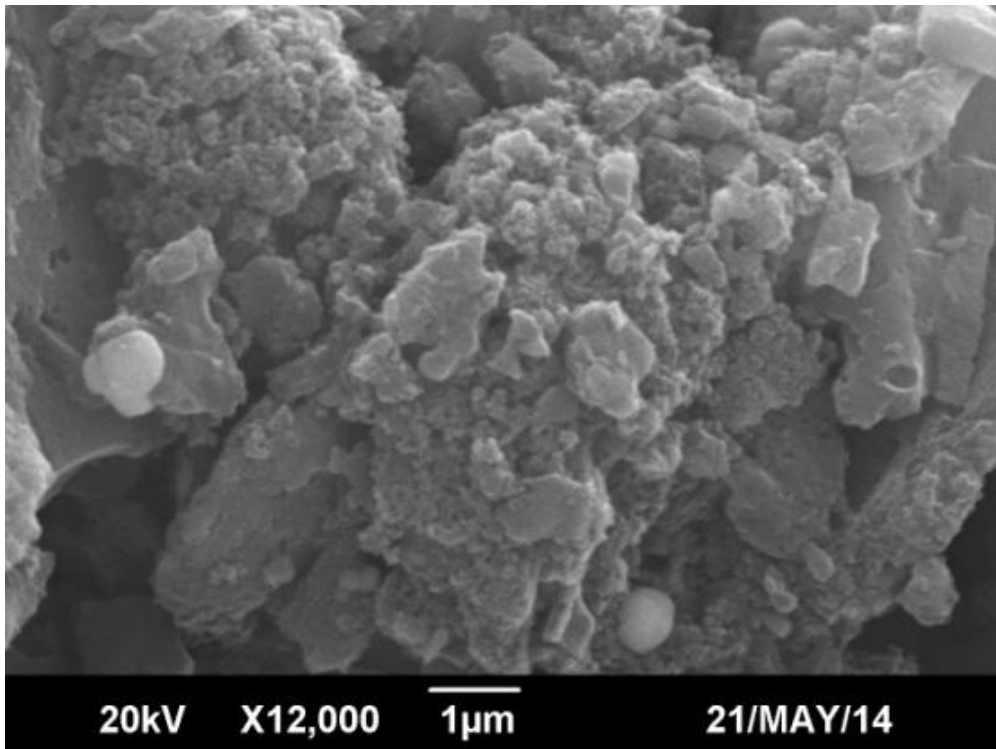


Figure 16 SEM at 12,000X Resolution

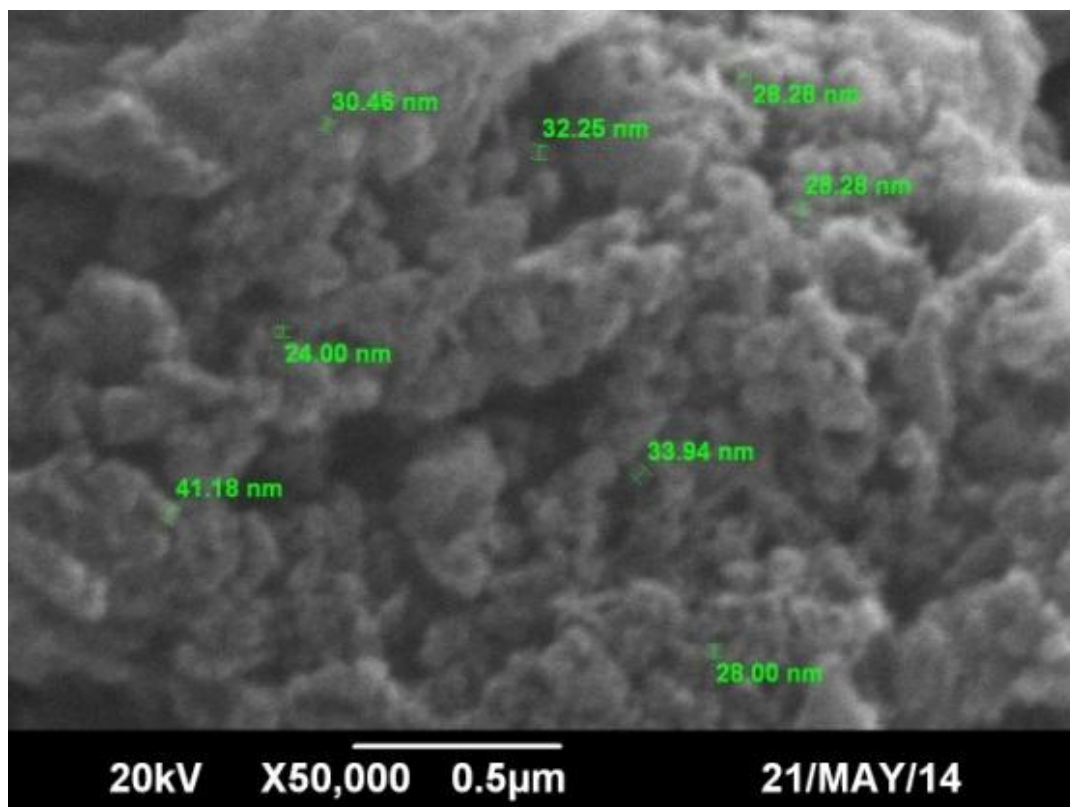


Figure 17 Pore Size through SEM

The above SEM image shows different pore sizes at different areas of the electrode. As the electrodes were prepared manually therefore there is quite a difference between pore sizes. The average pore size from figure 17 comes out to be about 30 nm.

#### 4.9 Pore Size Analysis

Activated carbons were characterized by nitrogen adsorption at 77 K. Before adsorption experiments, all the carbon samples were degassed at 523 K for 5 h. The BET surface areas of carbons were obtained from nitrogen adsorption in the relative pressure range from 10<sup>-6</sup> to 1.0 using Micromeritics, ASAP2020. Pore volumes were estimated to be the liquid volume of adsorption (N<sub>2</sub>) at a relative pressure of 0.99. The pores size distribution of carbons was obtained by employing the Density Functional Theory. The characteristics of activated carbon electrode used are listed in Table 10 below.

Table 10 : Pore Size Analysis

<b>Surface Area</b>	
Single point surface area at p/p <sup>o</sup>	0.250167325: 544.5992 m <sup>2</sup> /g
BET Surface Area	539.7669 m <sup>2</sup> /g
Langmuir Surface Area	759.1025 m <sup>2</sup> /g
Micro pore Area	295.2526 m <sup>2</sup> /g
External Surface Area	244.5143 m <sup>2</sup> /g
<b>Pore Volume</b>	
Single point adsorption total pore volume	0.258070 cm <sup>3</sup> /g
Micro pore volume	0.143589 cm <sup>3</sup> /g
Adsorption cumulative volume of pores	0.081121 cm <sup>3</sup> /g
<b>Pore Size</b>	
Adsorption average pore width (4V/A by BET)	19.1246 Å
Adsorption average pore width (4V/A)	20.433 Å

## 5. Conclusion

The CDI system consistently achieved acceptable NDWQS limits over the entire test period of 3 months. There was a very slight decrease of around 3-4% in the efficiency of electrodes during the 3 months experimentation period which was observed from the two readings obtained at 1.8V. Study was done for both batch and continuous systems, the continuous system was observed to be efficient in different parameters compared to the batch system. The continuous system showed 4-5% higher TDS removal efficiency than the batch system. The continuous system treated 10% more volume of water in single run before the electrodes saturation occurred. Optimum retention time required for continuous system was 2 hours while it was 3 hours in case of batch system. Applied voltage was also an important parameter; increase in voltage showed a positive impact on the removal of salts from the water but with the increase of voltage beyond 1.8V electrode surface started cracking. Electrodes regeneration can be done by using tap water having TDS in the range of 300-500 mg/L. Desorption was studied with and without switching the charge on electrode and there was no considerable difference in efficiency of both the methods, no use of electric energy in the desorption phase decreases operation and maintenance cost.

## 6. Recommendations

The technology has several dimensions to study in future to increase process efficiency.

Performance of different types of adsorbents like carbon aerogel, carbon black and carbon cloth can be studied.

Adsorption potential of the electrodes can be increased by mixing KOH or TiO<sub>2</sub> nanoparticles in the activated carbon, this increase as reported by M.-W. Ryoo, G. Seo (2003) is due to the increase in surface area of the electrode.

The relation between the increase in number of electrode pair and treatment efficiency can be studied.

The capacitive deionization unit up-scaling shall be performed to achieve higher efficiency.

Performance of the system can be studied at higher TDS concentration i-e 4000-5000 mg/L.

Concept of salinity gradient solar ponds can be developed to recover solar energy from rejected Brine as reported by C. Karim et al (2010).

Armed forces convoys can use our handy systems to have clean drinking water in remote areas of Pakistan.

Our gadget can be registered by NUST after full scale testing by the armed forces.

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