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Study of the Desalination Efficiency for Different Configurations of Microbial Desalination Cell (MDC)

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DEDICATION

This thesis is dedicated to the soul of my beloved brother, my parents, husband and parents in law.

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Praise be to God, the one who hears my voice when I was weak and gave me the power to attain this research, this research was a sensuousness journey combined between the anxiety and the pleasure, and I hope I could conclude this research in well.

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Abstract

The Gaza Strip is suffering from the drinking water scarcity, where the essential water source in the Gaza Strip is the ground water which salted by the intrusion from seawater, and the remaining water is not suitable for human uses. One of the solutions for this problem is seawater desalination, unfortunately the desalination techniques is an energy consuming techniques and Gaza don't have enough energy to desalinate water. For this reason this research aims to study a new desalination method to reduce the required energy for desalination, by using the wastewater bacteria to produce electricity and desalinate water. This method depends on the bio-electrochemical systems, the reactor is called Microbial Desalination Cell (MDC) and consists of three chambers cathode, anode and desalination chamber, where the desalination chamber lies between the cathode and anode chambers. Anion Exchange Membrane (AEM) separates between the desalination chamber and the anode chamber, while Cation Exchange Membrane (CEM) separates the desalination chamber and the cathode chamber. By placing bacteria and wastewater in the anode chamber, bacteria breakdowns the organic matter in the wastewater and produces electrons, these electrons moves from the anode to cathode by external electrical connectors, and this creates an electrical current in the cell which causes the negative ions to move from the desalination chamber to the anode through the AEM and the positive ions to transfer to the cathode chamber through the CEM thus the salt water in the desalination chamber would be desalinated. In this research four MDC configurations were implemented to study the ability of improving desalination efficiency and electrical generation. The best desalination efficiency and electricity generation was seen in the Photosynthetic Microbial Desalination Cell (PMDC), where the desalination rate reached to 94% through 11 days, and produced power generation equal to 1.1 W/m^3.

ملخص الدراسة

يعاني قطاع غزة من شح في المياه الصالحة للشرب حيث ان الخزان الجوفي لا يكفي لسد حاجة قطاع غزة من المياه، غير أن كمية الطاقة اللازمة لتحلية مياه البحر او المياه المالحة في الابار هي أكبر من قدرة القطاع على توفيرها. الهدف من هذه الدراسة ان تتم دراسة طريقة جديدة لتحلية المياه المالحة دون الحاجة الى استهلاك كميه كبيرة من الطاقة عن طريق استخدام البكتيريا الموجودة في المياه العادمة لانتاج كمية من الكهرباء القادرة على تحلية المياه بنسبة جيدة. من هنا يمكن وصف تصميم جهاز التحلية على أنه خلية كهروكيميائية تشبه الية عمل الخلية الجلفانية حيث ينقسم الجهاز الى ثلاثة غرف المصعد (أنود) ، المهبط (كاثود) وغرفة التحلية، تقع غرفة التحلية ما بين غرفتي الانود والكاثود ، ويفصل غرفة التحلية عن الانود غشاء خاص لتمرير الشحنات السالبة فقط ، بينما يفصل غرفة التحلية عن الكاثود غشاء خاص لتمرير الشحنات الموجبة فقط، يتم وضع البكتيريا في غرفة الانود لتعمل على انتاج الكترونات عن طريق تكسير المواد العضوية الموجودة في المياه العادمة وتتحرك الالكترونات في الخلية عن طريق أسلاك كهربائية موصولة ما بين الانود والكاثود، مرور تيار كهربائي في الخلية يعمل على تحريك ايونات الكلور السالبة لتنتقل الى غرفة الانود بينما تتحرك أيونات الصوديوم الموجبة الى غرفة الكاثود وبهذه الطريقة يتم تحلية المياه الموجودة بغرفة التحلية.

في هذا البحث تم دراسة اربعة تصاميم من الخلية الميكروبية للتحلية لتحسين القدرة على تحلية المياه المالحة وتحسين الانتاج الكهربائي للخلية الميكروبية.

أظهرت النتائج النهائية أن أفضل نسبة تحليه كانت في الجهاز الثاني (الخلية الضوئية الميكروبية) حيث كانت وصلت نسبة التحلية الى 94% خلال 11 يوم ، وكانت الطاقة الناتجة عنها تكافئ 1.1 واط / م^3 .

LIST OF CONTENT

LIST OF ABBREVIATIONS

AEM	Anion Exchange Membrane
CEM	Cation Exchange Membrane
MDC	Microbial Desalination Cell
PMDC	Photosynthetic Microbial Desalination Cell
SPMDC	Stacked Photosynthetic Microbial Desalination Cell
SSAMDC	Stainless Steel electrodes in Algal Microbial Desalination Cell
MFC	Microbial Fuel Cell
COD	Chemical Oxygen Demand
TDS	Total Dissolved Salts
EC	Electrical Conductivity
DI_{Water}	Deionized Water
OLR	Organic Loading Rate
CE	Coulombic Efficiency
FC	Faradic Efficiency
DO	Dissolved Oxygen
SS	Stainless Steel
HRT	Hydraulic Retention Time
mV	Milli Volt
mW	Milli Watt
mA	Milli Ampere
A/m^3	Ampere per cubic meter
W/m^3	Watt per cubic meter
NADH	Nicotinamide adenine dinucleotide
NADHP	Nicotinamide adenine dinucleotide phosphate
Qd	Desalination Rate
Aver. Qd	Average Desalination Rate
P	Power
PMFC	Photosynthetic Microbial Fuel Cell
SPMFC	Stacked Photosynthetic Microbial Fuel Cell
SSAMFC	Stainless Steel Electrodes in Algal Microbial Fuel Cell

g/L	Grams per liter
mg/L	Milli grams per liter
mS/cm	Milli semen per centimeter
mL	Milli liter
Ω	Ohm
GAC	Granular activated carbon
RO	Reverse Osmosis

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Chapter 1: Introduction

1.1 Introduction

Water is one of the most vital, essential components of life. As a result of population explosion the global water demand is extremely increasing, unfortunately the most fresh water resources are contaminated by various physical, chemical, and microbiological species which include bacteria, viruses, and toxic material such as heavy metals. One of the solutions to elevate the available drinking water is the water desalination techniques. The desalination of seawater and brackish water for use as potable drinking water is costly due to the amount of energy required to remove the dissolved salts from the water when accomplished by either evaporation (650 $kW/h.m^3$ for single-stage evaporation) or reverse osmosis (RO) (3.7 $kW/h.m^3$), (Mehanna et al., 2010).

There are upcoming increases in the worldwide desalination capacity, and this would threaten the global energy production where energy accounts for 40 percent of the total cost of desalination (Miller, 2006).

The membrane separation techniques are preferable for water desalination in order to reduce the contaminants in the water (Brastad, 2015).

Microbial Desalination Cell (MDC) is a new method for water desalination using electrical energy generated by bacteria (Cao et al., 2009). MDCs are environmentally friendly technology for removing ions from water. The concept is similar to water electro dialysis except the MDC don't need an external power to drive the ions from the saline water.

MDC is an extended bio electrochemical system from Microbial Fuel cells (MFC), which utilizes the bacteria produce electrical energy from the energy stored in chemical bonds of organic compounds (Betts et al., 2009).

1.2 Introduction to Microbial Fuel Cells

The Microbial Fuel Cells (MFCs) study is a blossoming and miscellaneous field incorporating microorganisms and power generation. It is difficult to define and characterize the MFC in both design and concept because of the diversity of the field. This diversity is due to every single MFC component and concept is variable except

one - microorganisms must be used in at least one of processes that shares in the Energy production.

The following literature review will discuss the microbial fuel cells with its types, bacteria mechanisms, the different types of electron transfer, Losses that happens in the microbial fuel cells, and electrodes that was used previously. This chapter will also discuss the Microbial Desalination Cell (MDC), its principle, electrode materials and Biocathodes approach used in the MDC.

1.1.2 Types of Microbial fuel cell

There are two structure types of MFCs the first type in which one chamber is exist, Anode chamber, the cathode is merged with the reactor where it interface the internal electrolytes in one face and the external air in the other face this type is called a single-chamber MFC.

A double-chamber MFC contain two compartment anode and cathode chamber separated by Ion Exchange Membrane (IEM). The organic matters is in the anode chamber where the oxidation reaction is happened by bacteria, whereas the cathode chamber contains the catholytes that include electron acceptor such as oxygen (Fig 1.1), (Degrenne, 2012).

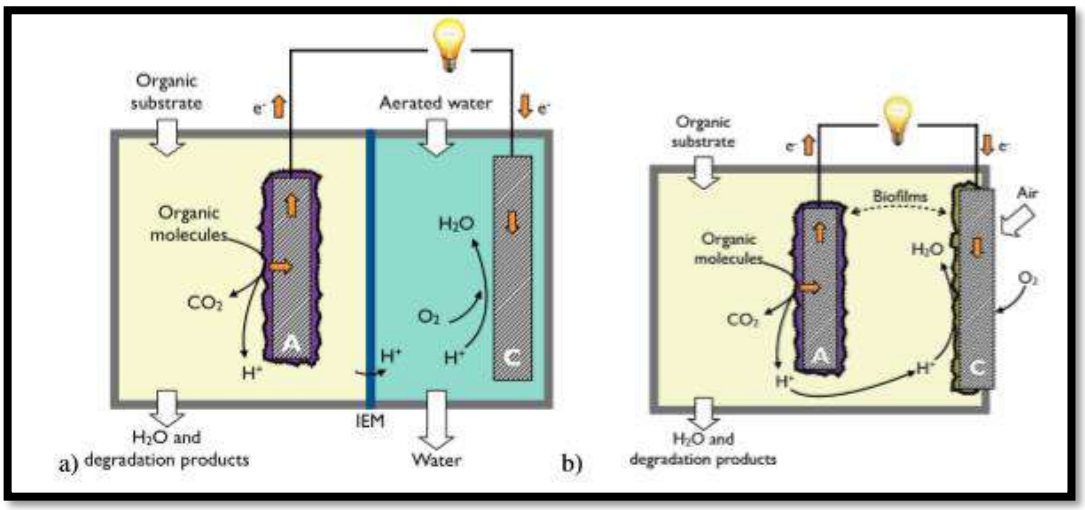

Figure 1.1: Schematic of a double-chamber (a) and single-chamber (b) MFC

1.1.3 Microbial Desalination Cells (MDCs)

The MDCs have the same principle of bio electrochemical reactions in MFCs. The MDC conjugates ionic current in the electrolyte with electric current at the electrodes, through bio electrochemical organic oxidation takes place at the anode and electrochemical reduction at the cathode respectively. The discussion in following subsections is applicable to both MDCs and MFCs.

1.2 Problem Statement

The Gaza Strip or simply Gaza is a very small area (365 km^3) lies along the Mediterranean Sea, Gaza depends on the groundwater from the coastal aquifer as the main source of water.

The Gaza Strip suffers from the scarcity of renewable water resource where the annual discharge rate from the coastal aquifer is about 200 MCM, while the annual recharge is about 55-60 MCM/ Y from the rainfall, and this led to deficiency in the per capita water resources. Fifty two percent of the groundwater is utilized for irrigation and the residual is used for domestic water supply and industry. The unbalance in the recharge-extraction equation results of a dropping in the groundwater level which led to seawater intrusion and water quality deterioration (PWA 2013).

Desalination sea water and brackish water is the main option for mitigation of water problem in Gaza, unfortunately the Large-scale desalination process requires high amount of energy which is not available due to severe fuel shortages in Gaza, for that reason Gaza needs a better solution that relieve the water crises besides the lack of energy.

1.3 Justification

The Gaza Strip is one of the areas that cannot meet people needs for drinking water, furthermore the population in Gaza is extremely increases and it’s hard to get sufficient energy for water desalination processes. For this reasons it’s important to found an alternative techniques to decrease the required energy for desalination processes. We believe that Microbial Desalination Cells (MDCs) will be a good option for mitigate the deficiency in the potable water through using it as a pretreatment process before the reverse osmosis which in turn will decrease the water salinity thus the required energy for desalination.

1.4 Objectives

This research aims to study the microbial desalination cell and investigate the desalination efficiency through it. The objectives of this research are:

- To study a four types of the microbial desalination cells reactors for desalination enhancement purpose.
- To investigate the output power from each reactor.
- To study the COD removal by bacteria.
- To investigate the coulombic efficiency of each MDC reactor.

1.5 Research Questions

Abundant questions about the microbial desalination cells are in demand to be addressed, this research attempted to handle some of them, for instance:

- Would the microbial desalination cell be a good solution to obtain a potable water?
- Could the microbial desalination cell minimize the required energy for desalination process?
- How will the microbial desalination cell contribute to create a clean environment?

1.6 The structure of the thesis

- **Chapter 1**

  It displays general background, the problem that the research aims to handle, the objectives to accomplish, and research questions.
- **Chapter 2**

  In this chapter an introduction to the MFC and its types were provided, also it offers the biochemical reactions occur in the bio electrochemical systems, the losses happens within MFC. It highlights the MDCs system with a description of the electrodes and ways to elevate the power production along with the survey of the previous researches related to this research.

- **Chapter 3**

  Describes the research methodology of this research.

- **Chapter 4**

  This chapter represents the results of the study include the desalination efficiency, electricity and power generation, wastewater treatment efficiency and the electron transfer efficiency results of the MDC reactors.

- **Chapter 5**

  Provides conclusion and recommendation of the study.

Chapter 2: Literature Review

2.1 Microbial fuel cell principle of operation

Microbial Fuel Cells (MFC) is a system that is designed to utilize the chemotrophs metabolism for generating electrical energy. It relies on the separation of oxidation-reduction reactions in order to harvest the available fraction of the produced energy from these reactions. Bacteria in microbial fuel cell are set in the anode chamber with organic materials, and the anode electrode are placed as the natural electron acceptors. Anode electrode is connected with the cathode electrode by electrical connections. The electron acceptor such as oxygen is placed in the cathode chamber in order to constrain the bacteria for oxygen utilization as the final electron acceptor. Electrons which are produced from oxidation of organic matters in the anode chamber are moved to cathode chamber to be reduced (Degrenne, 2012).

The bacteria that are used in MFC is exoelectrogens which are capable of exocellular electron transfer (Logan et al., 2006). Bacterial consortium produce a protons in the same time of electrons production and organics degradation. This protons are important for the reduction reaction at the cathode, therefor cathode chamber (containing the solid cathode) is positioned besides the anode chamber where protons can migrate through an ion exchange membrane (Degrenne, 2012).

2.1.1 Bacteria involved in MFCs

Bacteria has a plenty metabolic pathways for their growth and maintenance (Aelterman, 2009). Bacteria can be categorized based on the energy type they uses:

- Phototrophic bacteria which uses the sunlight.

- Chemotrophic bacteria that obtain energy by oxidation of chemical compounds, and this type include organtrophic bacteria (which utilize the organic compounds) and lithotrophic bacteria (which utilize the inorganic compounds).

Chemotrophic bacteria (chemotrophs) are the types that used in the microbial fuel cells (MFC). This type of bacteria (respiring bacteria) oxidize the chemical substances and uses the oxygen as electron acceptor, the oxidation reaction produces an energy that could be used to synthesize ATP to make their metabolisms. Chemotrophs could

be aerobic or anaerobic where the aerobic chemotrophs uses the oxygen as electron acceptor, but the anaerobic chemotrophs uses other inorganic compounds as nitrate to be its electron acceptor (Degrenne, 2012).

2.1.2 Biochemical reactions that occur at the electrodes of MFCs

The oxidation reaction in the microbial fuel cell takes place at the anode chamber when the electrons released to the anode and the protons at the solution, the released electrons travels through an external circuit to the cathode where the corresponding reduction reaction is occurred, the protons transfer through the PEM and combine along with electrons and with the terminal electron acceptor which is most cases the oxygen. The proton exchange membrane (PEM) which is selective only for protons is used to prevent the fuel from being crossed over to the cathode and the oxygen from flowing to the anode. A schematic of the reactions that occured in a microbial fuel cell is shown in Fig. 2.1 (Gunawardena et al., 2012).

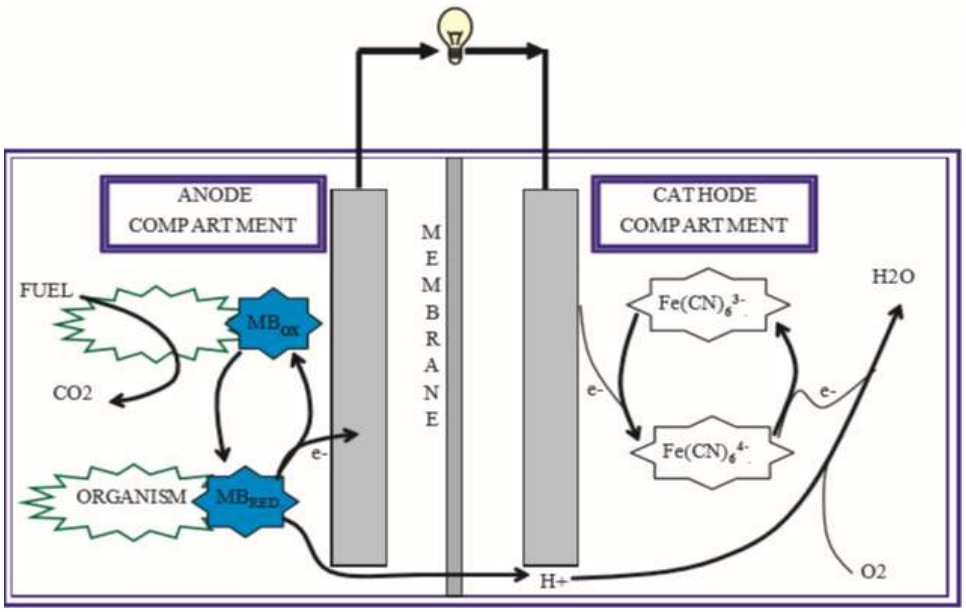

Figure 2.1: Schematic diagram of a microbial fuel cell and its operation.

2.1.2.1 Catabolic pathways involved in energy production from microbes:

Chemotrophic bacteria obtain the energy required for their life and growth through the mechanisms of oxidation-reduction reactions. In these mechanisms the substrates which are the reactants (organic matters) is transformed into water and carbon dioxide (products). The fuel oxidation process produces a free energy, a part of the free energy is retained by the microbes for their catabolic activities and the remaining could be

utilized to produce electricity Respiration and fermentation are the two metabolic pathways used for bacterial energy conversion (Mahadevan et al., 2014).

The oxidation of glucose in the aerobic conditions obtained by four steps:

1) Glycolysis, 2) Krebs Cycle, 3) Electron transport chain, 4) Oxidative phosphorylation.

The aerobic respiration is the essential mechanism for energy production in the organisms. However some organisms have the ability to produce energy under anaerobic condition. Some organisms undergoes the lactic fermentation while other organisms as the yeast follow alcohol fermentation. In anaerobic catabolism for MFC microbes, carbohydrate are broken down in the absence of oxygen, the co-enzymes inside the microbial cell help the microbes in the carbohydrate oxidation, and then the electrons and protons transported outside the cellular membrane. The overall fermentation reaction of MFC is given in Equation (2.1). The reaction in MFC can be divided in to half reactions (Equation 2.2& 2.3) where after carbohydrates were broken down by bacterial activity the produced electrons transferred to anode and the protons transport to cathode through the PEM, thus the electrons travel via an external circuit containing external load and consequently enter the cathode (Fig 2.3) (Mahadevan et al., 2014).

$$C_6H_{12}O_6 + 6O_2 = 6CO_2 + 6H_2O \quad (2.1)$$

$$C_6H_{12}O_6 + 6H_2O = 6CO_2 + 24H+ + 24e^-, \ E^0 = 0.014V \quad (2.2)$$

$$O_2 + 24H+ \ 24e^- = 12H_2O, \ E^0 = 1.23V \quad (2.3)$$

Some researchers used acetate as the substrate in the laboratory experiments because of its good assimilation by bacteria. In the oxidation process, acetate is broken down to bicarbonate according to Equation 2.4 which is counter balanced by Equation 2.5 (Degrenne, 2012).

$$CH3COO- + 4H2O \rightarrow 2HCO- 3 + 9H+ + 8e- \quad (E_0 = 0.187V), \quad (2.4)$$

$$2O2 + 8H^+ + 8e^- \rightarrow 4H2O \quad (E0 = 1.229V), \quad (2.5)$$

The corresponding standard potentials E_0 for acetate/bicarbonate couple were obtained from the Gibbs free energy data arranged in (Thauer and Jungermann, 1977) and from (Bard and Faulkner, 1981) for the oxygen/water couple.

Therefore the EMF in standard conditions is equal to 1.024V. According to the Nernst equation the effective EMF relies on temperature and on reactant and product concentration (Logan et al., 2006). With acetate as an oxidation substrate (HCO^-_3 = 5mM, CH_3COO^- = 5mM, pH=7) and oxygen as an electron acceptor (partial pressure pO_2 = 0.2, pH =7), the maximum attainable EMF (cell voltage) would equal to 0.805-(-0.296) =1.101V (Logan et al., 2006).

2.1.2.2 Electron transfer mechanisms

Electron transfer mechanism combines between electrochemistry, biochemistry and microbiology.

When the electrons reach the anode surface, they had been passed through several irreversible enzymatic reactions and finally the reversible electrochemical reactions of the electron transport chain (Busalmen et al., 2008). Electrons depend on the mediator such as cytochromes, proteins (such as PQQ), bound or soluble redox mediators to take place at the anode surface and share in the reversible reaction (Labelle & Bond, 2009). Numerous electron transfer mechanisms have been reported involving direct and indirect electron transfer mechanism. From these different processes the direct contact mechanism in which a monolayer of microbes are formed on the anode surface thus a direct transfer of electrons from the cell membrane to the anode is facilitated (Mahadevan et al., 2014).

The specific Fe (III)-reducing bacteria (Shewanella putrefaciens) reported to have the ability to transmit electrons to the electrode surface with no need of synthetic shuttles as shown in. Cytochrome, a mainly outer membrane redox protein causes direct electron transfer through its electrochemical activity of reducing the soluble Fe (III) in the water (Kim et al. 2002).

Direct transfer mechanism has a negligible gap between microbes and electrode therefore it produces to the extracellular lowest potential losses. However, the total number of bacteria contacted directly to the anode can limit this transfer mechanism (Torres et al., 2010).

A new discovery regarding the direct electron transport (DET) mechanism in MFC is the pili growing observed in bacteria (Geobacter sulfurreducens).Pili which also

called bacterial nanowires are tiny flexible structure made of pillin protein. Pili function is to help the bacteria to adhere to surfaces and recognize materials in its surroundings. These pili allow charge transfer via several layers of biofilms on the anode surface by being electrically conductive and also forming internal networks, in this way pili could overcome the limitation of pervious mechanism (Fig.2.2) (Malvankar et al., 2011).

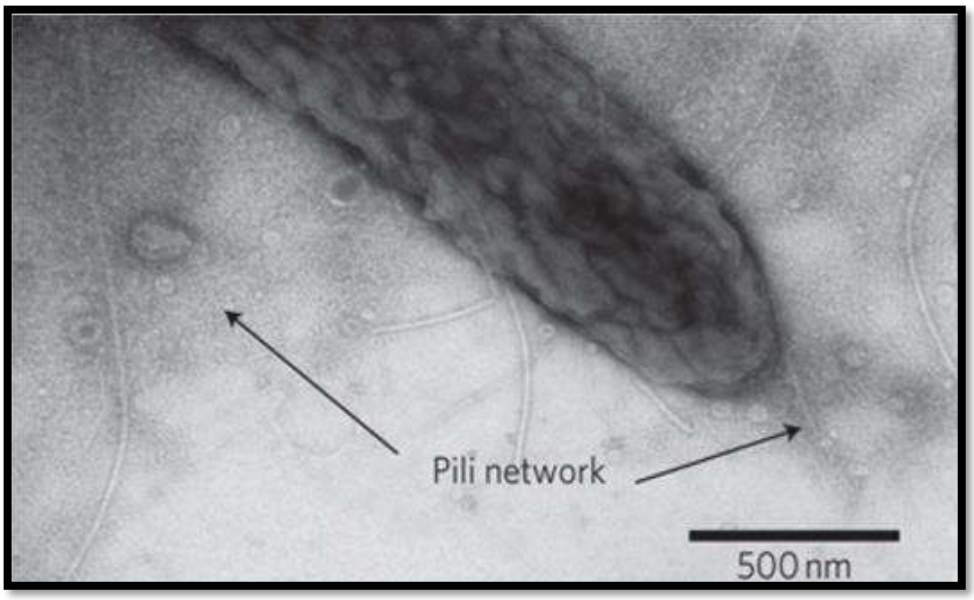

Figure 2.2: TEM image showing pili formed by the strain KN400 forming an interpenetrating network on the anode biofilm

The indirect electron transfer mechanism could be classified based on the kind of mediator used to connect the microbial catabolism with the surface of the anode. A good mediator is sufficiently soluble, has high membrane permeability, possess efficient electron transport rate, biocompatible to microbial cells and non-biodegradable. Theoretically, mediators with low redox potential (e.g. SO_4^{2-}) are suitable for MFCs, the reason is that electron usually moves from the low redox potential (mediators) to the high redox potential (electron acceptor or anode). Although, mediators possess high redox potential have better ability to draw electrons from the electron carriers in the cell (Schröder, 2007).

Some of synthetic shuttles were used to transport the electrons in MFC systems such as phenazines, phenothiazines, phenoxazines and quinones. However utilization these mediators has a several drawbacks which makes their use to be unsustainable and impractical, low current densities, problems in electron transport over heavy biofilm,

requires continuous changing in the mediator, and the toxicity. For that reasons, it was essential to employ the generation of metabolites in microbes for electron transfer destination (Mahadevan et al., 2014).

Microorganisms has the ability to produce endogenous metabolites through primary and secondary pathway to implement many biological mechanisms. Microbial catabolic oxidation of substrate (anaerobic respiration and fermentation) produces primary metabolites like H_2 could be used as redox mediator (Sekoai et al., 2014).

Also several secondary metabolites have been used as mediators for MFC applications such as phenazine-1carboxamide, pyocyanine (Pseudomonas aeruginosa) (Luo et al., 2009), neutral red, anthraquinone-2,6disulfonate (AQDS), thionine, methyl viologen, methyl blue, humic acid (Thygesen et al., 2009) and 2-amino-3 carboxy-1,4-naphthoquinone (ACNQ) (Bifidobacterium longum) (Yamazaki et al., 1999).

These mediators exhibit cyclic redox performance, in other word it could be used continuously for electron transfer mechanism, which is sustainable and applicable for long range electron transfer in the anodic biofilm thus a constant and enhanced current density (Mahadevan et al., 2014).

2.2 The concept of Microbial Desalination Cell (MDC)

Because the present techniques for desalination is energy intensive, a microbial fuel cell was improved through creating a third chamber (desalination chamber) by placing two membranes between the anode and cathode. Anion Exchange Membrane (AEM) was placed next to the anode and Cation Exchange Membrane (CEM) was adjacent next to the cathode (CEM). Through these ion exchange membranes a certain ions is passed based on the size and charge (+ or -) of the ions. For AEMs only the anions are allowed to pass through it, while CEM allow to the cations to pass through it figure 2.3.

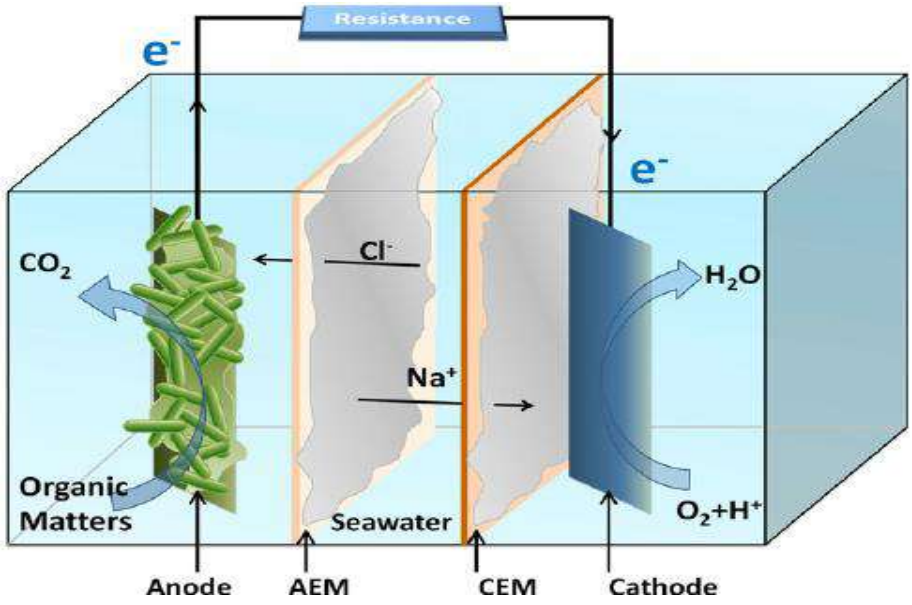

Figure 2.3: Schematic diagram of microbial desalination cell (MDC)

The driving force for ions transport is provided through the electrical potential difference (i.e., voltage) and the concentration gradient. When the current was produced by bacteria on the anode chamber the ions in the desalination chamber (middle chamber) were transferred to the anode and cathode chambers through the IEMs causing the water in the middle chamber to be desalinated without any water pressurization (Cao et al., 2009).

The last versions of MDCs contain a three chamber MDCs, microbial desalination-electrolysis cells (MECs), bipolar MDC, and osmotic MDCs (MODCs) and stacked MDC (SMDC) which stacking more than one membrane pair between anode and cathode thus the desalinating capacity could be enhanced (Chen et al., 2011; Luo et al., 2011; Mehanna et al., 2010; Mehanna et al., 2011; Kim et al., 2011)

2.2.1 Physiological Conditions (Anode)

The main role of microbes in the anode chamber is to harvest the energy from the fuel (substrate) and turn it to a suitable form for oxidation mechanism and then in to electrical energy (Schroder et al., 2010).

ATP (Adenosine Tri Phosphate) produces by the microbes through cascading redox reactions, and finally transporting the electrons from organic fuel to the solid anode. bacteria that used in the MDC systems is called Anode Respiring Bacteria because

bacteria uses the solid anode as a terminal electron acceptor they (ARB) (Lee et al., 2008).

The growth rate of ARBs relies on the variance between redox potential of the electron donor and the actual potential of the anode. In the other hand lower anode potential leads (negative potential) to higher voltage gradient which increases the possibility of higher current densities in MDCs. Various factors influences the anode potential such as the type and concentration of electron donor, electrical properties of MDC, the choice of electrode and membranes, and physiological conditions (e.g. pH, temperature, concentrations of micronutrients and vitamins, and mixing conditions) (Borole et al., 2011).

2.2.2 Electron Acceptors and Biocathodes of MDCs

The MDCs electron acceptor is a chemical oxidant, some studies used the ferricyanide as a laboratory electron acceptor in the cathode chamber. Ferricyanide affect positively on the power generation where it offer high cathodic potential. However, due to its toxicity and high cost such these chemicals is limited in the laboratory and couldn't be used in scaled up systems. Oxygen was used as a terminal electron acceptor (TEA) which is better than ferricyanide due to its high reduction potential and availability. When the oxygen is used as the TEA the cathode is called air cathode, the main problems with the air cathode, it's slowly redox reaction which require an expensive catalyst material (e.g. platinum) for reducing activation over potential with oxygen reduction. Another disadvantage is the need of mechanical equipment to maintain optimal dissolved oxygen concentration (Gude et al., 2013).

Logan et al. 2010 displayed a new strategies to minimize some of the disadvantages with air cathode of MFCs, these strategies are also applicable to MDCs: 1) MDCs cathode could be exposed to the atmosphere to minimize the need of aeration, 2) also to reduce the aeration costs a passive methods could be used to achieve oxygen transfer in the cathodes, 3) for minimizing the catalyst requirement, ultra high surface area carbon substrate (e.g. activated carbon) can be used.

An innovative approach to create sustainable cathodes is the biocathodes which uses the microbes as catalysts to facilitate electrochemical reduction on the cathode surface. The biocathodes offer a flexibility in producing valuable commodities and eliminate the need for chemical catalyst. The biocathode needs an optimal

physiological conditions that allow microbial growth on the cathode surface. The biocathode microbes should have the capability to receive electrons from cathode surface (He et al., 2006; Zhang et al., 2012).

2.2.3 Algal Biocathodes in MDCs

Because the global energy needs are increasing and the available energy cannot meet the global needs, the researches go to the biofuels produced from renewable sources. Algae one of the biofuels which can produce a green renewable energy (Strik et al., 2011).

Algae are the major oxygen producers in the oceans which covers a 71% of the earth's surface (Harrison et al., 2005).

Zou et al., 2009 used microalgae in the cathode chamber of MDC and some advantages were achieved such as: 1) production of oxygen in the cathode chamber, 2) reduction of oxygen in the cathode, 3) substituting the chemical-based catholyte with a green-design by using the algae, and 4) utilizing the sunlight in the system where it never ends. This advantages could enhance the microbial desalination cell to be self-sustainable system depending on the sunlight.

One of the marine microalgae that was chosen before to be utilized in bio electrochemical systems is Nanochloropsis because of its ability in the nutrient removing figure 2.4 (Cai et al., 2013).

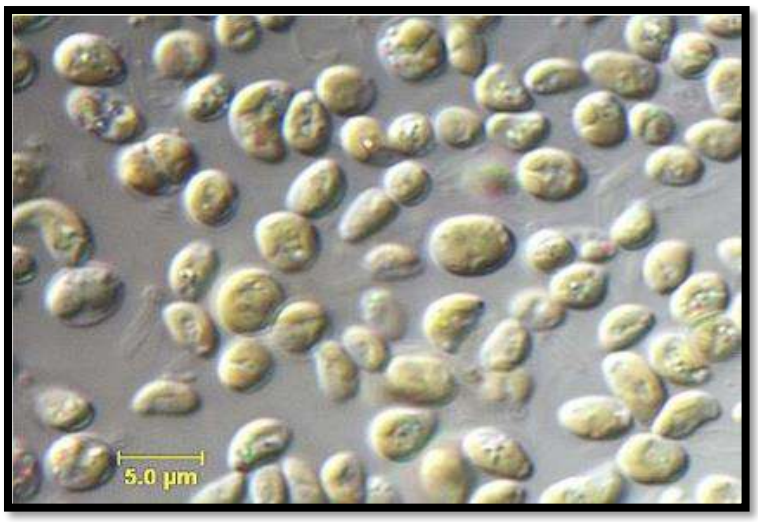

Figure 2.4: Nanochloropsis salina under a compound microscope (40x magnification)

Chlorella vulgaries, a fresh water microalgae, was also used in the cathode chamber of microbial desalination cell for its tolerance of high CO_2 levels and high efficiency in utilizing it via its photosynthesis (Kokabian and Gude, 2013).

2.2.4 Electrode Materials in the MDCs

The type of electrode affect significantly in the electrical performance of microbial desalination cells. The basic features that the electrode should has are large surface area with accessible pores, high electrical conductivity, low cost, biocompatibility, mechanical strength, scalability, good mass transfer characteristic and chemical stability. The actually utilized carbon electrodes (e.g. graphite felt, graphite rod, graphite foam, vitreous carbon and carbon cloth) were primarily designed for chemical fuel cells which may not be the best option for MFC applications. Also these material lack the large surface area (Gude et al., 2013).

Dumas et al. 2008 reported the probability of stainless steel plate as the anode both the anode and biocathode electrodes in an MFC, and indicated a power density values of 23 mW/m2. Similarly, Erable and Bergel, 2009 evaluated the use of stainless steel grid as anode material.

Also the cathode type affects the performance of MDCs. For example, it has been discovered that the cathode material influences the growth and performance of microbial communities on the biocathode surface. The electrodes vary in conductivity, surface area and porosity and thus affect the performance of biocathode in MDCs. These variances influence the adhesion and biofilm progress characteristics of microbial consortium or algae on the cathode surface (Gud et al., 2013).

Sun et al. 2012 assessed four different electrode materials (i.e., granular activated carbon (GAC), granular semicoke (GS), granular graphite (GG) and carbon felt cube (CFC)) on the development of microbial consortium in the biocathodes. Their results proven that the electrode materials affects the type and composition of microbial species in biofilm communities. The dominant phyla in the four materials were the microbes in the kind of Bacteriodetes and Proteobacteria.

2.2.5 Factors that Decrease Cell Voltage (losses within MFCs):

The produced energy from an MFC is hindered by a numbers of losses in the operation which lowers the cell voltage. The MFC losses can be categorized in to voltage drops and current drops as described in (Larminie and Dicks, 2003).

Voltage losses

The theoretical maximum voltage of MFC is equivalent to the EMF. Because of voltage drops this voltage cannot be completely obtained by MFCs. A fraction of the energy stored in the substrate is captured by bacteria for their growth and maintenance through picking a certain voltage V_{BAC} from EMF. This voltage drop (V_{BAC}) can be involved in the more general definition of **activation drop** since the bacteria is activating the reaction, which includes other phenomena in the cathode. These are caused by the requirement to have a local potential difference, overcoming energy barriers, before a reaction occur at the electrodes surface. A part of the produced voltage is lost in the beginning of the chemical reactions that transfer the electron to or from the electrode. This voltage drop is extremely non-linear. The linear resistance to the electrons flux via the solid electrode material and the different inter connections is the **ohmic losses**, also it is the resistance to the ions flow in the electrolyte and separator membrane. Both, the ion and electron flux resistance follow Ohm's law. Therefore, the ohmic drop is proportional to the current density:

η (ohm) = IR, where I is the current flow and R is the total cell resistance. Including electronic, ionic and contact resistances.

The **concentration drop** is often explained as a mass transfer limitation, indicates to the limitation of fuel and oxidant concentrations at the respective electrode surface. The electrode potentials is directly influenced by the local concentrations according to the Nernst Equation 2.6 (Bard and Faulkner, 1981). Concentration losses are significantly increased for high current densities, where the reactants are consumed rapidly at electrodes surface.

$$E = E_0 + (RT/nF) \ln([\text{reactants}]/[\text{products}]), \qquad (2.6)$$

Where R is perfect gas constant.

The overall theoretical energy available from each electron involved in the redox reactions is divided between the bacteria, the electrical load and the losses. Potential efficiency (PE) is the representative unit of the voltage drop. Therefore the PE is affected by the current and decreases for high current densities.

PE is the fraction of the actual output voltage versus the theoretical potential of the involved reaction (2.7).

$$PE = V_{OUT} / (E_{RED} - E_{OX}), \qquad (2.7)$$

Where V_{OUT} is the output voltage of MFC.

Current losses

In the ideal MFC. The electron acceptor obtainable to bacteria for oxidation of substrate is the anode. However, virtually a part of electrons may transfer to the cathode via the electrolyte or may react with other electron acceptors such as oxygen and inorganic oxidants. Because the oxygen could leaks to the anode chamber, also the non-organic electron acceptors such as the nitrate may present in the electrolytes naturally. In the lack of feasible electron acceptor some of the bacteria could follow fermentative metabolism pathways.

The current drop is high when the electrophilic attraction of the anode (related to anode potential) is low. The short-circuit of MFC is caused by similarity in the anode and cathode potentials hence the anode is strongly attractive, thus the bacteria will utilize the anode as an electron acceptor.

Diffused oxygen is one of the relatively strong alternative electron acceptor which could divert electrons. In contrast, in the open-circuit mode, bacteria will choose another electron acceptors instead of the anode, which does not pulls any electrons, such as diffused oxygen, non-organic acceptors and also fermentation. The deduction is that the more generated voltage the less attractive anode, therefor the more electrons to be attracted by the alternative electron acceptors. Current drop can be represented by Coulombic efficiency (CE), the portion of electrons efficiently used as a current against the full number of electrons n (mole) involved in the internal reactions (Eq. 2.8, 2.9).

$$CE = Q_{effective} / Q_{total} \qquad (2.8)$$

$= \int Idt/ (n \times F)$ (2.9)

Where $Q_{effective}$ is the amount of charges transported to the anode and Q_{total} corresponds to the total amount of charge produced by the oxidation reaction. I is the produced current. "Quenched electrons" (I_Q) are the electrons have not transported to the anode.

Reducing the losses to maximize power output

The MDCs have specific internal resistance for each of the cathode and anode, and this internal resistance can be reduced to promote energy recovery. Cross sectional area of anode has a very important role affecting on the internal resistance, internal resistance could be decreased by increasing the cross sectional area of the anode (Strik et al., 2011).

2.5 Integration of MDCs with algae harvesting systems

Most of the MDC studies uses synthetic wastewater to study the desalination performance, the organic removal efficiency and power production.

It is important to use a system with real wastewater.

Luo et al. 2012 tested MDCs with a real wastewater in the anode compartment. The results indicates that the output power from wastewater was four time greater than the control MFC without desalination function. Furthermore the desalination ratio was 66% and COD removal was improved by 52%. The real wastewater enhanced the desalination of MDCs through elevating the conductivity by 2.5 times and stabilizing anolyte PH thus decreasing the internal resistance of the system.

The results revealed that MDC can function as a viable choice for integrated wastewater treatment, power production, and desalination. Hence it is applied to integrate microbial desalination cells with standing wastewater treatment systems (Figure 2.5). So MDCs and the wastewater treatment system could processed separately or in a combined system.

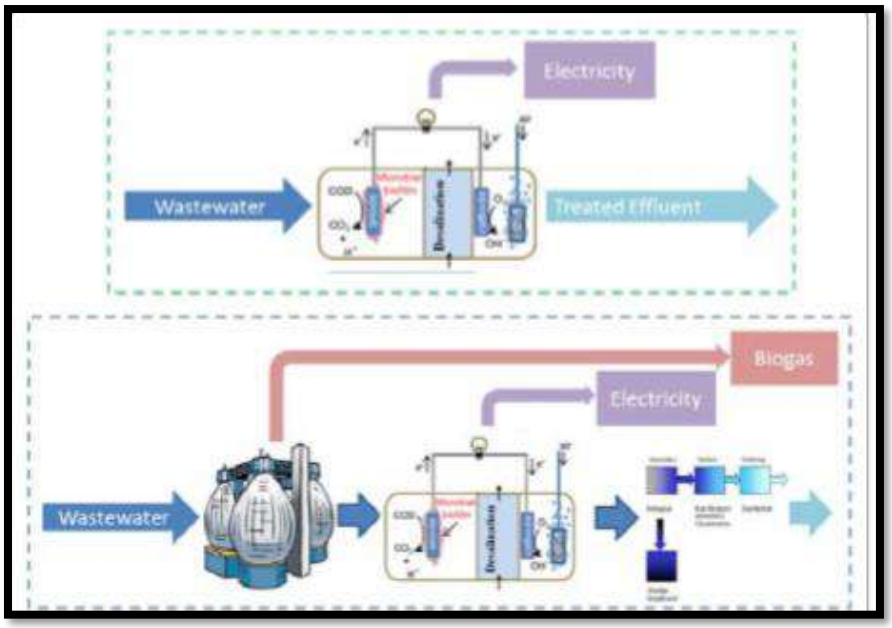

Figure 2.5: Integration of Microbial Desalination cell (MDC) with wastewater treatment

Using algae in the cathode chamber could enhance the electricity production due to increased dissolved oxygen concentration released by algae (Kokabian and Gude, 2013).

Wang et al., 2010 reported the MDC system can be sustainable process with high value algal biomass if the CO_2 could harvested and introduced to the cathode chamber as a substrate for algal cell growth.

As the PH raises in the cathode chamber due to hydroxide releasing from the reduction process, the CO_2 recycling can control the PH rise. Because there are just a few studies that focused on the nutrient deletion using MFCs, MFCs have restricted feasibility to remove nutrients as the phosphorus from wastewater. For that reason Lundquist, 2010 studied an innovative approach which is the introducing the CO_2 and organic substrate released from the anode chamber to the algal bio-cathode compartment, where algae have a composition of C: N: P ratio of 50:8:1 while domestic wastewater has a composition of 20:8:1.

Schamphelaire et al., 2009 reported that by adding a carbon source, wastewater can function as a perfect medium for algal growth. Nitrogen and phosphorus are used in microalgae biomass production as well as carbon dioxide for photosynthetic and oxygen production, the produced biomass can be utilized for biofuels production.

Chapter 3: Research Methodology

3.1 Chemicals and reagents used in the experiments:

F2 media defined by Guillard and Ryther (1962) where used in the Algal cathode chamber of MDCs, the composition of the F2 media illustrated in table 3.1, 3.2.

Table 3.1: Stock solutions for F2 media

Stocks	***Per Liter***
$NaNO_3$	75g
$NaHPO_4.2H_2O$	5.65g
Trace elements	
Na_2EDTA	4.16g
$FeCl_3$	3.15g
$CuSO_4.5H_2O$	0.01g
$ZnSO_4.7H_2O$	0.022g
$CoCl_2.6H_2O$	0.01g
$MnCl_2.4H_2O$	0.18g
$Na_2MoO_4.2H_2O$	0.006g
Vitamin mix	
Cyanocobalamin (Vitamin B_{12})	0.0005g0
Thiamin HCl (vitamin B_1)	0.1g
Biotin	0.0005g

Table 3.2: F2 Medium composition

Medium	**Per Liter/100ml sea water**
$NaNO_3$.	1.0ml
$NaHPO_4.2H_2O$	1.0ml
Trace elements stock solution (1)	1.0ml
Vitamin mix stock solution (2)	1.0ml

In the MDC's air-cathode chamber, the phosphate buffer was used table 3.3.

Table 3.3: Composition of the phosphate buffered solution

Salt	**Concentration g/L**
NaCl	8.0
KCl	0.2
KH_2PO_4	0.24
K_2HPO_4	1.42

The composition of synthetic wastewater used in the anode chamber for bacterial growth is presented in the table 3.4.

Table 3.4 Composition of the synthetic wastewater

Material	**Concentration mg/l**
$NaHCO_3$	1500
NH_4Cl	318
$CaCl_2.2H_2O$	250
$MgSO_4.7H_2O$	64
KH_2PO_4	9
K_2HPO_4	27
Sodium Acetate	1000
$FeSO_4$	10
$MnSO_4$	0.526
$ZnSO_4$	0.106
H_3BO_3	0.106
$CuSO_4$	0.0045

3.2 Laboratory equipment used during the experiments:

During the experimental process, equipment that were used are mentioned in table 3.5:

Table 3.5: equipment used in the experiments

Equipment	Type
Electronic balance	BOECO balance
Multi meter:	Fluke115
Conductivity meter	HI98188 HANNA
Incubator	M12-TB
Potentiometer	Variable resistor
Air pump	90L/H Aquarium Air Pump
Cell chambers	Polycarbonate blocks
Ions exchange membranes	(CMI 7000 Membranes International), (AMI 7001 Membranes International)

3.3 Preparation stage

In this stage preparing synthetic wastewater for bacterial acclimation and media for microalgae nutrition was accomplished.

3.3.1 Sludge microbes and the Anode

Microbial consortium was collected from the aerobic sludge of wastewater treatment plant in Al Sheikh Eglin in the Gaza Strip.

The sludge was grown at 35^{o}c in anaerobic bottle in synthetic wastewater (table 3.4) for 3 months (Fig. 3.1). The acetate was used as a non-fermentable carbon source.

The measured pH for synthetic wastewater was in the range of 7 - 7.5.

Figure 3.1: Acclimated sludge in anaerobic bottle

3.3.2 Algal culturing and the Cathode

Nanochloropsis Salina, a marine water microalgae was selected for the cathode chamber of the MDC. The N. Salina was obtained from the Islamic University-Gaza Strip (Fig 3.2) and was cultured at microbiological lab at Al-Azhar University-Gaza Strip, (Fig. 3.3).

Figure 3.2: N. Salina sample obtained from Islamic university

The growth medium for this microalgae was F2 medium table 3.1 and 3.2, pH was adjusted to 8.0 with 1M NaOH or 1M HCl.

The solution was serialized by autoclave. Culture were maintained in laboratory bottle and fish tank air pump was used for Continuous aeration and mixing under artificial light (PL lamp) and natural sun light at room temperature.

Figure 3.3: Microalgae and sludge cultures

3.4 Conducted Experiments:

Four experimental runs were conducted for water desalination purpose.

3.4.1 Experiment 1 'Air cathode-MDC'

Microbial Desalination Cell (MDC) was conducted as the control cell. The experimental period was 25 days (10 days for biofilm formation and 15 days for desalination process).

3.4.1.1 System Design and operation

- **MDC Electrodes:**

  A mixed of packed and planed electrodes were used in this experiment (Fig. 3.4). Half of the anode and cathode chambers were filled with Granular Activated Carbon (GAC) after it was washed three times with distilled water to remove the impurities. Two graphite plates of 1cm^2 (1cm * 1cm) were washed in HCl for 24 hours and then with NaOH for another 24 hours, finally graphite plates washed with distilled water before placing them in the anolyte and catholyte chambers. The resistance of the graphite plates was less than 1 Ω at any point on the surface. The electrodes were connected externally with external copper wires. In order to prevent slipping and secure the connection, a portion of the electrode that connected with the wire was soldered with tin solder.

Figure 3.4: Mixed of GAC and graphite electrodes

- **Biofilm formation (MFC stage):**

  Microbial Fuel cell (MFC) was established for biofilm formation purpose. The biofilm function is to enhance the electrons motion hence the electricity generation.

  MFC consisted of anode and cathode chambers separated by CEM with 9.6 cm^2 ($A = \pi r^2$) surface area. Two 25cm^3 (5x5 cm^2 * 1cm thickness) polycarbonate plates were used to cover the terminal ends of the reactor, To create a system with the option for anaerobic cultivation and the possibility to

add or remove liquid, the chambers are fitted with ports. Three holes were established on the top of each of the cathode and anode chambers, two of them for feeding and sampling and the third was for the copper wires used in the external circuit. Rubber gaskets were used in the cell to prevent the leakage. For setup and inoculation, the cathode chambers were injected with 40 ml of phosphate buffered (PBS) solution table 3.3, through a syringe attached with spinal 22GX3 needle.

After the catholyte was injected in the cathode, the anode chamber of the reactor was injected with 50ml of previously prepared synthetic wastewater containing 2g/L acetate as a source of electron donor to increase the organic load and enhance biofilm formation. A 40ml of the acclimatized sludge was inoculated in to anode chambers through spinal 22GX3 needle. N_2 gas was sparged to the anode chambers through an intravenous (IV) tube for 10 minutes to expel oxygen out by ventilation port. After the anode chamber has been inoculated the ports on the top of anode chamber were closed by using silver epoxy.

For the system startup, MFC was incubated at 35^o C for 10 days to accelerate the formation of the biofilm by bacteria. Through the incubation/startup period, bacteria was fed with 20ml of nutrition media daily. In this stage COD measurements were not proceeding, this stage was focused on biofilm formation.

- **The MDC Chambers:**

  Three chambers anode, cathode and desalination chambers were used in the air MDC, the cell compartments were a three polycarbonate block with an open cylindrical chamber inside each block, the internal diameter of the cross section of anode chamber was 5 cm and the effective volume was 98 ml ($V = \pi r^2$h) with a 5 cm thickness, while the internal diameter of the cross section for both of the cathode and desalination chambers were 3.5 cm and the effective volumes were 48ml for each of them with a thickness of 5 cm.

- ***MDC operation:***

  After the 10 days of incubation, the control MDC was established by adding a desalination chamber between anode and cathode chambers, new Cation Exchange Membrane (CEM) was inserted between the cathode and desalination chambers to allow cations to travel between the chambers (Fig 3.5). Anion Exchange Membrane (AEM) was inserted between anode and desalination chambers to allow anions to transport between the chambers, the exposed surface area of the membranes was 9.6 cm^2. Rubber gaskets was placed between the chambers to insure the system is air-tight. The blocks and endplates were held together by four threaded rods. In MDC the approximate distance between anode and cathode is 8 cm.

  Catholyte in cathode chamber was replaced with another fresh PBS medium. A 48ml of synthetic brackish water with 7.5 g/L of NaCl was introduced to the desalination chamber. A 50ml of the anode effluent were replaced by 50ml of synthetic waste water to feed bacteria after incubation process in MDC as the first fed batch cycle. Since the anode chamber requires substrate replacement for microorganism's nutrition the nutrient solutions should be replaced every 48 hours. After the first batch cycle the anode chamber was fed every batch cycle with a 40ml of nutrient with OLR equals to 0.5 kg/ m^3.d. The effluent of anolyte (liquid from the upper layers) were existing through a hole on the top of the chambers, media for both cathode and anode were supplied to the reactors through a nutrition hole on the top of chambers using a 22GX3 needle. Since the cathode chamber has a constant evaporated portion of the solution, PBS was added continuously to the cathode chamber.

  Fish tank air pump was introduced to MDC cathode chamber to provide the oxygen to the system, the external resistance for the system was 500 ohm.

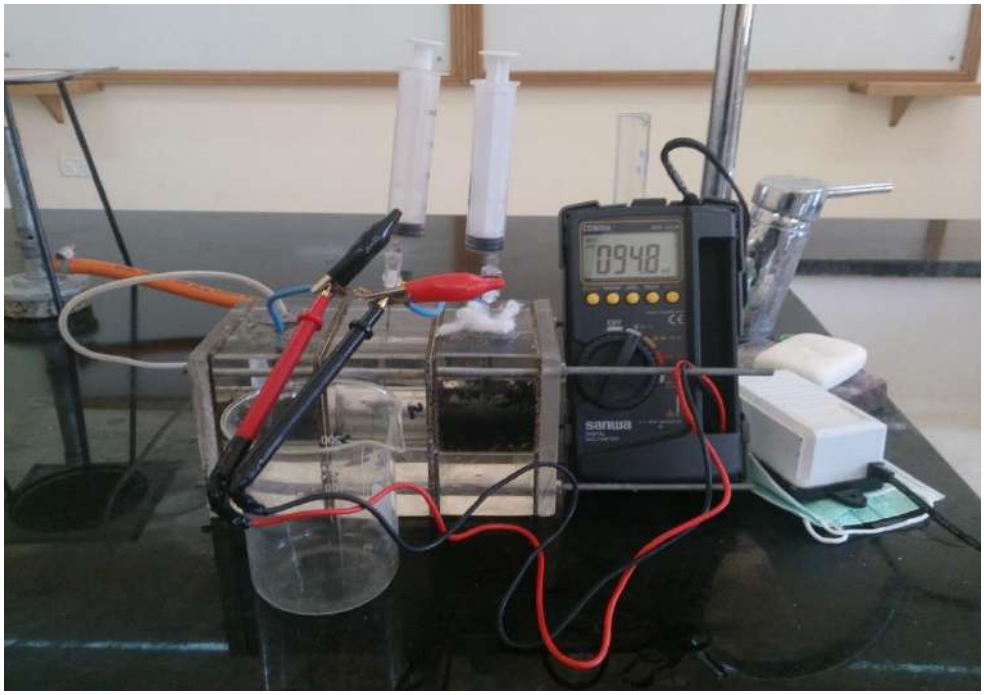

Figure 3.5: Microbial Desalination Cell (MDC)

3.4.2 Experiment 2 'Photosynthetic Microbial Desalination cell (PMDC)'

In Photosynthetic Microbial Desalination Cell (PMDC) an algal biocathode was used, the whole PMDC experiment was lasted for 21 days (10 days PMFC and 11 days PMDC).

3.4.2.1 System design and operation

- **The cell Electrodes:**
  As the MDC electrodes, PMDC electrodes were a mixed of packed and planed electrodes.
- **Biofilm formation (PMFC stage):**
  PMFC was constructed in the same manner of MFC, PMFC reactor consists of a cathode and anode chambers separated by a CEM (Fig 3.6). The setup, inoculation and startup processes for PMFC were the same as MFC processes.

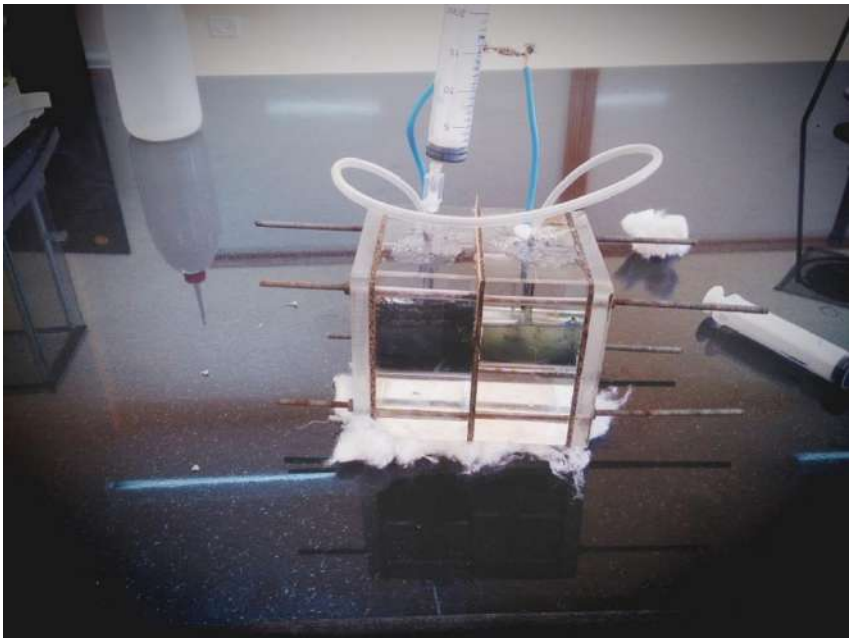

Figure 3.6: PMFC for biofilm formation

- **PMDC chambers:**

  Three polycarbonate chambers were used for this experiment with the same ambient condition and the same diameter of the MDC.

- **PMDC operation:**

  After the 10 days of incubation the photosynthetic microbial desalination cell was established by adding a desalination chamber between anode and cathode chambers (Fig 3.7).

  Cathode chamber was cleaned from the catholyte and replaced by 20ml of synthetic F2 media (table 3.2) and 20ml of previously cultured microalgae through a syringe, Nannochloropsis algae in the cathode chamber was fed every batch cycle with 20ml of F2 media. Fish tank air pump was introduced to PMDC cathode chamber to provide carbon dioxide to the microalgae where it's needed for photosynthesis process. A 50ml of the anolyte were refreshed, and all the other condition related to the anode was similar the MDC anode conditions.

  A synthetic brackish water with 7.5 g/L of NaCl was introduced to the desalination chamber. The external resistance that was used is 500ohm.

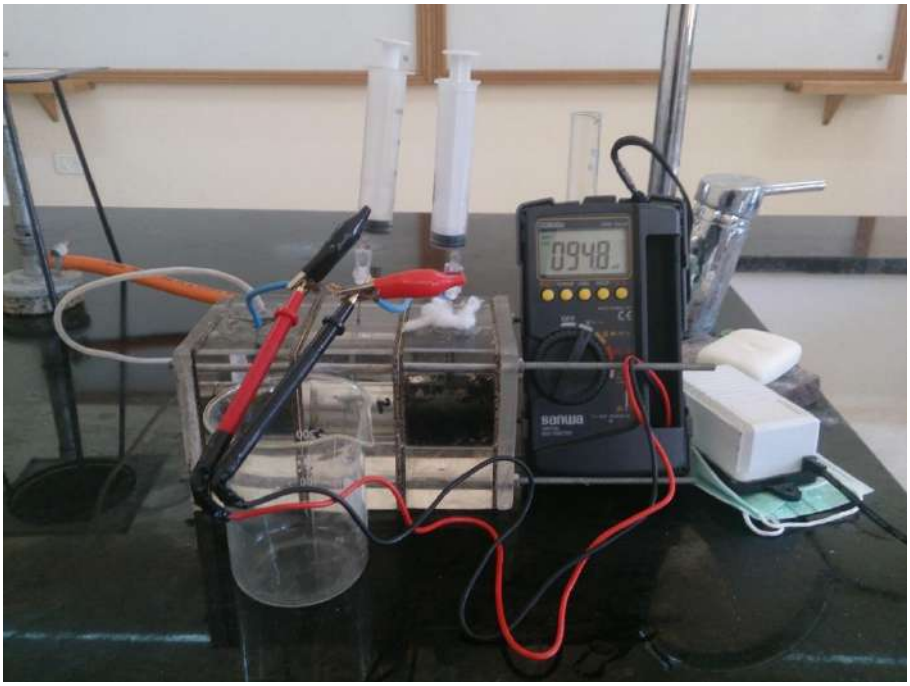

Figure 3.7: Photosynthetic microbial desalination cell

3.4.3 Experiment 3 'Stacked Photosynthetic Microbial Desalination Cell (SPMDC)'

This experiment was lasted for 25 days (10 days SPMFC and 15 days SPMDC)

3.4.3.1 System Design

- **The cell electrodes**

  In this experiment we used the same electrodes that were used in PMDC experiment.

- **SPMFC stage (biofilm formation)**

  SPMFC was established in the same way of MFC through placing a CEM between the anode and cathode chambers. The setup, inoculation and operation of the SPMFC were also the same technique as the MFC technique.

- **SPMDC chambers**

  In this experiment cathode, anode and stacked desalination compartment consists of two desalination chambers and one concentrated chamber. The cathode, anode and concentrated chambers were the same diameters of the MDC chambers. In addition two poly acrylic plates with a cylindrical chamber inside were the desalination chambers. The effective volumes was 9.6 ml for each desalination chamber.

One desalination chamber was separated by one AEM and one CEM, respectively. The AEM was on the side adjacent to the anode while the CEM was on the other side adjacent to the cathode. Between two desalination chambers laid one concentrated chamber, which collects ions moving out from the desalination chambers. Different chambers and ion exchange membranes (IEMs: AEM and CEM) were clamped together with gaskets to provide a water seal between the chambers and insure the system is air-tight. The effective surface area for each membrane was 9.6 cm^2. In SPMDC the approximate distance between anode and cathode is 8cm (Figure 3.8).

- ***SPMDC operation:***

  The cathode chamber refreshed in the same way as the PMDC cathode

  The anode chambers was inoculated as how the control MDC has inoculated.

  The same concentration of synthetic brackish water (7.5 g/L) was used for the desalination and concentrated chambers.

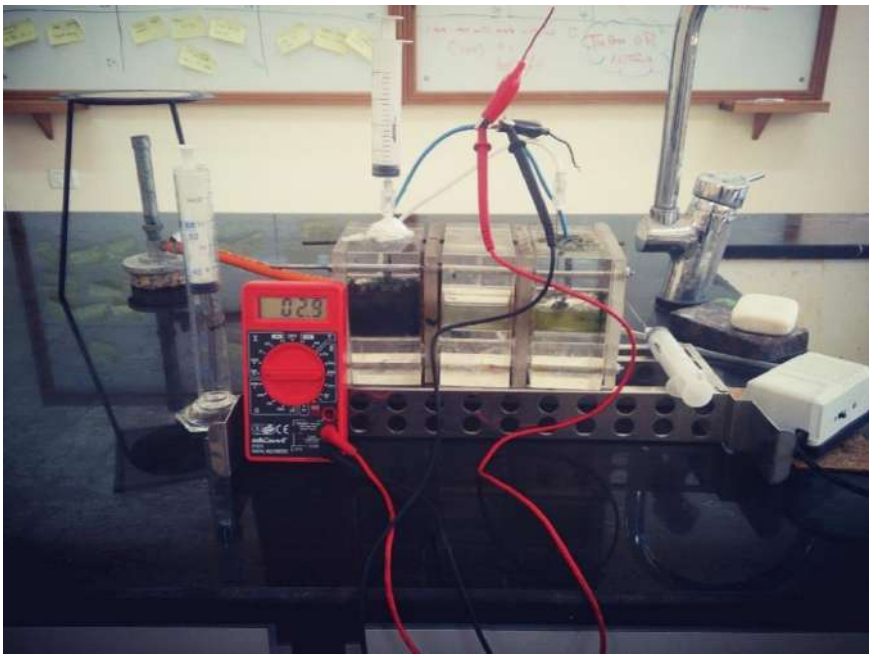

Figure 3.8: Stacked Photosynthetic Microbial Desalination Cell (SPMDC)

3.4.4 Experiment 4 'Algal microbial Desalination cell with stainless steel electrodes (SS-AMDC)'

This experiment was lasted for 19 days (10 days for SSAMFC and 9 days SS-AMDC).

3.4.4.1 System design:

- **Stainless steel (SS) electrodes:**

  Since we are in the Gaza Strip, there was scarcity of the materials that required for this research. Carbon/graphite paper, carbon cloth or carbon felt were not available to be used in the experiments, for this reasons we tried to use alternatives to complete the research. 304Stainless steel SS sheets were used in this experiment as anode and cathode electrodes. Multiple holes were drilled randomly in the electrodes to help bacteria in biofilm formation. Multiple electrodes system were used in the anode which were three sheets of stainless steel with effective surface area of 254 cm^2 for each one, the whole projected surface area was 762 cm^2. While the cathode electrode was one sheet of stainless steel with the surface area of 254 cm^2. SS sheets washed with distilled water before placing them in the anode and cathode compartments. The electrodes were connected externally with a copper wire to be used as current collector (Fig. 3.9).

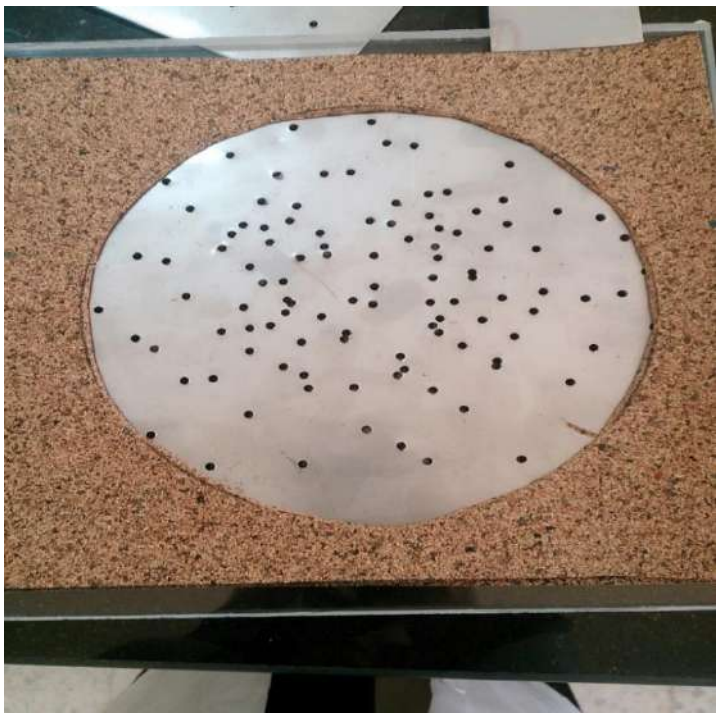

Figure 3.9: Stainless steel sheets with drilled holes.

- **Biofilm Formation (SS-AMFC)**

  Constructing the AMFC with stainless steel electrodes for biofilm formation was done by setting the reactor with the anode and the cathode chambers.

  The anode compartment was consisted of four poly acrylic plates, each plate has a cylindrical chamber and between every two plates one stainless steel sheet was placed. Therefore a three stainless steel sheets was used as the solid anode electrode.

  The cathode compartment was consisted of two poly acrylic plates with a cylindrical inside, one stainless steel sheet was placed in the middle of the compartment. A CEM was positioned between the anode and the cathode compartments in order to avoid the anolyte and catholyte from mixing and transport specific selected ions (Fig.3.10).

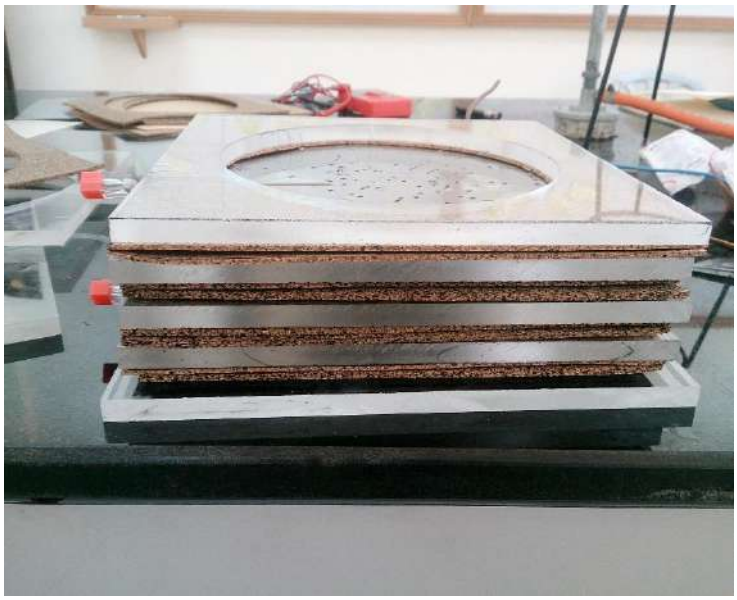

Figure 3.10: Constructing the SSAMDC reactor

Two hole were established in each plate one on the top of the plate for removing effluent and the other down to the left side of the chamber for feeding. Two poly acrylic 30*30 cm^2 plates were used to close the reactor.

For setup and inoculation, the cathode compartment of the reactor was injected with a 500 ml of phosphate buffered solution, Then the anode compartment of the reactors were inoculated with 600 ml of previously prepared synthetic wastewater and 400 ml of sludge.

N_2 gas was sparged to the anode chambers through an IV tube for 10 minutes to expel the oxygen out through a ventilation port and establish anaerobic environment. After the anode chamber has been inoculated the needles in the ports on the anode chamber were closed.

For startup and biofilm formation, MFC was incubated at 35^o C for 10 days. Through the incubation/startup period, bacteria was fed with 150ml of nutrition media daily.

- **The SSAMDC chambers**

  Three chambers were used for this experiment anode, cathode and desalination chambers.

  4 poly acrylic plates performed as the anode chamber each plate has a cylindrical chamber inside with internal diameter of 18cm and 1cm thickness, effective volume for whole anode chamber was 1017 ml. The cathode compartment was 2 poly acrylic plates, the whole cathode volume was 508 ml. One poly acrylic plate performed as the desalination chamber with effective volume of 254 ml. The volume ratio of anode, cathode and desalination compartments was 4:2:1.

- ***SS-AMDC Operation***

  After biofilm formation, a desalination chamber was inserted between the anode and cathode compartments.

  An oil bubbler was used as one way valve to transfer CO_2 gas from anode chamber to microalgae in cathode chamber. The system compartments were held together by four clamps. A spinal 22GX3 needles were fixed on the hole using nonconductive silver epoxy.

  The experiment was operated under fed batch conditions. The cathode chamber of the reactor was cleaned from the catholyte inside (PBS) and re-injected with 300 ml of synthetic F2 media and 200 ml of previously cultured microalgae. A 400 ml of the anolyte were replaced by 400 ml of synthetic waste water. The Cathode chamber was fed every batch with 100 ml of F2 media where the anode chamber was fed every batch cycle with 150ml (OLR= 0.5 kg/ m^3.d) of the synthetic waste water, by maintaining hydraulic retention time HRT of 48 hours.

The effluent of catholyte and anolyte have been exited through the effluent holes, media for both cathode and anode have been supplied to the reactors through the nutrition holes (Fig 3.11), (Fig 3.12).

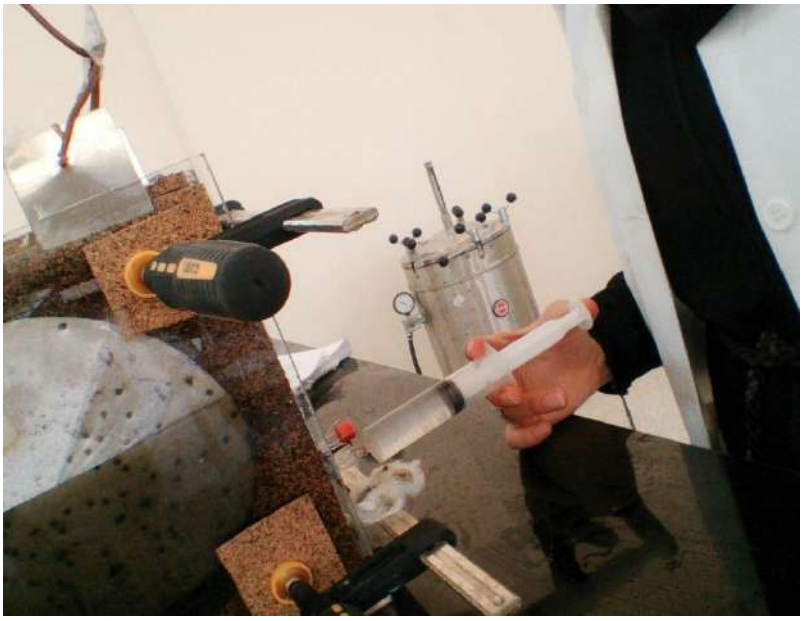

Figure 3.11: Injecting media through the feeding port

The external resistance which used in the system was 500ohm.

Figure 3.12: The SSAMDC with using mercury bubbler

3.5 Analysis and calculations:

TDS and EC was measured and recorded every batch cycle to monitor the progress of desalination profile, after the experiment was completed, EC with time curve, salinity removal with the time curve and the desalination rate were determined.

The reactors were allowed to reach a steady state. At this point, the polarization curves were drawn. This was done by varying the external resistance in the circuit from 10000 to 10Ω and measuring the voltage changing. Current and power density were evaluated, on the maximum power the cell reaches, the internal resistance were determined.

Current (I) was calculated using Ohm's law (I = V/R) with power estimated by P = IV, where **I** is cell current and **V** is the cell voltage.

Chemical oxygen demand (COD, mg O_2/L) was measured using standard methods (Standard Method). COD removal (%) was calculated based on influent and effluent COD of a single batch cycle (APHA, 2005).

Coulombic efficiency (CE) was calculated as described in (Logan et al., 2006) through the following equation:

$$CE = \frac{M \int Idt}{FbVan\Delta COD}$$

Where M= 32 the molecular weight of oxygen, F is Faraday's constant (96485 C/mole), b= 4 which is the number of electrons exchanged per mole of oxygen, V_{an} is the liquid volume in the anode chamber and ΔCOD is the change in COD during the time t.

Desalination Ratio was calculated according for the MDC, PMDC, and SS-AMDC through: $\eta = \frac{\sigma(n)}{\sigma 0} * 100\%$ where σ_n is the EC at n batch cycle and $\sigma_0$is the initial EC used in the experiment. For the SPMDC the desalination ratio was calculated by:

$\eta = \{1- (V_1 * \sigma_1 + V_2 * \sigma_2 \ldots..+V_N \sigma_N)/ (V_1 +V_2 \ldots\ldots+V_N)*\sigma_0 \}*100\%$

Here V_N and σ_N refer to the volume and EC in the N desalination chamber at a certain batch cycle, respectively.

The desalination rate (g/h) Calculated through the next equation:

Or Qd = (C0 – Ct)/ T, where C0, Ct is the initial and final TDS in the middle chamber over a batch cycle of time t.

Faradic efficiency or current efficiency (η_f) was calculated as the ratio of the theoretical amount of coulombs (Q_{th}) required to remove the NaCl to the actual coulombs harvested through the electrical circuit (Q) supposing that elimination of one mole of NaCl will require one mole of electrons, where Q and Q_{th} can be calculated by the following equations:

$$Q = \int Idt \,,$$

$$Qth = \eta \ * 0.128\, mol/l * Vdes \ * F$$

Where η: is the desalination ratio, 0.128 mole/L is the initial molar concentrated of the salt water in the desalination chamber, V_{des} is the volume of the desalination chambers, in case of the SPMDC because two desalination chamber were used the total volume was used in the equation ($V_1 + V_2$), and F is faraday constant, the Faradic efficiency equation was reported in (Chen et al., 2011).

Chapter 4

Results and Discussion

4.1 Desalination Ratios and Electrical conductivity (EC) in MDCs:

Four types of MDCs were operated under fed-batch mode (48 hours) at the same external resistance (500 ohm), All MDCs exhibited a similar overall trend of desalination process.

The initial electrical Conductivity (EC), Total Dissolved Salts (TDS) and initial concentrations for the four experiments were 15.27 mS/cm, 7670 ppm and 7.5 g/L respectively.

The EC and TDS of the salt water for the four MDC types were measured at the half and the end of each feed batch cycle (every 24, 48 hour).

There was a reducing in the electrical conductivity for MDC, PMDC, SPMDC and SS-AMDC (Fig 4.1). The EC was reduced to 1.24 mS/cm for the control MDC after 360 hour. By comparing the other three types of MDC with control MDC:

- SPMDC had achieved a comparable results to the control, where SPMDC final EC value was 0.99 mS/cm and this value has obtained through 360 hour.
- The PMDC had achieved better desalination efficiency where the EC was reduced to 0.911 in 264 hour.
- The EC value for SS-AMDC was reached to 1.3 mS/cm through 240 hour, which is better than control MDC and SPMDC values, and a comparable to PMDC value.

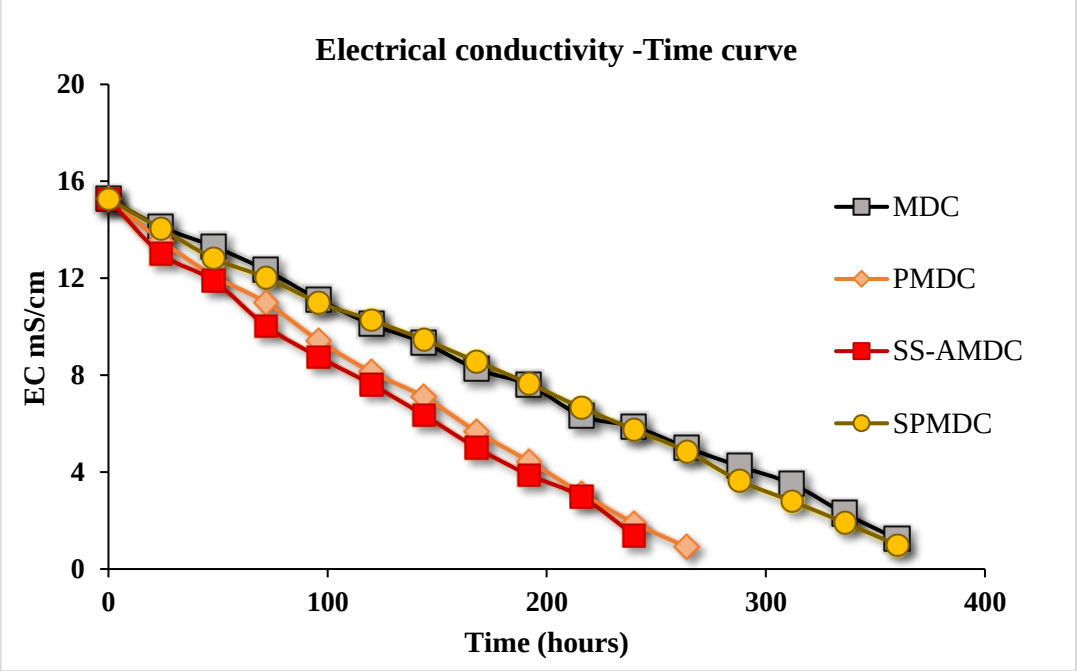

Figure 4.1: Electrical conductivity for MDC, PMDC, SPMDC and SS-AMDC

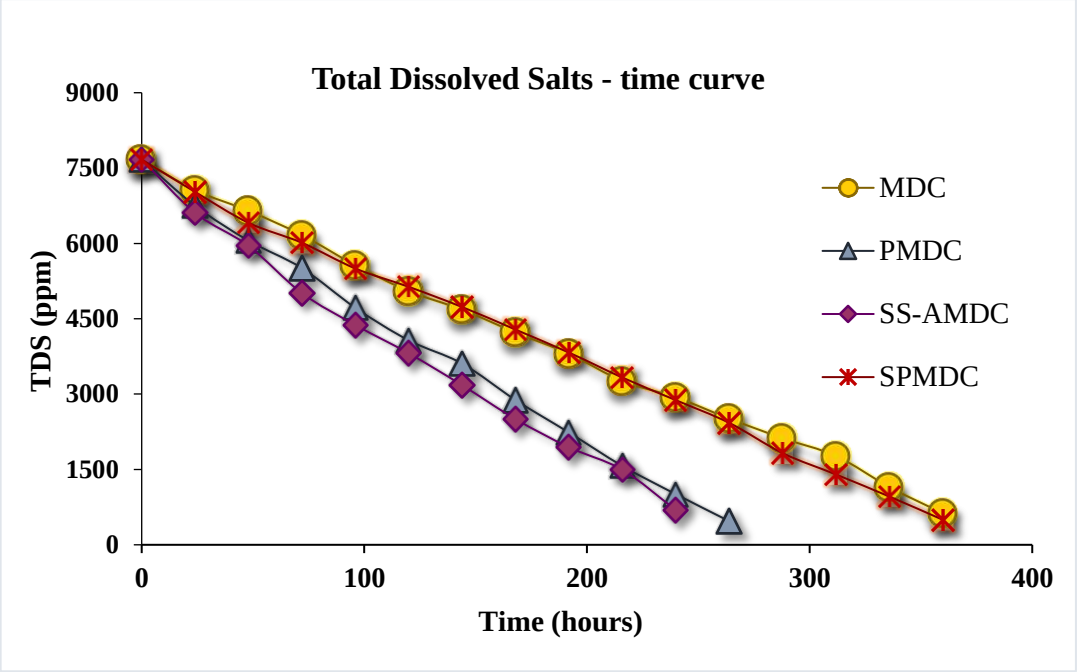

Figure 4.2: Total Dissolved Salts (TDS) for MDC, PMDC, SPMDC, SS-AMDC

As the electrical conductivity, the Total Dissolved Salts (TDS) and desalination ratios had displayed an analogous overall trend for all MDC types Fig.4.2, 4.3.

Control MDC has decreased the TDS from 7670ppm (7.5 g NaCl in 1L of D.W) to 624 ppm in 15 days (360 hours) which means that air-cathode MDC could remove 91.87% of salts in 15 days. By comparing the other three types of MDC with the control MDC:

- The TDS for SPMDC has reduced to 495 ppm through 15 days and the desalination ratio was 93.5%.
- The PMDC shown a better results where the TDS was decreased to 457 ppm over 11 days of operation, in other words PMDC has removed 94.03% of salts in 11 days of operation time.
- SS-AMDC results was good enough to be compared with the other types of MDCs where it had removed 90.9% of salts through 10 days (524 ppm over 240 hour), which is similar to PMDC results.

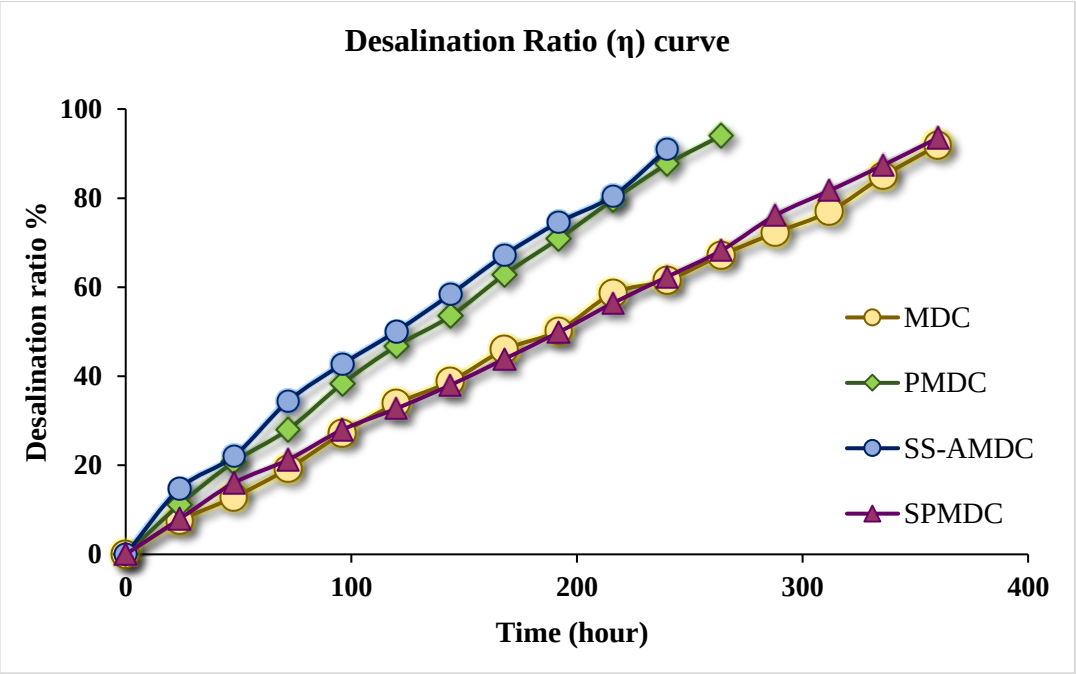

Figure 4.3: The Desalination Ratio for control MDC, PMDC and SPMDC and SS-AMDC

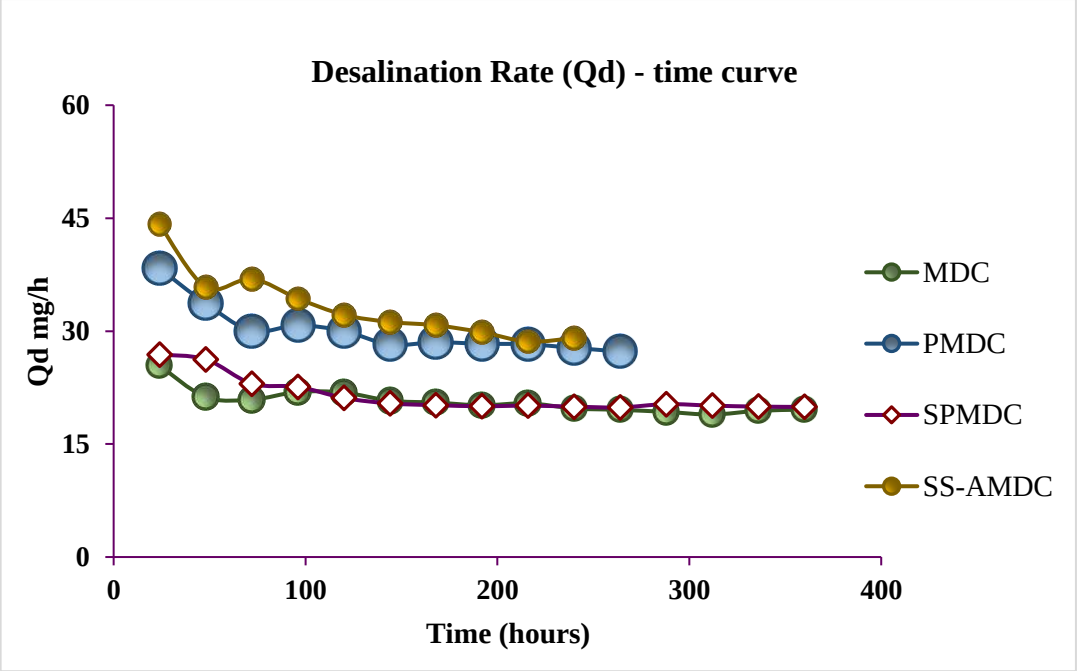

Figure 4.4 Desalination Rate Qd mg/h through the whole experiments

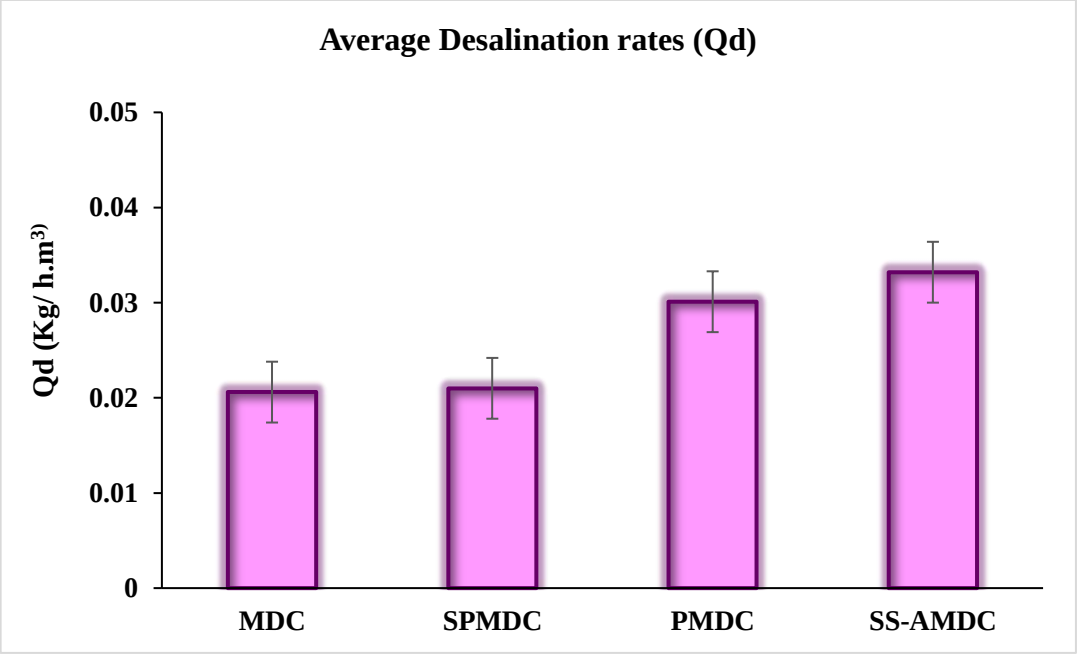

Figure 4.5 Average desalination rates for the four types of MDC

Regardless of the difference in salt-solution volumes that was used, SS-AMDC has accomplished best desalination rates (Qd) (Fig 4.4), where the SS-AMDC had an average desalination rate (Qd) equal to 0.039 kg/m3.h.

The Qd of PMDC, MDC and SPMDC equal to 0.031, 0.021 and 0.02 kg/m3.L (Fig 4.5).

In MDCs with one pair of ion exchange membranes, when one electron passed through the external circuit, a pair of cation and anion will be separated from desalination chamber to maintain the charge balance.

The PMDC exhibited higher desalination efficiency of the control air-MDC because the using of algal bio cathode creates high potential difference between anode and cathode which simulates the transfer of the ions in the middle chamber to anode and cathode chambers, this results agree with the results of (Kokabian and Gude, 2013) where it was approved that the usage of bio-cathode chamber enhances the desalination efficiency.

The SPMDC has slightly higher desalination efficiency than the control MDC because by using a composite middle compartment (two desalination chambers with one concentrated chamber) the charge transfer efficiency could be increased because by one electron passed through the external circuit two more pairs of ions will be separated.

However by comparing the desalination efficiency of the SPMDC to the PMDC's it was found that because the number of the middle chambers had increased, the distance between the electrodes was elevated resulted in rising of the internal resistance and this lower the desalination efficiency which presented by the previously five diagrams. Furthermore the salt gradient between desalination chamber and concentrated chamber creates an electric potential what will contribute the decrease of Qd because the transfer of ions from desalination chamber toward concentration chamber hindered by this electric potential. This phenomena will occur as well as the desalination is proceeding, this results are agree with (Chen et al., 2011) results where it was reported that the more desalination cells the less desalination efficiency at relatively high external resistance and it was discovered that for better desalination efficiency by the stacked microbial desalination cell a low external resistance has to be used.

SS-AMDC illustrates the best desalination efficiency, this is due to the high surface area of used membranes which allows more ions to transport through it and this approves that the membrane surface area is a limiting factor of the desalination

efficiency, also the Nannochloropsis algae was used in the cathode chamber of the SS-AMDC which will improve the desalination by the created potential difference between anode and cathode chambers.

It should be mentioned, most of the previous desalination studies found that the MDCs could desalinate water with high salt concentration ~ 30-35 g/L (sea water) more efficiently and with shorter time than the (brackish water) with salt concentration of ~5-10 g/L.

4.2 Electrical Profile for the four different types of MDC

4.2.1 Voltage production:

Figure 4.6 exhibited the voltage generation profile for control MDC, PMDC, SPMDC and SS-AMDC across the 500 Ω external resistance Load for one feed batch cycle, the operation time for one feed cycle was 48 hours.

During the 48 hours the voltage was recorded every 10 minutes, unfortunately our lab doesn't have data logger for voltage parameter, because of that, there was a miss in the voltage data (for 30 hours of 48 hours), the summation hours of the recorded voltage data was 16 hours for each MDC feed cycle. The voltage of the four experimental runs have the same comprehensive tendency which increased slightly in the first seven hours, after 7 hours there was no recorded results for about 16 hours. 24 hours later the voltage was stable in steady state for 6 hours and then it started to decrease slowly, the voltage had dropped sharply in the last 10 hours of the feed cycle, it was observed that when the feed solutions were renewed the voltage regain to increase gradually. Some previous studies mentioned that because of the microbial lag phase the voltage production exhibited a sigmoidal increase but in this study it was not obviously noted because this study is fed-batch mode and the sigmoidal increase was observed in the continuous feed mode, besides there are missing in the voltage data.

The control MDC generated a maximum voltage equal to 0.21 V after 25 hour and 18min of the feed batch cycle, the voltage production results of the other three types of MDCs are:

- The SPMDC produced a peak voltage of 0.198 V after 25 hours and 30min which is slightly less than the control air-MDC.
- For PMDC the produced voltage was better than the control MDC voltage where PMDC produced a maximum voltage of 0.23 V after 24 hours and 30min.
- SS-AMDC has a very high voltage in comparison with the control MDC, where SS-AMDC generated a maximal voltage of 0.655 V over a 25 hour and 30min.

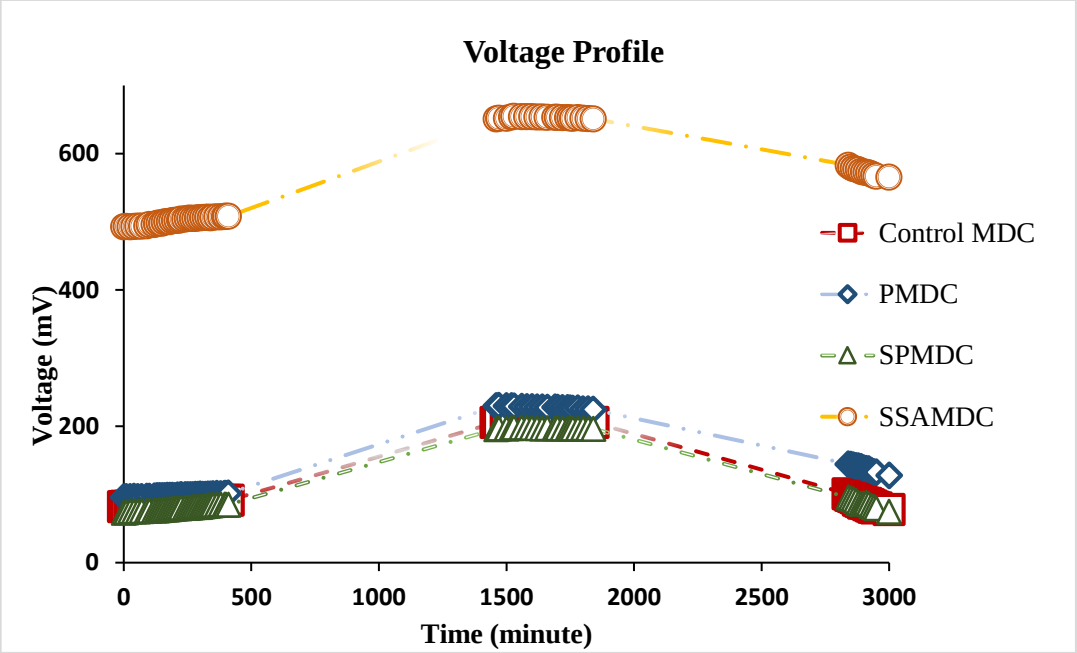

Figure 4.6: Voltage generations as a function of time for different types of MDC

The produced voltage from the control MDC is around the voltages produced by previous studies. This generated voltage was promoted through using the biocathodes in the PMDC which creates high potential difference between the anode and cathode what will improve the produced voltage, this explains why the PMDC generates higher voltage than the air-MDC and also this higher voltage indicates that the biocathode could be faster in reduction of the protons and electrons.

The SS-AMDC has the best voltage data (higher potential) and this mainly because of the different reactor volumes where it's logical that the larger reactor produce higher voltage than the smaller one and that is reason of the more reduction process according to the higher catholyte volume.

4.2.2 Electricity generation

The electricity generation of the four types of MDC have exhibited similar overall trend, with three stages 1) the increasing stage, 2) steady-state stage and 3) the dropping phase, figure 4.7 exhibited the current generation (mA) and figure 4.8 displayed the volumetric current density (A/m^3).

The generation of electricity for air MDC has slowly increased over the first ~7 hours (after the cell was fed) with an average current and current density of 0.174 mA and 1.938 A/m3 respectively. After 24 hours of operation the current/ current density reached a steady state for ~6 hours where the values were ranges between 0.410 – 0.415 mA/ 4.557-4.608 A/m^3, then the current, current density decreased to 0.156 mA, 1.56 A/m^3 respectively in the end of the fed batch cycle.

SPMDC has produced an average current, current density of 0.159 mA and 1.773 A/m^3 respectively over 6 hours and the current and current density still increased over 24 hours and it became relatively stable at 0.392-0.396 mA and 4.35 – 4.41 A/m^3, after that the current and the current density were decreased to 1.49 mA and 1.49 A/m^3, due to decreasing anolyte PH, depletion of substrate and increasing in the catholyte PH, this current results are slightly less than the control MDC results.

PMDC's electricity generation has the same trend as air-MDC with higher values of current and current density, where in the initial period of the operation (the first 6 hours) the average of current and current density were 0.197 mA and 2.198 A/m^3, an stilled increase for 24 hours till it reached a steady state with a current ranges between 0.4492-0.4604 mA and a current density ranges between 4.995-5.115 A/m^3, after ~6 hours of steady state the current, current density decreased to 0.256 mA and 2.56 A/m^3.

The average current and current density of SS-AMDC was 0.391 mA and 0.385 mA/m^3 in the first 7 hours of the operation, after 24 hours the current and current density was ranges between 0.594 – 0.604 and 0.584 – 0.594A/m^3 for 6 hours, the last part of the curve shows that the current and the current density decreased to 0.355mA and 349.5 mA/m^3respectively.

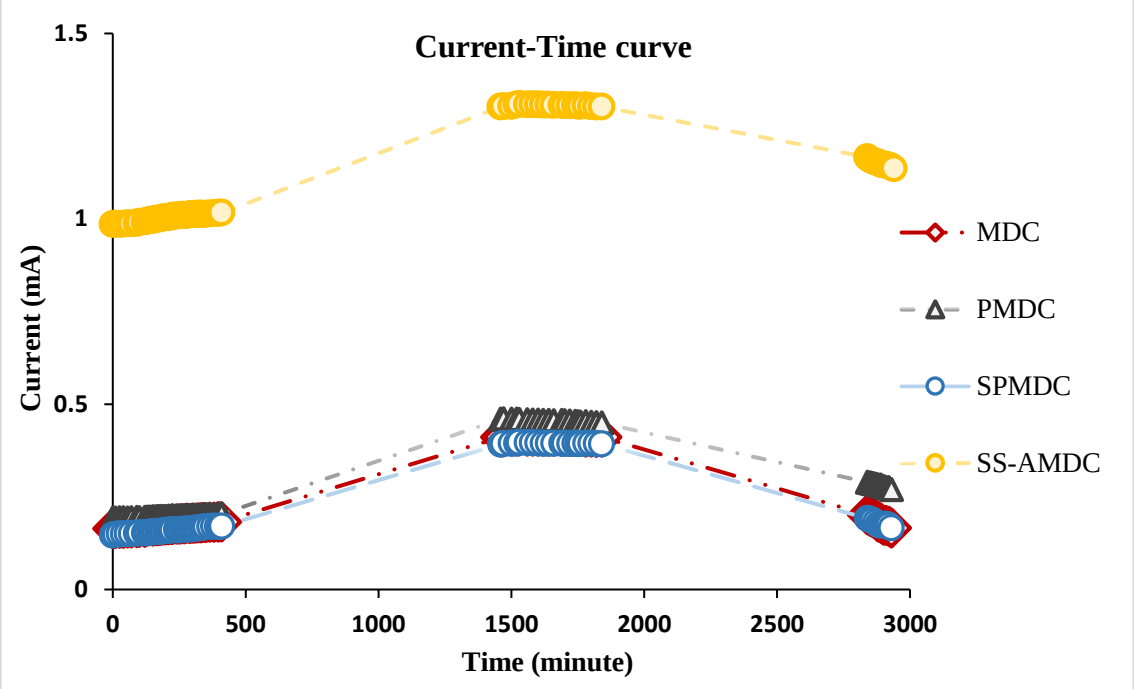

Figure 4.7: Current generation (mA) of MDC, PMDC, SPMDC and SS-AMDC

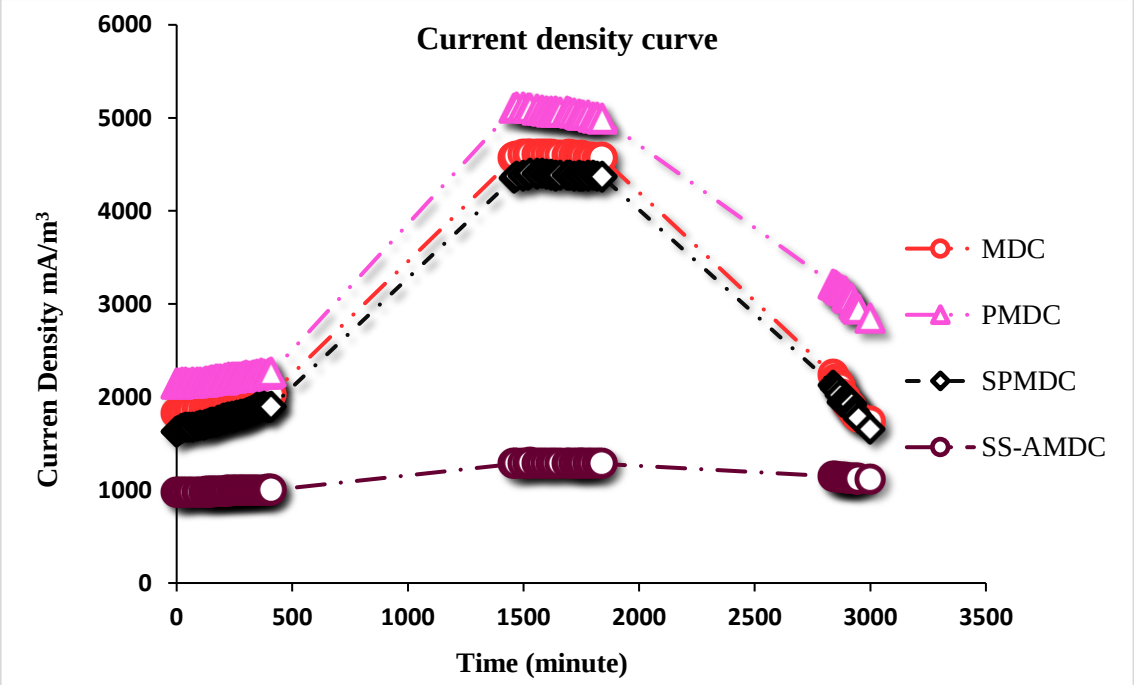

Figure 4.8: Current density (mA/m^3) of MDC, PMDC, SPMDC and SS-AMDC

The electrical generation (mA) has the same behavior of the voltage production where the current results showed that the SPMDC has a lower generated current than the control Air-MDC. This is mainly because of the high ohmic resistance, the total resistance in an SPMDC consisted of internal resistance and external resistance. This former was affected by the desalination chamber number. Therefore, the variation of internal resistance is mainly a result of the change of the desalination chamber number. Since a pair of AEM and CEM, together with salt solution of two chambers (one desalination chamber and one concentrated chamber), were increased into the system when another desalination cell was added, it is reasonable for the decrease of the maximum current due to the increased internal resistance caused by the extra added desalination cell. The current density exhibited the same results for the SPMDC in respect to the control MDC.

According to the current (mA) data SS-AMDC has the best produced current and the major reasons of that; the surface area of stainless steel anode used in SS-AMDC experiment is 763 times bigger than graphite electrodes surface area what will allowed to transfer the electrons in higher rates also the volume of anolyte solution (organic matter) was 1000 ml which is about 11.1 times greater than the volume of anode chamber for the other MDCs (90 ml), by this large volume advanced electrons amount could be produced by organic matter oxidation. However, the volumetric current density the SS-AMDC showed a lower values than the control MDC, the volumetric current density is the generated current in one cubic meter of anolyte. One of the main reasons for lowering the generated electricity from SS electrodes is that the stainless steel has higher resistivity and lower conductivity than the graphite electrodes, furthermore (Flint et al., 2000) reported that the importance of biofilm formation is to make a natural bridge for electrons transfer to the electrode surface hence improves the electricity generation, the more biofilm thickness the higher electrical activity, to form a strong biofilm the electrode should have a roughness surface (Ra) in the range of the size of microbial cells. This was verified in the current density results where the 304 SS sheets that was utilized have a smooth surface what was one of the main reasons to generate volumetric current density lower than the graphite electrodes.

Also (Malvankar et al., 2012) reported that the more thicker biofilm the higher electrical generation and that is because of the bacteria nanowires (pili) which is responsible of transferring electrons from bacteria to electrode surface.

By comparing the PMDC to the control MDC, PMDC has better generated current (mA), the reason as mentioned before could be the higher reduction process in the biocathode than the air cathode, also the PMDC has higher potential difference than the MDC. For the current density (A/m^3), the PMDC exhibited the best current density results and this essentially because the ohmic resistance of the reactor is lower than the three other experimental MDC types.

4.2.3 Volumetric Power Density:

The generated power (mW/ml) were obtained from the produced voltage and current through a certain external resistance (500 ohm) in one feed batch cycle. The volumetric power density presented the power data in one cubic meter of organic material.

Control MDC, SPMDC, PMDC and SS-AMDC have similar behaviors through the whole feed cycle. However, the SS-AMDC has a bit of differences in the data values, where the power of the three similar MDCs increased rapidly through the first 6 hours with significant difference between the values in the first period and in the steady state period, unlike the SS-AMD which seems to have a close-matched power values and that's mainly returns to the similarity in its voltage data Figure 4.9.

The control MDC has a maximum volumetric power density of 0.955 W/m^3, which is better than the SPMDC power density of 0.874 W/m^3.

PMDC has better results than the control MDC where it generated a maximum power density with the value of 1.18 W/m^3 and this value was the best between the four experiments.

SS-AMDC's maximum power density was 0.842 W/m^3 which is nearly the same as SPMDC result.

It's obvious that the produced power by the four different types of MDC is not efficient enough to scale it up, however MDCs purpose is to desalinate salt water more than power production and if we want to go to producing energy it must to use MFCs because it has a different conditions and aspects in addition it's specified to produce

power, furthermore in previous studies for improving the generated power a platinum catalyzed air-cathode was used.

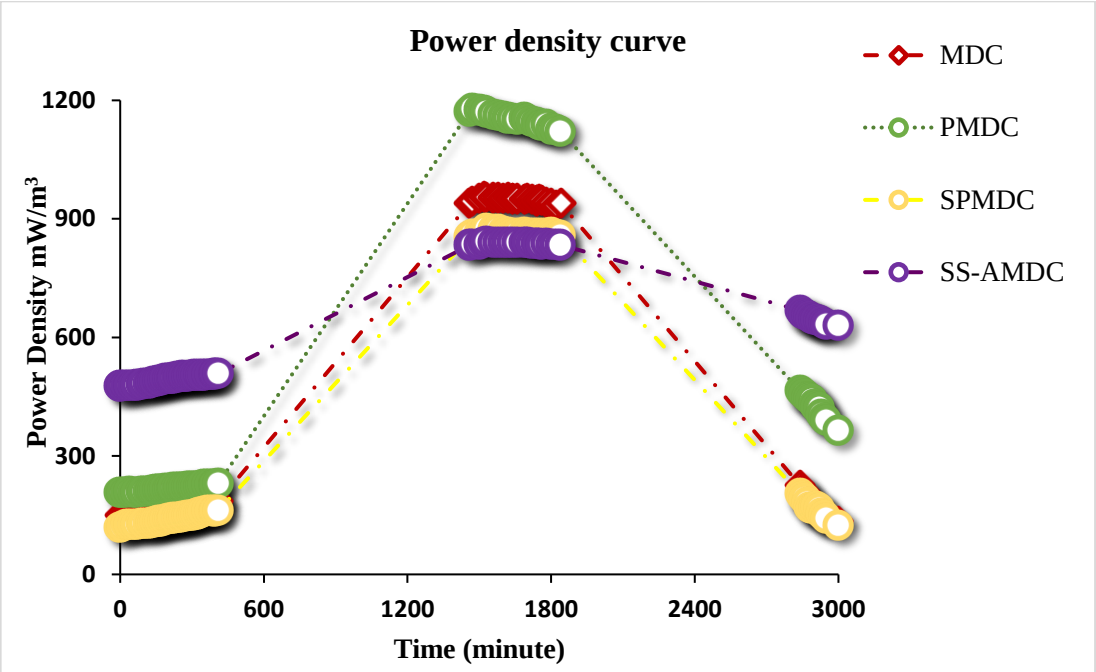

Figure 4.9: Power density (mW/m^3) of MDC, PMDC, SPMDC and SS-AMDC

Because the PMDC has a higher current density and generated voltage than air-MDC (control) its predictable to have higher volumetric power density (mW/m^3).

As it was shown before the internal resistance (R_{in}) of the SPMDC is higher than PMDC internal resistance, it's logical that the volumetric power density of the PMDC larger than the power density of the SPMDC, (Chen et al., 2011) reported that the performance of the MDC with a more than one desalination chamber could be improved by decreasing the external resistance to a suitable level.

For the SS-AMDC, as a result to had the lowest current density its decreases the power density to be the lowest value, and this results indicates that the conductivity of the stainless steel (SS) electrodes is not good as well as the graphite electrodes. Also the oil bubbler that was used to transport the carbon dioxide from the anode to the cathode chamber could has low transfer rate according to the amount of the produced CO_2 and this can affect on the oxygen production by the algae in the cathode chamber therefore it can decreases the amount of the electron acceptor (oxygen) generally that would

affect on the whole oxidation process and thus on the generated power. Even though the SS-AMDC has performed in a comparable level to the SPMDC.

4.2.4 Polarization Studies:

The polarization curves is a curve in which the voltage is a function of current and could be accomplished by using the periodical decrease of the load and recording the voltage, from the voltage current and power are calculated.

Polarization curves obtained for the four MDC configurations by using the single-cycle method (20 min intervals). Polarization was performed after the MDCs were fed and thus when the voltage was stabilized. By conducting various external resistance across the MDC, the internal resistance can be calculated. Each resistance was connected for 20 min and by a digital multi-meter the voltage data was recorded over single batch cycle, based on the voltage and resistance value, parameters such as current, current density, power and power density could be figured out.

The control MDC showed a peak volumetric power density of 1.019 W/m^3 based on anolyte volume at ~600 ohm and volumetric current density of 4.509 A/m^3. Thus the internal resistance of the control MDC is a round of 600 Ω.

The maximum power production was 0.0988 mW at current of 0.405 mA, where the voltage was 243.5 mV correspondingly (Figure 4.10).

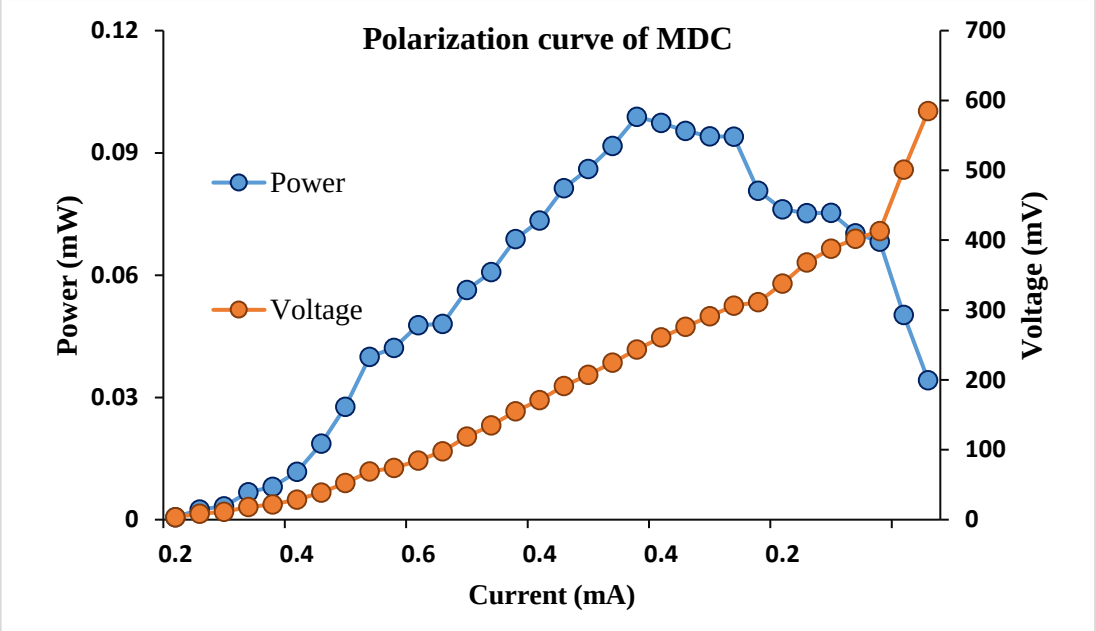

Figure 4.10: Voltage and power generated as a function of current in control MDC

The PMDC display a maximum volumetric power density of 1.175 W/m^3 based on anolyte volume at ~ 550 ohm and volumetric current density of 5.07 A/m^3, which means the internal resistance of the PMDC is around 550 Ω.

The maximum power production was 0.114 mW at current of 0.456 mA, where the voltage was 251 mV correspondingly (Figure 4.11).

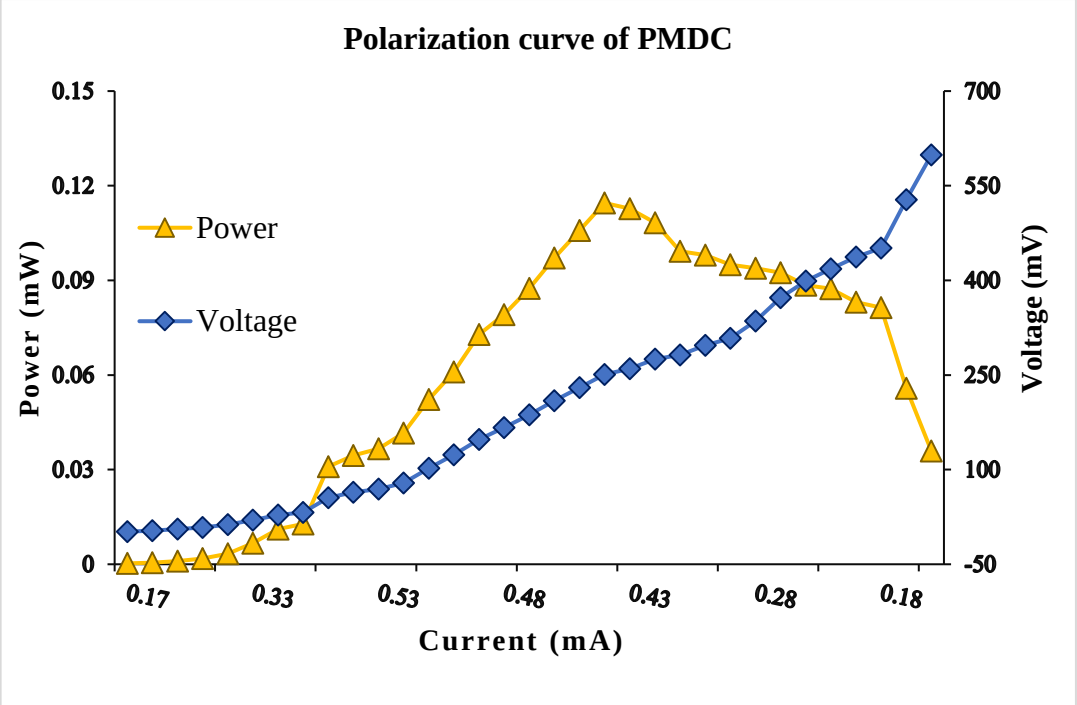

Figure 4.11: Voltage and power generated as a function of current in PMDC.

In SPMDC the maximum volumetric power density was 1.064 W/m^{3}based on the anolyte volume at ~ 700 ohm and current density of 4.111 A/m^3, and this indicates that the internal resistance of SPMDC is about 700 Ω.

The maximum power production was 0.095 mW at current of 0.37 mA, where the voltage was 259 mV correspondingly (Figure 4.12).

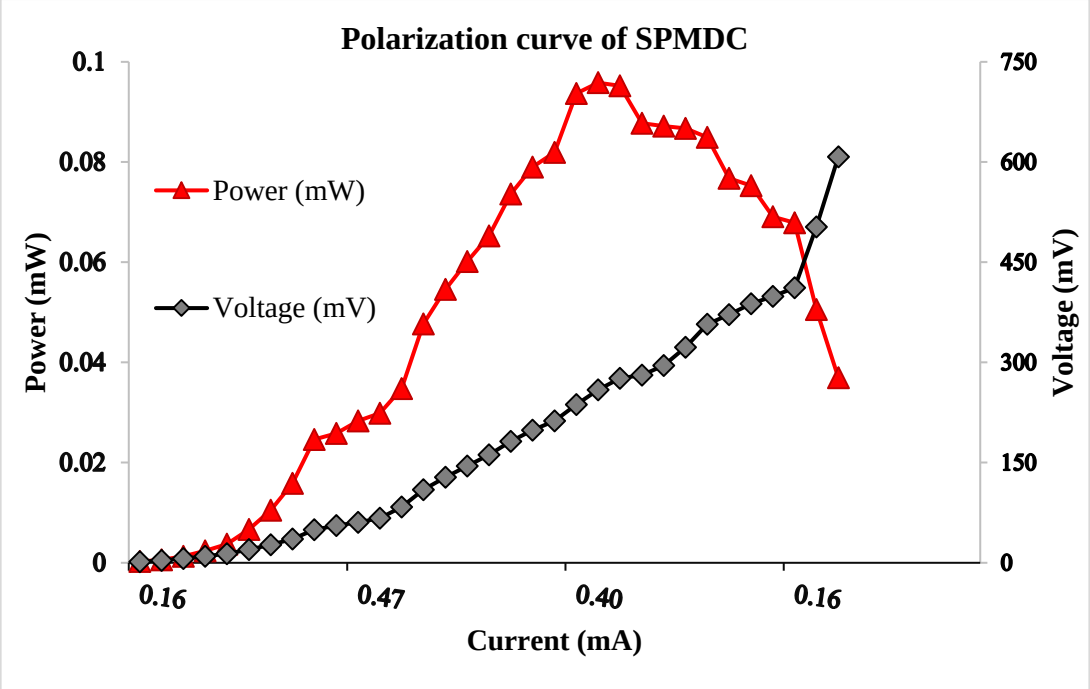

Figure 4.12: Voltage and power generated as a function of current in SPMDC

For SS-AMDC the maximum power density of 0.886 W/m^3 based on the anolyte volume (1017ml) at ~ 800 ohm and current density of 1.043A/m^3, which means that the internal resistance of the SS-AMDC is around 800 Ω.

The maximum power production was 0.901 mW at current of 1.06 mA, where the voltage was 848.9 mV correspondingly (Figure 4.13).

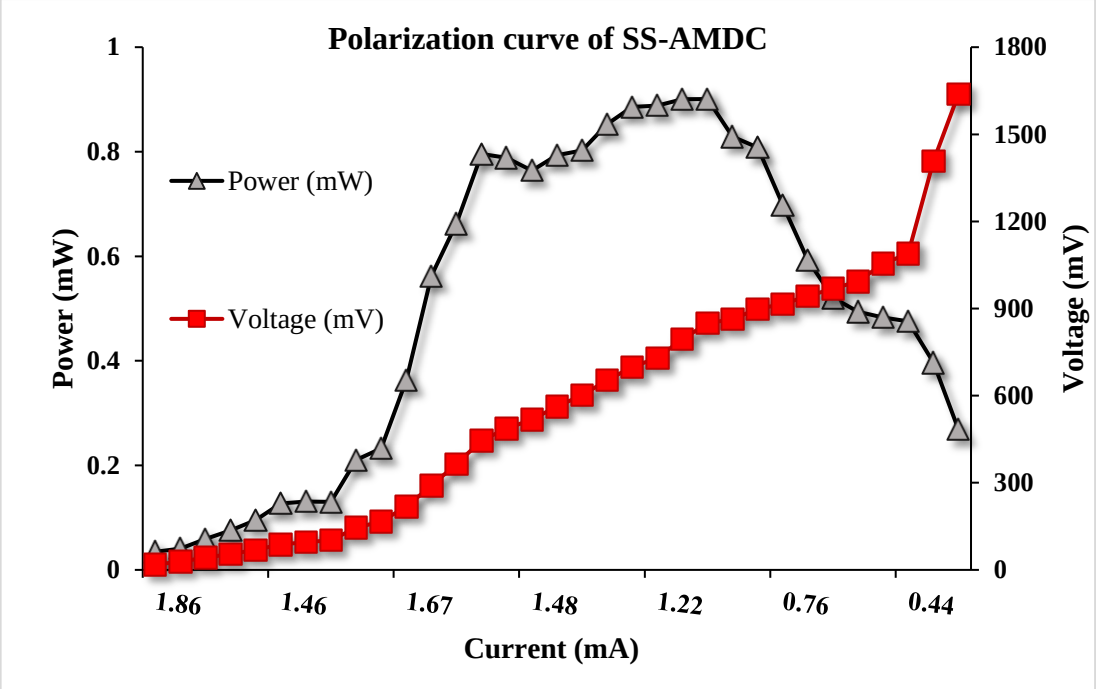

Figure 4.13: Voltage and power generated as a function of current in PMDC

Table 4.1 comparison of electrical properties of the four MDC configurations

MDCs types	Voltage with 500 Ω load (V)	Volumetric Power density with 500 Ω load (W/m^3)	Maximum volumetric power density (W m^{-3})	Approximate internal resistance (Ω)
Air-MDC	0.21	0.95	1.02	600
PMDC	0.198	1.18	1.18	550
SPMDC	0.23	0.87	1.06	700
SS-AMDC	0.65	0.84	0.89	800

The four polarization curves showed that by decreasing the external ohmic resistance the maximum current was increased, the current reaches to the maximum level and then it starts to decrease along the batch cycle, even though when the external resistance was decreased from 90 Ω to 10 Ω the currents decreased sharply, this phenomena also happened with (Chen et al., 2011) where it was explained by the disability of the exoelectrogenic bacteria to produce enough electrons at very low resistance.

One of the main factors contributing to lower power density is the high internal resistance, and this also affect negatively on the COD removal efficiency.

The presence of bio-cathode in the reactor raise the cell potential which means that it could decrease the ohmic resistance of the reactor.

The more desalination chambers implies higher distance between the electrodes which in turn would increase the internal resistance of the reactor, Stacked microbial desalination cell has a higher distance between the electrodes than the control air-MDC which explain the high internal resistance of the SPMDC, this results is compatible with the results found by (Ye et al., 2011) which reported that the closer electrodes the lower internal resistance.

The SS-AMDC shows the highest internal resistance, the smooth surface of the SS electrodes and the use of the oil bubbler could be from the reasons to increase the internal resistance of the system.

4.3 COD removal in MDCs

The four configurations of MDC were operated under the fed batch mode to support attachment of bacteria to the anode surface, with an OLR of 0.5 kg COD $m^{-3}d^{-1}$.

COD removal in the anode chamber for SS-AMDC was about 88.2% over a fed batch cycle, PMDC about 79.4%, SPMDC 76.4% and for MDC was about 61.7%.

The influent and effluent for MDCs anode chamber was shown in figure 4.14.

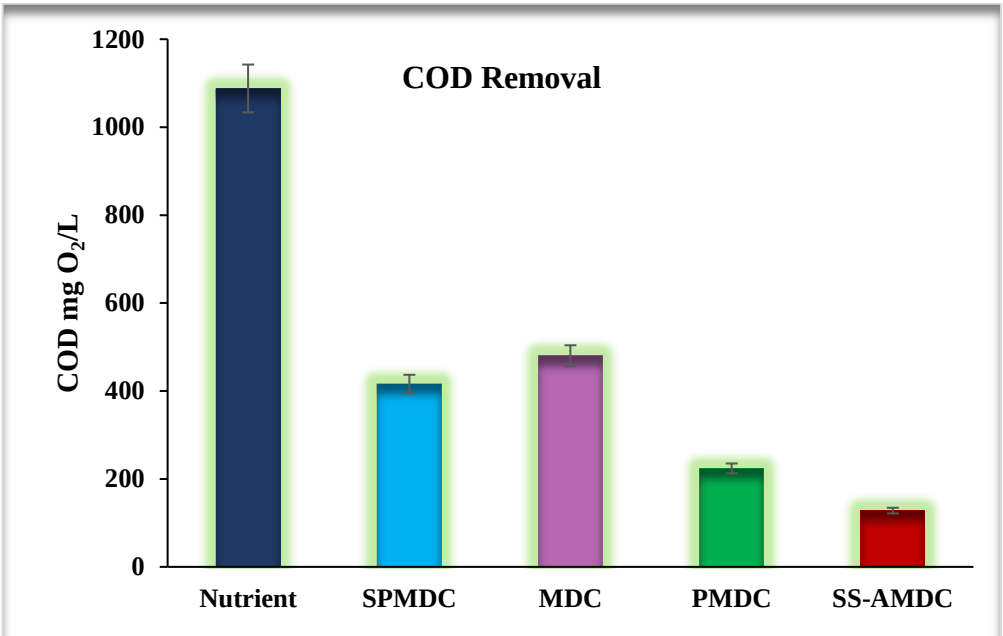

Figure 4.14: Chemical Oxygen Demand (COD) of the four different types of MDCs

The more produced electrons (higher produced voltage) the more degradation of anode organic matter and the more COD removal. So the SS-AMDC which has the highest voltage would has the lowest COD of its effluent (the highest COD removal) compared to other MDCs, furthermore the volume of bacterial consortium in the SS-AMDC is higher than the others and this implies more organic consumption.

Also in SS-AMDC the higher removal of COD means the higher carbon dioxide production to be transferred to the cathode chamber as well as higher oxygen generation in the cathode chamber as electron acceptor.

COD removal efficiency of PMDC is good enough to be compared to SS-AMDC despite of the difference of chamber volumes and surface area and that's return to the different in electrode types that were used in the experiment.

4.4 Faradaic efficiency (Current efficiency)

Faradaic efficiencies of 125.6, 241, 250.9, and 346% were observed with SPMDC, MDC, PMDC and SS-AMDC, respectively.

The theoretical coulombs required to facilitate the observed salt removal were 1.2, 2.4, 2.5 and 3.4 times higher than the actual coulombs observed in the system with SPMDC, MDC, PMDC and SS-AMDC respectively.

The Faradaic efficiency observed to be least for SPMDC, because the entirely desalination chambers volume is (19.2 ml) which is the smaller than 40ml for PMDC/MDC and 254 ml for SS-AMDC

Faradaic efficiencies of beyond 100% refers that electric current contributed to some TDS removal while other factors as the water osmosis and dialysis also shared in salt removal in the MDC.

The PH was measured at the end of the feed batch cycles for each of MDC, PMDC, SPMDC and SS-AMDC and it was ranges between of 5.8-6.7 for the four MDCs types.

4.5 Coulombic efficiency

Coulombic efficiency (CE %) is the fraction of electrons transported to the anode compared to the total electrons released by substrate oxidation.

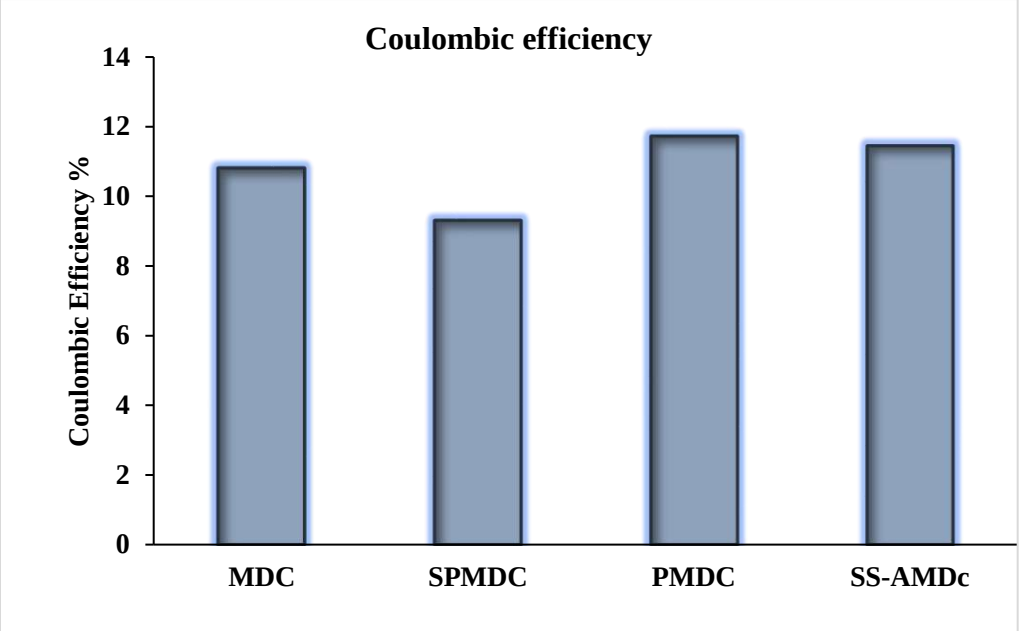

Figure 4.15: Coulombic efficiency % for the four MDCs configurations.

The PMDC and SS-AMDC have comparable levels of CE where the PMDC's CE equals 11.7% and the SS-AMDC's CE equals 11.46%.

Both of PMDC and SS-AMDC have higher CE values than the (control) air-MDC with CE equals to 10.79%. While the SPMDC exhibited the lowest CE value equals to 9.3% (Fig 4.15).

The CE in the four types of MDCs was less than 50% which could be resulted from the fermentation of substrate, methanogenesis process or even the aerobic oxidation of the substrate in the anode. The low CE indicates that fermentation process happens in the anode chamber due to the deficiency of NO_2 sparging as it was mentioned by (Zhang et al., 2012). Also (Kokabian and Gude, 2015) reported that the enrichment of microbial consortium could decreases the fermentation process thus increases the CE.

This is agree with (Logan et al., 2006), where he reported that the coulombic efficiency can be minimized by the alternative electron acceptors which could be present in medium or diffused to the anode (such as oxygen when the system is not tightly closed), also the bacterial growth could decrease the coulombic efficiency, so the bacteria that didn't have the ability to use the electrode as the electron acceptor could utilize the substrate for fermentation.

Table 4.1 exhibited the differences of the performance of MDC, PMDC, SPMDC and SS-AMDC.

Table 4.2: Comparison of efficiencies of the four MDC types

	COD removal%	**CE%**	**TDS removal%**	**FE %**	**Operation time (hours)**
MDC	76.4	10.79	91.8	241	360
PMDC	79.4	11.7	94.03	250.9	264
SPMDC	61.7	9.3	93.5	125.6	360
SS-AMDC	88.2	11.43	90.9	346	240

Also (Li et al., 2011) reported a different factors for decreasing the coulombic efficiency one of them was the distance between the anode and cathode electrodes which represented by the SPMDC in this research where it's coulombic efficiency is lower than the PMDC.

From these low CE results, it's predictable that aerobic oxidation, methanogens or fermentation process may be happened in the anode chambers of the MDC configurations.

Chapter 5

Conclusion and Recommendation

In this chapter the essential results of the research will be presented.

5.1 Conclusion

- In this research four different configurations of the Microbial Desalination Cell (MDC) were investigated to enhance the desalination efficiency and electricity generation.
- The usage of the nanochloropisis microalgae as a biocathode (PMDC) showed an increase in the desalination efficiency (Desalination ratio, Qd and decreasing of EC) and increase in the power and electricity generation along with increasing in the capability of removing organic matters from wastewater in the anode chamber, furthermore the usage of the algal biocathode displayed improving of the CE%.
- By adding desalination chambers and concentrated chambers to the basic system of MDC the desalination ratio was improved. However the increasing of desalination chambers lowers the current due to the elevation in the internal resistance.
- Utilization of the 304 Stainless Steel (SS) electrodes with the algal biocathode ,which serves as oxygen generator without the need of mechanical aerator (SS-AMDC), exhibited high desalination efficiency, high COD removal and CE, in addition the usage SS electrodes is cost effective method.
- Also the 304 SS electrodes with smooth surface showed the ability to produce a fair power density, but not as much as the graphite electrodes, however by improving the electrodes topography.
- Utilization of the oil bubbler is not the best way for transfer the CO_2 from anode to cathode chamber.
- The desalination rate of the MDC could reach more than 94% by improving the system parameters.
- The best desalination efficiency was seen in the PMDC and SS-AMDC with desalination ratio equals to 94% and 91% respectively.

- Nevertheless the MDC proved to be appropriate pretreatment technique before the RO.

5.2 Recommendation

- The stainless steel electrodes must have a roughness surface (Ra) in the range of the microbial cell size to improve the electricity generation hence the desalination efficiency.
- The desalination compartments shouldn't be increased without boundaries, the external resistance, the chambers and the material/electrodes should be optimized to have the best desalination efficiency and electrical generation.
- For better transport of the CO_2 from the anode to the cathode, specific valve should be used what will affect on the generated power.
- The low cost separator could be used in future developments for economical MDC technology.
- Further developments of this research should involve a way for reducing the internal resistance thus elevating the generated power.
- Continuous mode instead of the feed-batch mode would be preferable to generate a stable current and potential.

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APPENDIXES

A.1 Appendix 1 "MDC/PMDC reactor designs"

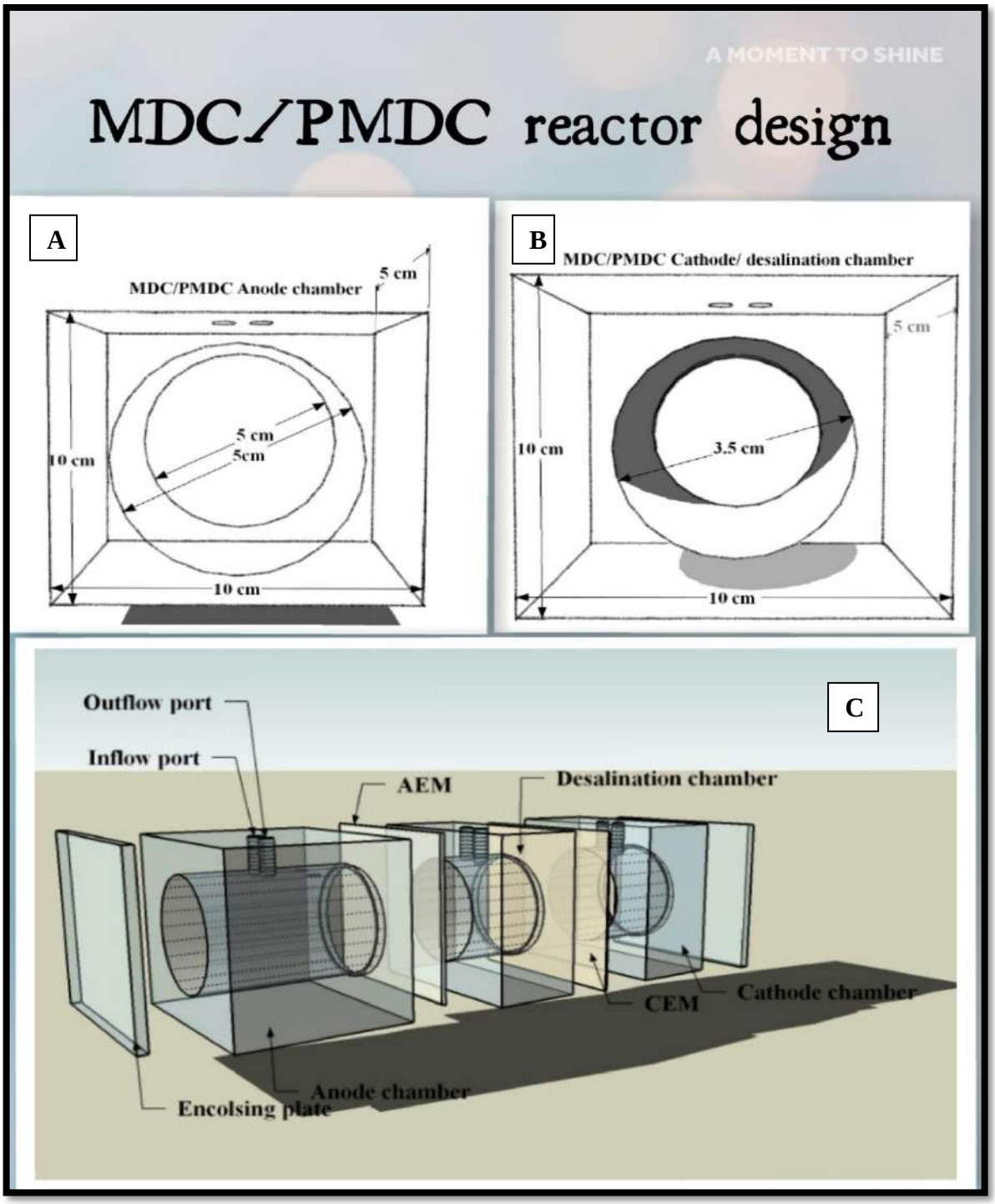

Figure 6.1: A) Schematic diagram of MDC/PMDC Anode chamber, B) Schematic diagram of MDC/PMDC cathode/Desalination chambers, C) Overall MDC/PMDC reactor design

A.2 Appendix 2 “SPMDC reactor designs”

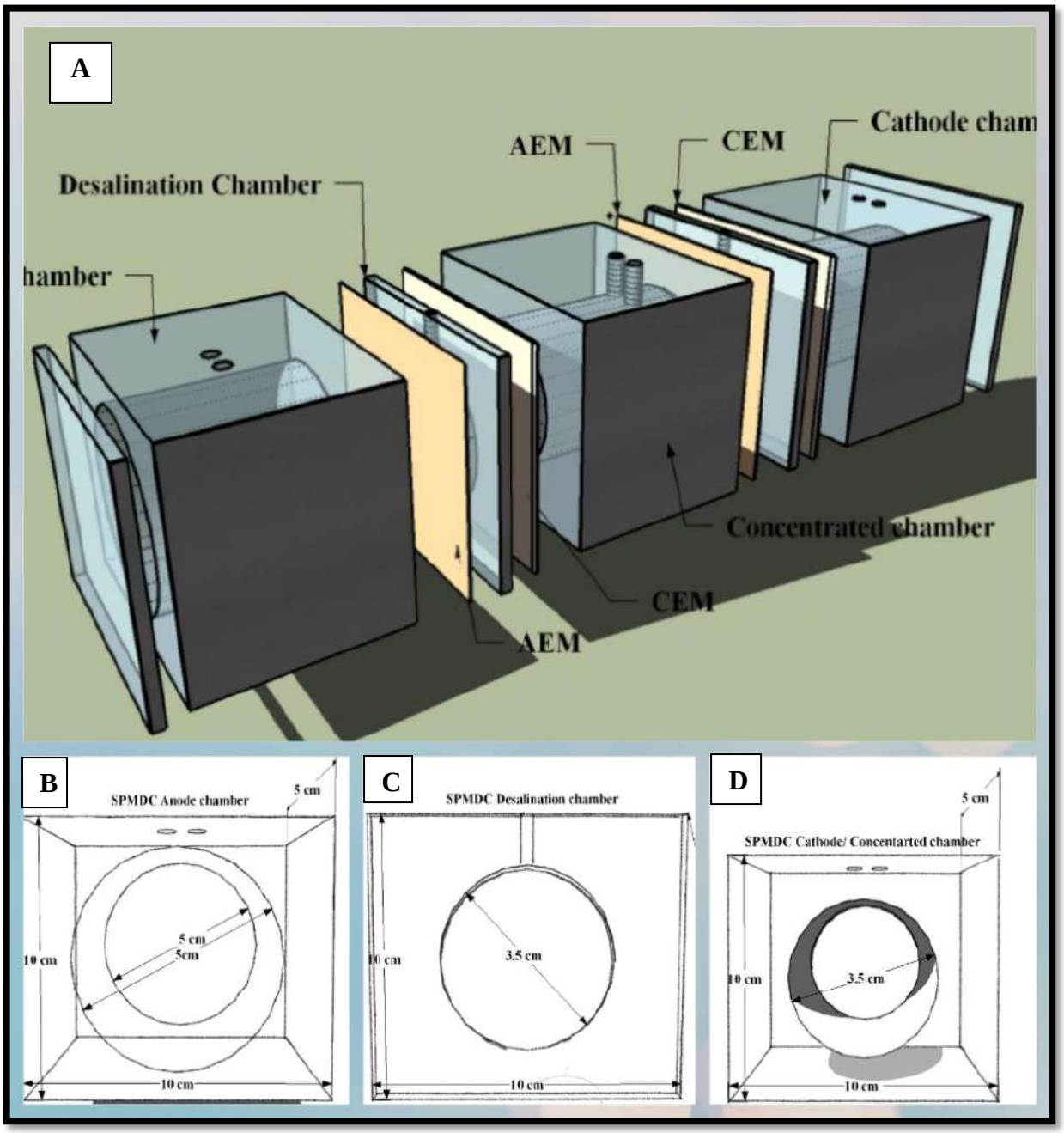

Figure 6.2: A) Overall SPMDC reactor design, B) Schematic diagram of SPMDC Anode chamber, C) Schematic diagram of SPMDC desalination chamber, D) schematic diagram of SPMDC cathode/concentrated chambers

A.3 Appendix 3 “SSAMDC System designs”

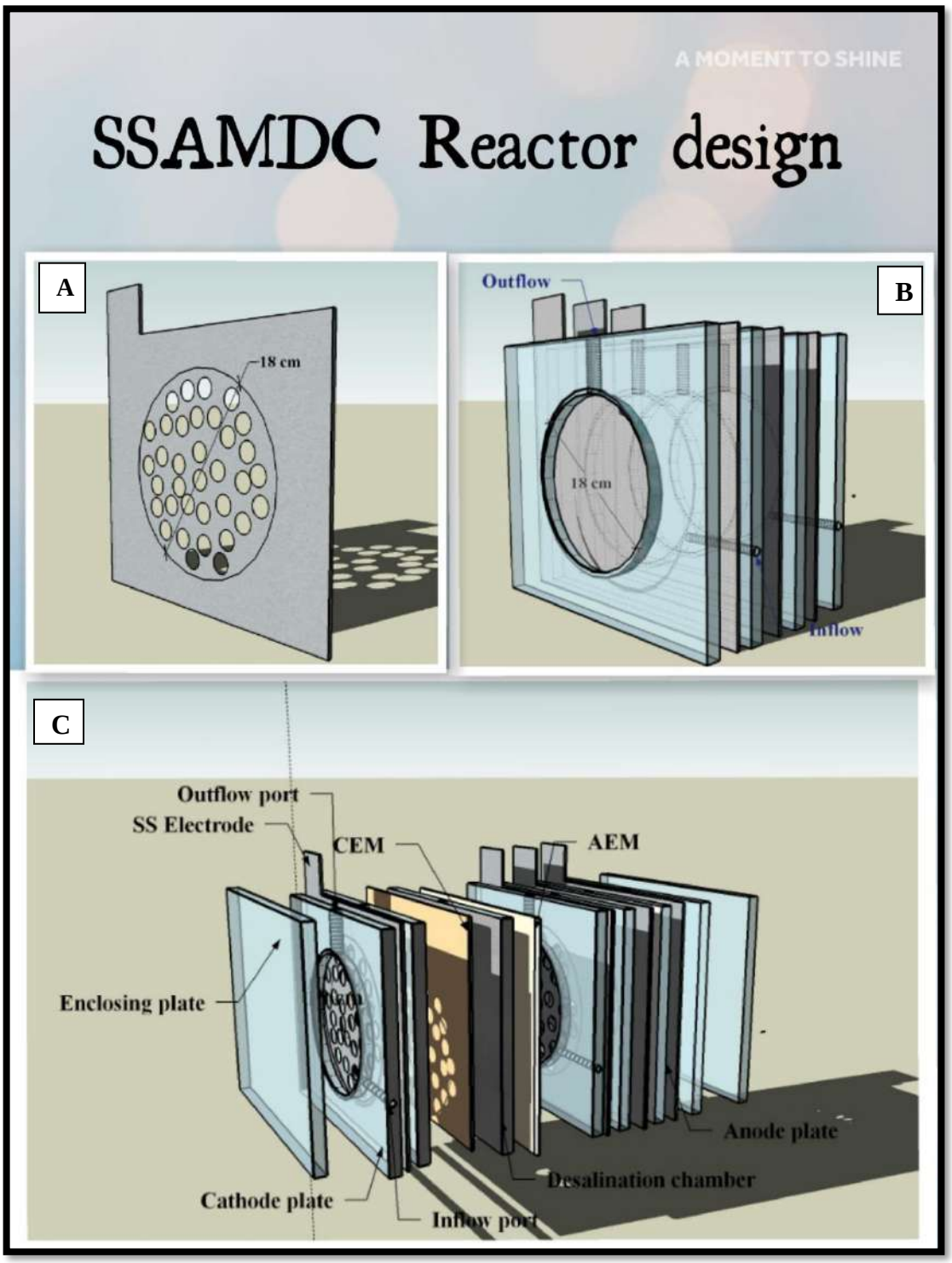

Figure 6.3: A) diagram of Stainless Steel electrode used in SSAMDC reactor, B) diagram of SSAMDC anode chamber, C) Overall SSAMDC reactor design