TREATMENT OF BRACKISH WATER BY USING CAPACITIVE DEIONIZATION (CDI) TECHNOLOGY

A thesis submitted in partial fulfillment of the requirements for the degree

Of

Master of Science

In

Environmental Engineering

By

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(2015)

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DEDICATION

This work is dedicated to my beloved Parents and elder brother, their support and encouragement brought me to this stage today!!!

ACKNOWLEDGMENTS

I would like to express my thoughtful gratitude to my kind supervisor ***Dr. Sher Jamal Khan***. Working under his kind guidance as a *Research Assistant* was an honor for me. His innovative suggestions and valuable comments were a source of motivation for me during the study.

I am sincerely appreciative of ***Dr. Yousuf Jamal*** and ***Dr. Zahir-ud-Din Khan*** for giving me stimulating suggestions and ample encouragement throughout the study. A special thank is address to ***Engr. Muhammad Naveed (WaterAid, Pakistan)*** for accepting me to guide as an external supervisor. His extensive knowledge and his logical way of thinking have been of a great value for me.

I am also thankful to ***Dr. Fouzia Malik (RCMS, NUST)*** and ***Dr. Arshad Hussain (H.O.D Chemical Engineering SCME, NUST***) for conducting cyclic voltammetry and Scanning electron microscope analysis for my project. I would also like to acknowledge graduated student ***Mr. Hussain Kamran*** for his motivational and inspirational support throughout the study.

Fawad Ahmad

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

Abbreviations	**Description**
Q	Adsorption capacity (mg-NaCl/g-adsorbent)
Ci	Influent concentration (mg/L)
Ce	Effluent concentration (mg/L)
Cf	Feed concentration (mg/L)
Cp	Lowest product concentration (mg/L)
V	Volume of effective product (L)
M	Mass of adsorbent (g)
SEM	Scanning electron microscopy
CV	Cyclic voltammetry
TiO_2	Titanium dioxide
PAC	Powdered activated carbon
DI	Deionize water
EDL	Electric double layer
PTFE	Polytetrafluoroethylene
EIS	Electrical impedance spectroscopy
AC	Activated carbon
ACC	Activated carbon cloth
BET	Brunauer, Emmett and Teller
RO	Reverse Osmosis
ED	Electrodialysis

CDI	Capacitive deionization
PVDF	Polyvinylidene Fluoride
MVR	Multi Vapor Compression
IUPAC	International Union of Pure and Applied Chemistry
TTB	Titanium Tetrabutoxide
EtOH	Ethanol

ABSTRACT

Capacitive Deionization (CDI) is a desalination technology utilizing electrosorption and desorption of ionic salts. CDI has pulled in much consideration as an alternative to traditional deionization technologies due to environmental friendly and low energy requirements. Carbon materials are the main components of electrodes used while organic and inorganic materials added to bind the electrodes on graphite sheet enhance the desalination performance.

In this study, powdered activated carbon (PAC) as well as PAC combined with titanium dioxide (TiO_2) electrodes was prepared. The deionization performance was evaluated using three CDI systems. Feed solution having concentration of 2,000 mg/L was used in small and laboratory scale CDI systems. PAC + TiO_2 electrodes showed 28% more salt removal as compared to PAC electrodes in the small-scale CDI system using one pair of electrodes. Laboratory-scale CDI system using six pairs of PAC + TiO_2 electrodes showed adsorption capacities of 2.64, 4.30, and 6.67 mg NaCl/g-adsorbent at 1.3, 1.6, and 1.8 volts, respectively. Pilot scale CDI system using 20 pairs of PAC + TiO_2 electrodes at 1.8 volts showed maximum salt removal of 84, 82, and 71% for the feed NaCl concentrations of 2,000, 2,500, and 3,000 mg/L with adsorption capacities of 7.7, 10.4, and 11.2 mg NaCl/g-adsorbent, respectively. As the amount of salt ions to adsorbent increases, the exchangeable sites on the adsorbent structure become saturated, which results in decrease of salt removal efficiency, while the adsorption capacities increased with increase in concentration due to elevated mass transfer rate of salt ions inside the pores. The developed electrodes were characterized using cyclic voltammetry (CV) and scanning electron microscopy (SEM).

INTRODUCTION

1.1 Background

Water is a major requirement to support life on earth. Regrettably, Pakistan is thought to be among one of those nations on the planet which are confronting water shortage. Water deficiency is one of the real issues that need a great deal of consideration regarding water management. In excess of 780 million individuals without access to an enhanced drinking water source (WHO/UNICEF report, 2012). Currently Pakistan is ranked 80 among 120 nations regarding drinking water quality as its drinking water sources, both surface and ground water, are contaminated with coliforms, toxic metals and pesticides. Furthermore nearly one-quarter of individuals on the earth live in territories where the ground water is consistently exhausted speedier than it can be substitute (Gleeson *et al*., 2012). Even though over 70% of the surface of the earth is secured with water, access to clean water remains a basic issue around the world (Gleick, 1996). Provision of clean water in a protected, cheap and energy-saving manner is amongst the most difficult technological challenges facing humanity the coming decades (Shannon *et al*., 2008). The world's natural fresh water assets are shrinking due to expanding requirements, so other possibilities for water contribution are being sought after (Ayoub *et al*., 2014). The average per capita supply of clean water will lessen by one third and it is estimated to be happening in next 20 years (UN Report 3, 2009).

The foremost choice for producing water of drinking quality from brackish/seawater is desalination which has been serving many parts of the world, but energy and capital intensiveness are the main concerns for water desalination technologies (Shannon *et al*., 2008).

For the supply of artificial freshwater, immense large scale desalination will therefore serve the need, with treated water coming on stream at a rate of 40-50 million cubic meters per day and estimated to grow up to 100 million cubic meters per day in 20 years (Fritzmann *et al*., 2007).

Water scarcity has been a standout amongst the most genuine social, economic and natural issues all throughout the globe and its significance is clear by the way that per capita water accessibility has decreased in numerous parts of the world. The per capita water availability in West Asia and North Africa region was 1000 cubic meters per year in 2000, which was previously 3600 cubic meters per year in 1960 that is virtually a 75% decrease (Kharraz *et al*., 2012).

The ever increasing population of world, industrial expansion, unsustainable water usage and with several such reasons water demand is increasing which as a consequent decrease per capita water availability. The world is compelled to discover answers for the issues which arise due to expanding trend of lessening water resources. Some of the possible answers are reuse of water by treating water and wastewater, sustainable life style, cutback water consumption, conserving rain water etc. The urge to make freshwater from saline water is more vital consistently every day and the answer to strive against this issue is desalination, which is the most applicable one.

Conventional desalination technologies like reverse osmosis (RO), ion exchange, electrodialysis (ED) are mostly adopted to separate salts from water (Strathmann, 2004; Younos *et al*., 2005). These technologies have various pros and cons, like the energy cost for these processes is very high although the processes are simple and provide high quality freshwater. In RO and ED technologies, there are scaling as well as maintenance of specific permeate flux problems. In the ion exchange process resins are costly, require regular regeneration and produces brine (Younos *et al*., 2005; Zou *et al.*, 2008; Xu *et al.*, 2008). The advantages like low pressure, non-membrane process, make capacitive deionization (CDI) technology competent and alternate technology for desalination (Pekala *et al.*, 1998; Gabelich *et al.*, 2002).

In this study small, laboratory and pilot scale CDI systems were developed. The electrodes were manufactured on graphite sheet by the addition of titanium dioxide particles 12% by weight of powdered activated carbon. Electrodes effectiveness was investigated by evaluating the desalination performance. The developed electrodes were characterized using cyclic voltammetry (CV) and scanning electron microscopy (SEM).

1.2 Objectives

- Designing, installation and operation of small, laboratory and pilot scale CDI systems.
- Comparison of treatment performance of small scale CDI system using powdered activated carbon (PAC) and PAC incorporated titanium dioxide (TiO_2) electrodes.
- Comparison of treatment performances of laboratory scale CDI system at different voltages using the electrodes which give optimum performance in terms of salt removal efficiency in small scale CDI system.
- Comparison of treatment performances of pilot scale at different salt water concentration solutions with optimized voltage at laboratory scale and assess the amount of treated water produced under 1000 mg/L at pilot scale CDI system.

1.3 Scope of Study

During the research study small, laboratory scale and pilot scale CDI systems were operated. The scope of the study can be separated into three phases:

i. **Phase 1**

Small scale CDI system operated at 1.3 Volts for salt water concentration of 2000 mg/L, using PAC and PAC+TiO_2 electrodes to assess electrodes performance in terms of salt removal efficiency and further tested in laboratory and pilot scale CDI systems.

ii. **Phase 2**

Laboratory scale CDI setup consisting of three pairs of PAC+TiO_2 electrodes operated at 1.3, 1.6 and 1.8 volts, at fixed volumetric flow rate of 25 mL/min with salt water concentration of 2000 mg/L to determine optimum voltage at which maximum desalination efficiency achieve.

iii. **Phase 3**

Pilot scale CDI setup consisting of twenty pairs of PAC+TiO_2 electrodes operated at optimum voltage find in laboratory scale CDI system, at fixed volumetric flow rate of 25 mL/min with salt water concentration of 2000, 2500 and 3000 mg/L to find optimum salt water concentration with maximum desalination efficiency.

The following parameters were analyzed during the study.

- Effluent water quality in terms of measuring TDS/Conductivity, adsorption capacity and salt removal percentage.
- Surface morphology of electrodes and characteristics of powdered activated carbon.
- Cyclic voltammetry analysis to discover electrochemical properties of electrode.

LITERATURE REVIEW

About 96.5% of the world's water is spotted in the seas, moreover the water which is brackish or saline resides in saline lakes and ground water forms 1% of earth’s water leaving only about 2.5% of fresh water on earth, from which only 1% water can consumed by human.

Desalination has a long history, a process which eliminates salts from water. Initially desalination was used to acquire potable water from sea water. Now a day a number of technologies have been developed and implemented throughout the world for desalination in which major technologies are distillation, reverse osmosis, nano filtration, ion exchange, electro deionization which are used to remove inorganics or in some case organics impurities.

2.1 Overview of desalination technologies

Existing data, concerning the different desalination technologies and more particularly CDI, was reviewed to support the design, operating and fabrication of CDI test systems along with testing methods. To adequately assess the CDI as a substitute deionization/desalination technology, a systematic understanding of various existing desalination technologies was vital.

Table 2.1 outlines the desalination technologies based on the operating principles. Ion exchange technology is also listed in desalination technologies, though a usual ion exchange technology do precisely what, as meant by its name, it replace unwanted ions from water with more tolerable ions on the solid resin surface. Thus, rely upon the resin type used; the general total dissolved solid content of the water does not actually decrease. Nevertheless, housing water softening units (Sodium chloride regenerated) are widely in use nowadays, and CDI is a possible substitute to conventional ion exchange water softeners.

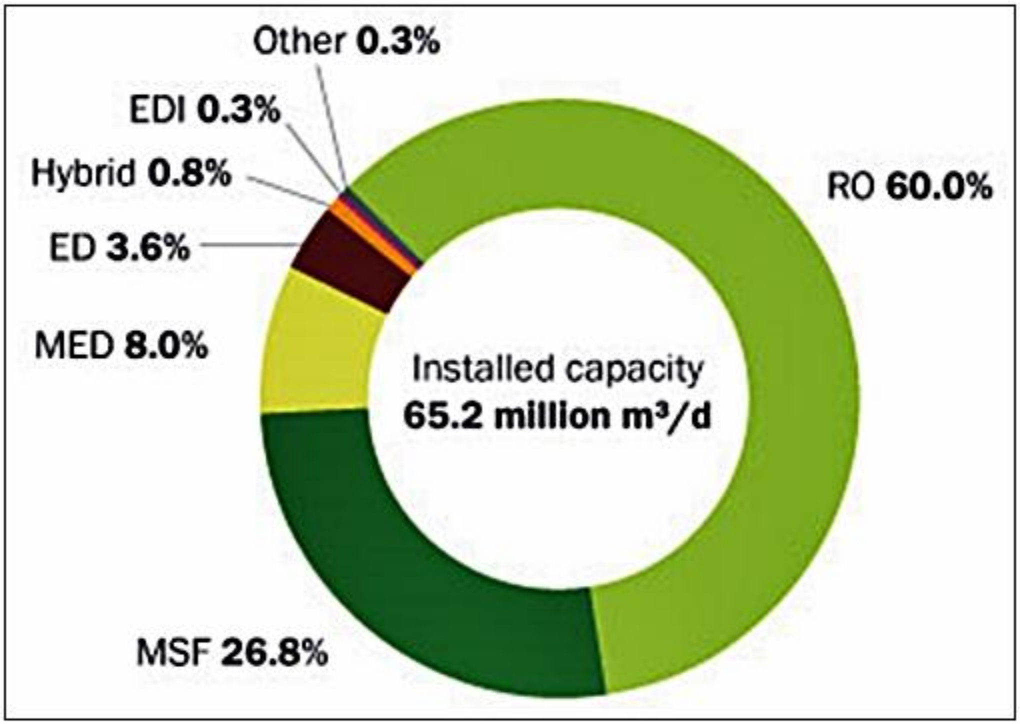
Table 2.1: Desalination technologies and operating principles

Technology	**Operating Principle**	**Typical application**
Thermal Processes		
Multistage Flash Evaporation	Thermal evaporation	Desalination of sea water
Multiple Effect Distillation with (MED) Mechanical Vapor Recompression (MVR)	Thermal evaporation with enhanced energy efficiency	Desalination of sea water
Multiple Effect Distillation with Thermal Vapor Recompression	Thermal evaporation. Less efficient than MVR but more effective than direct distillation	Desalination of sea water
Membrane Processes		
Reverse Osmosis	Driven by pressure and diffusion managed membrane operation. Eliminate particles down to 0.0001 micrometers	Desalination of sea and brackish water
Nano-Filtration	Driven by pressure and diffusion managed Eliminates particles down to 0.001 micrometers	Industrial-water/waste-water and drinking water treatment
Ultra-Filtration	Driven by pressure but does not remove ions. Elimination is based on sieving up to 0.01 micrometers	Industrial-water/waste-water and drinking water treatment
Micro-Filtration	Driven by pressure but does not	Industrial-water/waste-

	remove ions. Elimination is based on sieving up to 0.1 micrometers	water and drinking water treatment
Electrodialysis	Charge driven membrane process that eliminate ions, not turbidity	Primary brackish water desalting
Ion Exchange Processes		
Anion/Cation Exchange	Positive and negative ions in a source water are exchanged from more wanted and less bothersome ions	Feed water for boiler and water softening
Electro-deionization	Charge driven ion exchange process	Ultra pure water production

Date source: Farmer *et al*, 1995

The global desalination capacity of about 90% by volume is symbolized by membrane and thermal desalination technologies already discussed in Table 2.1. Additional desalination technologies include freezing distillation, solar distillation, electrodialysis, hybrid (membrane/power/thermal) and other promising technologies. Figure 2.1 illustrates the globally installed desalination processes (capacity by volume) in 2010.



Date source: Desalination.com, 2012

Figure 2.1: Globally installed desalination processes (capacity by volume) in 2010. Other: Freeze, thermal distillation, nano-filtration and other desalination processes; EDI: Electro-deionization; ED: Electrodialysis; MED: Multiple effect distillation; MSF: Multi stage flash distillation

2.2 Capacitive deionization technology

Capacitive deionization (CDI) is cost effective, performance efficient and environmental friendly desalination technology in which ionic salts are removed electrochemically from brackish water (Huang *et al.,* 2014). CDI involves application of very low electric field between two electrodes which forces the ionic species to adsorb on oppositely charged electrodes. These ions make electrical double layer (EDL) near the surface of electrodes, get held and thus it acts like energy stored in super capacitors (Tsouris *et al.,* 2011). Ions are desorbed from the surface of electrodes by eliminating the electric field and washing with Demonized (DI) or treated water thus results in the regeneration of electrodes (Farmer *et al.,* 1996).

2.2.1 Basic electrochemical cell

To completely clarify capacitive deionization, it is important to survey some fundamental electrochemical principles. The simple electrochemical cell includes two electrodes which are immersed in a solution (electrolyte) which allows current to flow through it. The basic electrochemical cell is illustrated in Figure 2.2

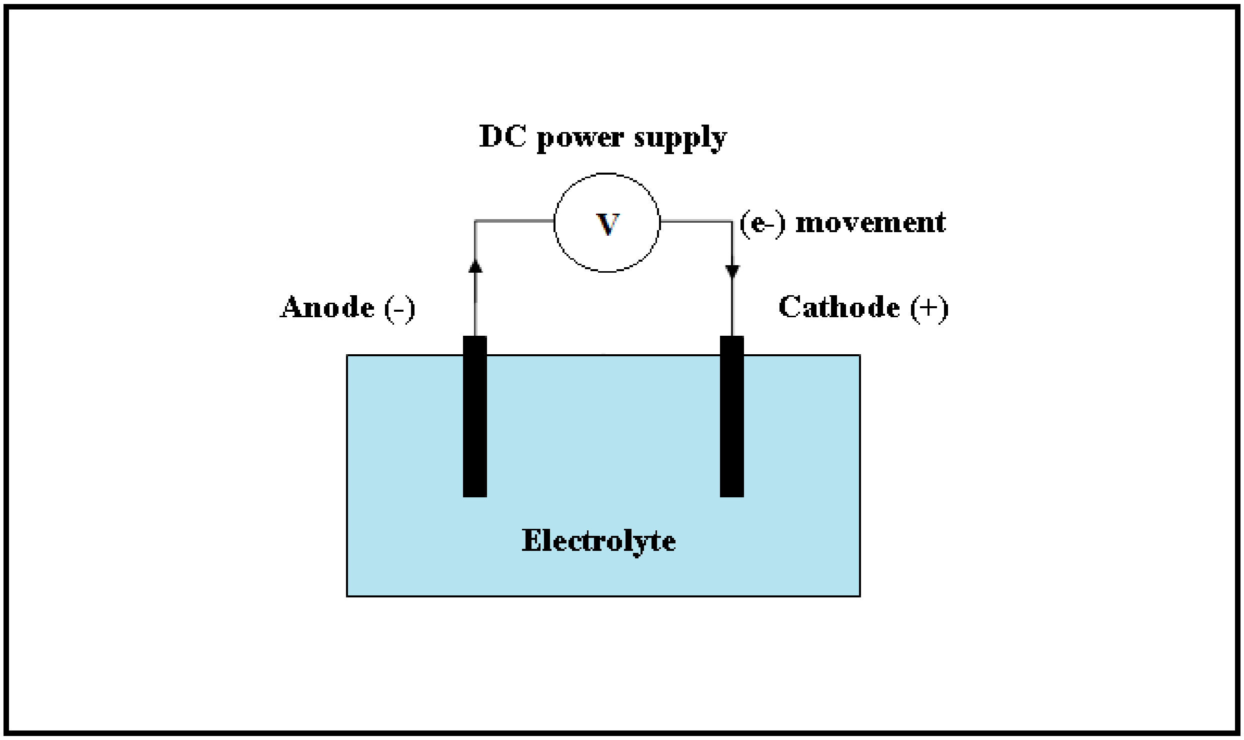


Figure 2.2: Basic electrochemical cell

It is not necessary that anode/cathode must be made up of metals. In the case of CDI the material of electrodes can be any materials which are based on inert carbons like activated carbon, carbon aerogel or other nanostructure carbon. At the point when two different metals with individual electrochemical potentials are utilized as the anode and cathode, a current will stream in the external connection, without the requirement for a power supply. When the anode is prepared by low carbon steel the usual reaction at anode is written as follows:

$$Fe \rightarrow Fe^{+2} + 2^{e-}$$

The aforementioned chemical reaction is termed as typical corrosion reaction which takes place at the surface of low carbon steel (anode) when it comes in contact with any electrolyte. To complete the reaction, the cathode which contacts with the anode by the electrolyte, absorbs the electrons. Common cathode reactions are as follows:

$O_2 + 4H^+ + 4^{e-} \rightarrow 2H_2O$ (Reduction of oxygen in acidic electrolyte)

$\frac{1}{2}O_2 + H_2O + 2^{e-} \rightarrow 2OH^-$ (Reduction of oxygen in basic/neutral electrolyte)

$2H^+ + 2^{e-} \rightarrow H_2$ (Hydrogen liberation from acidic electrolyte)

$2H_2O + 2^{e-} \rightarrow H_2 + 2OH^-$ (Hydrogen liberation from water)

The above mentioned basic electrochemical principles are applicable to entire water treatment technologies which also include CDI. In water treatment technologies the basic aim is to eliminate unnecessary particles (charged or uncharged) from water, in result treating the water.

2.2.2 Surface chemistry of electrode

The electrodes essentially used in CDI and other electrodes generally usually pursue electric double layer theory. This theory expresses that if an electrode is charged negatively and submerged in an electrolyte, then positive charged particles are adsorbed onto the surface, which in result forms a layer of positive charge on the negatively charged electrode surface. This positive layer attracts the negative particles in the electrolyte towards itself, thus forming a second layer of negatively charged particles. The second layer bounds loosely with the first layer and also contains smaller amount of negatively charged particles as compared to the first layer which was positively charged. Figure 2.3 depicts the basic concept of electrical double layer theory.

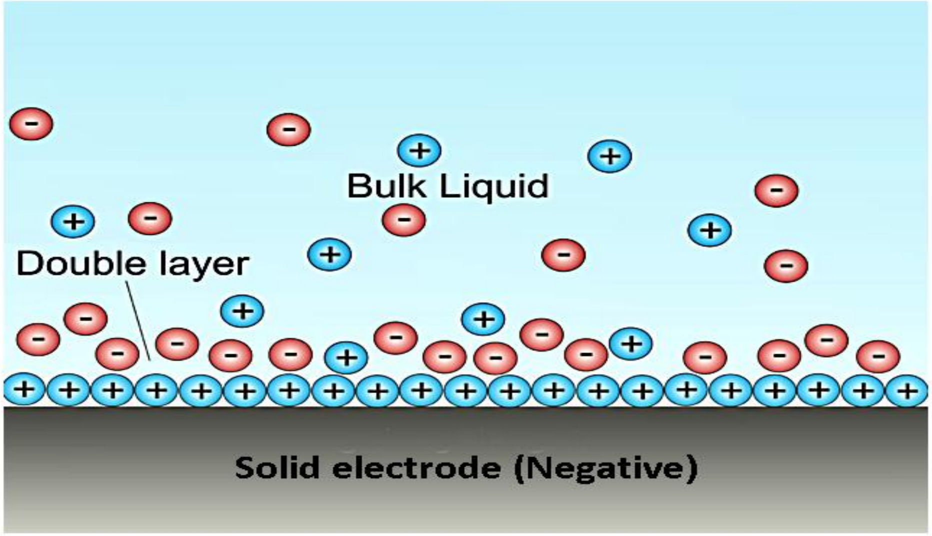


Figure 2.3: Electrical double layer theory

2.2.3 Capacitance

A parallel capacitor is made by submerging two parallel plates in an electrolyte solution. When the charged electrical potential is applied to the capacitor the electrical energy begin to store in it. The electrical energy stored in terms of capacitance is calculated by the following equations.

$$C = Q/V$$

$$C = \frac{\kappa . \varepsilon_o . A}{d}$$

κ = Dielectric constant for a specific medium

= 80.4 for water at 20 °C and 78.5 for water at 25 °C

ε_0 = $8.85 \times 10^{-12}\ C^2/N.m^2$

A = Area of electrode plates

d = Distance between the plates

There are two ways for connecting capacitors, either parallel or series. The equivalent capacitance can be calculated by using following equations.

$$\frac{1}{Ceq} = \sum_n Cn \qquad \text{Capacitors in Parallel}$$

$$\frac{1}{Ceq} = \sum_n \frac{1}{Cn} \qquad \text{Capacitors in Series}$$

2.3 Capacitive deionization

CDI employ all of the aforementioned principles in order to eliminate dissolved charged particles from water. Figure 2.4 depicts the basic operating principle of CDI. An effluent stream is allowed to flow between the electrodes. During its adsorption step, ions are adsorbed onto the surface of porous electrodes by applying a low voltage (1-2 Volts). The negative electrodes attract positively charged ions, similarly the positive electrodes attract negatively charged ions. The ions get held on the surface of electrode by forming electric double layer (EDL). The adsorption step continuous until saturation of electrode. During the regeneration of electrodes the applied potential is removed and electrodes are flushed with DI or treated water. The regeneration stream has high level of salts as compared to effluent stream, because the adsorbed ion gets detached from the electrode thus results in regeneration of electrodes.

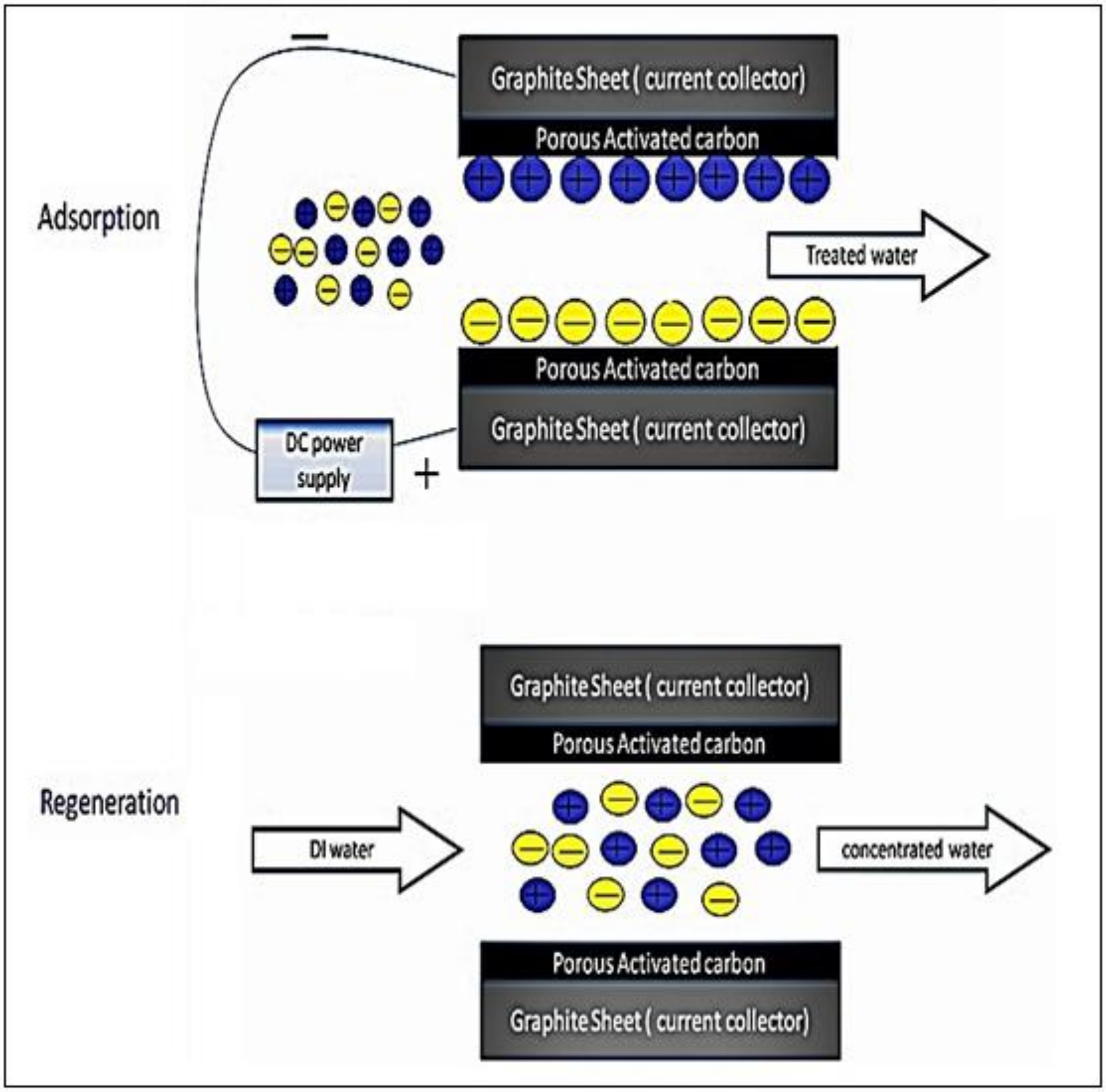
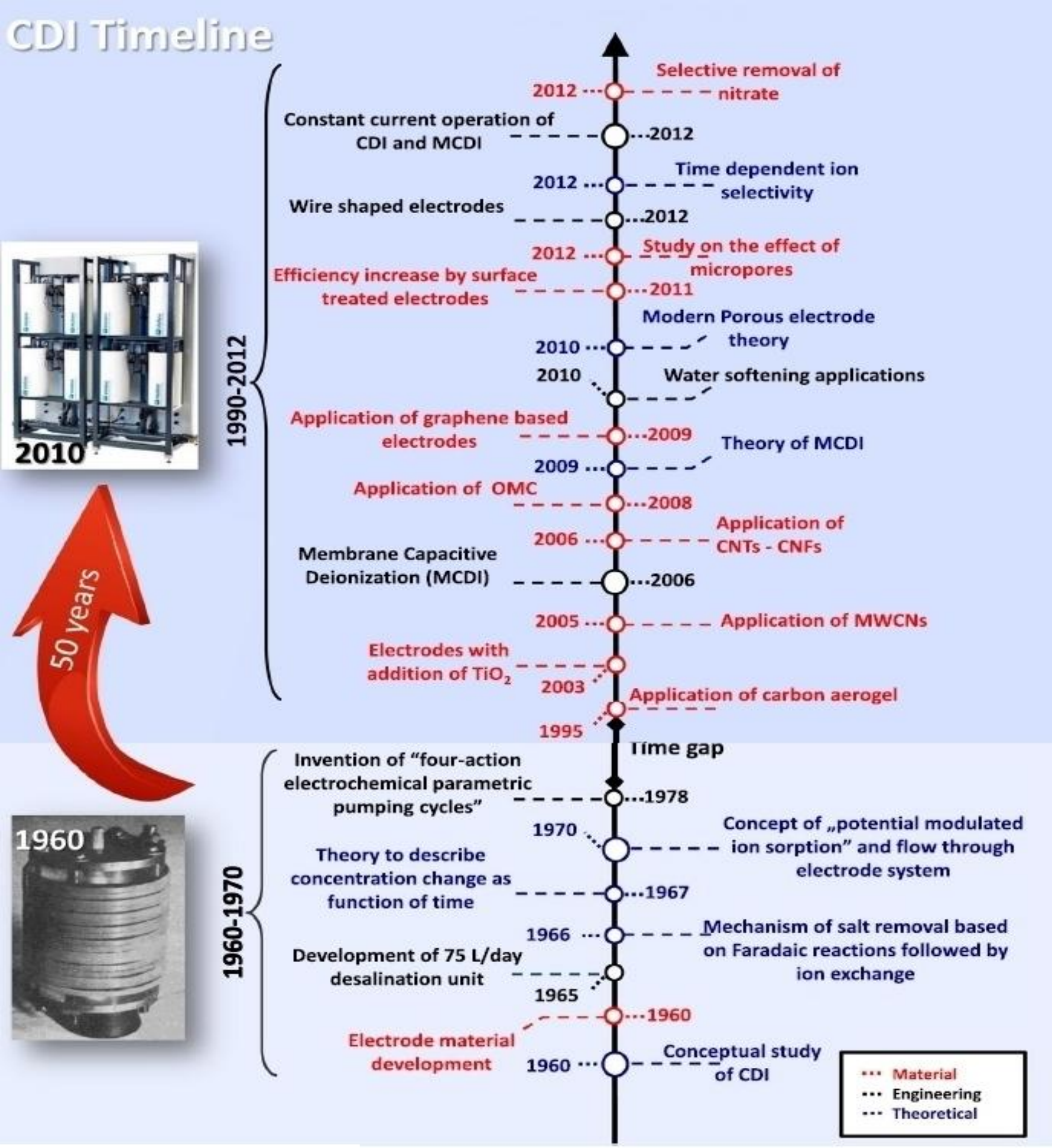


Figure 2.4: Capacitive deionization process

2.3.1 History of CDI development

In this section an outline is being presented from 1960 to 1995, which demonstrates early stages of CDI development as sketched in Figure 2.5. A thorough debate of carbon based electrode development for CDI after 1995 is presented in next section.



Data source: Porada *et al*, 2013

Figure 2.5: Development phases of CDI.

Revolutionary work on desalination of water based on the idea of electrochemical demineralization was first executed by Blair and his team near the beginning of 1960 and persisted till the late 1960s. (Blair *et al*., 1960; Arnold *et al*., 1961; Murphy *et al*., 1697; Murphy *et al*., 1969). At that time it was supposed that ions can only be detached from water only when specific chemical species present on the surface of electrode undergo either reduction or oxidation which results in forming an ionic bond between the salt ions present in the water and the specific chemical species on the surface of electrode. According to Blair et al., 1960, the majority of the forms of carbon used for making electrodes, were hypothetically positive ions attractive which was due to the occurrence of hydroquinone-quinine combination and other supposed positive ions attractive groups. This was the motive why throughout the stages of CDI improvement, more concentration was paid on the progress of a technique to differentiate among the positive and negative ion selective behavior of electrode material, and on the research on negative ion selective electrode material by merging molecules containing organic groups (Arnold et al., 1961).

Evans at al. (1966) studied the mechanism of “electrochemical desalination” by using mass balance and coulometric analysis. Evans concluded that the desalination of water is a two step process. The 1st step required was the occurrence of faradic reactions on the cathode, result in the production of hydroxyl ions and to adsorb hydrogen. The 2nd step is based on ion-exchange mechanism in which the hydroxyl ions, which was produced in the 1st step provides suitable circumstances for the breaking of weak acid groups which take part in demineralization reactions. The regeneration of electrodes was done by reversing the voltage with the intention to reduce the pH which results in the desorption of adsorbed ion. At that time it was understood that to attain an efficient desalination step, the voltage must be inverted for the duration of regeneration step and it was obvious that the salt removal efficiency was verified by the surface group concentration. Preceding sections of literature review denies these classical concepts on the basics of desalination of water, as those views are now being outdated and have been overturned by the modern concepts like capacitance of electrodes resulted by the electrical double and consequently electrodes bases on carbon materials are appropriate for both positive and negative ions, while electrochemical or faradic reactions are well though-out to be of principal value in carrying out the CDI process.

Murphy et al. (1967) provided a mathematical modeling of desalination by CDI. In this study transport and mass balance equations were combined to illustrate concentration of salt with respect to time, and the mathematical model was applied to explain real time experimental results which were gathered by various operational conditions. Another study by Murphy et al., 1969, paid attention on the properties related to surface of carbon based electrode materials by treating them with chemicals. For instance when the carbon based electrodes were treated with concentrated nitric and sulfuric acids the positive ion responsive electrode worked on ion-exchange mechanism due to the treatment of sulfuric acid which provided carboxylic groups to the electrode. Further thorough work on CDI and transport mechanism was carried out by Evans et al., 1969 and Accomazzo et al., 1969.

Reid et al. (1968) studied the commercial application and sustainable operation of desalination unit with no considerable loss of ion adsorption capacity with respect to time. The study confirmed that not only chloride and sodium ions can be removed but magnesium, nitrate, calcium, sulfate and phosphate ions also can effectively be removed.

Johnson et al., 1970, provided a ground breaking concept, known these days as electrical double layer theory (EDL) for electrochemical desalination. EDL was held responsible for the removal of ions from saline water and also the concept of half cycle non symmetrical operational conditions was established. The use of non symmetrical approach was significant because it proved that by utilizing asymmetrical half cycle time or by improving voltage during adsorption step, we can get better results from system with no reversal of voltage. The same study also concluded that the faradic reactions might result in electrode degradation. Furthermore this study provided cost studies for CDI process from economical prospects of the system with condition; if electrode produced for CDI were stable. Further studies by Johnson et al., 1971, developed an electrode model based on porous carbons to investigate ion adsorption, voltage and charge dependency of porous carbons. The results of this study were; the adsorption capacity of electrodes relies on EDL thickness, surface area of electrodes and the voltage applied.

After the introduction of EDL concept, massive studies on EDL and additional topics were initiated by Oren et al. (1978) and still being a topic of debate till present (Soffer et al., 1972; Oren et al., 1983; Oren et al., 2008; Avraham et al; 2009). The research offered by Soffer et al., 1972, focused on the development of a procedure to explore EDL effects in porous carbon electrodes. The same study concluded that whatever the pore size is, even in the range of 0.5 to 0.3 nm, is wettable and takes part in removal of ions in CDI process.

A growing number of published articles were seen from 1990s which mainly focused on the development of efficient carbon based electrode materials for CDI. Carbon aerogel is one of the carbon based electrode material which was invented by Farmer et al. (1995). Carbon aerogel instantly took attention of CDI researchers due to it exceptional properties like good electrical conductivity, low electrical resistivity, very high surface area and monolithically arrangement. More studies were conducted using carbon aerogel to get rid of various salt ions from brackish water. For instance, Farmer et al. (1996, 1997) studied the removal of $NaNO_3$ and chromium using carbon aerogel.

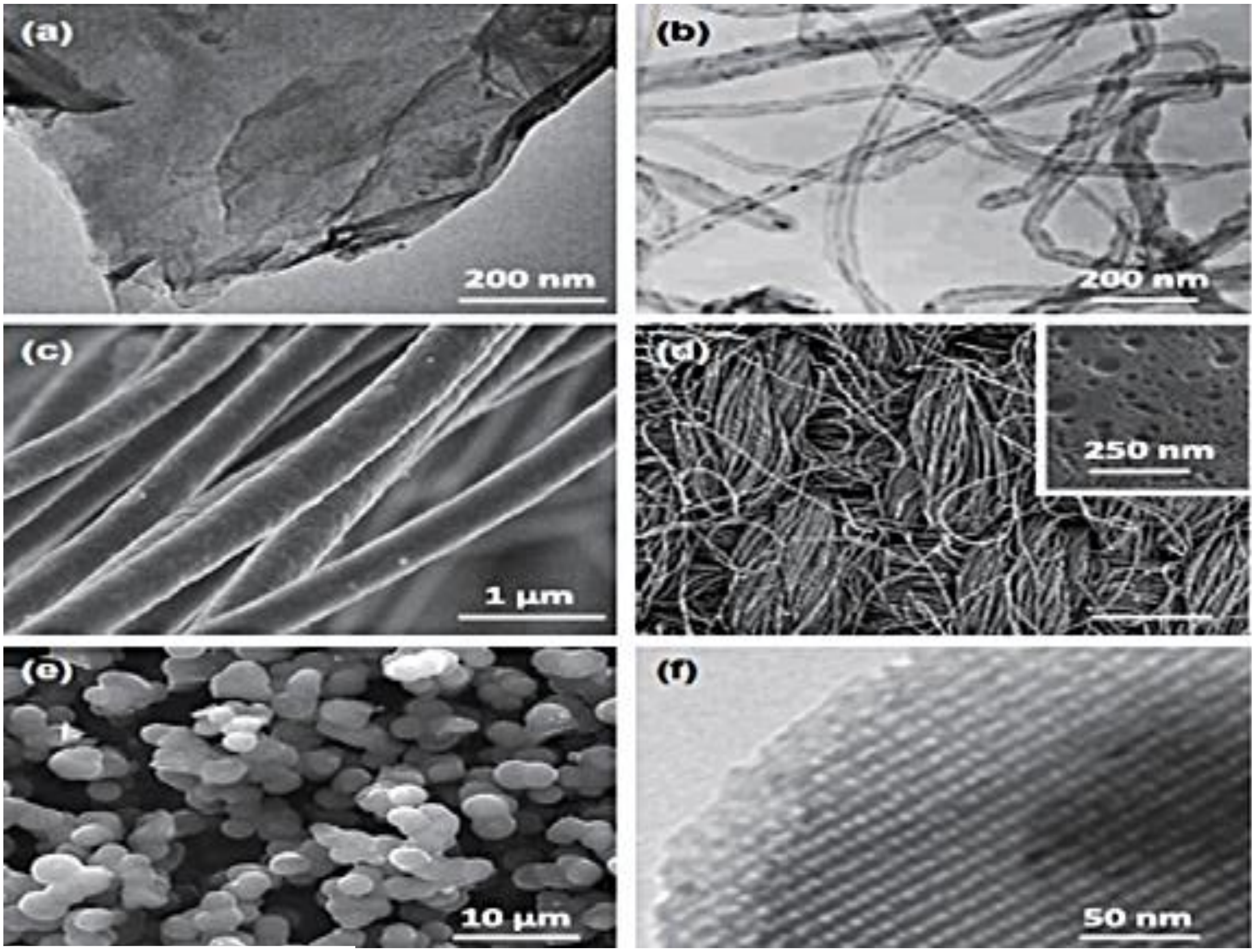
2.3.2 Carbon based electrode materials for CDI

The porous carbon based electrode material is the vital element in all CDI applications, a condition analogous to that in the situation of devices which store energy on the principle of capacitance. Carbon is the key material for developing porous electrodes in both fields. CDI performance is dependent on thickness of electrode, spacing between electrodes, spacer shape and size, CDI cell design and operational parameters. Figure 2.6 provides an overview of different carbons used for electrode development like activated carbon, carbons derived from carbide, graphene and carbon nanotubes etc.

CDI will never be a contender to the already developed desalination technologies like RO without efficient electrode materials and this prospect has seen major development with the continues research in electrodes materials for CDI. A number of carbon materials such as activated carbon (Zou *et al.*, 2008; Chia-Hung *et al.*, 2013), carbon aerogels (Pekala *et al.*, 1998; Gabelich *et al.*, 2002; Xu *et al.*, 2008; Kohli *et al.*, 2012) activated carbon cloth (Han-Jun *et al.*, 2005), carbon black (Nadakatti *et al.*, 2011), carbon nanotubes and nanofiber (Liu *et al.*, 2013), etc. have been reported as electrode materials for CDI.

The performance of CDI based on carbon electrodes not only depends on pore size distribution, pore volume, connectivity of pores, but it is also dependent on electrical conductivity, electrochemical inertness and cost of CDI development. The subsequent listings are the most vital necessities for CDI carbon based electrode materials.

1. High surface area
2. Electrochemical inertness over the applied voltage and pH range.
3. Rapid ion movement within the structure of pores
4. High electrical conductivity
5. Low electrical resistance
6. Good wettability of electrode material



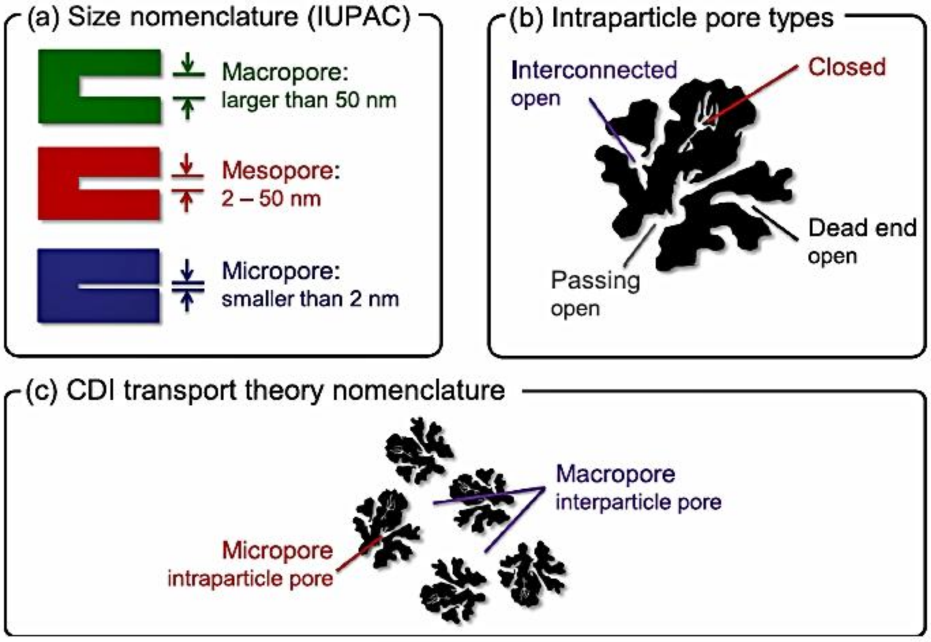
Data source: Porada *et al*, 2013

Figure 2.6: Carbon based electrode materials for CDI. (a) Graphene carbon flakes, (b) Multi walled carbon nano tubes, (c) Electrospin fibres, (d) Activated carbon cloth, (e) Carbon aerogel, (f) meso porous carbon

7. Low cost material
8. Flexible process ability
9. Natural occurrence and low carbon emissions
10. Not prone to bio fouling

The structure of pores has its effects on CDI desalination performance. The international union of pure and applied chemistry (IUPAC) defined pore sizes as follows. Figure 2.7 presents the pore nomenclature according to IUPAC.

1. Macropores larger than 50 nm
2. Mesopores between 2 and 50 nm
3. Micropores smaller than 2 nm



Data source: Porada *et al*, 2013

Figure 2.7: Pore nomenclature according to IUPAC. (a) Size nomenclature (IUPAC), (b) Inter particle pore types, (c) CDI transport theory nomenclature

2.3.3 Performance overview of carbon based electrodes for CDI

In Table 2.2**,** the summary of literature review for the important property of adsorption capacity per gram of carbon based electrode material is reported. The data is provided as a function voltage and salinity, per gram of one pair of electrode collectively. The study in all mentioned cases was done in a symmetric CDI cell with one pair of electrode with equal material and mass. From the Table 2.2, it can be inferred that the information differ in huge range from 0.7 to 15 mg-adsorbed salt per gm for one pair of electrode collectively.

From Table 2.2, it can be inferred that the research conducted using batch mode CDI system with low initial salinity values showed low adsorption capacity values. The reason for low adsorption capacity might be attributed to the limited amount of salt in the system, which does not allow the system to further drop the concentration. Therefore, CDI should be operated either using single pass mode or when using batch mode, the system should be operated at high initial salinity, so that the system should show at least 50% salt removal efficiency. Moreover, salt concentration for CDI experiments should be varied instead of using particular value of salt concentration, in order to assess the salt removal percentage at different concentrations.

Table 2.2: Overview of performance data for carbon based electrode materials for CDI

Author	**Carbon based electrode material**	**Experimental Conditions**				**Adsorption capacity (mg/gm)**
		Feed concentration (mg/L)	**voltage (V)**	**Carbon content (%)**	**Mode of operation**	
Farmer et al, 1996	Carbon aerogel	50	1.2	N/G	CDI (BM)	1.4
		500	1.2	N/G	CDI (BM)	2.9
Dai et al, 2005	Multi walled carbon nano tubes	3000	1.2	N/G	CDI (BM)	1.7
Wang et al, 2006	Carbon nano tubes & nano fibres	110	1.2	100	CDI (BM)	3.3
Zou et al, 2008	Ordered mesoporous carbon	25	1.2	78	CDI (BM)	0.68
Li et al, 2009	Ordered mesoporous carbon	50	0.8	78	CDI (BM)	0.93
H. Li et al, 2009	Graphene	25	2	100	CDI (BM)	1.8
Kim et al, 2010	Activated carbon	200	1.5	N/G	CDI (SP)	3.7
	Activated carbon	200	1.5	N/G	O-MCDI(SP)	5.3
Zhao et al, 2010	Commercial activated carbon	292	1.2	N/G	CDI (SP)	10.9
		1070	1.4	N/G	CDI (SP)	13

H.Le et al, 2010	Graphene like nano flakes	25	2	80	CDI (BM)	1.3
H.Le et al, 2011	Single walled carbon nanotube	23	2	70	CDI (BM)	0.75
Biesheuve et al, 2011	Commercial activated carbon	292	1.2	N/G	CDI (SP)	10.5
		292	1.2	N/G	O-MCDI(SP)	12.8
		292	1.2	N/G	r- MCDI(SP)	14.2
Yang et al, 2011	MnO_2 Activated carbon	25	1.2	N/G	CDI (BM)	1.0
Wang et al, 2012	Carbon nano fiber webs	95	1.6	100	CDI (BM)	4.6
Jia et al, 2012	Sulfonated graphite nano-sheet	250	2	72	CDI (BM)	8.6
Zhang et al, 2012	Graphene carbon nanotube	29	2	90	CDI (BM)	1.4
H. Li et al, 2012	Reduced grapheme oxide- activated carbon	50	1.2	N/G	CDI (BM)	2.9
Peng et al, 2012	Carbon CNT's ordered mesoporous	46	1.2	80	CDI (BM)	0.63
Suss et al, 2012	Monolith of carbon aerogel	2922	1.5	100	CDI(BM)	9.6
Wang et al, 2012	Reduce grapheme oxidate resol	65	2	80	CDI (BM)	3.2

In all experiments NaCl solution was used. SP: Single pass; BM: Batch mode; N/G: Not given; O-MCDI: CDI with ion exchange membranes, ions released at zero cell voltage; r-MCDI: Ions released at reverse voltage.

2.3.4 Role of titanium dioxide (TiO_2) in carbon based electrode materials

Titanium dioxide (TiO_2) modifications with various carbon based electrode materials for CDI were also reported in order to evaluate the effect of TiO_2 on desalination efficiency.

Kim *et al.* (2014) coated the carbon electrode with TiO_2 sol–gel spray. In this method the carbon electrode was made by using activated carbon powder (specific surface area 2300 m^2/g) and carbon black and stirred with polytetrafluoroethylene (PTFE) as a binder and ethanol as solvent to make slurry. The slurry then allow to mix for 30 minutes to prepare a viscous fluid which was used in making the sheet type carbon electrode and dried in an oven at 60 ^oC for 12 hours. The recipe for this electrode included 86%, 8% and 8% of wt% of activated carbon, carbon black and PTFE respectively. After the electrode was dried in the oven the TiO_2 coating was carried with sole gel spray method. Titanium butoxide was used with isopropyl alcohol at 10% (V/V) concentration and sprayed through a nozzle sprayer to load the carbon electrodes with TiO_2 particles. Afterwards the electrode was well heated at 250^oC for 2 hours under normal conditions. This study proved that the desalting efficiency of TiO_2 loaded carbon electrode proved to provide two time greater desalination efficiency than simple carbon electrode. Also it was suggested that the specific capacitance of simple carbon based and TiO_2 loaded carbon electrodes did not differ appreciably, so the enhanced desalination efficiency was due to high wettability of TiO_2 loaded carbon electrode.

Liu *et al.* (2013) made nano structure anatase activated carbon electrode modified with TiO_2 in two step microwave assisted ionothermal synthesis method which is relatively short time method done in less than 2 hours and at 150^oC. Crystallization is the first step in this method which include the ionic fluid acting as a hydrothermal correlation function in motivating the surface anatase crystallization of amorphous TiO_2 nanoparticles created in the second step i.e. reaction step. The study concluded that the TiO_2-AC electrodes have greater electrical conductivity and higher electrode wettability. The AC electrode showed electrosorption capacity of 5.43 ± 0.91 mg/gm, while TiO_2-AC electrode showed 8.05±0.34 mg/gm. In addition, CV results showed the electrodes have higher specific capacitance and desalting performance.

Lee *et al*. (2012) made composite carbon electrodes modified with TiO_2 nanoparticles and sulfonated polystyrene. The TiO_2 nanoparticles were mixed with ion exchange polymer and the mixture was coated on the carbon electrode surface to give the carbon electrode decreased electrical resistance and sustain the ion selectivity of the electrodes. The results after performing cyclic voltammetry (CV) and electrical impedance spectroscopy (EIS) of electrodes indicated that the electrical resistance reduced considerably as the TiO_2 content in the electrodes was amplified. On the other hand the ion selectivity reduced as TiO_2 content increased which resulted in the pore formation amongst the particles. This study also purposed that the most favorable TiO_2 content in the making of electrodes proved to be approximately 10 wt% of activated carbon. Moreover, after performing desalination experiments it was revealed that the desalting efficiency of TiO_2 modified composite carbon electrodes were enhanced roughly 30% as compared to uncoated composite carbon electrode.

Zou *et al.* (2008) synthesized TiO_2 nanoparticles by hydrolysis of titanium butoxide to prepare a homogenous sol gel in which activated carbon (AC) was submerged to load it with TiO_2 sol gel particles, dried at ambient conditions and heat treated at 200^oC. Study finds that when AC was loaded with TiO_2 nanoparticles, the TiO_2 nanoparticles made bond with polar groups of AC and produced much established metal oxides which resulted in less physical adsorption of AC. The reduction in physical adsorption give rise to electrosorption of electrodes which in return enhanced the adsorption capacity of AC loaded TiO_2 electrodes by 10% as compared to simple AC electrodes.

Ryoo *et al.* (2002, 2003) made the CDI electrodes from activated carbon cloth (ACC) and modified it with TiO_2. The ACC cloth had BET surface area of 2000 m^2/g. The ACC was submerged in anhydrous ethanol solution accompanying metal alkoxides which included titanium (IV) butoxide, zirconium (IV)-n-propoxide, 3-trimethoxypropylsilane and aluminum isopropoxide. The solution was stirred to enable alkoxide to react with ACC at room temperature for the duration of 48 hours. Anhydrous ethanol was used to remove non reacting alkoxides from the surface of ACC, and then allowed to dry it for 24 hours in an oven. The reported result indicated that the incorporation of TiO_2 in activated carbon cloth increased electrosorption and decreased physical adsorption which notably enhanced the ion removal capacity.

MATERIALS AND METHODS

3.1 Preparation of electrodes

3.1.1 Preparation of titanium dioxide (TiO_2)

Titanium dioxide (TiO_2) was prepared by the hydrolysis of Titanium Tetrabutoxide (TTB) in alcoholic medium by using H_2O as a hydrolysis agent. In the preparation, there is no use of any catalyst (acid or basic) for the hydrolysis reaction. TTB (Aldrich, 90%), ethanol (EtOH, Aldrich) for synthesis and distilled H_2O were used as raw materials. The hydrolysis reaction was carried out at 25 °C by maintaining a vigorous stirring during the whole process. In this study the molar ratio TTB/EtOH/H_2O used was 1/4/4 as per method describe by Velasco *et al.,* 1999. First of all TTB and EtOH is added in a beaker placed on the stirrer, The water was added drop by drop with the help of burette in such a way that it took two hours for the whole volume of water to be added in the solution of TTB and EtOH. The resulting solution kept stirring for seven days vigorously. Then the suspensions in the solution allowed to settle down for 24 hours and then suspension was allowed to dry at room temperature to obtain the sol gel particles. Dried suspension was grinded with the help of pestle and mortar to get fine particles of TiO_2. Figure 3.1 summarize the steps involved in making of TiO_2.

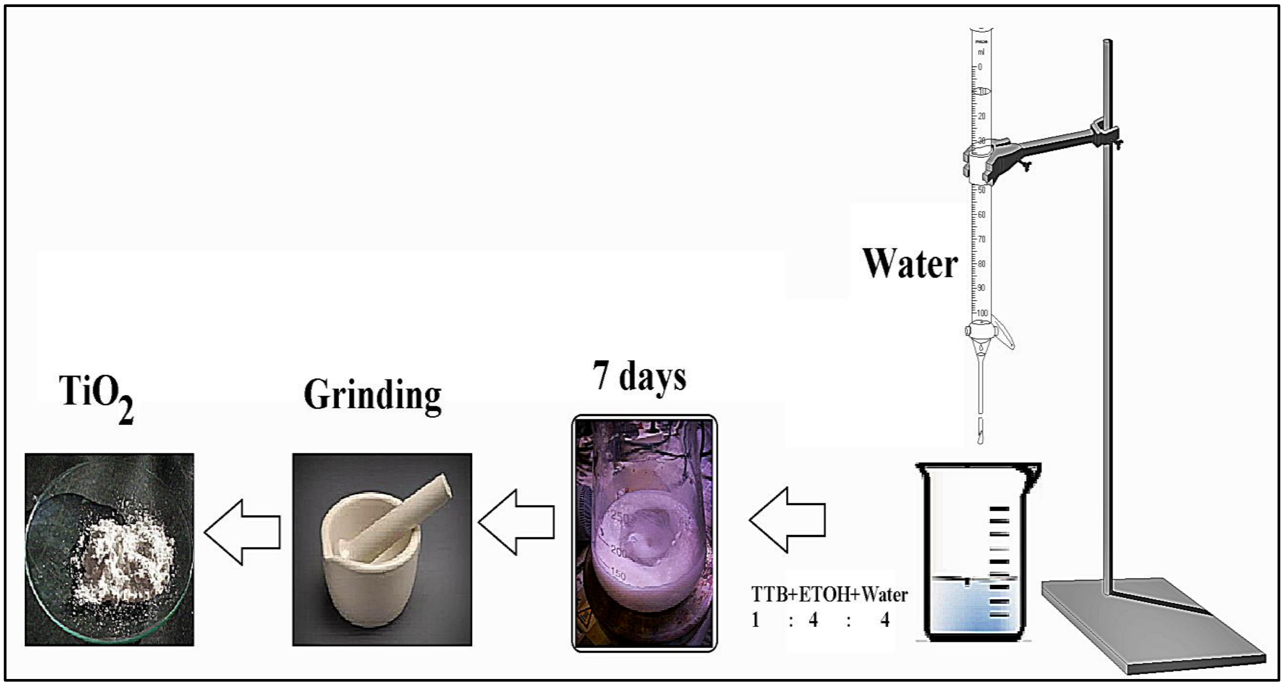


Figure 3.1: Steps involved in making TiO_2

3.1.2 Preparation of simple PAC and PAC electrodes modified with TiO_2

The electrodes slurry was prepared by mixing powdered activated carbon (PAC) (Acros, USA), polyvinylidene fluoride (PVDF) (International laboratory, USA) used as polymer binder in an organic solvent, N, N-Dimethylacetamide solution (>99%, Merck, USA). Furthermore, TiO_2 were added in the slurry which was obtained by reacting Titanium (IV)-butoxide (>97%, Sigma Aldrich, USA) and absolute ethanol (99.8%, laboratoryscan, Poland) according to the method by Velasco *et al*. (1999), with slight modification i.e. absolute ethanol is used instead of n-butanol. The slurry was made homogeneous by blending the mixture vigorously using magnetic stirrer for 7 hours. Electrodes were oven dried at 120^{o}C for 2 hours to evaporate the organic solvent after the electrode slurry was casted on to graphite sheet (Asia-Pacific Sealing Technologies, Pakistan). Polymer binder and TiO_2 content in the fabricated electrode were 10 and 12 wt% respectively. Same above procedure was adopted for the PAC electrode without addition of

TiO_2. The details of electrodes are given in Table 3.1. Figure 3.2 Summarizes the steps involves in making of electrodes.

Table 3.1: Details of electrodes

Types of CDI system	Electrode	Electrode dimensions (mm)	No. of electrodes	Mass of adsorbent (gm)
Small Scale	PAC	203.2 x 76.2 x 1.5	2	11.8
	PAC+TiO_2	203.2 x 76.2 x 1.5	2	11.8
Laboratory scale	PAC+TiO_2	203.2 x 76.2 x 1.5	12	71
Pilot scale	PAC+TiO_2	304.8 x 152.4 x 1.5	40	336

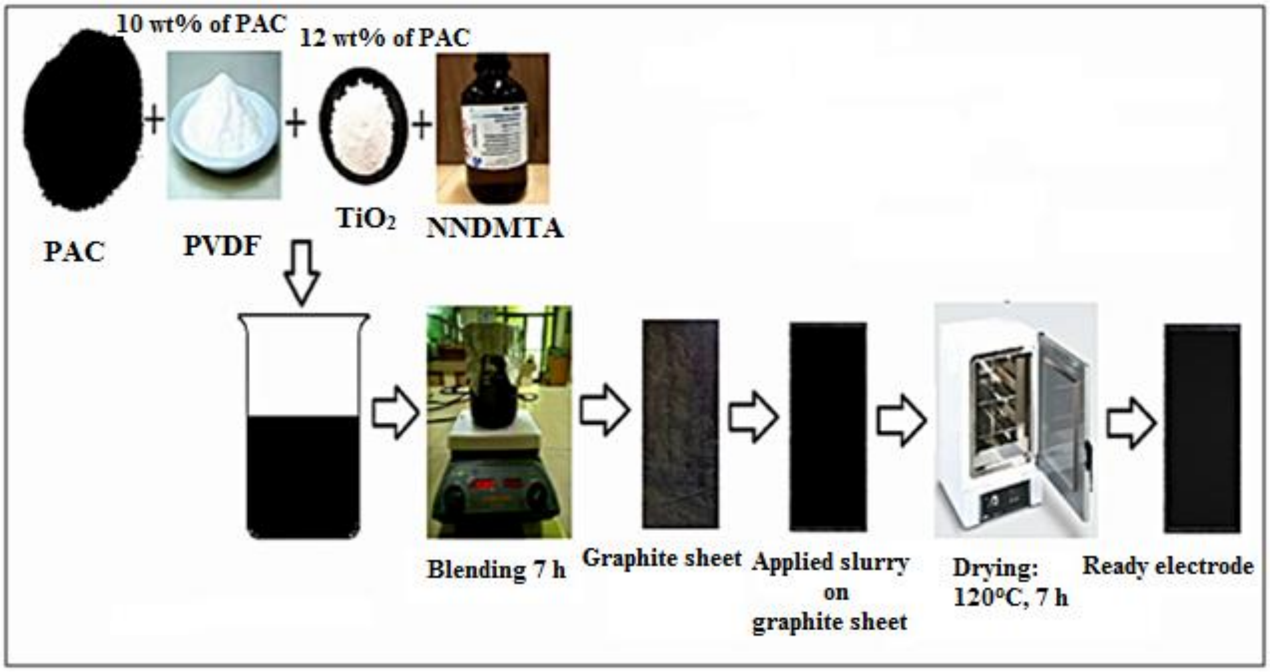


Figure 3.2: Steps involved in making of electrodes

3.2 Experimental setups

3.2.1 Small scale CDI system

The small scale CDI system consisted of one pair of electrode fabricated in acrylic sheets. The pair of electrode was separated by a rubber spacer to avoid short circuit and maintain a distance of 2 mm between them. Each electrode was attached with copper shin and wires which were connected to DC power supply to give them potential. The influent enters from bottom of the system and exit from top. Figure 3.3 is the schematic diagram of small scale CDI system and figure 3.4 is the actual setup installed at Water and Wastewater (laboratory, IESE, SCEE).

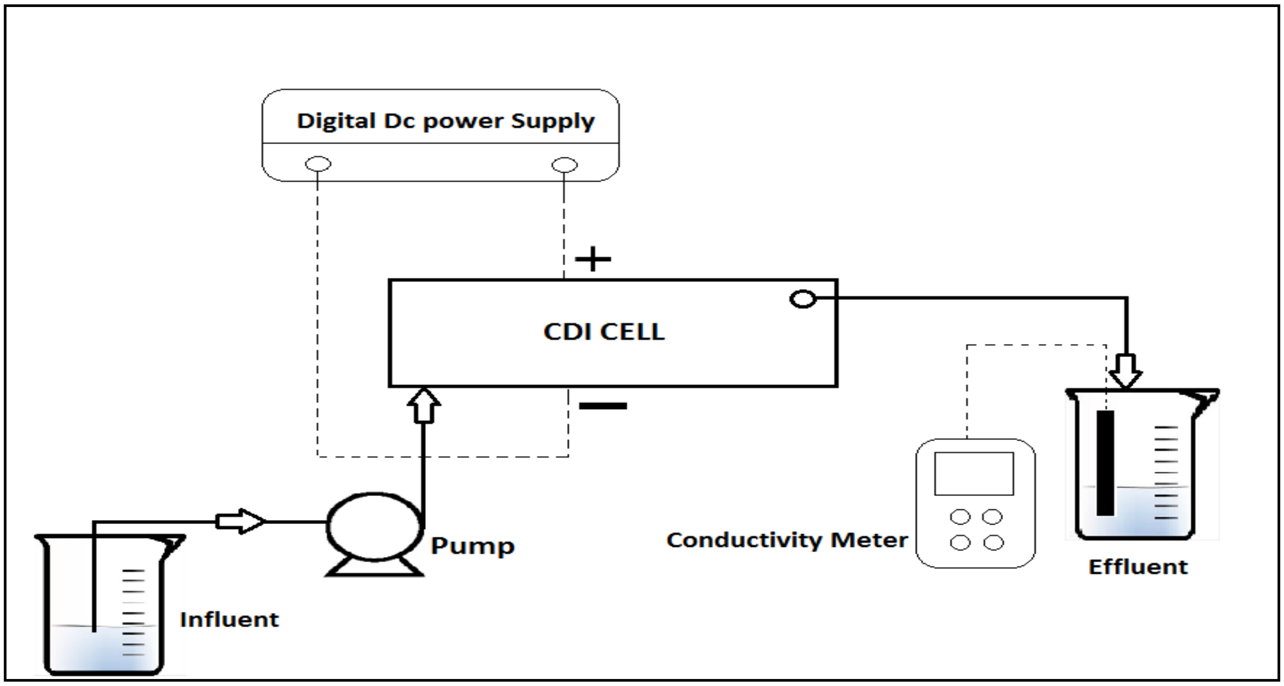


Figure 3.3: Schematic diagram of small scale CDI system

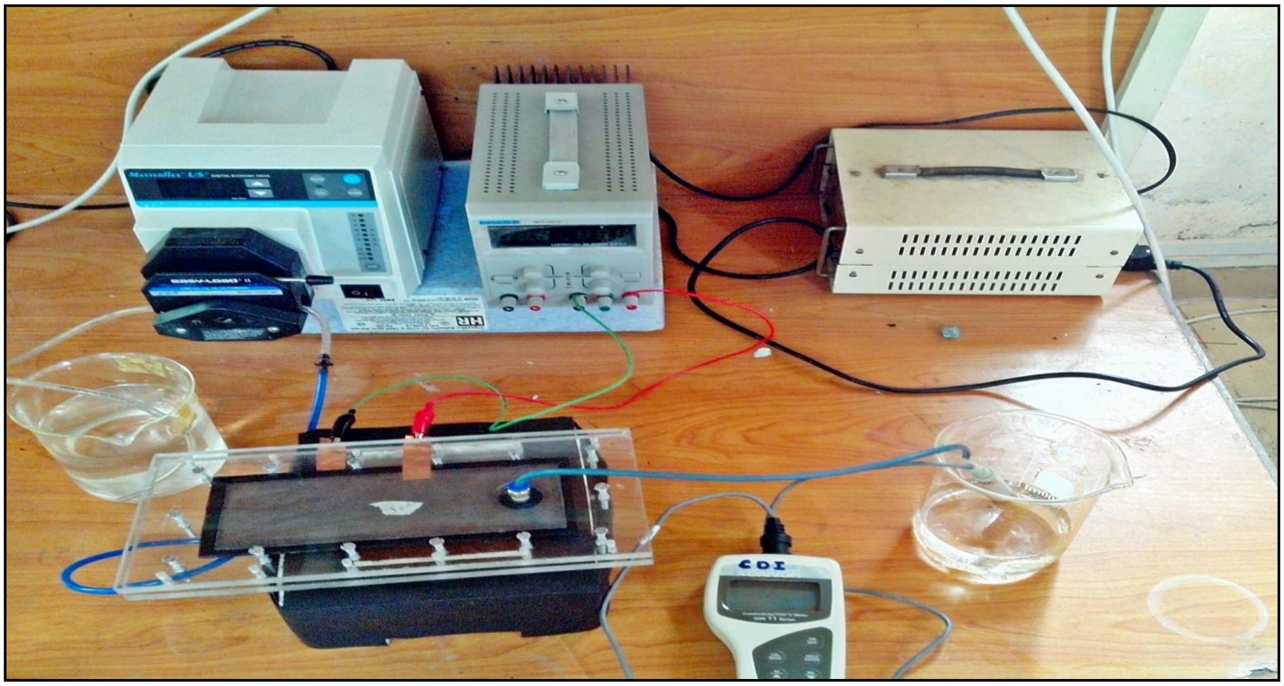


Figure 3.4: Actual setup of small scale CDI system

3.2.2 Laboratory scale CDI system

The laboratory scale CDI system consisted of three unit cell assembly (each cell having two pair of electrodes) connected in series with each other using a pump flow system as shown in Figure. 3.5. The electrodes were stacked over each other and provided with holes to create flow channel. The pair of electrodes was separated by a separator made of non conductive thin rubber gasket material to avoid short circuiting. Space of approximately 2 mm was kept between electrodes by a putting a non conductive rubber spacer and individually connected with digital DC power supply. Acrylic sheets were attached on the back of the electrodes in the CDI cells assembly. Figure 3.6 shows the actual laboratory scale CDI system installed at Water and Wastewater (laboratory, IESE, SCEE).

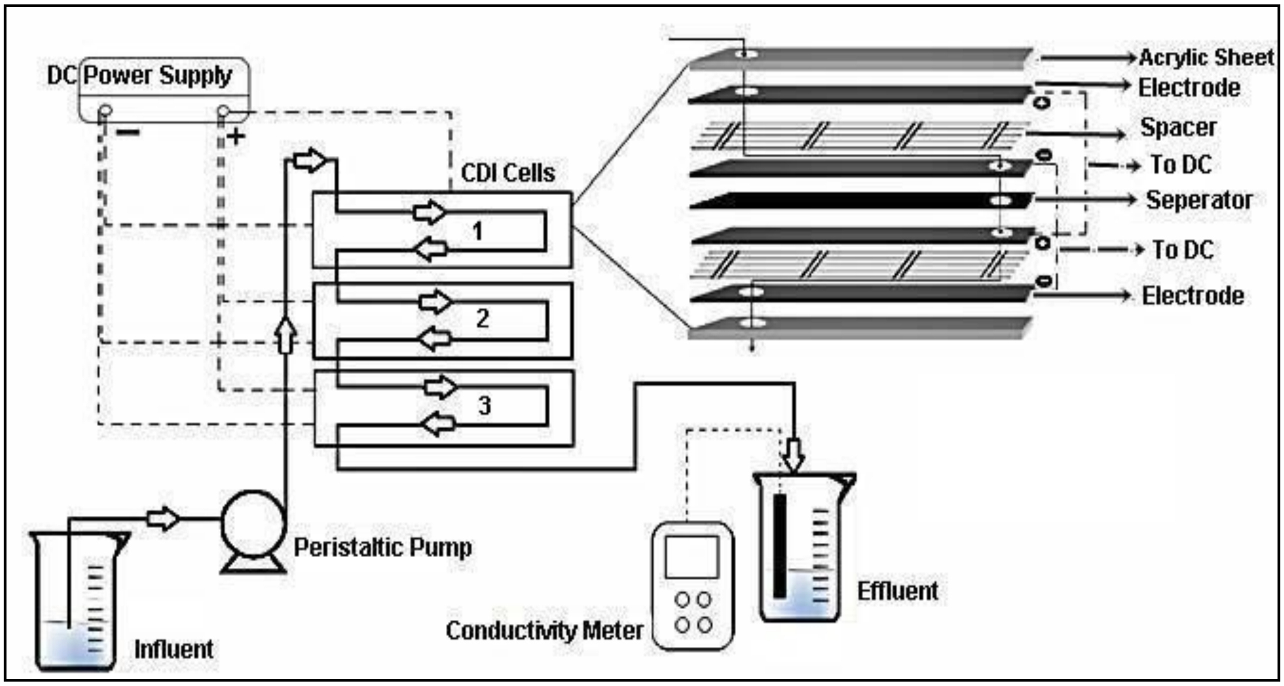


Figure 3.5: Schematic diagram of laboratory scale CDI system

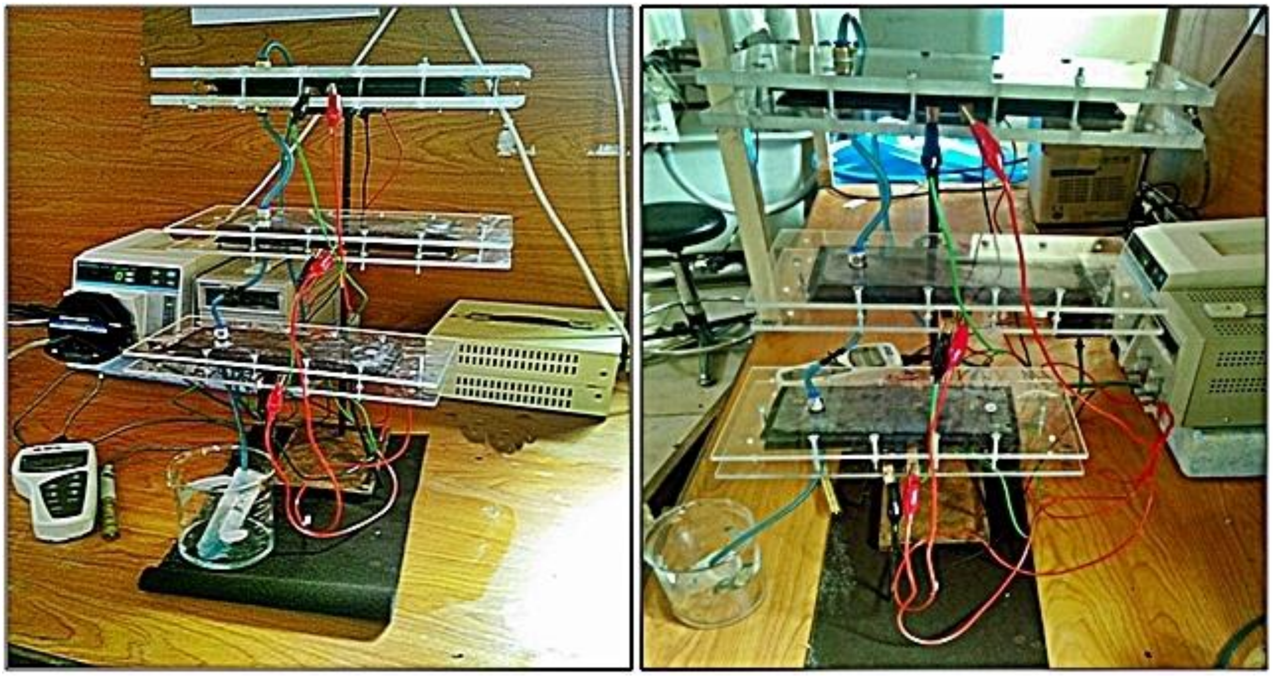


Figure 3.6: Actual setup of laboratory scale CDI system

3.2.3 Pilot Scale CDI system

Pilot scale CDI system was developed as same configuration of laboratory scale CDI system consisting of twenty pairs of electrodes using a pump flow system as shown in Figure 3.7. The system was developed in single unit. Figure 3.8 shows the actual Pilot scale CDI system installed at Environmental Chemistry (laboratory, IESE, SCEE).

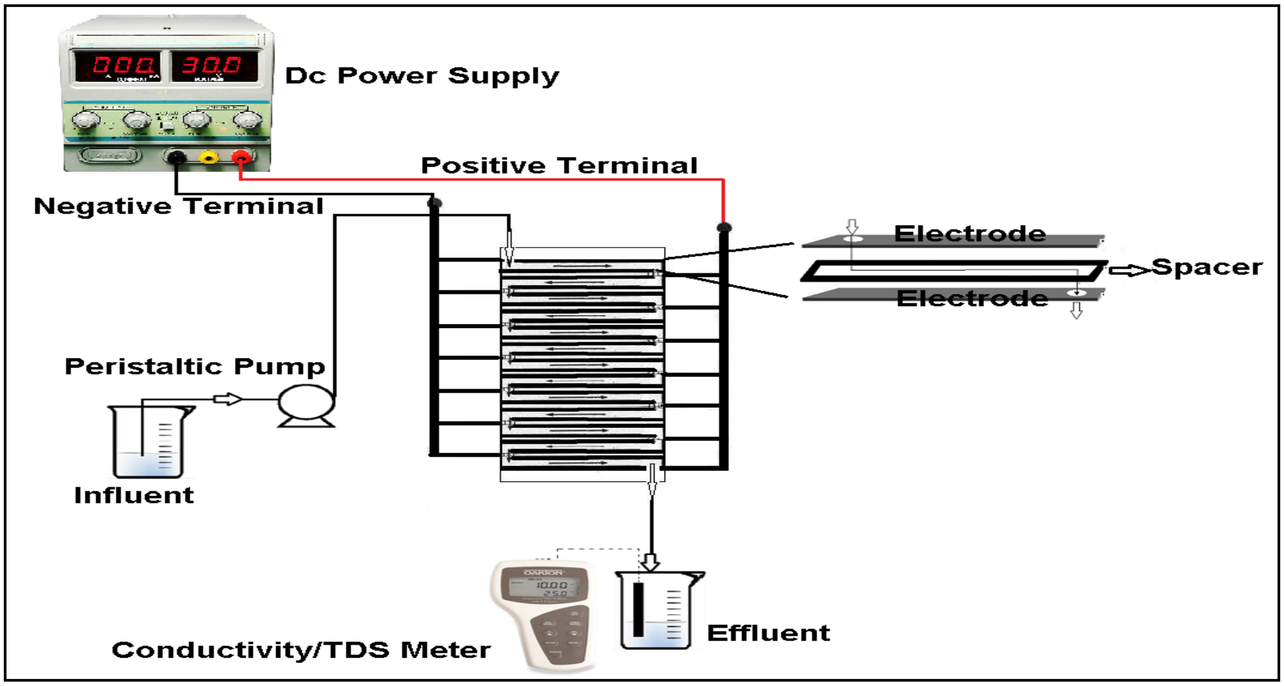
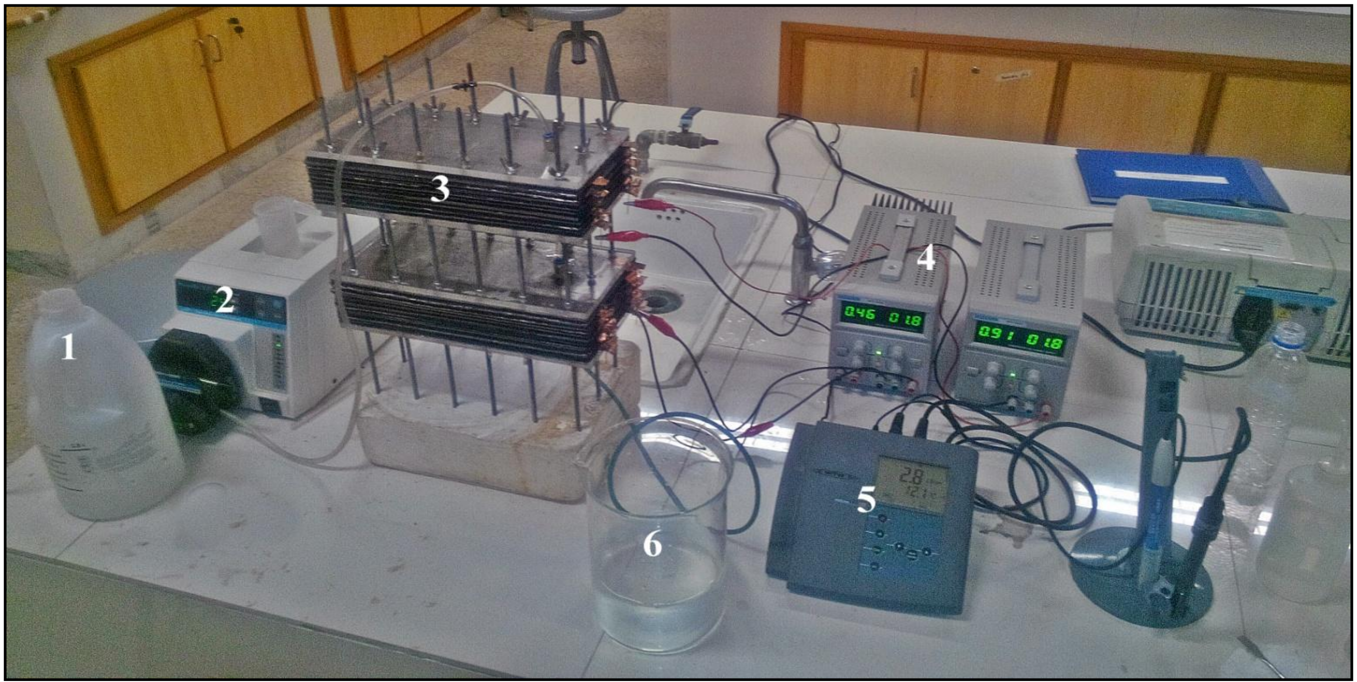


Figure 3.7: Schematic diagram of pilot scale CDI system



1. Influent container 2. Peristaltic pump 3. CDI unit 4. DC power supplies
5. Conductivity/TDS meter 6. Effluent beaker

Figure 3.8: Actual setup of pilot scale CDI system

3.3 Testing procedures

3.3.1 Scanning electron microscopy (SEM)

The surface morphology analysis of the PAC+TiO_2 electrode was carried out with scanning electron microscope, expanded to an analytical SEM by the addition of optional EDS (JSM-6490, JEOL, Japan). The images were recorded at a magnification of 5000.

3.3.2 Energy dispersive X-ray spectroscopy (EDS)

The EDS analysis of electrode carried out to qualitatively/quantitatively investigate the electrodes with the same machine used for SEM images (JSM-6490, JEOL, Japan). EDS makes utilization of the X-ray beam range radiated by a solid sample shelled with a centered light emission to acquire a limited chemical analysis. In principle all the elements between atomic number from 4 to 92 can be detected.

Qualitative analysis involves the identification of the lines in the spectrum and is fairly straightforward due to the simplicity of X-ray spectra. Quantitative analysis facilitates measuring line intensities for each element in the sample and for the same elements in calibration Standards of known composition.

3.3.3 Cyclic voltammetry

To examine the electrochemical properties of the prepared electrodes cyclic voltammetric measurements were performed using a potentiostat (DY2113, Digi-Ivy, Inc., USA) with three electrode system. The reference electrode was an Ag/AgCl electrode while counter electrode is made up of a thin Platinum wire and working electrode were PAC and PAC+TiO_2. Cyclic Voltammetry was performed at room temperature using 0.5 M NaCl solution. The potential range was -0.6 to +0.6 at scanning rate of 50 mV/s.

3.3.4 Surface area analysis

PAC was analyzed for its pore size, pore volume and its surface area using Surface Area Analyzer (Micromeritics, Gemini VII 2390, USA).

3.3.5 Desalination performance of capacitive deionization (CDI) systems

3.3.5.1 Small scale CDI system

Initial desalination performance experiments were conducted on a small CDI system. The tests were conducted using NaCl feed solution concentration of approximately 2000 mg/L at 1.3 V and flow rate of 25 mL/min was maintained. This setup compared the desalination efficiency of PAC and PAC+TiO_2 electrodes.

3.3.5.2 Laboratory scale CDI system

The NaCl feed solution concentration of approximately 2000 mg/L was supplied to laboratory scale CDI system by peristaltic pump (Masterflex, USA) at 25 mL/min. The salt removal tests were conducted by charging electrodes with a potential of 1.3V until there was no significant change observed in concentration of effluent. Once electrodes sites were saturated, the desorption of ions was performed by changing the potential to 0V and washing the electrodes with DI water at 50 mL/min. Same procedure was repeated with potentials of 1.6V and 1.8V and salt removals were determined at each voltage. The conductivity/concentration changes in effluent were measured with a conductivity meter (CON 110, Oakton, USA) at different intervals of time.

3.3.5.3 Pilot scale CDI system

The NaCl feed solution concentrations used in the pilot scale CDI system was 2000, 2500 and 3000 mg/L while keeping pumping rate constant at 25mL/min. The salt removal tests were performed at 1.8V, while the regeneration was studied for 20 minutes at 0V and DI water flow rate of 25mL/min. All the experiments were performed in triplicate in order to get representative results.

3.3.6 Adsorption capacity and salt removal percentage

The adsorption capacity was calculated by the change in concentration during the charging/discharging step of the CDI cells assembly. Here the adsorption capacity (Q) (mg-NaCl/g-adsorbent) was determined as described by Wang *et al.* (2012).

$$\mathrm{Q} = \frac{(\mathrm{C_i} - \mathrm{C_e})}{\mathrm{M}} \times \mathrm{V} \qquad (1)$$

Where C_i (mg/L) is influent concentration and C_e (mg/L) is the effluent concentration during adsorption. V (L) is the volume of the product during the adsorption process and M (g) is the mass of adsorbent.

For the comparison of performance under different applied voltages, the desalted product was expressed as the salt removal rate as described by Park *et al*, (2007).

$$\text{Salt Removal (\%)} = \frac{\mathrm{C_f} - \mathrm{C_p}}{\mathrm{C_f}} \times 100 \qquad (2)$$

Where C_f (mg/L) represents the feed concentration and C_p (mg/L) represents the lowest effluent concentration during adsorption.

RESULTS AND DISCUSSION

4.1 Surface morphology of electrodes

Figure 4.1, shows the SEM image of TiO_2 modified powdered activated carbon electrode. It can be observed that there is continuous irregular network with presence of powdered activated carbon, binder and TiO_2 particles. Figure 4.2 shows the surface structure of the electrode with different pore sizes, mainly mesopores. Electrosorption capacity is greatly dependant on pore size distribution of electrode. The significant number of macropores (>50 nm) leads to low surface area and low electrosorption capacity while mesopores (2–50 nm) are very suitable for electrosorption due its pore size (Liu *et al.*, 2013).

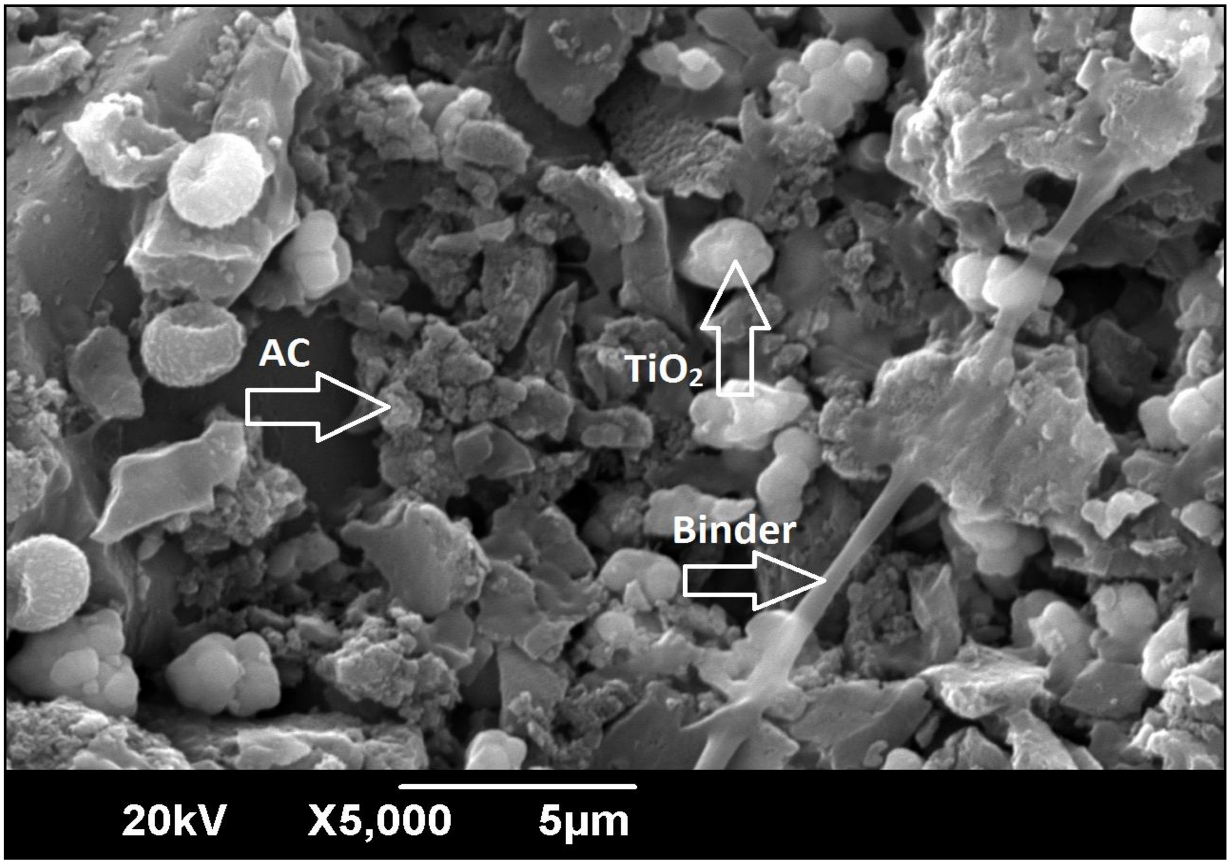


Figure 4.1: SEM image (magnification 5,000X) of the PAC+TiO_2 electrode

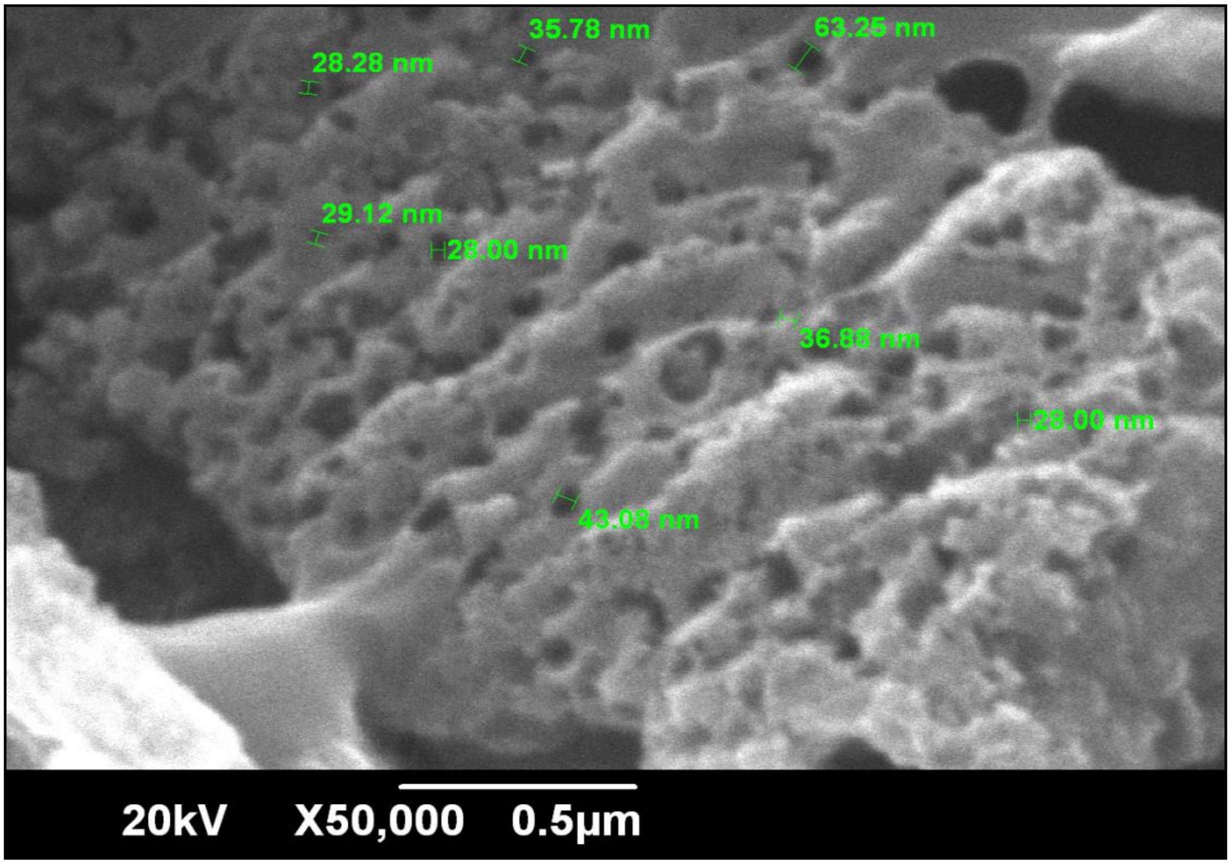


Figure 4.2: SEM image (magnification 50,000X) of the PAC+TiO_2 electrode

4.2 Energy dispersive X-ray spectroscopy of electrodes

EDS of PAC+TiO_2 electrode were performed without any standard sample of known composition. Electrodes were mainly analyzed for their qualitative analysis because it was important to know the presence of TiO_2 on the electrode. It is evident from Figure 4.3 that most number of counts was obtained for PAC, because the main constituent of electrode was PAC. 2nd and 3rd counts were obtained for nitrogen and oxygen respectively. The reason for the presence of nitrogen and oxygen could be attributed to the entrapped air molecules inside the pores of the electrodes. The presence of oxygen can also be justified due to presence of two oxygen molecules with each titanium atom. Nitrogen presence can also be justified by the organic solvent used in the making of electrodes containing N, N-Dimethylacetamide which is also a source of nitrogen. 4th most counts were obtained for fluorine. Fluorine presence can be confirmed due to the presence of binder (PVDF) on electrodes which also contain Fluorine. 5th most counts were obtained for Titanium, which is evidence of presence of TiO_2 on the electrode. Slight counts were found of elements like Magnesium, Aluminum, Silicon, Potassium, Calcium and Iron, which was due to impurities in materials and chemicals used in the making of electrodes.

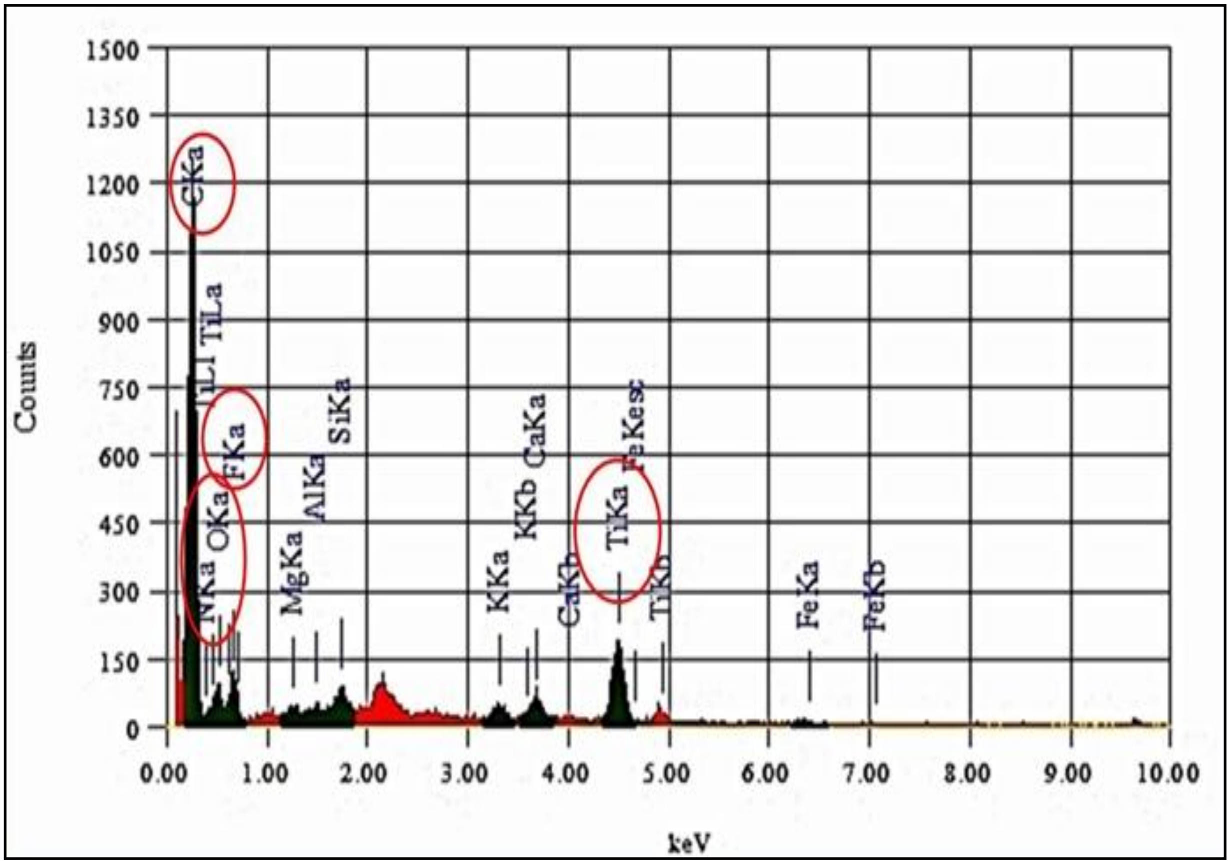


Figure 4.3: EDS analysis of PAC+TiO_2 electrode

4.3 Characteristics of powdered activated carbon

Powdered activated carbon was analyzed for its properties including pore size, pore volume and its surface area using Surface Area Analyzer (Micromeritics, Gemini VII 2390, USA). The main textural characteristics of powdered activated carbon used in the preparation of the PAC-TiO_2 electrodes are listed in Table 4.1. Pore volume was calculated according to the following equation (Zhao *et al.*, 2013)**.**

Pore volume: $V_{meso} = V_{total} - V_{micro}$

Table 4. 1: Main textural Characteristics of powdered activated carbon

Bet surface area (m^2/g)	Total pore volume (cm^3/g)	Meso pore volume (cm^3/g)	Micro pore volume (cm^3/g)
540	0.2581	0.1145	0.1436

4.4 Electrochemical properties of electrodes

Cyclic voltammetry (CV) was performed to study the electrochemical properties of electrodes. Figure 4.4 shows cyclic voltagrams acquired in the electrosorption and desorption of NaCl on the PAC and PAC+TiO_2 electrodes. There is no major evidence of oxidation/reduction reactions on both types of electrodes, as balance growth and drop in current with electric potential was noticed. The CV results showed that the main contribution of the salt ions removal from the solution was electric double layer on the surface of electrode under the charged potential and there were no major Faradic or electrochemical reactions (Frackowiak *et al.,* 2001; Chen *et al.*, 2011). In CDI cell the loops corresponds to sweeping area in cyclic voltagrams, which actually demonstrate the adsorbed amount of salt ions on the surface of electrode. The sweeping area of PAC+TiO_2 electrode is greater than PAC electrode which exhibit the increase in electrosorption of salt ions by the addition of TiO_2 in PAC.

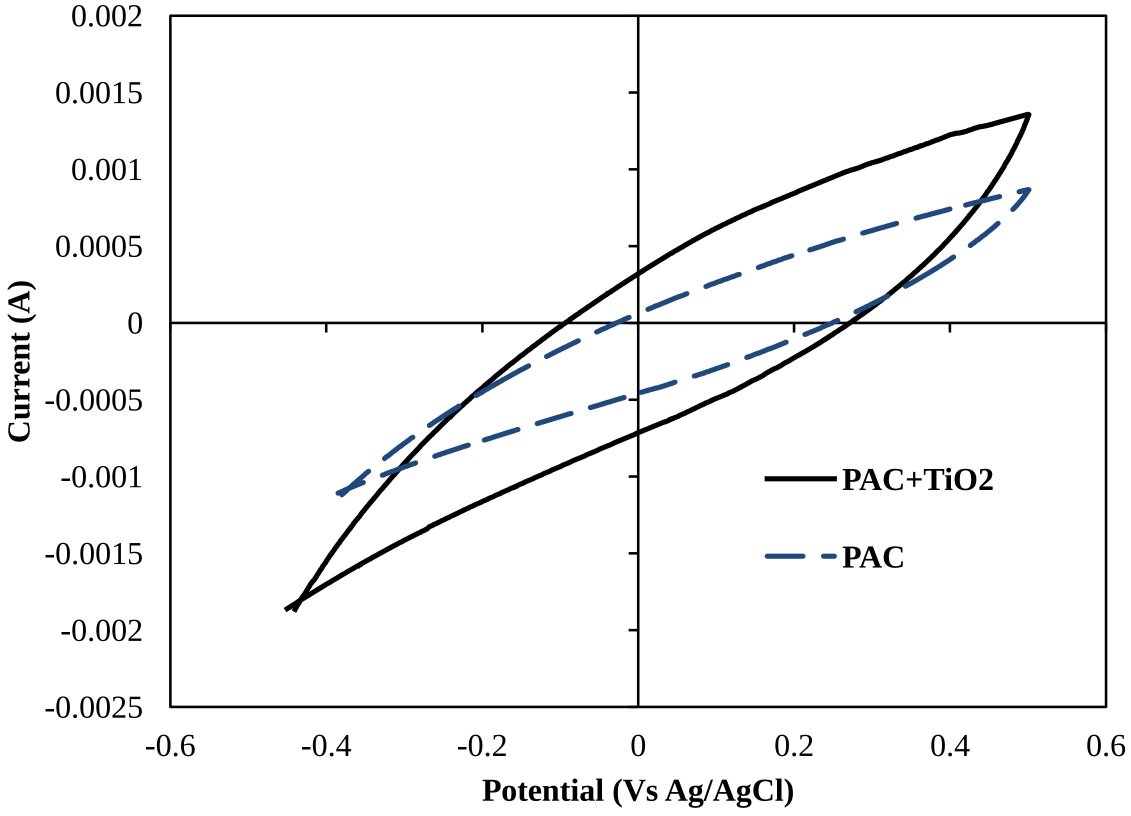


Figure 4.4: Cyclic voltagrams of the electrodes

4.5 CDI performance of PAC and PAC+TiO_2 electrodes

4.5.1 Adsorption

4.5.1.1 Small scale CDI system

Figure 4.5 shows concentration variations of effluent for small scale CDI system. Once the voltage was applied, the concentration of effluent decreased sharply to 1916.3 mg/L for PAC and 1883 mg/L for PAC+TiO_2 electrodes after first 5 minutes of adsorption operation. The ions were electrosorbed onto the electrodes surface and the concentration was decreased until there was no significant change noted in the effluent concentration over time. PAC+TiO_2 electrodes showed 28% more salt removal as compared to PAC electrodes. This increase in salt removal % can be explained by the facts that the addition of TiO_2 decreased physical adsorption while promoting electrosorption and high wettability of electrodes (Ryoo *et al.*, in 2003; Kim *et al.*, in 2014).

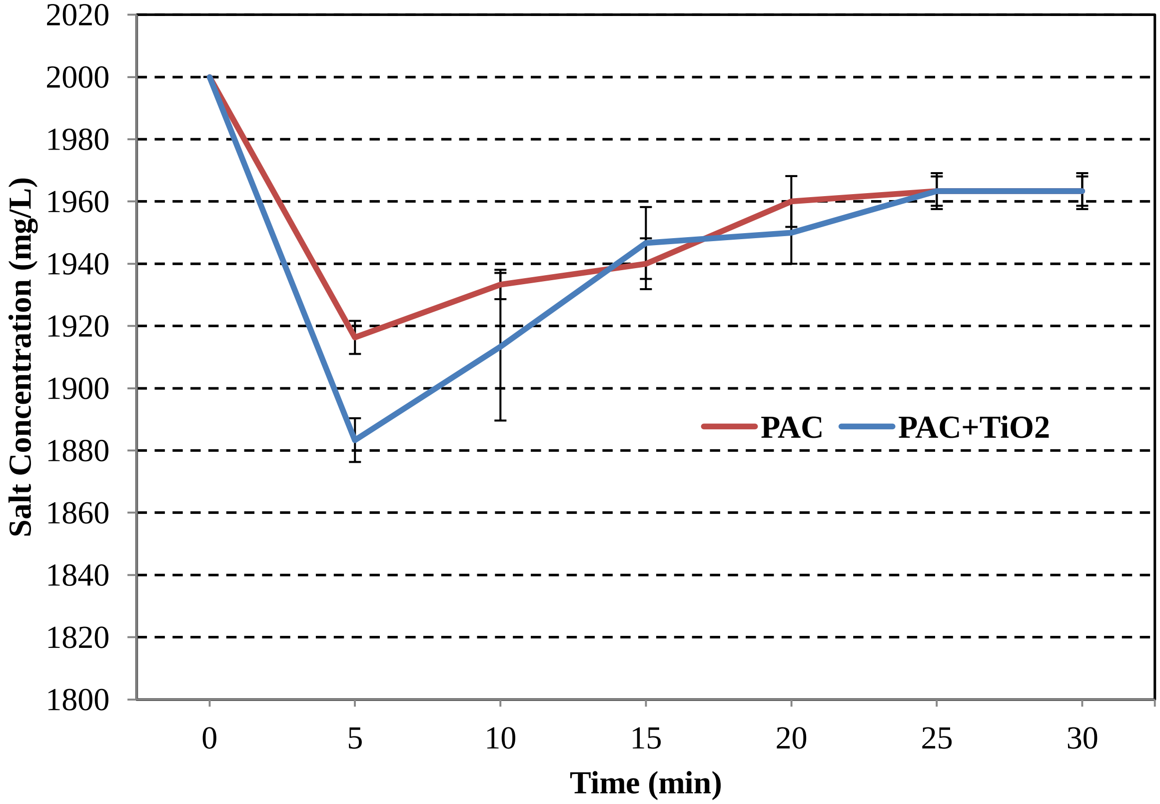


Figure 4.5: Concentration variations for small scale CDI system at 1.3V using PAC versus PAC+TiO_2 electrodes

4.5.1.2 Laboratory scale CDI system

Further experiments were conducted on laboratory scale CDI system using PAC+TiO_2 electrodes. Figure 4.6 shows concentration variations of effluent at different applied voltages. It can be observed that maximum reduction in concentration of effluent appeared for all the voltages within 8-10 minutes of adsorption operation, meanwhile the concentration tend to get closer to the influent concentration after 28 minutes for 1.3 and 1.6 V but at 1.8 V the concentration went to 1846 mg/L after 44 minutes of operation. This means greater the electrode potential, longer will be the saturation time and greater will be the salt removal. Higher voltages exert stronger electrostatic forces and thicker EDL, so the electrosorption capacity increases with the enhancement of the cell voltage (Zhao *et al.*, 2014)**.**

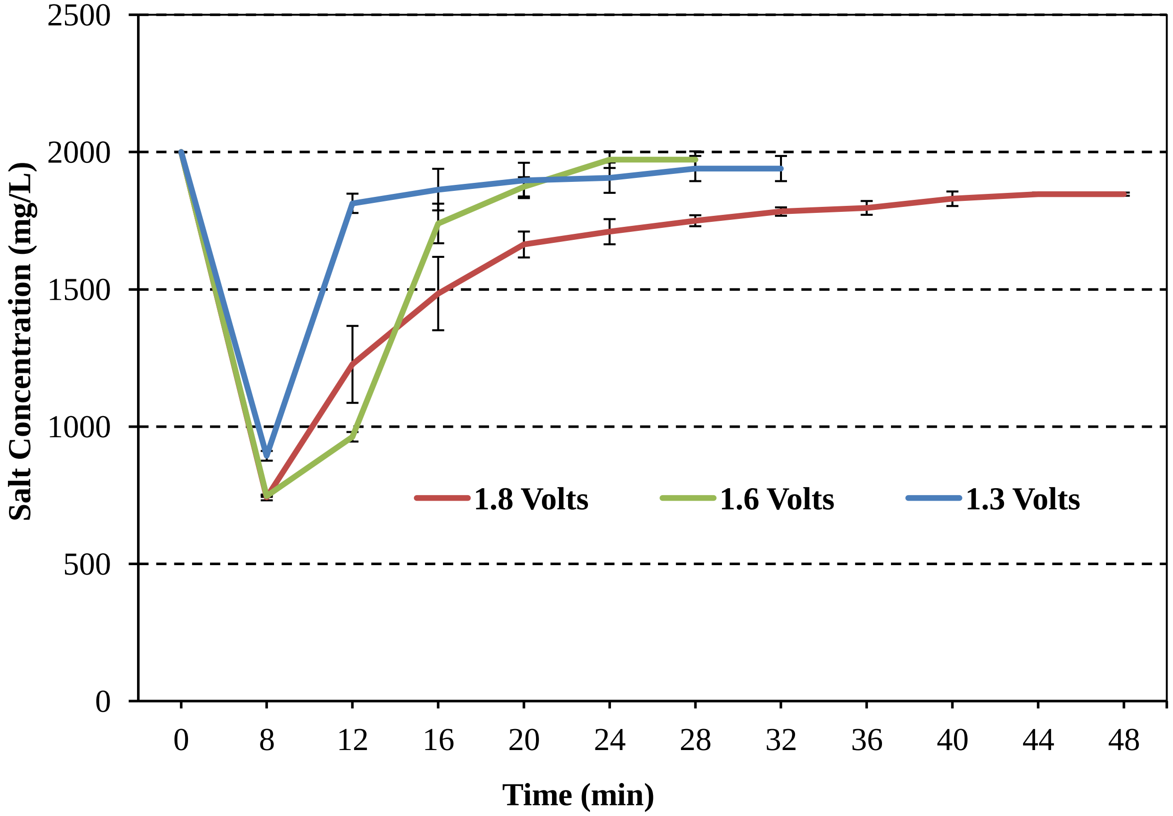


Figure 4.6: Concentration variations of laboratory scale CDI system at different applied voltages using PAC+TiO_2 electrode

The ion removal increased with the increase in voltage range from 1.3 to 1.8 V. Greater ion removal performance was observed at 1.8V in terms of 64% salt removal and adsorption capacity of 6.67 mg-NaCl/g-adsorbent. Concentration of NaCl solution maximum dropped to 882 mg/L at 1.3 V, 744 mg/L at 1.6 V and 731 mg/L at 1.8 V. No visible gas bubbles were observed during experiments which indicate that no electrolysis reaction occur at applied potentials (1- 2V) (Kim *et al.*, 2010; Li *et al.*, 2010). The cyclic voltammetry results also revealed no electrochemical reactions occurred**.** The salt removal characteristics and adsorption capacities at different applied voltages are presented in Table 4.2.

Table 4.2: Salt removal characteristics and adsorption capacities for laboratory scale CDI system.

Voltage (V)	Volumetric flow rate (mL/min)	Salt removal %	Adsorption Capacity (Q) (mg NaCl/g-adsorbent)
1.3	25	56	2.64
1.6	25	62	4.30
1.8	25	64	6.67

4.5.1.3 Pilot scale CDI system

Figure 4.7 shows concentration variation of effluent for pilot scale experiments conducted at 1.8 V with different concentrations of NaCl solutions using PAC+TiO_2 electrodes. Maximum salt removal of 84, 82 and 71% was observed for the salt water concentration of 2000, 2500 and 3000 mg/L with adsorption capacities of 7.7, 10.4 and 11.2 mg NaCl/g-adsorbent, respectively. The reason for a decrease in salt removal with increase in concentration is increase in the amount of salt to adsorbent and the saturation of the exchangeable sites on adsorbent structure. In this study the salt adsorption capacity increased with increasing concentration, which is due to elevated mass transfer rate of salt ions inside the pores and minimize overlapping effect by greater concentrations (Li *et al.*, 2009).

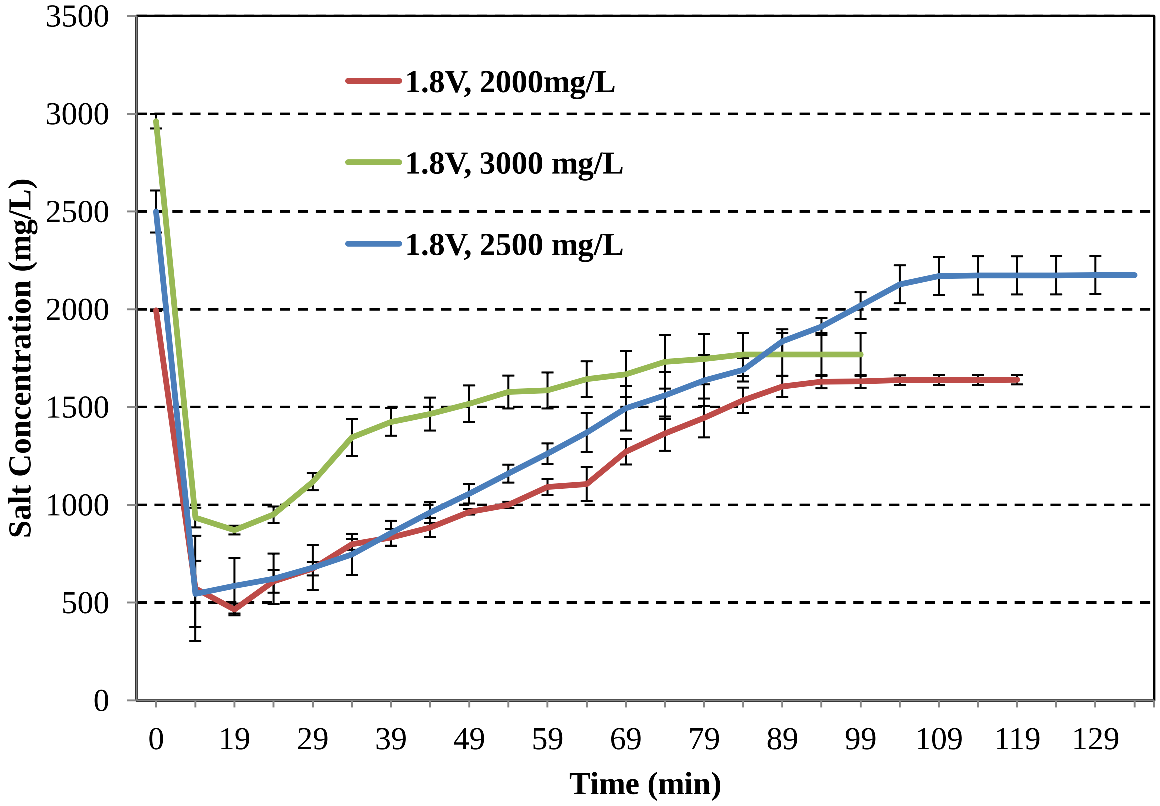


Figure 4.7: Concentration variations of pilot scale CDI system at 1.8 V using PAC+TiO_2 electrode for different feed concentrations

4.5.2 Regeneration

During the experiments, once the electrodes become saturated with salt ions, the performance of electrodes in terms of salt removal decreases over time. The performance was indicated by the effluent salt concentration which begins to show no significant changes in terms of conductivity/TDS with respect to time. It was a clear indication to regenerate the electrodes to get the electrodes back to initial stage adsorption efficiency.

The regeneration of electrodes was performed by reversing of voltage or removing the voltage supplied to electrodes and can be washed with treated or deionized (DI) water. In this study the regeneration was achieved by removing the voltage completely by switching off direct current (DC) power supply and flushing the laboratory scale CDI system with DI water. The disconnecting of DC power supply allows detaching the salt ions from electrode and DI water helps in flushing the salt ions from the system, thus producing concentrated effluent at the outlet. At the outlet the concentration of effluent was continuously monitored by conductivity/TDS meter.

Figure 4.8 and Figure 4.9 shows the regeneration curves for small and laboratory scale CDI systems respectively. It can be noted that during regeneration, the effluent concentration dropped within 10 minutes which can be considered as the regeneration time. Generally at the beginning of regeneration, the concentration should increases and then decreases showing regeneration of electrodes. The lower concentration values should be attributed to the flow rate used for regeneration in these experiments. Higher flow rate i.e. 50 mL/min for small CDI testing systems resulted in dilution of the spent stream and indicating low concentration values of the effluent.

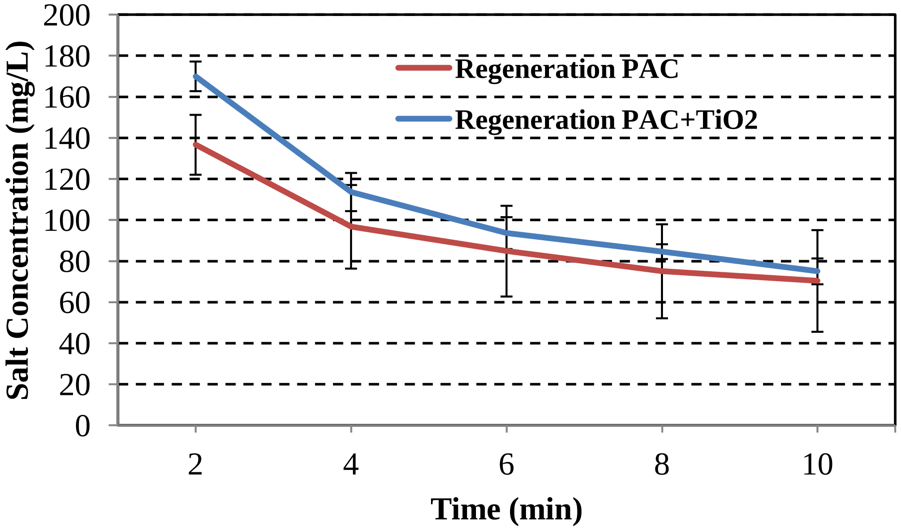


Figure 4.8: Regeneration concentration variations for small scale CDI system

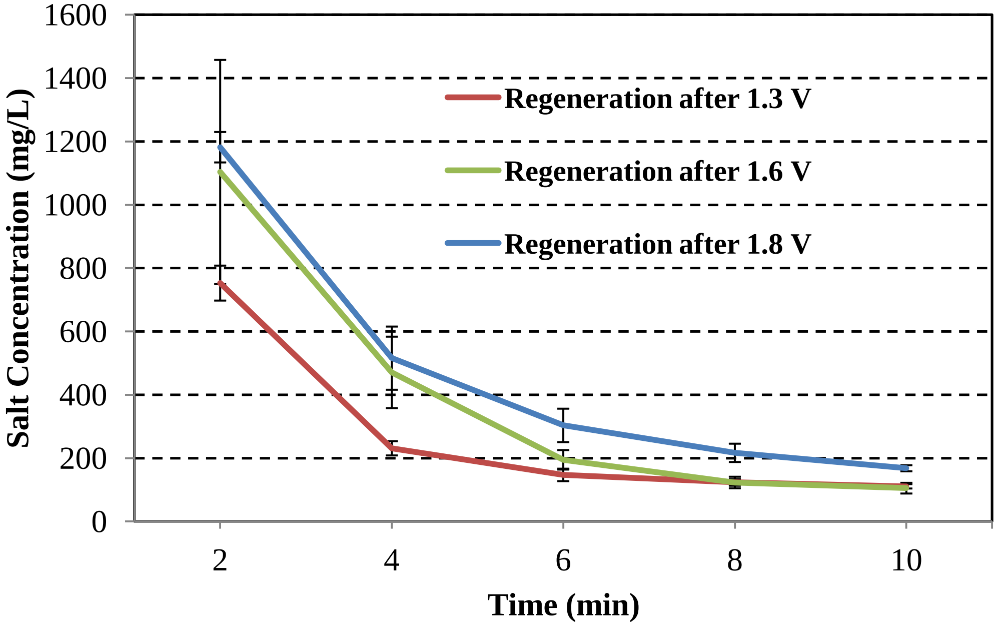


Figure 4.9: Regeneration concentration variations for laboratory scale CDI system

Fig 4.10 shows the regeneration of electrodes for pilot scale CDI system. As compared to small and laboratory scale regeneration flow rate the flow rate for pilot scale CDI system was kept at 25 mL/min to minimize the DI water use in the regeneration the electrodes. The lower flow rate did not dilute the spent stream from regeneration and the increasing trend in concentration of effluent indicated that the electrodes were being regenerated by flushing the adsorbed salt ions from the electrodes surface.

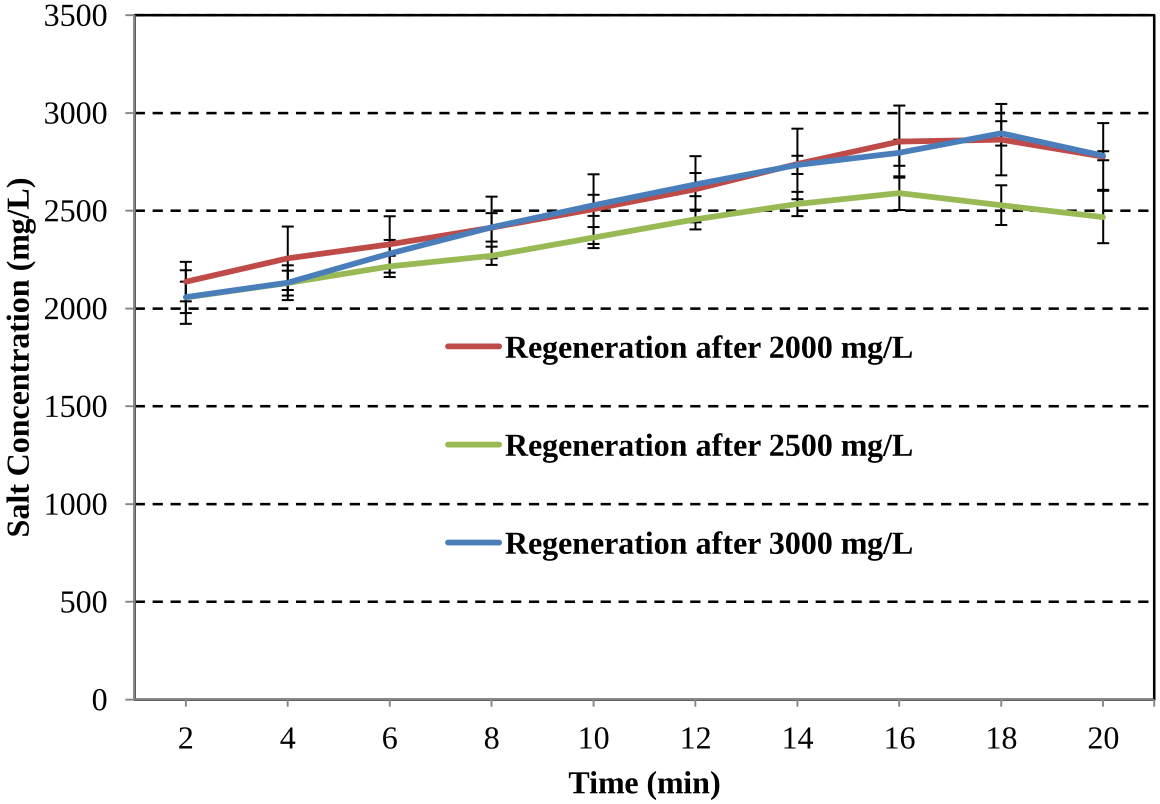


Figure 4.10: Regeneration concentration variations for pilot scale CDI system

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

In this study initial experiments were conducted using PAC and PAC+TiO_2 electrodes to access the salt removal efficiency of both electrodes. PAC+TiO_2 electrodes showed 28% more salt removal as compared to PAC electrodes. Further experiments were conducted using PAC+TiO_2 electrodes in laboratory and pilot scale setups. In laboratory scale CDI system the adsorption capacities were found to be 2.64, 4.3 and 6.67 mg NaCl/g-adsorbent and salt removals were 56, 62 and 64% for 1.3, 1.6 and 1.8 volts, respectively. Higher voltages exert stronger electrostatic forces and thicker EDL, so the electrosorption capacity increases with the enhancement of the cell voltages. Moreover pilot scale CDI system using 20 pairs of PAC+TiO_2 electrodes showed maximum salt removal percentage of 84%, 82% and 71% for the feed water concentrations of 2000, 2500 and 3000 mg/L with adsorption capacities of 7.7, 10.4 and 11.2 mg NaCl/g-adsorbent respectively. The amount of treated water under 1000 mg/L was 1.475, 1.1 and 0.6 liters for 2000, 2500 and 3000 mg/L respectively. The salt removal efficiency decreased with increase in concentration, as the amount of salt ions to adsorbent increases, the exchangeable sites on adsorbent structure become saturated which results in decrease of the salt removal efficiency. In comparison to salt removal efficiency, salt adsorption capacity increased with increasing concentration, which was due to elevated mass transfer rate of salt ions inside the pores and minimize overlapping effect by greater concentrations. The cyclic voltammetric results showed that the removal of ions was mainly due to the presence of electric double layer (EDL) near the surface of electrodes. The PAC+TiO_2 electrodes were very effective in terms of ions removal by providing electrosorption sites for ions which resulted in significant enhancement of electrosorption while decreasing the physical adsorption as reported in the literature. The results indicate the potential practical application of PAC-TiO_2 electrodes for CDI system.

5.2 Recommendations

In order to further assess salt removal efficiency using CDI technology, following research can be considered.

- Variations in flow rate.
- Different electrode materials.
- Varying electrodes distance

REFERENCES

Accomazzo, M.A., Evans, S. (1969) Electrochemically controlled ion exchange, *Journal of the Electrochemical Society*, 116: 309–311.

Arnold, B.B., Murphy, G.W. (1961) Studies on electrochemistry of carbon and chemically modified carbon surfaces, *Journal of Physical Chemistry,* 65: 135–138.

Avraham, E., Noked, M., Bouhadana. Y., Soffer, A. and Aurbach, D. (2009) Limitations of charge efficiency in capacitive deionization. II. On the behavior of cdi cells comprising two activated carbon electrodes, *Journal of the Electrochemical Society,* 56: 157–162.

Ayoub, G. M., Zayyat, R.M. and Al, H.M. (2014) Precipitation softening: a pretreatment process for seawater desalination, *Journal of environmental science and pollution research,* 21(4): 2876-2887.

Biesheuvel, P.M., Zhao, R., Porada, S. and van der Wal, A. (2011) Theory of membrane capacitive deionization including the effect of the electrode pore space, *Journal of Colloid and Interface Science*, 360: 239–248.

Blair, J.W., Murphy, G.W. (1960) Electrochemical demineralization of water with porous electrodes of large surface area, Saline water conversion, *American Chemical Society*, 206–223.

Chen, Z., Song, C., Sun, X., Guo, H. and Zhu, G. (2011) Kinetic and isotherm studies on the electrosorption of NaCl from aqueous solutions by activated carbon electrodes, *Desalination,* 267: 239–243.

Chia, H.H., Cheng, Y.H. (2013) A comparative study of electrosorption selectivity of ions by activated carbon electrodes in capacitive deionization, *Desalination*, 314: 124-129

Dai, K., Shi, L., Fang, J., Zhang, D. and Yu, B. (2005) NaCl adsorption in multi-walled carbon nanotubes, *Materials Letters*, 59: 1989–1992.

Evans, S., Accomazzo, M.A. and Accomazzo, J.E. (1969) Electrochemically controlled ion exchange, *Journal of the Electrochemical Society*, 116: 307–309.

Evans, S., Hamilton, W.S. (1966) The mechanism of demineralization at carbon electrodes, *Journal of the Electrochemical Society*, 113: 1314–1319.

Farmer, J.C., Bahowick, S.M., Harrar, J.E., Fix, D.V., Martinelli, R.E. and Vu, A.K. (1997) Electrosorption of chromium ions on carbon aerogel electrodes as a means of remediating ground water, *Energy & Fuels*, 11: 337–347.

Farmer, J.C., Fix, D.V., Mack, G.V., Pekala, R.W. and Poco, JF. (1995) The use of capacitive deionization with carbon aerogel electrodes to remove inorganic contaminants from water, *Low level waste conference, Orlando.*

Farmer, JC., Fix, D.V., Mack, G,V,, Pekala, R.W. and Poco, J.F. (1996) Capacitive deionization of NH_4ClO_4 solutions with carbon aerogel electrodes, *Journal of Applied Electrochemistry*, 26: 1007–1018.

Frackowiak, E., Beguin, F. (2001) Carbon materials for the electrochemical storage of energy in capacitors, *Carbon*, 39: 937–950.

Fritzmann, C., Lowenberg, J., Wintgens, T. and Melin, T. (2007) State-of-the-Art of Reverse Osmosis Desalination, *Desalination*, 216(1–3): 1–76.

Gabelich, C.J., Tran, T.D. and Suffet, I.H. (2002) Electrosorption of inorganic salts from aqueous solution using carbon aerogels, J*ournal of Environmental Science and Technology*, 36(13): 3010-3019.

Gleeson, T., Wada, Y., Bierkens, M. F. P. and Van, B.L. P. H. (2012) Water Balance of Global Aquifers Revealed by Groundwater Footprint, *Nature*, 488: 197-200.

Gleick, P.H. (1996) Basic water requirements for human activities: Meeting basic needs, *Water International*, 21(2): 83-92.

H. Strathmann (2004) Ion-Exchange Membrane Separation Processes, *Elsevier, Amsterdam.*

Han, J.O., Jong, H.L., Hong, J.A., Yongsoo, J., Young, J.K. and Choong, S.C. (2005) Nanoporous activated carbon cloth for capacitive deionization of aqueous solution, *Thin Solid Films*, 515: 220–225.

http://ga.water.usgs.gov/edu/earthwherewater.html, accessed on 7th January, 2015.

Huang, G.H., Chen, T.C., Hsu, S.F., Huang, Y.H. and Chuang, S.H (2014) Capacitive deionization (CDI) for removal of phosphate from aqueous solution, *Desalination and Water Treatment,* 52: 759–765.

Jauad, E.K., Alaa, E.S., Noreddine, G. and Eric, M. (2012) Water scarcity and drought in WANA countries, *Procedia Engineering,* 33: 14-29.

Jia, B., Zou, L. (2012) Wettability and its influence on graphene nansoheets as electrode material for capacitive deionization, *Chemical Physics Letters,* 548: 23–28.

Johnson, A.M., Newman, J. (1971) Desalting by means of porous carbon electrodes, *Journal of the Electrochemical Society,* 118: 510–517.

Johnson, A.M., Venolia, A.W., Wilbourne, R.G., Newman, J., Wong, C.M. and Gilliam, W.S. (1970) The electrosorb process for desalting water, *Washington, U.S. Dept. of the Interior*.

Kim, C., Lee, J., Kim, S. and Yoon, J. (2014) TiO_2 sol–gel spray method for carbon electrode fabrication to enhance desalination efficiency of capacitive deionization, *Desalination*, 342: 70–74.

Kim, Y.J., Choi, J.H. (2010) Enhanced desalination efficiency in capacitive deionization with an ion-selective membrane, *Seperation and Purification Technology*, 71: 70–75.

Lee, J.H., Choi, J.H. (2013) Ion-selective composite carbon electrode coated with TiO_2 nanoparticles for the application of electrosorption process, *Desalination and Water Treatment*, 51: 503–510.

Li, H., Lu, T., Pan, L., Zhang, Y. and Sun, Z. (2009) Electrosorption behavior of graphene in NaCl solutions, *Journal of Materials Chemistry*, 19: 6773–6779.

Li, H., Pan, L., Lu, T., Zhan, Y., Nie, C. and Sun, Z. (2011) A comparative study on electrosorptive behavior of carbon nanotubes and grapheme for capacitive deionization, *Journal of Electroanalytical Chemistry*, 653: 40–44.

Li, H., Pan, L., Nie, C., Liu, Y. and Sun, Z. (2012) Reduced graphene oxide and activated carbon composites for capacitive deionization, *Journal of Material Chemistry*, 22: 15556–15561.

Li, H., Zou, L., Pan, L. and Sun, Z. (2010) Novel graphene-like electrodes for capacitive deionization, *Journal of Environmental Science and Technology*, 44: 8692–8697.

Li, H.B., Lu, T., Pan, L.K., Zhang, Y.P and Sun, Z. (2009) Electrosorption behavior of graphene in NaCl solutions, *Journal of Material Chemistry*, 19: 6773–6779.

Li, L., Zou, L., Song, H. and Morris, G. (2009) Ordered mesoporous carbons synthesized by a modified sol–gel process for electrosorptive removal of sodium chloride, *Carbon*, 47: 775–781.

Liu, P., Chung, L., Shao, H., Liang, R. Ma, H.C.M. and Chang, M.C. (2013) Microwave-assisted ionothermal synthesis of nanostructured anatase titanium dioxide / activated carbon composite as electrode material for capacitive deionization, *Electrochimica Acta*, 96: 173–179.

Liu, Y., Li, H., Nie, C., Pan, L. and Sun, Z. (2013) Carbon nanotube and carbon nanofiber composite films grown on different graphite substrate for capacitive deionization, *Desalination and Water Treatment*, 51: 3988–3994.

Murphy, G.W., Caudle, D.D. (1967) Mathematical theory of electrochemical demineralization in flowing systems, *Electrochimica Acta*, 12: 1655–64.

Murphy, G.W., Cooper, J.L. and Hunter, J.A. (1969) Activated carbon used as electrodes in electrochemical demineralization of saline water, *Washington, U.S. Dept. of the Interior.*

Nadakatti, S., Tendulkar, M. and Kadam, M. (2011) Use of mesoporous conductive carbon black to enhance performance of activated carbon electrodes in capacitive deionization technology, *Desalination,* 268: 182–188.

Oren, Y. (2008) Capacitive deionization (CDI) for desalination and water treatment – past, present and future (a review), *Desalination,* 228: 10–29.

Oren, Y., Soffer, A. (1978) Electrochemical parametric pumping, *Journal of the Electrochemical Society*, 125: 869–875.

Oren, Y., Soffer, A. (1983) Water desalting by means of electrochemical parametric pumping. I. The equilibrium properties of a batch unit cell, *Journal of applied electrochemistry*, 13: 473–487.

Oren, Y., Soffer, A. (1983) Water desalting by means of electrochemical parametric pumping. II. Separation properties of a multistage column, *Journal of applied electrochemistry*, 13: 489–505.

Park, K.K., Lee, J.B., Park, P.Y., Yoon, S.W., Moon, J.S., Eum, H.M. and Lee, C.W. (2007) Development of a carbon sheet electrode for electrosorption desalination, *Desalination*, 206: 86–91.

Pekala, R.W., Farmer, J.C., Alviso, C.T., Tran, T.D., Mayer, S.T., Miller, J.M. and Dunn, B. (1998) Carbon aerogels for electrochemical applications, *Journal of Non-Crystaline Solids*, 225: 74-80.

Peng, Z., Zhang, D., Shi, L, and Yan, T. (2012) High performance ordered mesoporous carbon/carbon nanotube composite electrodes for capacitive deionization, *Journal of Material Chemistry*, 22: 6603–6612.

Porada, S., Zhao, R., Van Der Wal, A., Presser, V. and Biesheuvel, P.M. (2013) Progress in Materials Science Review on the science and technology of water desalination by capacitive deionization, *Prorgress in Materials Science*, 58: 1388–1442.

Reid, G.W., Townsend, F.M. and Stevens, A.M. (1968) Field operation of 20 gallons per day pilot plant unit for electrochemical desalination of brackish water, *Washington, U.S. Dept. of the Interior*.

Rouquerol, J., Avnir, D., Fairbridge, C.W., Everett, D.H., Haynes, J.M. and Pernicone. (1994) Recommendations for the characterization of porous solids (technical report), *Pure and Applied Chemistry*, 66: 1739–1758.

Ryoo, M.W., Kim, J.H. and Seo, G. (2002) Role of titania incorporated on activated carbon cloth for capacitive deionization of NaCl solution, *Journal of Colloid and Interface Science,* 264: 414–419**.**

Ryoo, M.W., Seo, G. (2003) Improvement in capacitive deionization function of activated carbon cloth by titania modification, *Water Research,* 37: 1527–1534.

Shannon, M.A., Bohn, P.W., Elimelech, M., Georgiadis, J.G., B.J. Marinas. and Mayes, A.M. (2008) Science and technology for water purification in the coming decades, *Nature*, 452: 301–310.

Soffer, A., Folman, M. (1972) The electrical double layer of high surface porous carbon electrode, *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*, 38: 25–43.

Suss, M.E, Baumann, T.F., Bourcier, W.L., Spadaccini, C.M., Rose, K.A and Santiago J.G. (2015) Capacitive desalination with flow-through electrodes, *Energy & Environmental Science*, 5: 9511–9519.

Tsouris, C., Mayes, R., Kiggans, J., Sharma, K., Yiacoumi, S., DePaoli, D. and Dai, S. (2011) Mesoporous carbon for capacitive deionization of saline water, J*ournal of Environmental Science and Technolog,*. 45: 10243–10249.

Velasco, M.J., Rubio, F., Rubio, J. and Oteo, J. L. (1999) Hydrolysis of titanium tetrabutoxide. Study by FT-IR spectroscopy, *Spectroscopy Letters*, 32: 289–304

Wang, G., Pan, C., Wang, L., Dong, Q., Yu, C., Zhao, Z. and Qiu, J. (2012) Activated carbon nanofiber webs made by electrospinning for capacitive deionization, *Electrochimica Acta*, 69: 65–70.

Wang, X.Z., Li, M.G., Chen, Y.W., Cheng, R.M., Huang, S.M and Pan, L.K. (2006) Electrosorption of NaCl solutions with carbon nanotubes and nanofibers composite film electrodes, *Electrochemical and Solid-State Letters*, 9: 23–26.

Wang, Z., Dou, B., Zheng, L., Zhang, G., Liu, Z. and Hao, Z. (2012) Effective desalination by capacitive deionization with functional grapheme nanocomposite as novel electrode material, *Desalination*, 299: 96–102.

Water in a Changing Worlds, The United Nations World Water Development Report 3, http://www.unesco.org/water/wwap/wwdr/wwdr3/, 2009.

WHO/UNICEF Joint Monitoring Programme (JMP) for Water Supply and Sanitation (2012) *Progress on Sanitation and Drinking-Water, 2012 Update.*

Xu, P., Drewes, J.E., Heil, D. *and* Wang, G. *(*2008) Treatment of brackish produced water using carbon aerogel-based capacitive deionization technolog, *Water Research*, 42*:* 2605–2617.

Yang, J., Zou, L., Song, H. and Hao, Z. (2011) Development of novel MnO_2/nanoporous carbon composite electrodes in capacitive deionization technology, *Desalination,* 276: 199–206.

Younos, T., Tulou, K.E. (2005) Overview of Desalination Techniques, *Journal of Contemporary Water Research & Education,* 132: 3–10.

Zhang, D., Yan, T., Shi, L., Peng, Z., Wen, X. and Zhang, J. (2012) Enhanced capacitive deionization performance of graphene/carbon nanotube composites, *Journal of Material Chemistry,* 22: 14696–14704.

Zhao, Y., Hu, X., Jiang, B. and Li, L. (2014) Optimization of the operational parameters for desalination with response surface methodology during a capacitive deionization process, *Desalination,* 336: 64–71.

Zhao, Y., Wang, Y., Wang, R., Wu, Y., Xu, S. and Wang, J. (2013) Performance comparison and energy consumption analysis of capacitive deionization and membrane capacitive deionization processes, *Desalination,* 324: 127–133.

Zou, L., Li, L., Song, H. and Morris, G. (2008) Using mesoporous carbon electrodes for brackish water desalination, *Water Research,* 42: 2340-2348.

Zou, L., Morris, G and Qi, D. (2008) Using activated carbon electrode in electrosorptive deionisation of brackish water, *Desalination,* 225: 329–340.

ANEXTURE A

Publications and Conference Presentation

1. Ahmad, F., Khan, S.J., Jamal, Y., Kamran, H., Ahsan, A., Ahmad. M. and Khan. A. Treatment of Inland Brackish Water by Using Capacitive Deionization Technology, presented at 7th International conference in Challenges in Environmental Science & Engineering, Johor Bahru, Malaysia, October 12-16, 2014.

2. Ahmad, F., Khan, S.J., Jamal, Y., Kamran, H., Ahsan, A., Ahmad. M. and Khan. A. (2015) Desalination of Brackish Water Using Capacitive Deionization Technology, *Desalination and water treatment*, Published online on 20th April, 2015.