A STUDY EXAMINING MDC UNITS COUPLE TREATING CARBOHYDRATE STREAM WASTE AND ARTIFICIAL SEAWATER

By

DINA FAISAL AHMED AL AZAWI

Bachelor of Science in Civil Engineering
Al Mustansyriah University
Baghdad, Iraq
1991

Master of Science in Civil Engineering
Al Mustansyriah University
Baghdad, Iraq
2000

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Dissertation Approved:

John N. Veenstra

Dissertation Adviser

Gregory Wilber

Dee Ann Sanders

A. J. Johannes

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Name: DINA AL AZAWI

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Title of Study: A STUDY EXAMINING MDC UNITS COUPLE TREATING CARBOHYDRATE STREAM WASTE AND ARTIFICIAL SEAWATER

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Abstract:

Investing the biomass energy production in microbial desalination cells (MDCs) to drive another process like desalination has gained a great attention these days pushing researchers to try to unveil the limiting factors and overcome problems in order to scale up the MDC units and make a better competitor to another well adopted water-wastewater treatment technologies. Addition of BES inhibitor to deactivate methanogens contributed in increasing the power of the upflow MDC by 23% and that increase in power enhanced salt removal to reach 71% for reactor with inhibitor and 64% for reactor without inhibitor. The percentage removal of SCOD dropped when BES inhibitor was used to be 55% for reactor with inhibitor and for reactor without inhibitor was 64%. The results demonstrated that methanogen bacteria grow and compete for food whenever the loading rate is greater than the equivalent transfer load when operating MDC. Practically, deactivating methanogens can be approached through aeration rather than adding chemical.

When two reactors were connected hydraulically in series, salt removal percentage reached 86% and 71% of the SCOD (1.7 g SCOD/L/day) removed in the first reactor while about 8% removed in second reactor. The power density reached 61mW/cm^3 while it was only 2.3 mW/cm^3 in the first experiment using individual reactor. The results indicated that stacking cells can improve both salt removal and organic reduction. Examining membranes integrity after long term operation using scanning electron microscopy SEM along with EDS analysis revealed accumulation of biofilms on membrane surface (anion exchange membrane AEM) that could seriously hinder the migration of anions from the cathode compartment to the anode. The influence of long term operation on cation exchange membrane (CEM) was not significant as AEM. Investing the electricity produced by MDC bacterial metabolism to drive salt removal is considered promising; however the ability of such system is just to handle low organic loading rate (max of 2 g COD/L/day) and above that with the performance will drop. That made such system fit perfectly as post treating system following another waste stream treatment such as a digester. While the reduced salt stream may need further treatment such as RO to fit the purpose it designed for.

List of Abbreviations

Abbreviation	Description
AEM	Anion Exchange membrane
BES	Bioelectrochemical System
BES	Bromoethansulfonate
CE	Coulombic Efficiency
CEM	Cation Exchange membrane
CBS	Cell Balance System
EDS	Energy Dispersive Spectroscopy
MFC	Microbial Fuel Cell
MDC	Microbial Desalination Cell
MEDC	Microbial Electrodialysis Cell
PBS	Phosphate Buffer
SEM	Scanning Electron Microscopy
SMED	Stacked Microbial desalination Cell
SWE	Saline Water Effluent
SWI	Saline Water Influent
WWE	Wastewater Effluent
WWI	Wastewater Influent

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CHAPTER I

INTRODUCTION

Clean and renewable energy nowadays is a perfect solution to face the stringent environmental regulations and prevent further environmental damage. Among all sources of clean and renewable energy such as solar, wind and waves; bioenergy acquired special attention not only due to human kind best or environmental rules but for the discovery of microorganism's capability to produce and transfer energy (electrons) into two different electron accepters (Lovely, 2008).

This phenomenon started to bear fruit through the invention of a bioreactor composed of an anode and cathode. The microbial fuel cell (MFC) has bacteria in the anode capable of extracting electricity from a wide range of complex organic substrate and oxygen for example, as a terminal electron accepter in the cathode to complete the oxidation - reduction reaction (Logan, 2006). The current produced in the anode compartment can be invested in different integrated processes such as desalination.

The microbial desalination cell (MDC) was the first bioreactor capable of integrating two different reactions by investing the current solely bacterially produced in the anode to separate the ions of saline water in the cathode and was built and examined by Cao (2009).

Optimizing the performance of such bioreactors to reach the ultimate goal of full size reactors is still ongoing; however the outline boundaries were set through the operating capabilities of these reactors. Bioelectrochemical reactors (BES) can only deal with low organic loading rates which make them efficient as a polishing operation devices following other processes such as anaerobic digesters to meet the strict environmental rules (Rabaey, 2010). And for integrating another process through the investment of the current produced for example a desalination process, such BES reactors could function well in a step that precedes reveres osmoses (RO) for example for energy saving through their low salinity effluent production.

The objective of this research was an attempt to answer the following questions:

1. What is the effect of using 6 mM bromoethansulfonate (BES), a methanogen inhibitor, on reactor overall performance when complex substrate (sucrose) is used?

Methanogen bacteria can exist and grow in an anaerobic environment where excess food is available. So naturally it will compete with other exoelectrogenic bacteria for food and may affect the power generation (He, 2005). To examine inhibition of methanogens; and how it will affect the power generation in an upflow microbial desalination cell, (UMDC) a bromoethansulphonate (BES) inhibitor will be used.

2. What is the effect of connecting two MDC reactors hydraulically in series on salinity removal?

One of the steps on the way to scale- up of the upflow microbial desalination (UMDC) cell is proposed to be conducted through connecting two reactors hydraulically in series and examine the performance of such connection using complex feedstock (sucrose) and artificial seawater.

3. What is the effect of long – term operating on MDC membranes?

Biofouling and scaling could be two limiting factors due to their deterioration effects on membranes associated with them. Biofilm generated by bacteria for cohesion and adhesion purposes along with inorganic precipitations will probably cover membranes and reduce their ultimate performance, (Luo, 2012). Scanning electron microscopy is proposed to be used to depict this phenomenon.

CHAPTER II

REVIEW OF LITERATURE

Bioelectrochemical systems (BESs) are simply devices capable of converting substrates (organic or inorganic) chemical energy into different useful forms of energy such as electricity via biochemical reactions (Jacobson 2012, Logan 2013). These systems emerged recently with a promising lead not only as an integrated water- wastewater treatment devices but also being energy producing rather than consuming. The inceptive application of these systems is the microbial fuel cell (MFC). Configurations, microorganism species and substrates and problem associated with MFC performance has been well studied although commercializing this device is facing difficulties due to unsolved scale- up issues (Lovley, 2008). Electricity produced from MFCs caused researchers (Cao, 2009, Jacobson, 2011) to benefit from the harvested electrons to further assist treating another wastewater. Cao (2009) modified a microbial fuel cell to treat two different wastewaters. A similar yet different technology is the microbial desalination cell (MDC) which is a two chambered reactor in which microorganisms in the anode chamber are responsible of extracting chemical energy from different substrates and converting it into another form like electricity. The electric potential gradient created will be of great benefit in the cathode chamber to desalinate salty water.

In the last few years, research on microbial desalination cells (MDC) has increased significantly in order to better understand the mechanisms of the limiting factors and practical bottleneck that should be overcome to reach better performance and lead to commercialization of this technology.

BES and Energy Content in Wastewater

In bioelectrochemical systems, the organic energy is dealt with in a sustainable and controlled manner to yield different forms of energy. A wide range of wastewaters, specifically sugar wastewater, potato-processing factories, and slaughterhouses have high energy content and the potential of microbial electricity generation. The potential energy content depends on the average oxidation state of the carbon in the food, i.e. the number of electrons that can be released per weight of substrate when the compound is fully oxidized (Rebaey, 2009).

The overall reaction in BES applications such as a MFC can be evaluated in terms of Gibbs free energy. Gibbs free energy in the MFC is the potential difference between the anode and the cathode and can be calculated as (Logan 2006)

$\Delta Gr = \Delta Gr^0 + RT\ln(\Pi)$ …………………………………………….. (1)

where ΔGr is Gibbs free energy in (J), ΔGr_0 is Gibbs free energy under standard conditions of 298.19 K, 1bar pressure and 1M concentration and it tabulated in Metcalf and Eddy (2003), R is gas constant (8.31447 J mol^{-1} K^{-1}), T is temperature in K and Π is reaction quotient which is defined as the activities of the products divided by that of the reactants.

An example of an anodic reaction in a MFC is when bacteria oxidize acetate in the anode compartment is

$2\ HCO3^- + 9\ H^+ + 8\ e^- \rightarrow CH_3COO^- + 4\ H_2O$ …….. (2)

And the standard electrode potential for this reaction is 0.187 V (consuming or reduction reaction), while the actual potential in one experiment using acetate is - 0.296 V (Logan 2006). If oxygen is the electron accepter in the cathode and reaction occurred at pH of 7 then we can write the reaction as

$O_2 + 4\ H^+ + 4\ e^- \rightarrow 2\ H_2O$ …… (3)

For the specific conditions of pH = 7 and pO_2 = 0.2 atm, the standard potential is 1.229 V and the actual potential is 0.805 V (Logan 2006). Such a cell with acetate oxidizing anode and oxygen reducing cathode has a potential of 1.101 V (0.805 + 0.296 V). Oxidizing more complex substrate like sucrose will follow a different path of hydrolysis to glucose and then fermentation later by bacteria to form acetate and hydrogen. Both acetate and hydrogen can play a role in producing current via exoelectrogenic bacteria and that implies that not all the available energy from complex organics is recovered as current but only the energy available from fermentation products can be recovered and transferred to the circuit (Hubertus et al. 2010). The following equations illustrate the above concept:

The anodic reaction (Hubertus et al. 2010)

$C_6H_{12}O_6 + 12\ H_2O \rightarrow 6\ HCO_3 + 30\ H^+ + 24\ e^-$ ……. (4)

The cathodic reaction (Hubertus et al. 2010)

$O_2 + 4\ H^+ + 4\ e^- \rightarrow 2H_2O$ ……. (5)

So dealing with simple wastewaters have advantages of being readily broken down to recover energy over using more complex wastewaters which need to go through different processes to be bacterially degraded (Pant et al. 2010 and Hubertus et al. 2010). He and coworker (2005)

demonstrated the role of different bacterial species on breaking down organics and recovering energy. They selectively inhibited methanogen bacteria allowing exoelectrogen species to act solely without substrate competitors and succeeded in increasing the reactor power density by 25%. Pant and coworker (2010) reviewed a variety of wastewaters (substrates) used in microbial fuel cell researches and their potential energy recovered in terms of electricity. In this review, Pant stated that pre-acclimated bacteria from microbial fuel cell (MFC) can produce a maximum of 0.8 mA/cm^2 current density when fed with 1g/L acetate, while in another research, 0.7 mA/cm^2 current can be recovered when 6.7 mM glucose is used.

While bacteria degrade organics in the anode chamber, electrons produced eventually follow three identified strategies to be transfer to the electrode and those strategies are first through direct electron transfer involving proteins located on the bacteria cell surface, second using mediators which are redox reactive molecules to shuttle electrons through diffusion to the electrode and last through bacterial nanowires (Pant et al. 2012). Figure 2.1 below, adopted from Lovely (2008), illustrates the above descriptive pathways.

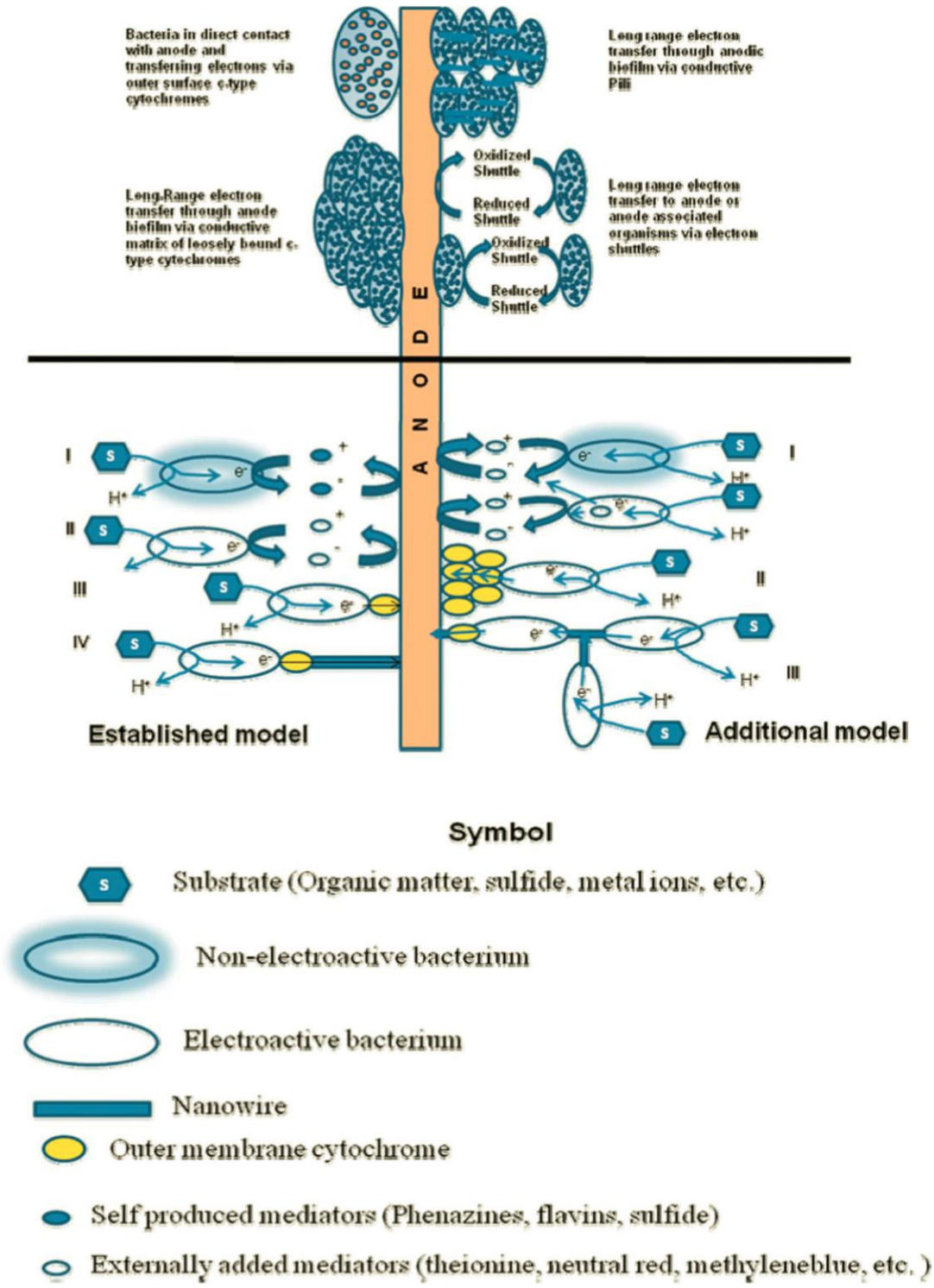


Figure 2.1: The strategies used to transfer electrons to the anode electrode (adopted from Lovely 2008).

Recent Publication and State of Art on Single Microbial Desalination Cell

Research on exploiting microbial activities to generate electricity integrated with salinity removal as two separated processes continued to explore the efficiency of desalination. Jacobson et al. (2011) examined a continuously operated microbial desalination cell for four months functioning in an up flow mode instead of batch flow operation to desalinate salt water with 30 g total dissolved solids (TDS)/L. The efficiency of NaCl removal was up to 99% and electricity recovered was 62 mA. Jacobson and his team (2011) continued in an attempt to scale up an up-flow microbial desalination cell by studying bioelectrochemical desalination with both salt water and artificial seawater. The up flow microbial desalination cell (UMDC) in this experiment treated 1 m^3 of seawater with 90% efficiency of TDS removal and produced energy of 1.8 KWh at the same time. They suggested that by using an up flow unit (UMDC) as a pre-desalination and energy saving approach before reverse osmosis, the net energy needed for RO will be lowered due to improved quality of the UMDC effluent (lowered TDS of salt solution). They also suggested that the location of an UMDC treatment plant could be centralized next to a wastewater treatment plant in a coastal area (Jacobson et al. 2011).

Both Mehanna et al. (2010) and Cao (2009), (Figure 2.2) used batch mode flow MDC. Mehanna used an open air cathode instead of using ferricyanide in the cathode compartment to desalinate different salinity concentrations (5 g/L and 20 g/L NaCl) primarily before RO treatment to save energy. They were able to reduce conductivity of 5 g/L salt water by 43 ± 6% and produced a maximum power density of 480 mW/m^2. For the 20 g/L salt water the conductivity was reduced by 50 ± 7%. They concluded that desalination of different salt concentrations up to a 43-50% reduction in conductivity is possible with equal volumes of water in both the anode and the cathode.

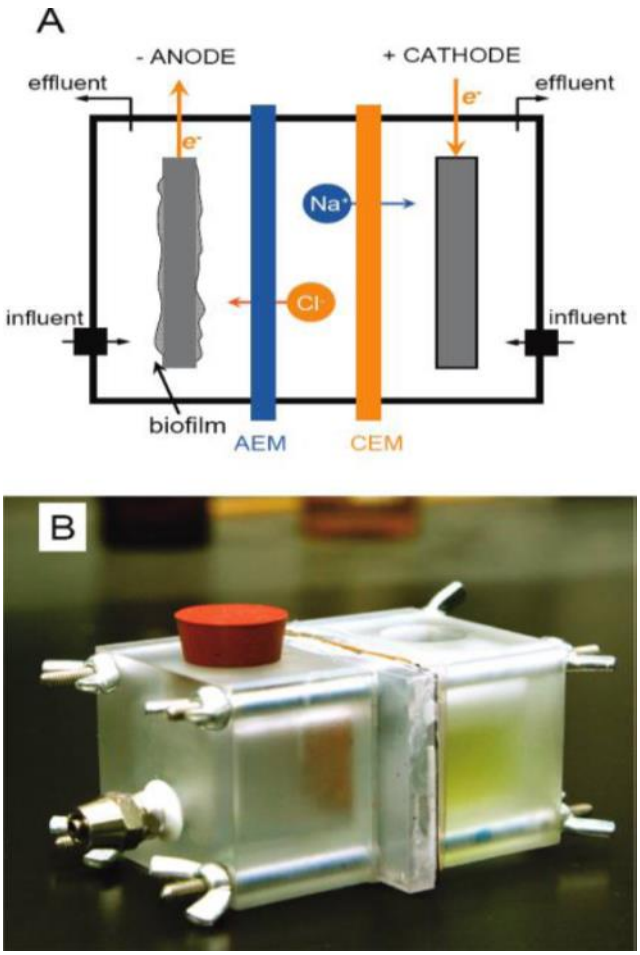


Figure 2.2: Schematic and a photograph for MDC (Cao et al. 2009).

Also MDC treatment could be used to primarily reduce salt concentration and energy demands for downstream RO processing, while producing electrical power at the same time.

In another attempt to boost voltage produced by bacteria, Mehanna et al. (2010) used an external electrical power source of 0.55 V to treat two different salty waters (5 g/L and 20 g/ L NaCl) in a microbial electrodialysis cell (MEDC). The cell composed of three chambers, the middle has the salty water and the anode has the waste water and the cathode has phosphate buffer solution (PBS). They were capable of reducing the overall conductivity up to 68 ± 3% in a single fed-batch cycle, and their electrical energy efficiencies reached 231 ± 59%. They also produced hydrogen with a rate of 0.16 ± 0.05 m^3 H_2/m^3d. They concluded that by applying an external

voltage they would better control electrode potentials and the hydrogen gas being produced will be considered self-sustaining with respect to electrical power requirements. In a similar approach at the University of Colorado, Luo et al. (2010) used 0.8 V as an external power source to produce 1.5 m^3/m^3 d hydrogen when treating salty water with concentration of 10 g/L. The achieved salt removal efficiency was up to 98.8% in a single batch cycle while it was 98.2% in a recirculation mode. Luo's current density recovered using microbial electrolysis desalination cell (MEDC) was 87.2 A/m^3 for the batch mode and 140 A/m^3, using anolyte recirculation.

Operational Problems Associated When Using Single Cell MDC

A complete oxidation of organics that lead to electricity production in most BES; can be hindered by many factors such as accumulation of protons in the anode chamber and poor buffer capacity that lower bacterial activity (Ren, 2007), optimizing organic loading rate (He, 2006) and reactor's configuration and design (Logan, 2006), reactor's long term performance operating with a variety of wastewaters and membrane's bio-fouling and/or scaling (Luo, 2012). Overcoming all these obstacles is a challenge for the best design of an economical reactor(s).

Microbial Desalination Cell in Series or SMDC

In China a new development to the MDC was done by Chen et al. (2011). Chen's team used a multi chamber microbial desalination cells which they called a stacked desalination cell (SMDC). The SMDC is composed of multi anion exchange membranes and multi cation exchange membranes to form the stacked desalination cell as shown in Figure 2.3 below.

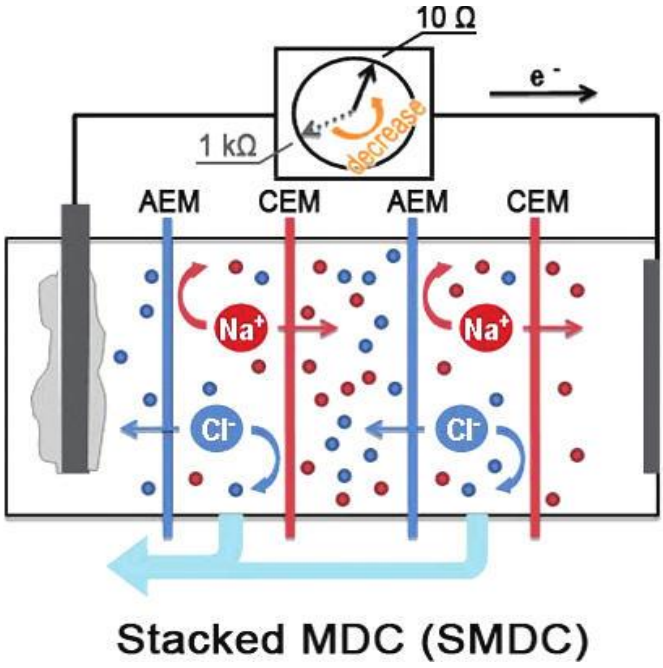


Figure 2.3: Stacked microbial desalination cell (Chen et al. 2011).

Chen and his team were able to increase the desalination rate with their development. The total desalination rate obtained was of 0.0252 g/h with external resistance of 10 ohm which proves the effectiveness of multiple desalination chambers.

At the same time, Kim and Logan (2011) developed a similar reactor with 20 pairs of desalination chambers (6 AEM and 5 CEM membranes); the cell has one anion and one cation electrodes to avoid cell voltage reversal (details to be given next section). Kim was able to reduce 44% of the salinity of 35 g/L synthetic seawater, eluded any catholytic buffer and recorded an 86% current efficiency.

Recently, Qu and coworkers (2013) used four MDC (three compartments) cells connected hydraulically in series to avoid cell reversal caused by cell voltage variations. They operated the cells in continuous mode where the anode solution from the first MDC flowed into the cathode, and then into the anode of the second cell and so on to avoid the anode pH dramatic change. The salt solution also transferred from the middle compartment of the first cell into the middle

compartment of the second cell and so on. Qu achieved 76% NaCl removal (HRT 1 day) and 97% (HRT 2 days). Also 60% of the wastewater COD was removed.

Operational Problems Associated When Using Stacked MDCs

In addition to the operational problems raised when using single cell MDC, researchers faced more hurdles associated when using stacked MDC, one of which is cell reversal. When BES stack cells are connected in parallel, they are actually operated at high current and lower voltage, while stack cells connected in series operate at high voltage and low current. Operating at low current may decrease energy loss across resistors and thin and inexpensive wires however stacks cells connected in series, due to the nature of the bioanode of acclimating the environment and colonizing the anode electrode can show inequalities in cells performance which can result in unfavorable potential due to start up and continuous operation (Andersen et al. 2013). Although the goal behind connecting BES cells in series is to increase voltage to a more useful value (Oh and Logan 2007), avoiding cell reversal needs a cell balance system. Anderson and coworker (2013) demonstrated a cell balance system (CBS) that controls individual cells connected electrically in series through allowing bacteria to drip feed excess electric current in the sensitive start period. This CBS is capable of accelerating start up and maximize cell performance during continuous operation.

Long Term Operating and Membrane Integrity

Problems associated with long term running of an MDC such as membrane fouling for example could be serious (Luo, 2012). Scanning electron microscopy (SEM) could be used to depict and investigate the problem. The ability of this device to conduct both elemental analysis and descriptive images helps to get better understanding of problems associated with membrane

fouling in MDC. Bond and Lovley (2004) used SEM to view the *G. fermentans* colonies on the graphite anode in a microbial fuel cell and how this species of bacteria is attached in a thick matrix and differ from other bacteria (from *Proteobacteria* family) in which the later appeared to be attached individually on the electrode surface without substantial extracellular material. Luo and Ren, (2012) examined MDC membrane integrity after 8 months of operation using advanced electrochemical microscopy and found that the anode membrane (AEM) was layered by bacteria causing the reactor performance to decline and the analysis showed a 47% decrease in current density and Couloumbic efficiency drop of 46% and 27% reduction in desalination efficiency.

CHAPTER III

MATERIALS AND METHODS

This chapter contains two sections. In section one, construction and operation of MDC reactor will be present, while in section two, construction and operation conditions of reactors connected in series will be introduced. In brief, the MDC reactor is composed of two chambers formed from membranes. The inner chamber is strengthened using two different structures. The first was a plastic structure composed of three rings and three columns was used to avoid membrane deformation during operation. The second structure was a hollow plastic netting cylinder that serves for same reason. Figure 3.1 below summarizes the processes of microbial desalination cell (MDC) construction, operation and the measurement conducted.

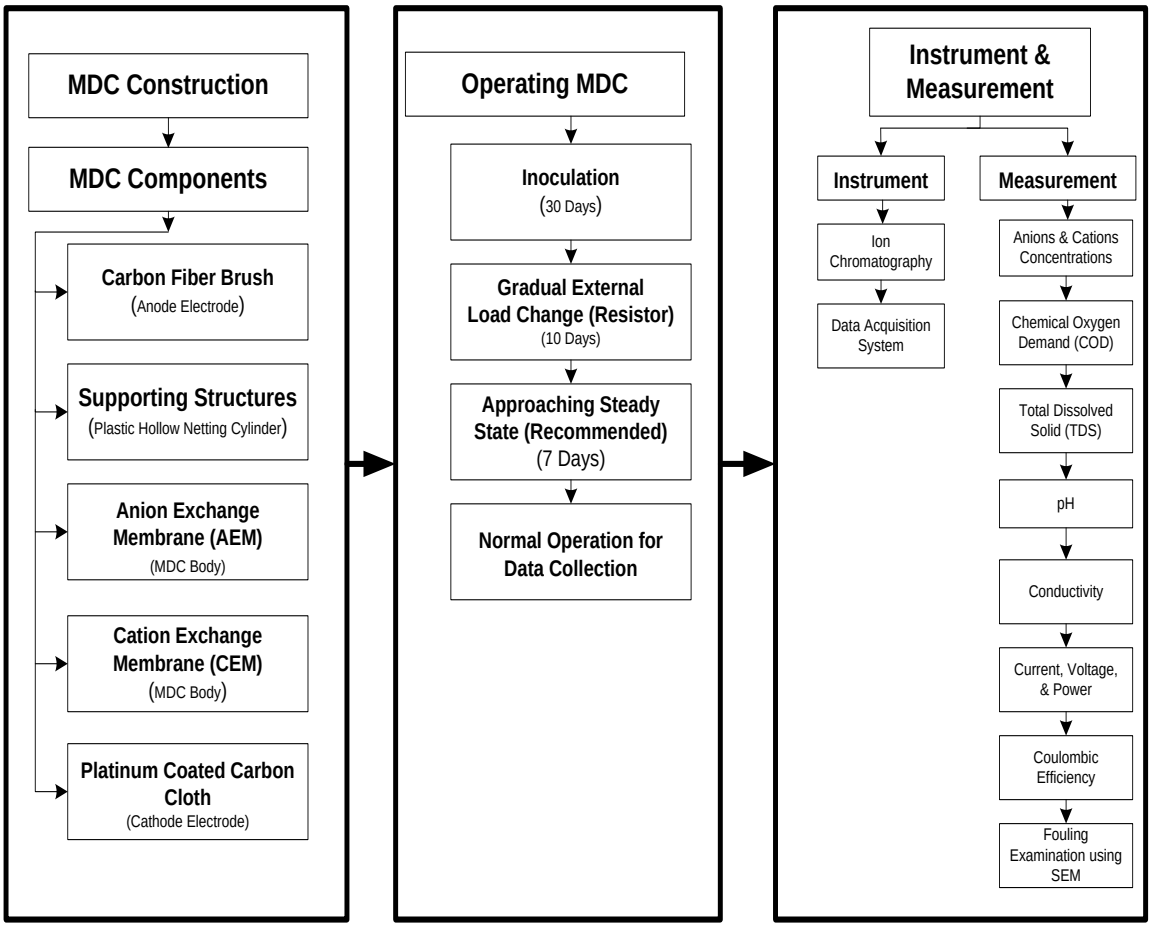


Figure 3.1 Flow chart showing MDC processes of construction, operation and measurements conducted.

SECTION 1

PART A MDC Construction and Operation

MDC Construction

The continuous upflow microbial desalination cell reactor was constructed in a cylindrical multi-chamber configuration.The anode or the inner chamber was formed

from an anion exchange membrane (AEM, AMI-710, Membrane International Inc., Glen Rock, NJ), 5.82 cm in diameter, 41.5 cm long, creating 1.11 L volume. This chamber was strengthened using a hollow plastic netting cylinder (Industrial Netting, Minneapolis, MN) to prevent the anode chamber deformation. The anode electrode was carbon brush (Golden Brush Mfg. Co., Inc., Commerce, CA) customized for the MDC reactor at 44 cm long.

The outer (cathode) chamber was 6.75 cm in diameter and 41.5 cm long with a volume of 350 mL composed of a cation exchange membrane (CEM, CMI-7000, Membrane International Inc., Glen Rock, NJ). The cathode chamber was covered with carbon cloth coated with platinum at 0.5 mg platinum /cm^2. The carbon cloth was wrapped in two layers (Fuel Cell Earth LLC, Stoneham, MA) to form the cathode electrode. Platinum wire of 0.5 m length was used to transfer electrons into an electric circuit (Good Fellow Cambridge Limited, Huntington, England). The external electric load (resistor) was set at 10 Ω. Flow meters were used to monitor the outer chamber feeding solution and inner chamber circulated solution (Gilmont Instruments, Barrington, II). The inner chamber feeding solution flow rate was measured manually due to the nature of the solution that caused high bacterial growth in the tubes at slow flow rate. Schematic diagrams in Figure 3.2 (illustrating the hydraulic streams), Figure 3.3 (illustrating electric circuit connections and MDC components) and Figure 3.4 (depict MDC assembling stages). Air breaking system (Figure 3.5) was added to decrease the buildup pressure.

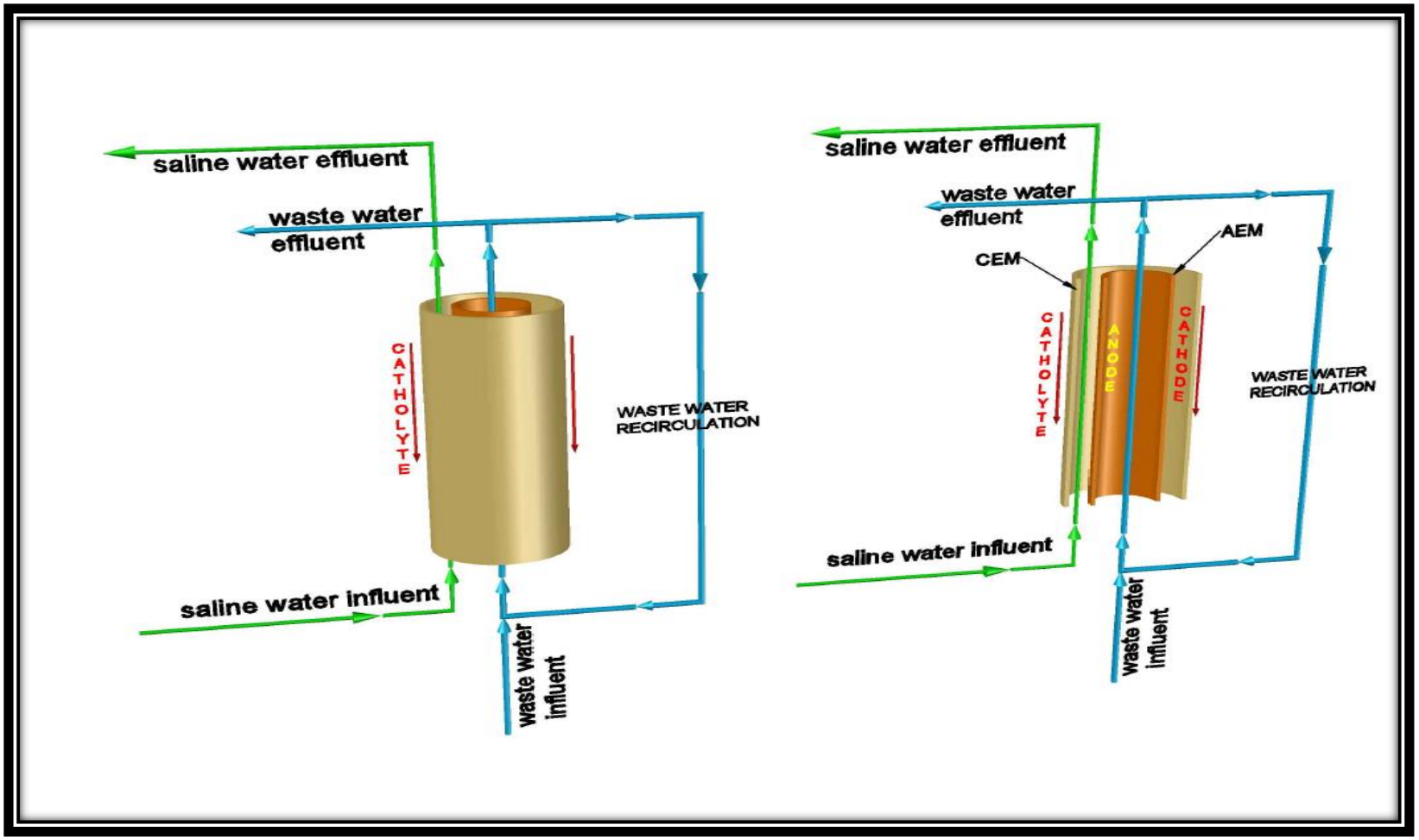


Figure 3.2: Schematic sketch illustrating MDC configuration.

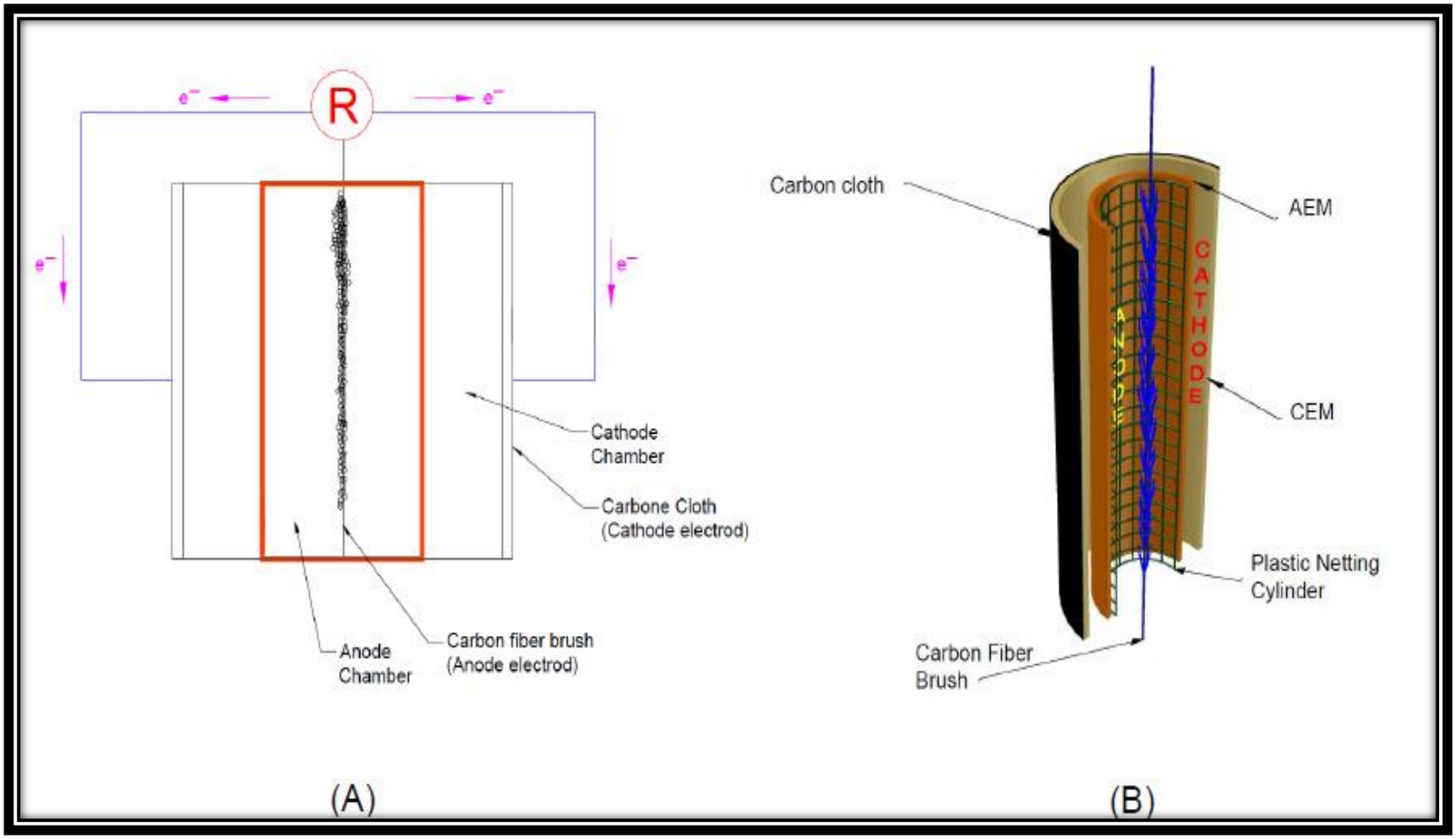
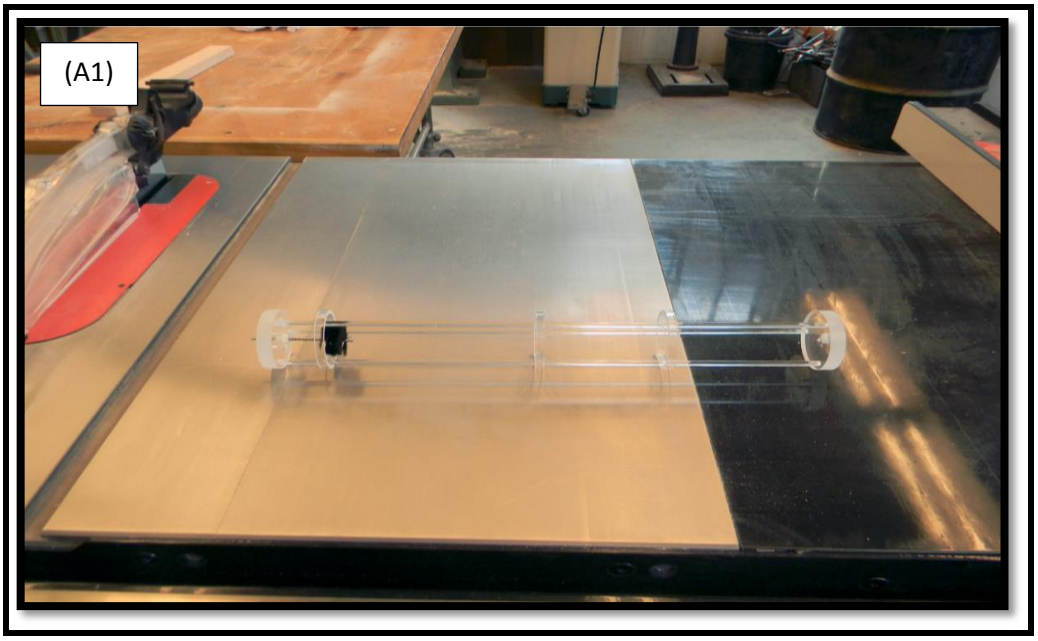


Figure 3.3: Schematic sketch illustrating MDC (A) electric circuit connections and (B) reactor components.



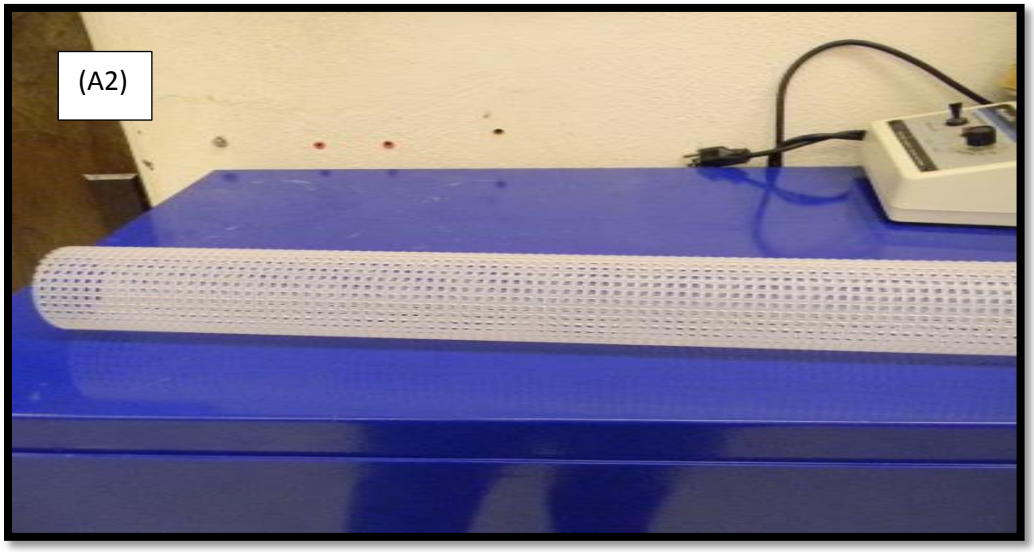


Figure 3.4: Photographs illustrated the stages of assembling the continuous upflow microbial desalination cell: (A1) 3 rods and 2 plastic rings for reactor support;(A2) the plastic support cylinder; (B) AEM membrane wrapped on the plastic tube; (C) CEM membrane wrapping the AEM membrane; (D) collecting catholyte pan.

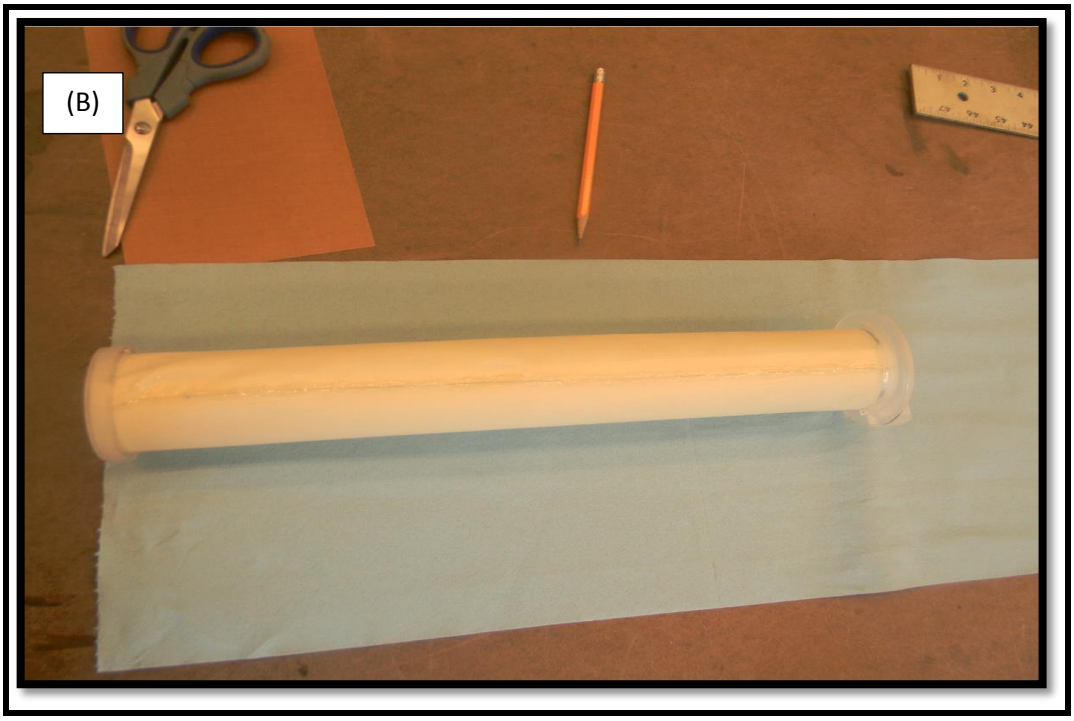


Figure 3.4 Continued

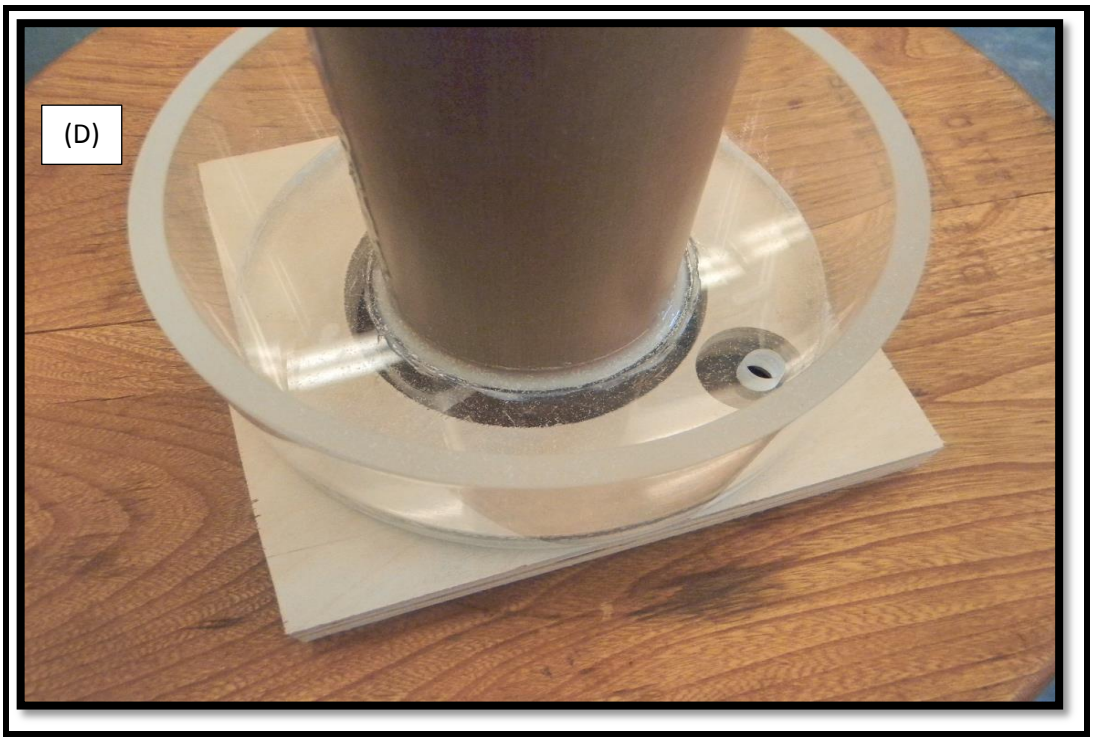


Figure 3.4 Continued

Biomass

Biomass used in the inoculation was collected from an industrial plant in Oklahoma City. Anaerobic bacteria in the biomass are pre- acclimated to carbohydrates. The inoculation process is described in the operation section.

Reagents

Solutions prepared for all experiments were made with reagent grade chemicals.

Synthetic wastewater

Sucrose was used to prepare the synthetic wastewater. 1.8 g/L of sucrose was dissolved in deionized water to prepare this synthetic wastewater (COD designed was 1200 mg/L). The

synthetic solution was buffered with 0.14 g/L potassium phosphate monobasic (KH_2PO_4) (Fisher Scientific, NJ), 2.45 g/L potassium phosphate dibasic (K_2HPO_4) (EMD, NJ) and 0.50 g/L sodium bicarbonate (EMD, NJ). 1 mL/ (L of synthetic wastewater) of 1 N sodium hydroxide (NaOH) (EMD, NJ) was added occasionally to adjust the anode pH. 1.5 mL/ (L of synthetic wastewater) of a trace element solution was added to the wastewater (Khandarker et al ,1995). The stock solution was autoclaved at 110^o C to eliminate both oxygen and bacterial growth to maintain pH inside the reactor between 6-8. Table 3.1 present the nutrient constituents added to the synthetic wastewater. Table 3.2 presents the constituents of the trace element solution used.

Table 3.1 Constituent of nutrient.

NH_4Cl	0.15g/L
NaCl	0.50g/L
$MgSO_4$	0.015g/L
$CaCl_2$	0.02g/L
Yeast extract	0.10g/L

Table 3.2 Constituent of trace element solution

$CoCl_2.6H_2O$	0.25 g/L
$FeCl_2.4H_2O$	2.00g/L
$MnCl_2.4H_2O$	0.05g/L
H_3BO_3	0.025g/L
$ZnCl_2$	0.025g/L
$NiCl_2.2H_2O$	0.025g/L
Na_2SeO_4	0.025g/L
$CuCl_2$	0.005g/L

Operating MDC

The reactor was operated in a continuous upflow mode all the time. At first the reactor was operated by inoculating the anode chamber with a mixture of carbohydrate's pre-acclimated anaerobic biomass (Industrial plant in OKC). The inoculation process with biomass helped developing a biofilm on the anode electrode. The inoculation proceeded for 3 cycles. Only in the beginning, of the inoculation, 10 mL of glucose (1.14 gm COD /L) plus 2 mL/L trace element solution was added to the biomass. The reactor operated in open circuit (OCV) and the voltage was recorded every 3 minutes and monitored so that when it drop below 0.1 V half of the biomass was discarded and replaced by fresh one. The content of the inner chamber of each reactor was circulated at 80 mL/min to avoid solid's settling. The step followed inoculation was feeding the bacteria with the synthetic wastewater. A peristaltic pump (Masterflex), (Cole Parmer, Chicago, II) was used to pump the wastewater with a flow rate of 1 mL/min (HRT 18.4 hrs.).

6 mM 2- bromoethanesulfonate (BES) inhibitor was added to one of the reactors (reactor 1) to inhibit methanogen bacteria (a structural analog of cofactor M which is involved in the final enzyme reaction of methane formation), (He, 2005).The wastewater effluent was discharged from the upper base port. The anode solution was recirculated at a flow rate of 80 ml/min to maintain a proper mixing (Zhang et al 2010). The saline water in the cathode chamber was prepared by dissolving 30 g/L Instant Ocean salt (an aquarium sea salt) (Instant Ocean United Pet Group, Blacksburg, VA) in deionized water and pumping into the reactor at a flow rate of 0.096 mL/min using a syringe pump (Harvard Apparatus, MA) (HRT 2.5 days). The ionic content of the Instant Ocean synthetic sea salt is shown in Table 3.3. Acidified water was used as a catholyte to rinse the cathode electrode. Composition of the acidified wash contains sulfuric acid diluted into deionized water. pH adjusted to 2.9 and the solution pumped with 3 mL/min using peristaltic pump (Masterflex), (Cole Parmer, Chicago, II).

Table 3.3 Composition of major ions of Instant Ocean synthetic sea salt.

Ion	Natural Seawater g/L	Instant Ocean g/L
Sodium (Na^{+})	10.781	10.78
Potassium (K^{+})	0.399	0.42
Magnesium (Mg^{++})	1.284	1.32
Calcium (Ca^{++})	0.4119	0.40
Strontium (Sr^{++})	0.00794	0.0088
Chloride (Cl^{-})	19.353	19.29
Sulfate (SO_4^{--})	2.712	2.66
Bicarbonate (HCO_3^{-})	0.126	0.20
Bromide (Br^{-})	0.0673	0.056
Boric Acid ($B(OH)_3$)	0.0257	
Fluoride (F^{-})	0.0013	0.001

PART B PROCEDURES AND MEASUREMENTS

Ion Chromatography

A Thermo Scientific Dionex ics-1100 was used to measure ion concentrations of the migrated ions in the reactor's chambers and those pumped into the reactor (APHA, 2005). Both anions and cations were measured although the emphasis was on major anions e.g. Cl- , PO4-3 and SO4-2.

Data Acquisition System

A data acquisition system (DAQ-Labjack, U12) was used to record reactor voltage. The connection and operation of the device is prescribed in the user's guide (Labjack User's Guide). Labjack U12 has 8 screw terminals for analog signals. The voltage range of the Labjack U12 is +/- 10 volt.

COD Measurements

Measuring the chemical oxygen demand COD was conducted with the aid of a spectrophometer (Hach DR/5000) (APHA, 2005). The device measuring range was 20 mg/l to 1500 mg/l. In all experiments, soluble COD was determined. The samples were filtered and diluted to the

appropriate dilution (1:20) before being transfer into the COD test tubes. The test tubes then heated in a digester at 110^{o}C for two hours, cooled and tested (Standard methods).

Total Dissolved Solid and Conductivity Measurements

The concentration of total dissolved solid was measured for the salt solution using the standard method. Samples were evaporated in a weighed dish at 103^{o}C until they dried then cooled in a desiccator and weighed again. Conductivity of the same samples was measured using conductivity meter (Fisher Scientific, NJ).

pH Measurements

Influent and effluent wastewater and salt water samples were collected for pH measurements daily. pH was measured using a pH meter (Accumet, Fisher Scientific, NJ).

Voltage, Currents and Power Measurements

A multimeter (Radioshack LCD NO. 22-182 auto range) was used to measure voltage, in addition to a data acquisition system board (LabJack, U12) that connected to a computer used to record voltage every 3 minutes. Power was calculated using the equation:

$$P = \frac{I^2}{R} \quad \text{..... (6)}$$

Where P is power in Watt, I is the current in ampere and R is the external load in ohm.

Coulombic Efficiency

Coulombic efficiency can be calculated by dividing output coulombs by coulombs input. Coulombs output is the electrons recovered and coulombs input is theoretical coulombs produced from the wastewater used. The following equations describe the above:

$$CE = \frac{C_p}{C_t} \times 100\% \quad \text{..... (7)}$$

$$C_p = \sum I \times t \quad \text{..... (8)}$$

$$C_t = \frac{96485\ (C/mol\ e^-) \times \Delta COD(gO_2/mL) \times W\left(\frac{mL}{min}\right) \times 4(mol\ e^-/O_2) \times t}{32\ (gO_2/mol\ O_2)} \quad \text{..... (9)}$$

Where CE is coulomb efficiency, C_p is the total coulombs, I is the average current generated in ampere A, t is time in minutes, C_t is the theoretical coulombs that can be produced from sugar wastewater, 96485 is Faraday's constant, ΔCOD is the consumed chemical oxygen demand in g/mL, 4 represents moles of electrons produced per mole of oxygen, W is anode flow rate in mL/min and finally 32 in the molecular weight of 1 mole of oxygen, (Liu, 2004).

Fouling Examination Using SEM

When all experiments were done, the MDC reactors were dissembled to collect random samples from both the AEM and CEM membrane for fouling examination using scanning electron microscope. The SEM was Zeiss Neon 40 EsB Cross Beam with an INCA Energy 250 Energy Dispersive X-ray Microanalysis system with Analytical Drift Detector. After autopsy, all samples were room dried and later coated with iridium before being scanned. 10 KV was the electron beam energy used to collect the spectra. A 100 second acquisition time was used to collect all the spectra. All samples were tested at OU scanning microscopy lab.

SECTION 2

MDC in Series, Construction and Operation

Two reactors were constructed same as previously described. Operating the MDC in series was done through hydraulically connecting the reactors. Inoculating for both anodes chambers was done with a mixture of pre acclimated anaerobic bacteria (same source of biomass) then pumping synthetic wastewater (sucrose) as (previously described) into the first reactor's anode chamber at a flow rate of 1.0 ml/min (with HRT of 18.4 hrs.) by peristaltic pump. The first reactor effluent then will be collected and pumped into the anode chamber of the second reactor at a flow rate of 1.0 mL/min. Each reactor's influent was circulated at 80 mL/min for better mixing and to avoid solids settling (Jacobson, 2011). For the cathode chambers, the first reactor receive untreated salt solution (≈ 26 g/L Instant Ocean sea salt dissolved in deionized water) pumped at 0.21 ml/min (HRT is 30 hrs.). The collected discharged effluent is then pumped into the second cathode chamber reactor at 0.21 ml/min (HRT is 30 hrs.) using a syringe pump. Both cathodes chambers were rinsed with acidified water (pH 2.9). External load of each reactor was set at10 ohm. Figures 3.5 and 3.6 illustrate MDCs in series set up and configuration respectively.

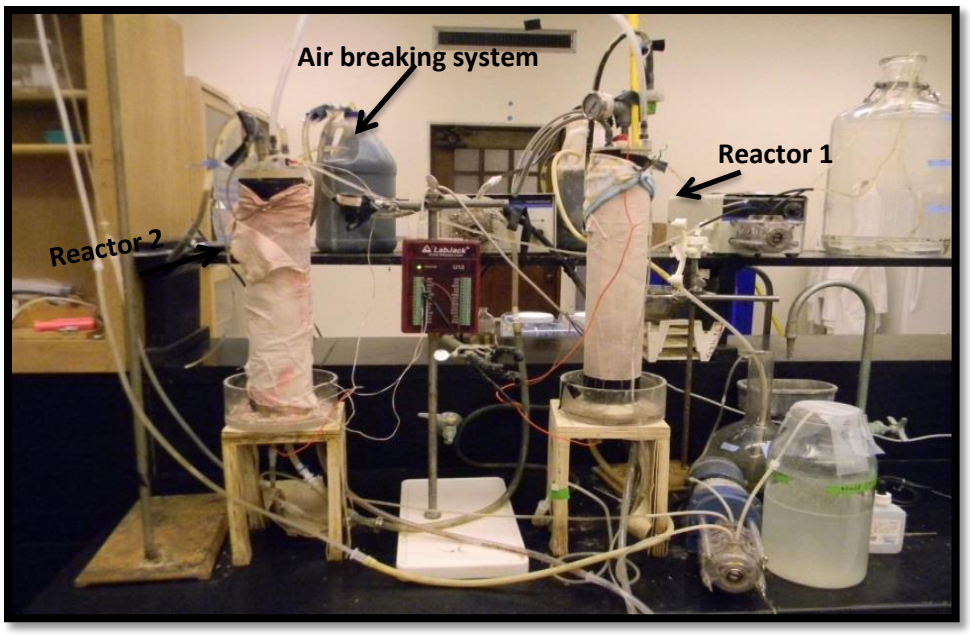


Fig 3.5 a photograph showing MDCs in series set up.

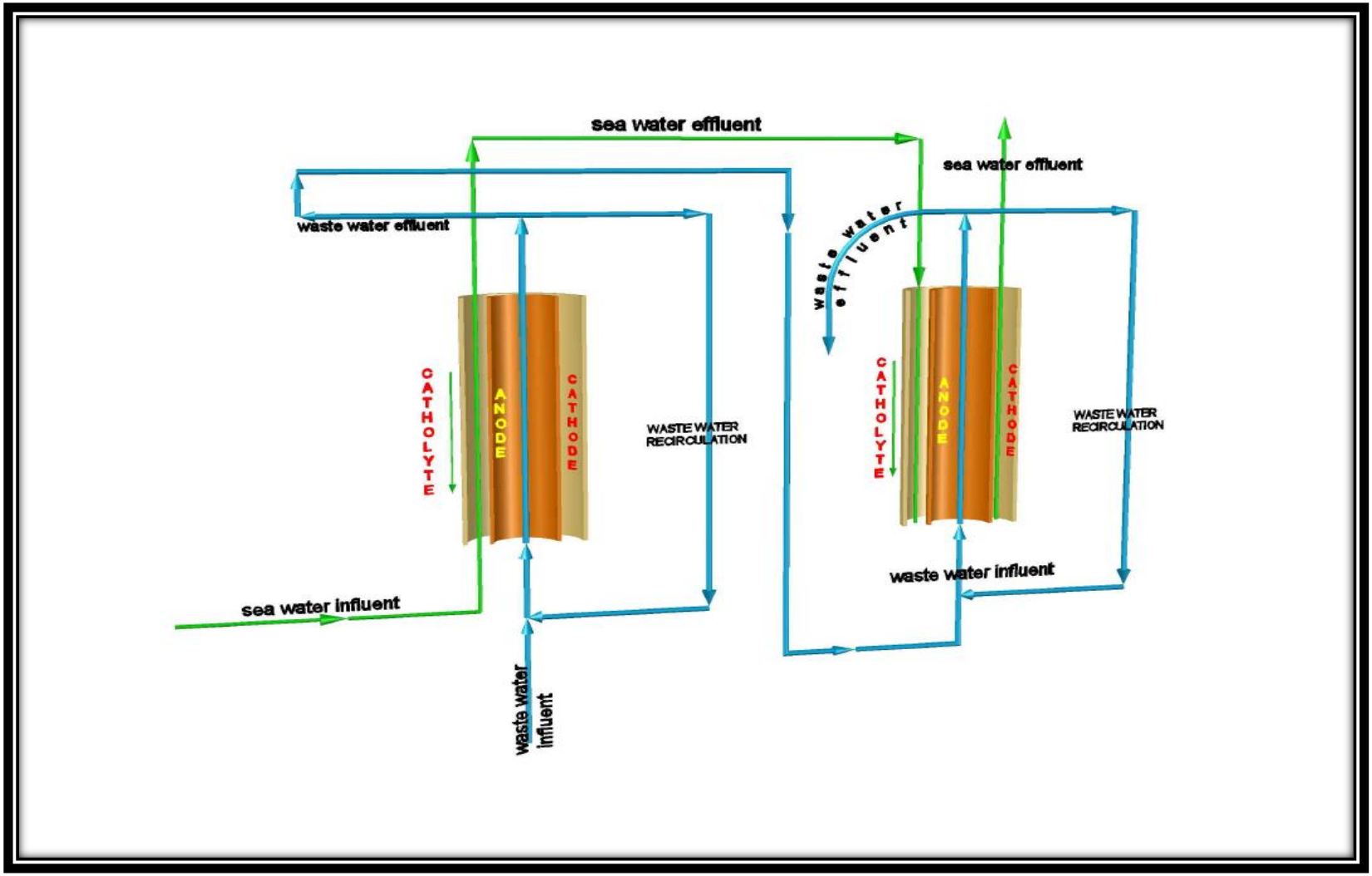


Figure 3.6: Schematic sketch illustrating MDC in series configurations.

CHAPTER IV

RESULTS AND DISCUSSION

Preliminary Experiment

Different air breaking systems were tested during MDC operation due to utilization of fermentable organic load and high anodic residence time. Such air breaking systems usage was not reported in literature because of the utilization of reduced substrate (acetate) and accordingly less residence time is required and less gas produced. The built up gases produced from breaking down organic applied pressure on the reactor's tubing that led to disconnection of the tubing joints. To overcome this problem, the recirculated anodic solution was collected in a 2L sealed bottle before being pumped to the reactor. The bottle size volume was larger than the reactor volume to maintain enough space for the gas phase of the recirculated solution. Figure 3.5 shows a photograph for the reactors set up including the air breaking system discussed above.

Reactors Electricity Generation Results

Two main experiments will be reported in the work, experiment one and experiment two. In experiment one, two reactors were used and both reactors were constructed and individually operated as previously described. 6 mM bromoethansulfonate was added to reactor (1). No methanogens inhibitor was added to reactor (2) since it was used as a controller.

In experiment two, a new reactor was built and the controller reactor (reactor 2 in the first experiment) was used as the lead reactor (reactor 1) in the second experiment. The two reactors were connected hydraulically is series.

The first experiment started with inoculating the two reactors (the lead reactor R1 and the controller reactor R2) with biomass (from Industrial wastewater) which has bacteria preacclimated to sugar wastewater. The reason to operate two reactors was to evaluate reactor's performance with a 6 mM BES inhibitor and without the inhibitor. The inoculation proceeded for 30 days, with the measured biomass COD to be approximately 5450 mg/L.

The reactors were operated in an open circuit. Voltage generated from electrodes potential was recorded every 180 second for both reactors using data acquisition system. Figure 4.1 presents the recorded voltage.

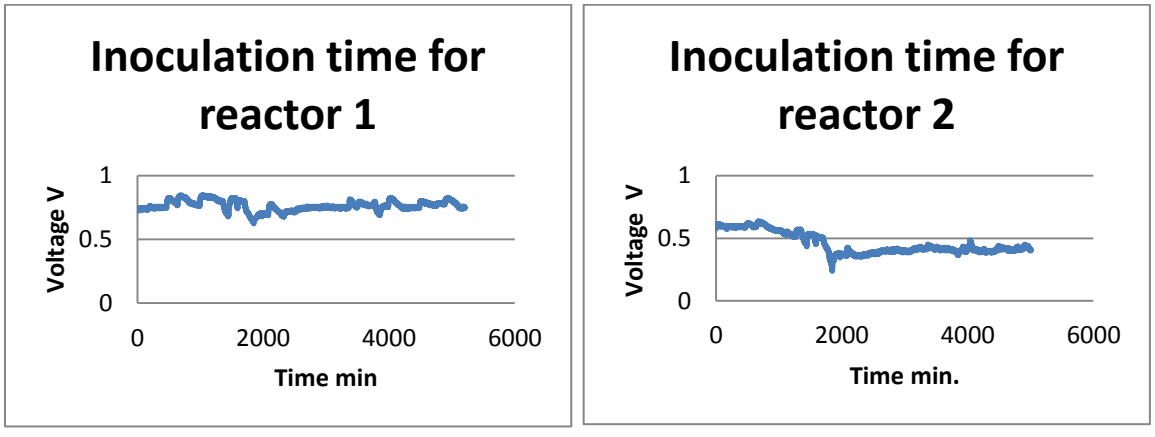


Figure 4.1 Voltage recorded for reactor 1 and reactor 2 during inoculation.

Inoculation helps in generating biofilm on the anode electrode (refer to Figure 2.1). When the biofilm is robust, electrons produced by exoelectrogenic bacteria will be enabled to transfer through the circuit into the cathode electrode. The reactors then were operated in a continuous mode and fed with synthetic sucrose wastewater at a loading rate of 1.63 g COD/L/day and a flow rate of 1.0 ml/min. The external electric load was set with a 1000 Ω resistor and reduced gradually (1000Ω for 2 days, 500 Ω for 2 days, 350 Ω for 2 days, and 100 Ω for 2 days and 50 for 2 days) to 10 Ω for the rest of the experiment. The reactors were producing electricity continuously, as shown in Figure 4.2 and 4.3.

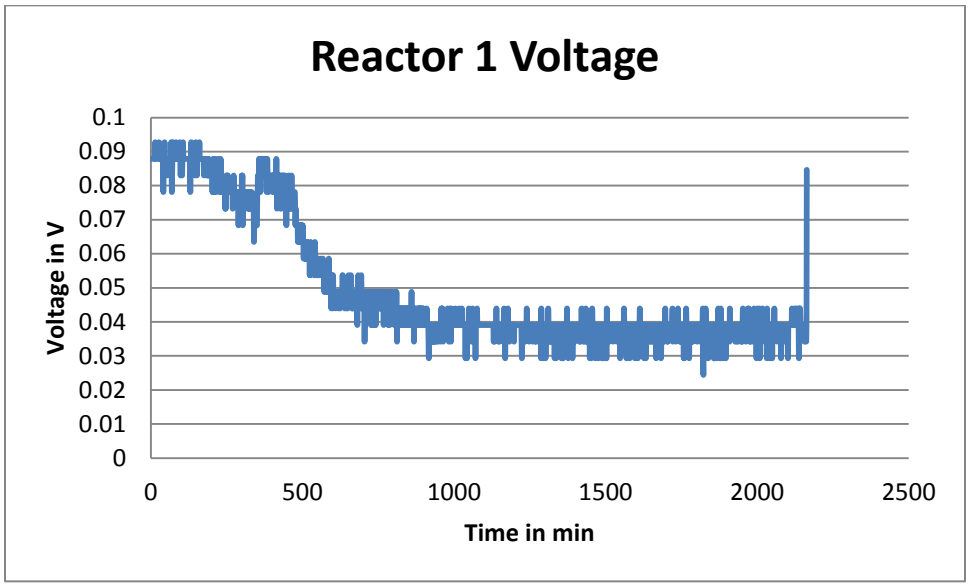


Figure 4.2 Voltage recorded for reactor 1 during normal operation (external load 10 Ω at time 0).

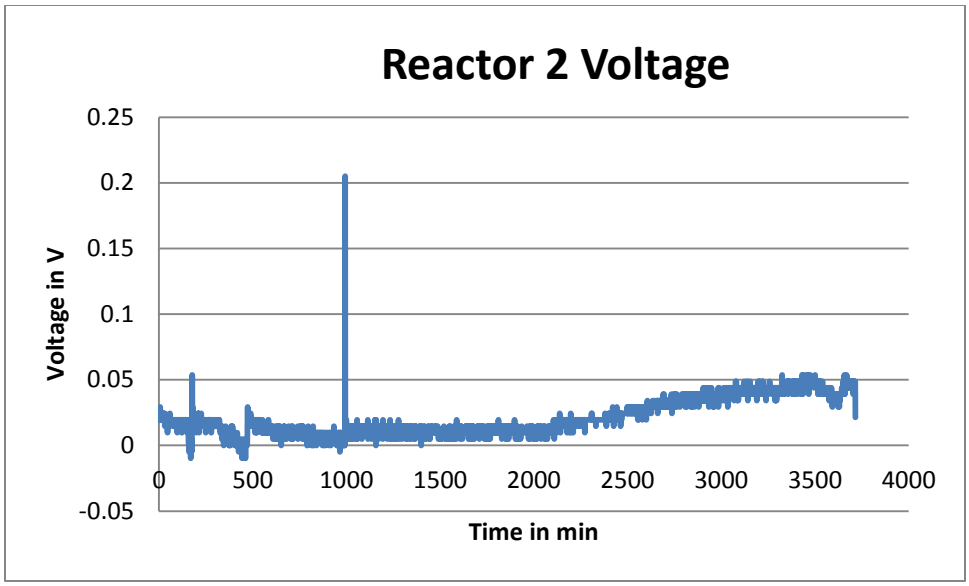


Figure 4.3 Voltage recorded for reactor 2 during normal operation (external load 10 Ω at time 0).

% SCOD Removal Results and pH Measurements

The results of the chemical oxygen demand removal for the two reactors used in the experiment varied according to the addition of BES inhibitor. When using BES inhibitor, only methanogen bacteria that aid in breaking down the sucrose were disrupted and the percentage SCOD removal dropped. Maximum SCOD removal was measured to be 64.9 ± 9.7% for the reactor without inhibitor and to be 55.2 ± 7% for the reactor with BES inhibitor. BES inhibitor is used to increase the cell power generation and to prevent methane accumulation (Kim, 2006; He, 2005). Figure 4.4 shows % SCOD removal of the two reactors in operation.

Measurements of pH were conducted daily on both wastewater and saline water influent and effluent. Maintaining pH at 6 to 7 in the anode chamber was essential to ensure a better bacterial functioning (Jacobson, 2011). Phosphate buffer along with sodium bicarbonate works well to maintain pH close to neutral (Metcalf and Eddy, 2003). The saline water effluent pH dropped

during operation time due to uncontrolled accumulations of protons. Inefficient cathodic reduction due to low current generation and the use of water proof cathode electrode could be the reasons behind this pH decrease. Table 4.1 shows pH measurements for the two reactors in operation.

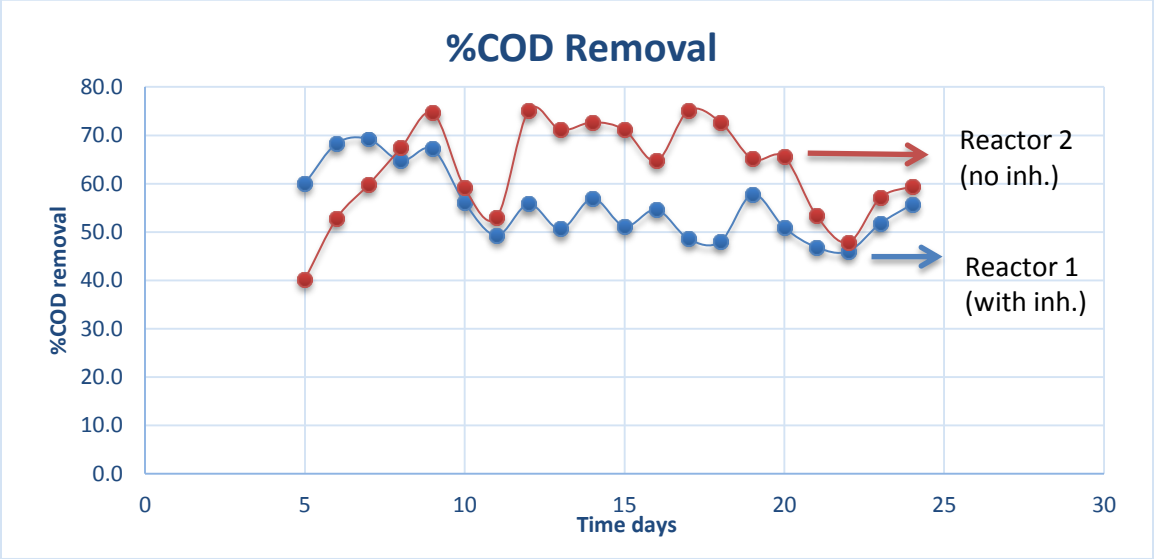


Figure 4.4: % SCOD removal of reactor 1 (with BES inhibitor), and reactor 2 (without inhibitor).

Table 4.1 pH measurements of both the anode and cathode influent and effluent. (Symbols descriptions are given earlier).

Days	pH SWE1	pH SWE2	pH SWI	pH WWE1	pH WWE2	pH WWI1	pH WWI2
1	7.91	7.42	8.21	7	6.74	8.17	8.7
2	6.9	6.42				8.2	8.56
3				6.79	6.25	8.14	8.54
4	7.15	7.24		6.8	6.3	8.2	8.57
5				6.64	6.05	8.22	8.52
6	7.12	7.12		6.48	6.11	8.16	8.54
7	7.04	7		6.08	6.06	8.26	8.35
8	7.02	5.33		6.63	6.02	8.13	8.23
9	6.9	6.81		6.53	5.94		
10	5.36	6.44		6.53	6	8.05	8.52
11	6.61	2.32		6.69	6.14	8.3	8.7
12	6.87	2.1				8.27	8.5
13	6.83	2.09		6.8	6	8.22	8.54
14	7	2.18		6.79	6.09	8.34	8.68
15	7.11	2.15				8.14	8.54
16	7.15	2.01	8.1	6.6	5.74	8.14	8.49
17	7.07	1.95	8.64	6.48	5.35	8.12	8.5
18	7.2	2.08				8.17	8.48
19	6.91	2.01		6.53	4.65	8.13	8.42
20	2.07	4.03		6.56	6	8.2	8.56
21	2.39	4.8	8.64	6.4	6.22	8.1	8.6
22	2.56	3.11		6.28	6.28	8.3	8.45
23	2.94	4.86		6.3	6.25	8.2	8.5
24	4.54	6		6.34	6.27	8.11	8.39

Total Dissolved Solid Removal and Anions Mass Transport Results

The microbial desalination cells were operated for 2 months (including the inoculation period) with both cells continuously producing electricity and reducing salinity while breaking down organic wastewater. The HRT of the cathode chamber was set to 2.5 days. TDS concentration dropped from 28 g/L to 7.7 g/L (71% max TDS removal) and 9.8 g/L (64% maximum TDS removal) for reactor with inhibitor and reactor without inhibitor, respectively. Figure 4.5 presents

the percentage salt removal of the reactor with inhibitor and the one without inhibitor, respectively. Conductivity was measured and the collected data was consistent with that of % TDS removal of both reactors. Figure 4.6 shows the conductivity measurements for both reactors.

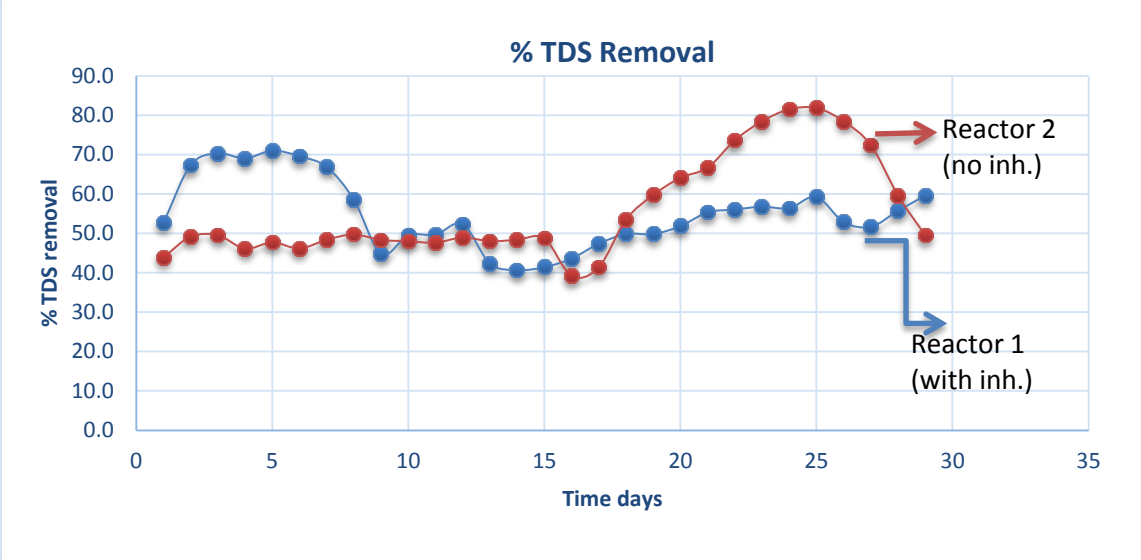


Figure 4.5: % TDS removal of reactor 1 (with BES inhibitor), and reactor 2 (without inhibitor).

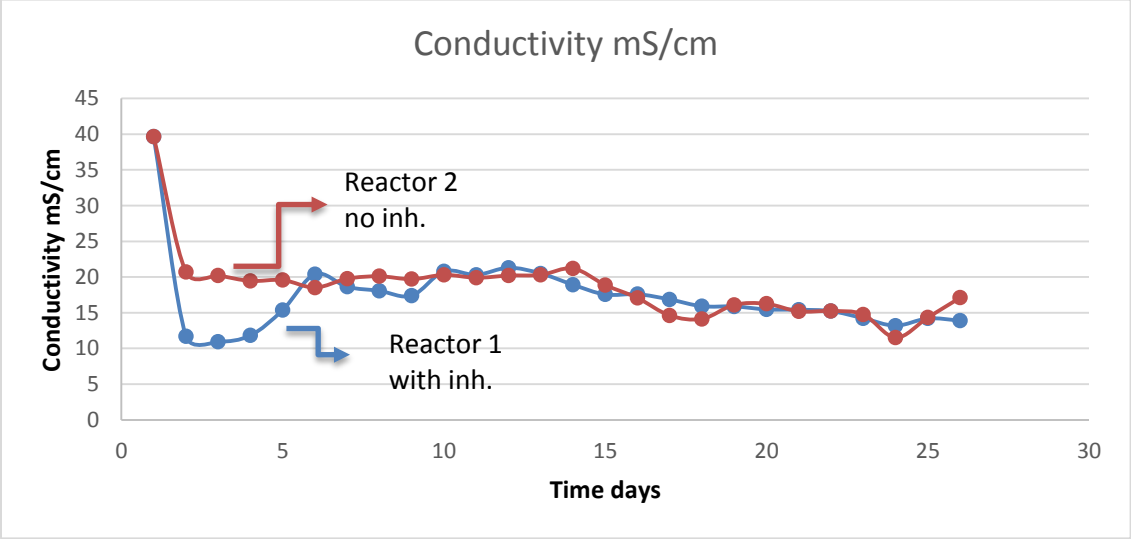


Figure 4.6: Conductivity measurements of reactor 1 (with BES inhibitor), and reactor 2 (without inhibitor).

For anions movement across the membranes, ion chromatography Figure 4.7 presents this migration for reactor 1 and data for reactor 2 is in the appendix.

Experiment 1 Discussion

The addition of BES inhibitor to deactivate methanogens in the MDC anode compartment had an impact on reactor performance in terms of %SCOD removal and power. The soluble COD removal rate dropped by 15% (from 64.9 %to 55.2%) as the methanogens activities was inhibited. Such drop suggested that methanogens compete for electrons (substrate) whenever excess food is available. An average of 64.9% SCOD (HRT 18.4 hours and the loading rate was 1.6 g COD /L/day) was removed from reactor 2 (without inhibitor) while the highest %SCOD removal rate reported was 90% (HRT 1 day and loading rate 2 g COD/L/day). He (2005) suggested the percentage COD removal can be increased with increasing the volumetric loading rate (He, 2005).

Addition of BES to inhibit methanogens increased the power density in reactor 1 (with inhibitor) by 23.4% at early stage (6.4 mW/cm^3 is reactor 1 power density, and 1.5 mW/cm^3 is reactor 2 power density) and after that the performance of both reactors were similar for no identified reason. The presence of methanogens and the competition with anodophilic bacteria on substrate can interfere with the reactor maximum equivalent electron transfer rate based on the operation loading rate causing reduction in power. In a full scale reactor, inhibition of methanogens can be achieved through periodic aeration (He, 2005).

In a separate experiment, it was found that 43% TDS (initial concentration was 29.9 g/L reduced to 16.9 g/L) removed in an open circuit condition. This reduction was possibly due to water osmosis from anode chamber, due to a concentration gradient to the cathode. This finding was consistent with Jacobson (2011). Maximum total dissolved solid reduction for the reactor with

BES inhibitor measured to be 71% (approximately 27.5 g/L initial concentration dropped to 7.7 g/L) while for reactor 2 (without inhibitor), the maximum TDS reduction was 48.7%. Although at certain times of the experiment, a higher TDS reduction was measured (81.8%) which can be explained due to bipolar electrodialysis. Or in another wards, water dissociation caused by the presence of bipolar membranes (cation and anion exchange membranes) could drive this bipolar process, (Jacobson, 2011). Also less cathodic reaction to consume excess protons leads to protons accumulation in the cathode compartment (Table 4.1). No reduction in conductivity was observed (Figure 4.6).

pH of the anodes chamber were maintained above 6 (6.58± 0.23 reactor with BES and 6.17±0.42 reactor without BES inhibitor) while originally being 8.52± 0.11. The addition of sodium carbonate $NaHCO_3$ plus the phosphate buffer and adjust the pH of feedstock solution with 2 mL of 1N NaOH whenever the pH measured below six helped in this regard, Table 4.1.

Relocating and/or precipitating of anions from the cathode compartment into the anode compartment are shown in Figures 4.7 and in elemental map in Figure 4.9. 70% of Cl^- was removed from the cathode compartment but only 30% were recovered in the anode compartment effluent and the rest precipitated on the AME membrane (Figure 4.9). Same for the sulfate, 62% removed from saline influent in the cathode compartment and only 17% were recovered in the anode compartment effluent and the rest precipitated on AEM membrane. This might be explained due to back diffusion of anions due to low current produced and the concentration gradient between the anode and the cathode compartment (Jacobson, 2011). Cations concentrations were not determined through the experiment but Energy Dispersive X-ray (EDS) spectrum analysis conducted at the end of all experiments illustrated Ca^+, Mg^+ and Na^+ precipitation on both AEM (saline water side) and CEM membrane as shown in Figure 4.8 (SEM images of AEM and CEM) and Figure 4.9 (the elemental map of the anions and cations).

In general, may factors could contribute to generate electricity and reducing TDS in MDC. Such factors include residence time of saline water in cathode compartment and wastewater in the anode compartment. Increasing HRT will allow more saline water to be involved in current generation (Jacobson, 2011). The volume of the anode to the volume of the cathode was (3.1:1). The larger this ratio the better reactor performance in terms of sufficient substrate flow and less salt will transfer away from the anode due to higher flux (Jacobson, 2011, Cao, 2009). Organic loading rate also played a role in current generation. MDC can perform best only with low organic loading rate. He (2005) demonstrated that increasing COD loading rate up to 2 g COD /L/day will produced the highest power density, after which no further increase will occur.

Long term operation can cause deterioration in MDCs performance in terms of biofouling and ions precipitation (two limiting factors that also enhanced by low current generation) (Jacobson, 2011, Luo, 2012). Such deterioration could be avoided through optimizing loading rate and MDCs configuration modification.

Last but not least the type of substrate is important. Reduced substrates like acetate are the key substrate for bioelectrochemical reactors (Logan, 2006). Fermentable feedstock such as sucrose, glucose and other complex substrates will not be used directly by bacteria to produce energy (releasing electrons) but instead bacteria will ferment these complex substrates to acetate to gain more energy from fermentation than that from producing electricity since the oxidation of acetate is at energy level of 0.289 V when it is solely used as substrate, while oxidation of glucose e.g. is at energy level of 0.429 V (Hubertus et. al., 2010). This explains the reason why less energy is produced from complex substrates than that from readily degradable like acetate.

Effect of Long Term Operation on MDC Membranes integrity with the aid of SEM

Long term operation of MDC reactor (e.g. one year continuous operation) has a serious effect on membranes in terms of biofouling and scaling. Examining the dissected membranes using a scanning electron microscopy (SEM) along with elemental analysis showed severe biofouling and scaling (Figure 4.8 and Figure 4.9). Evidences of biofouling and scaling of AEM membrane were revealed first through SEM image as for example in (Figure 4.8 B) which showing a plated like layer covering the membrane and second through accumulations of several elements like for example phosphorous, sodium, sulfur and silica which were accumulated on the membrane side facing bacteria (Figure 4.9 C) also the disappearance of fluorine; one of the intrinsic elements of the membrane revealed in (Figure 4.9 C). Also when comparing elemental maps in Figure 4.9 (A) and Figure 4.9 (C) we observed an approximate of 10% increase in percentage weight of other intrinsic elements like oxygen, carbon and chloride. All these finding of SEM images and EDS elemental map support hypothesis of biofouling. On the other side of the AEM membrane flint-like structures were shown in the SEM images e.g. Figure 4.8 (C). The composition of these aggregate elements was oxygen, fluorine, carbon, sodium, magnesium, calcium, potassium, silica and chloride (Figure 4.9 D). For the used CEM membrane, the aggregation on the membrane side facing the saline solution was limited. Sulfur increased by two folds (Figure 4.9 B and E) and calcium and magnesium were found on the CEM side facing saline water (Figure 4.9 E). Divalent cations such as calcium and magnesium with large radius (Ca^{+2} has 0.349 nm, Mg^{+2} has 0.429 nm) (Luo, 2012) will be hindered to transfer through CEM due to their size and such multivalent cations will complex with anions and precipitate on the membrane rather than being transferred (Luo, 2012). What was revealed from SEM images and EDS analysis was consistent to some extent with Lou et al. (2012) due to different configuration of their MDC reactor that was composed of three compartments with the desalination compartment located in the middle.

In general, the AEM membrane seemed to be affected significantly with long term operation through biofouling of the bacterial side face and scaling of the opposite side while the CEM has minor scaling fouling. This can be explained due to nature of the solution in the anode (bacterial stream) and the cathode (saline stream inside the chamber and acid wash of outer wall surface) chambers and the overall performance of the reactor during operation period.

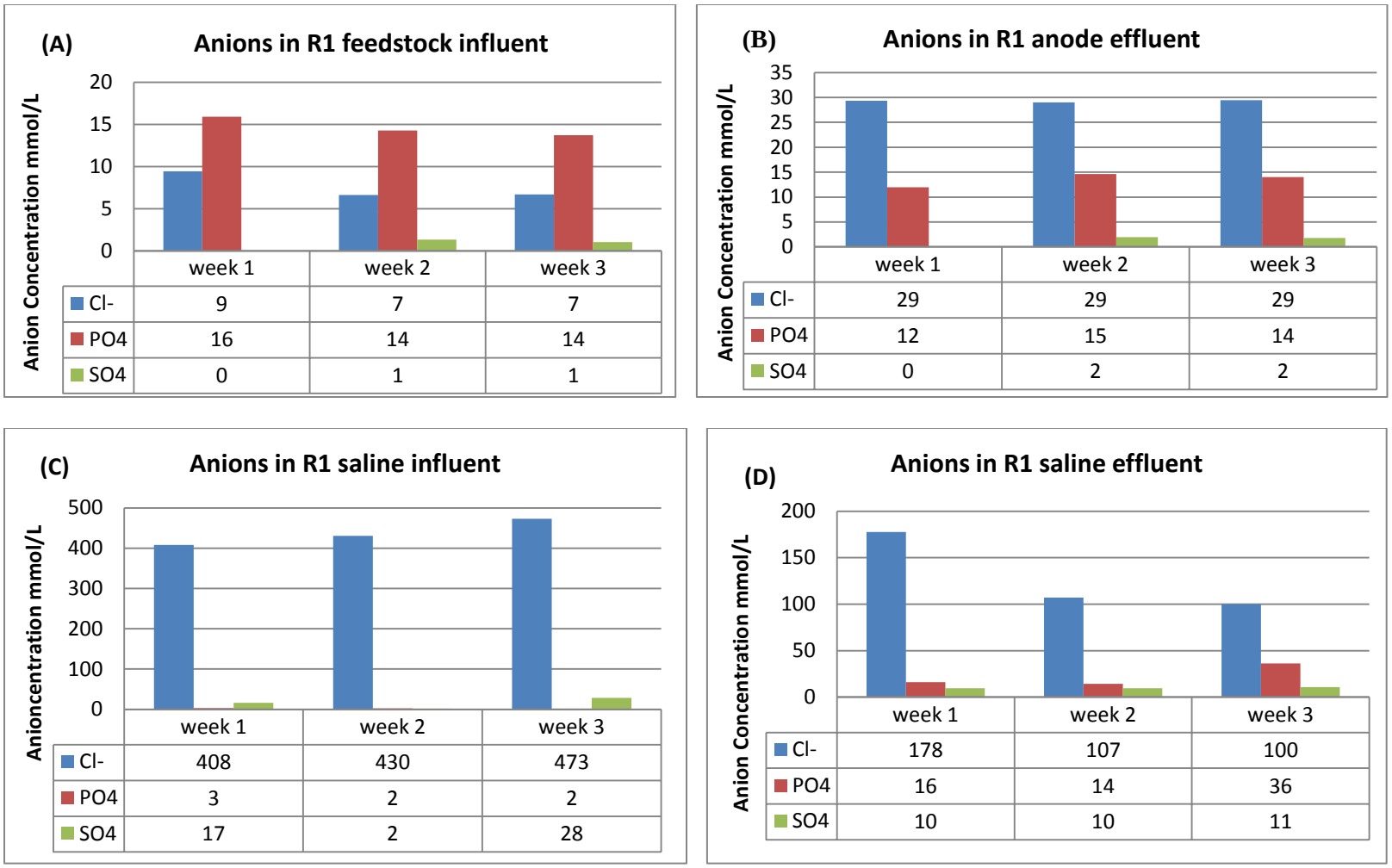


Figure 4.7 Anions concentration in mmole/L in measured for three weeks: (A) feedstock influent of reactor 1; (B) wastewater effluent of reactor 1; (C) saline water influent of reactor 1 and (D) saline water effluent of reactor 1.

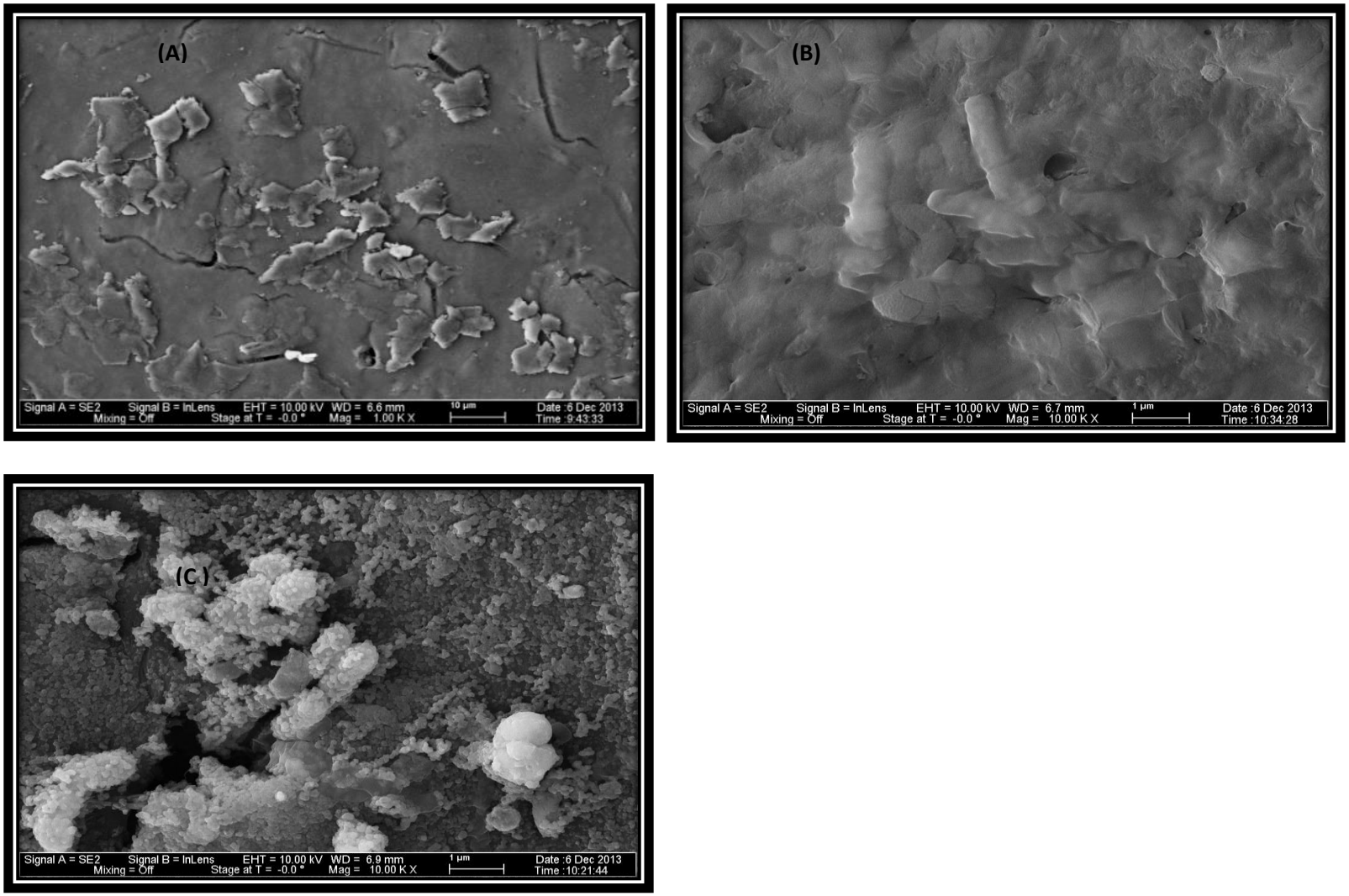
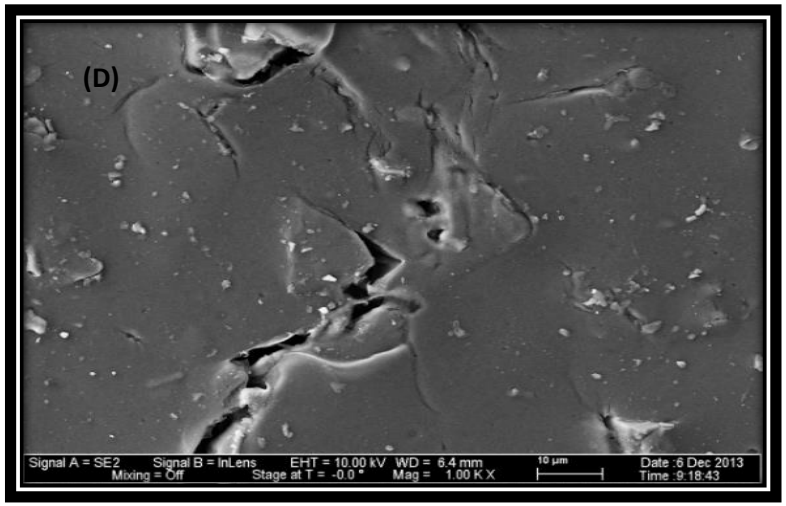
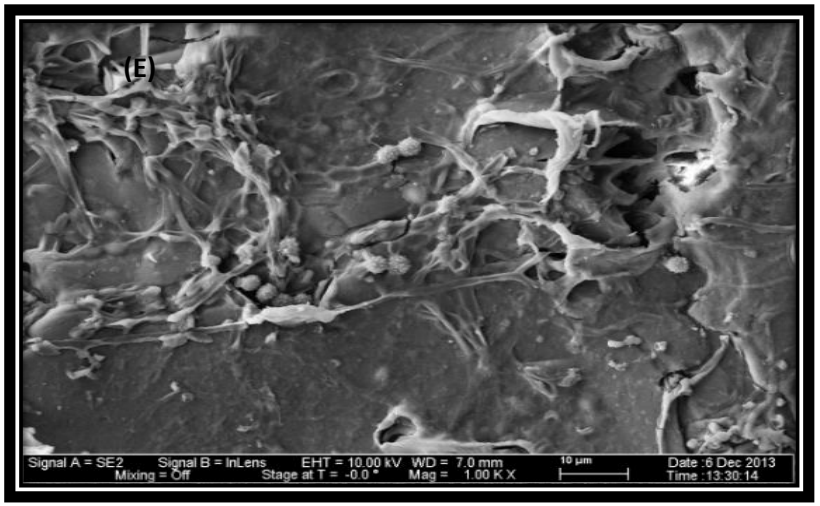


Figure 4.8 SEM images showing the surface of ion exchange membranes: (A) fresh AEM membrane; (B) Bacterial side of AEM; (C) saline water side of AEM; (D) fresh CEM membrane; (E) saline water side of CEM; (F) opposite side of CEM.





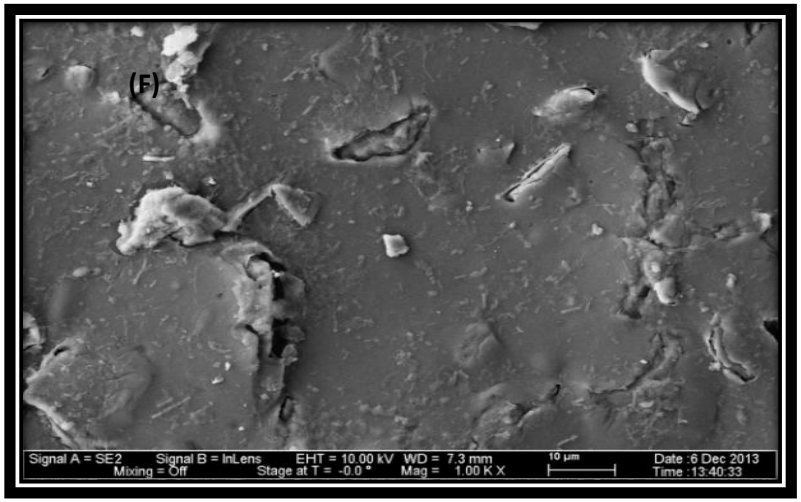


Figure 4.8 Continued

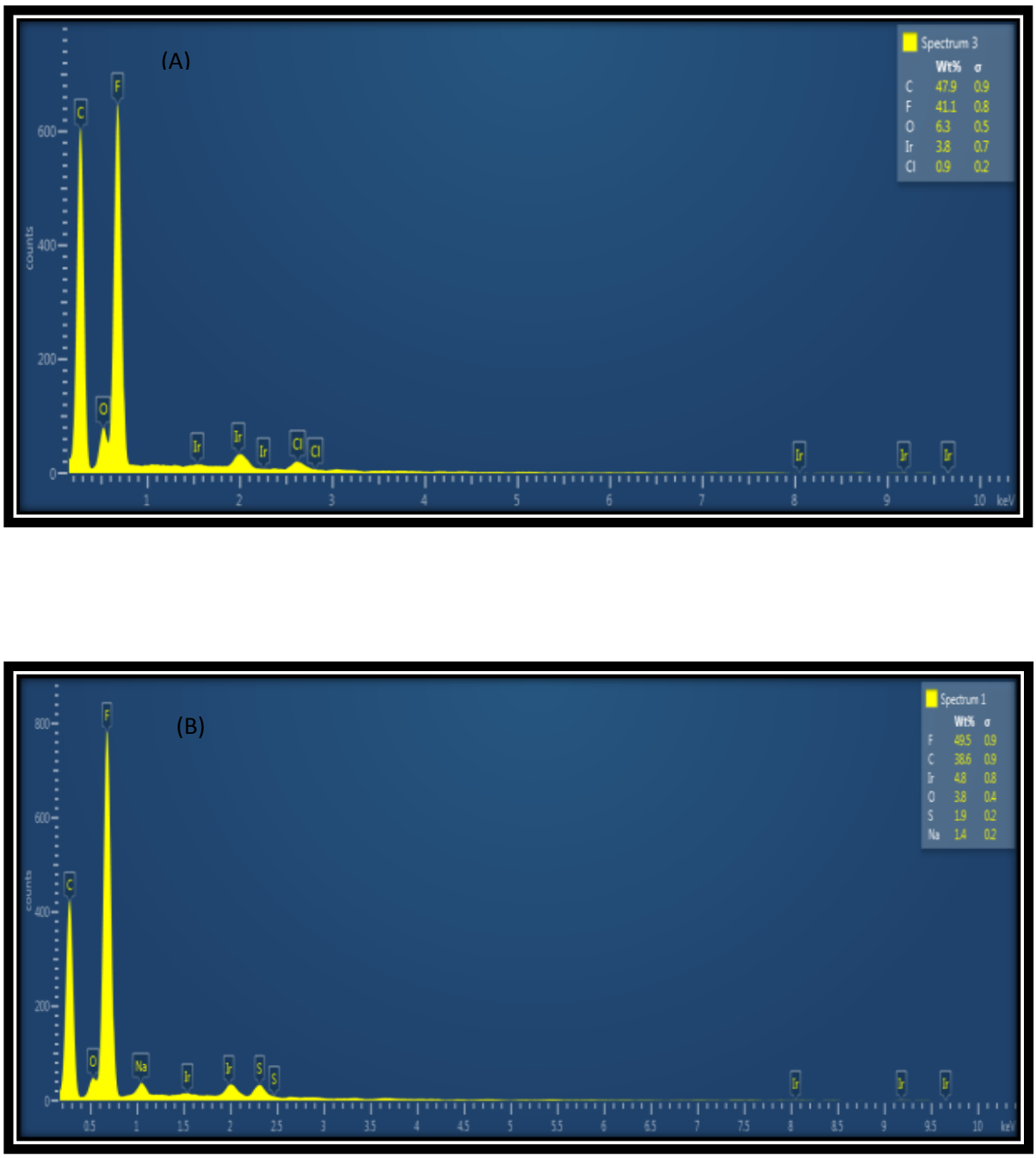
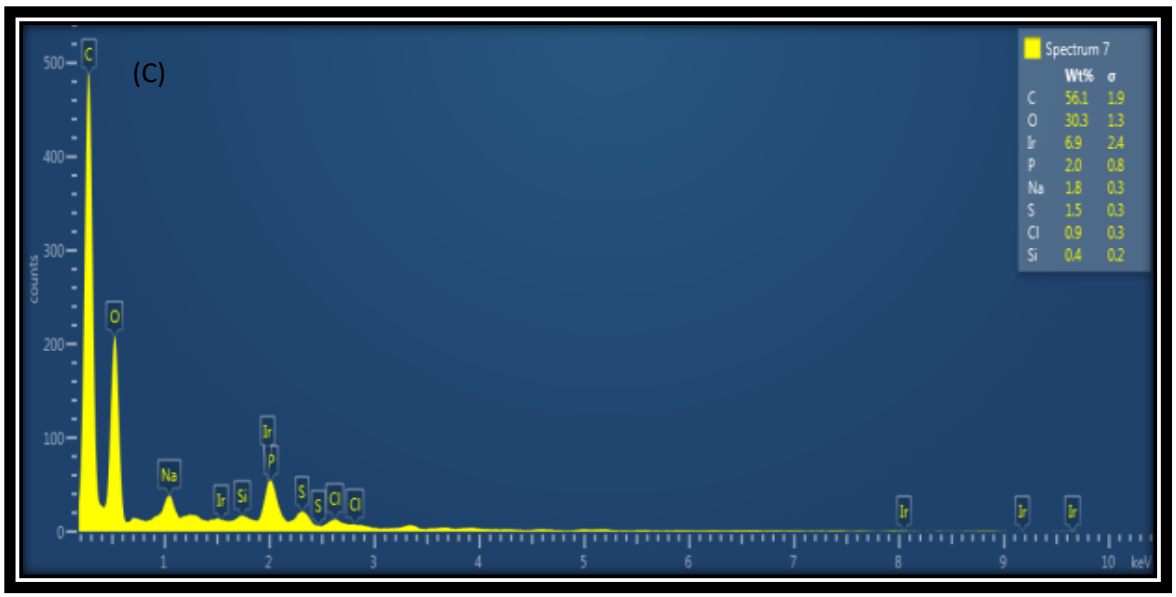


Figure 4.9 Elemental maps of the ion exchange membranes: (A) unused AEM membrane; (B) unused CEM membrane; (C) bacterial side of AEM; (D) saline water side of AEM; (E) saline water side of CEM; (F) opposite side of the CEM membrane.



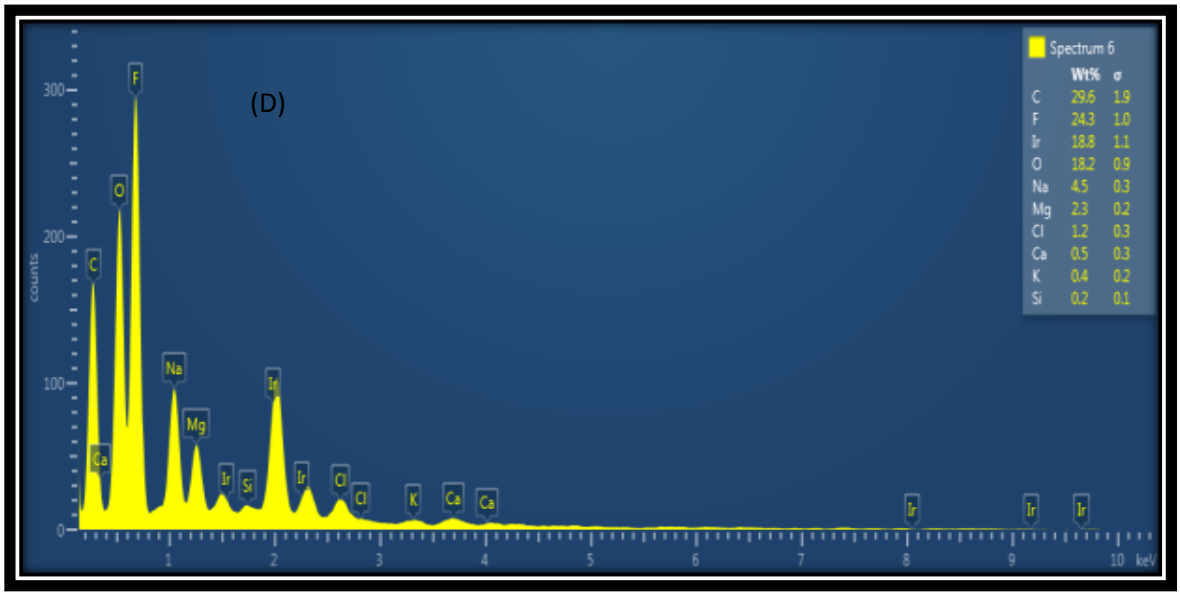
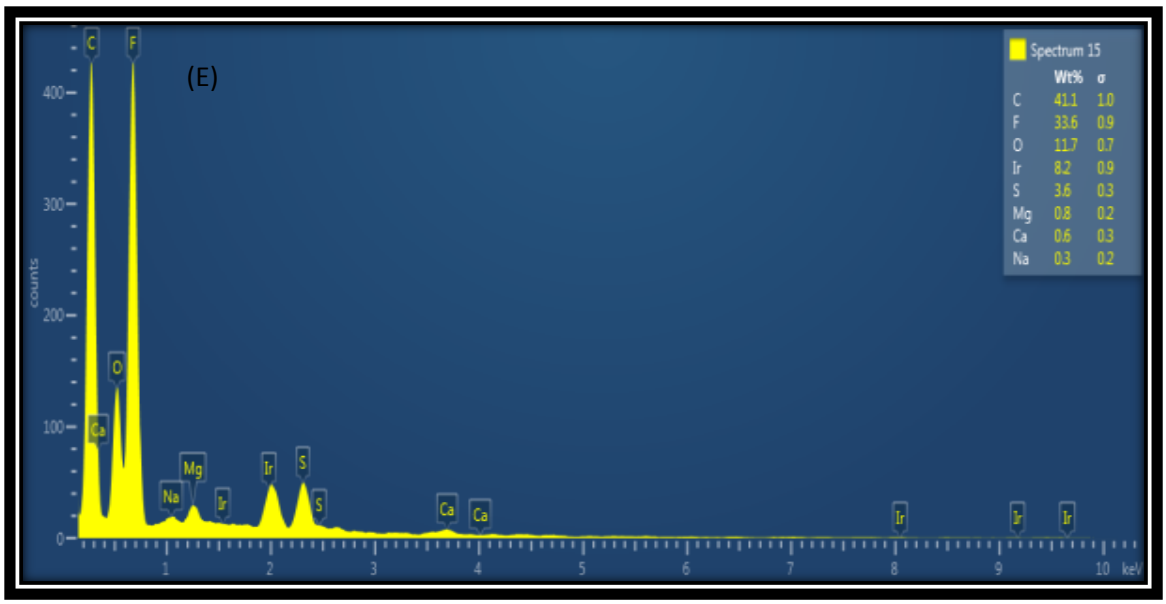


Figure 4.9 Continued



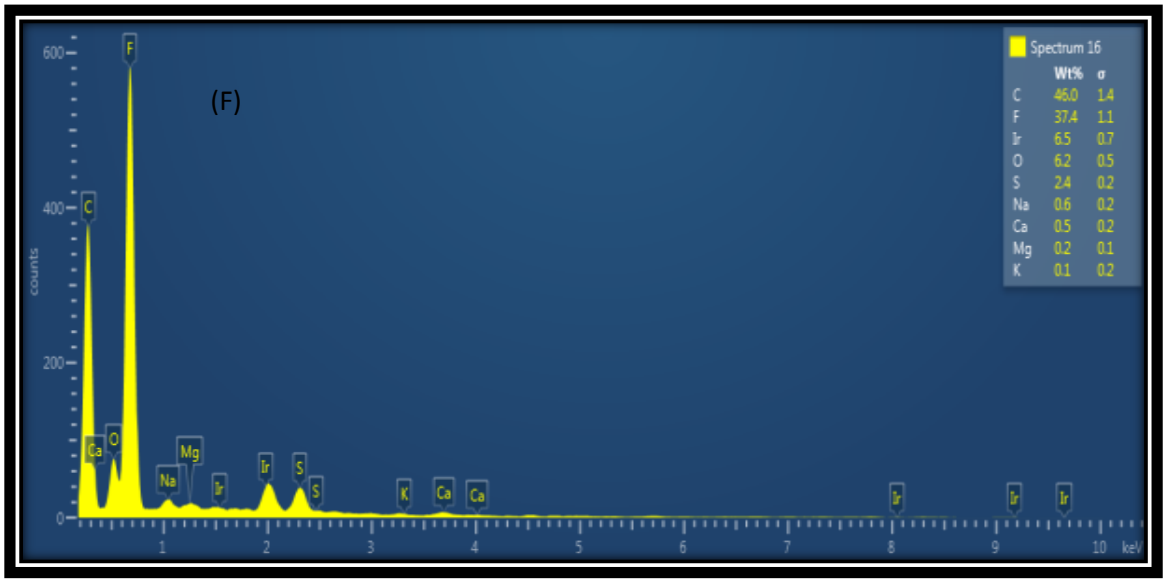


Figure 4.9 Continued

Reactors in Series Electricity Generation Results

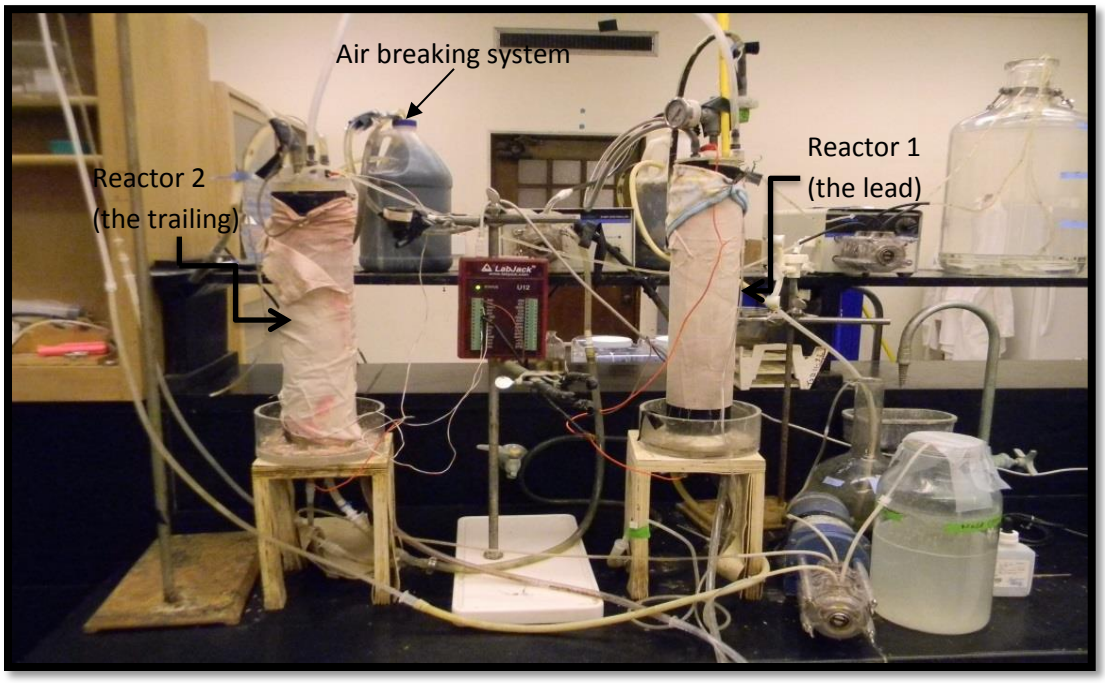
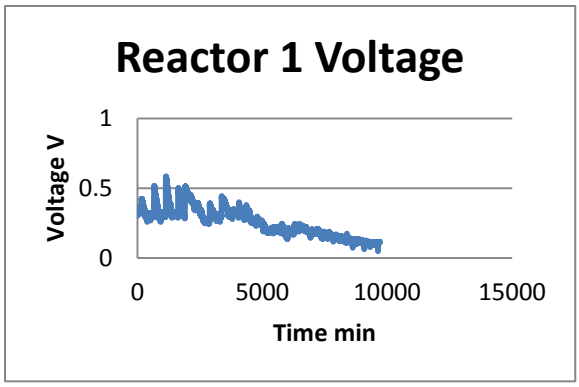


Figure 3.5: Reactors connected hydraulically is series set up.

The second experiment started by connecting two reactors hydraulically in series. One of the reactors was already in operation (reactor 1) while the second reactor was newly built. The inoculation process of the new reactor was conducted as prescribed earlier in Experiment 1. Same source of bacteria was used for inoculation (industrial wastewater). Both wastewater and saline water effluent streams produced in first reactor were considered as influent for the second reactor. Electrically, the two reactors were individually connected to one external load of 10 Ω during the entire experiment time and to the circuit. The voltage was recorded every 3 minutes using data acquisition system (LabJack) and the results are presented in Figure 4.10.



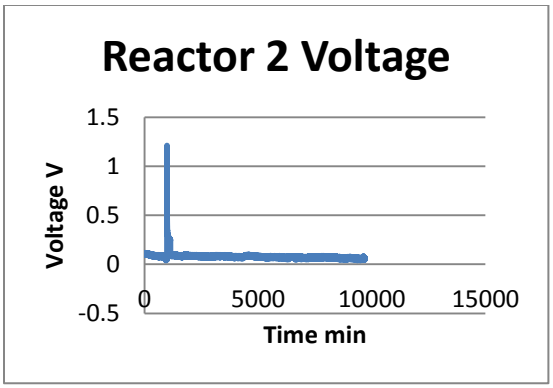


Figure: 4.10 Voltage recorded for reactor 1 and reactor 2 during normal operation (external load 10 Ω).

% SCOD Removal and pH for Reactors in Series

Soluble chemical oxygen demand measurements indicated better removal when connecting two reactors in series. 64.3 % ± 4.3 of organics were removed just in the first unit plus an extra removal of 7.9% ± 13.5 in the second reactor. The competition for carbon between methanogen and anodophilic bacteria was more intense in the second reactor due to reduction in the loading rate and the presence of volatile fatty acid as fermentation end products after predegradation in the first unit. Main volatile fatty acids reported produced from fermenting sucrose are acetate and propionate and a low level of butyrate (He, 2005). Figure 4.11 illustrate the percentage of COD removed in first reactor. Appendix A has all the COD measurements of both reactors.

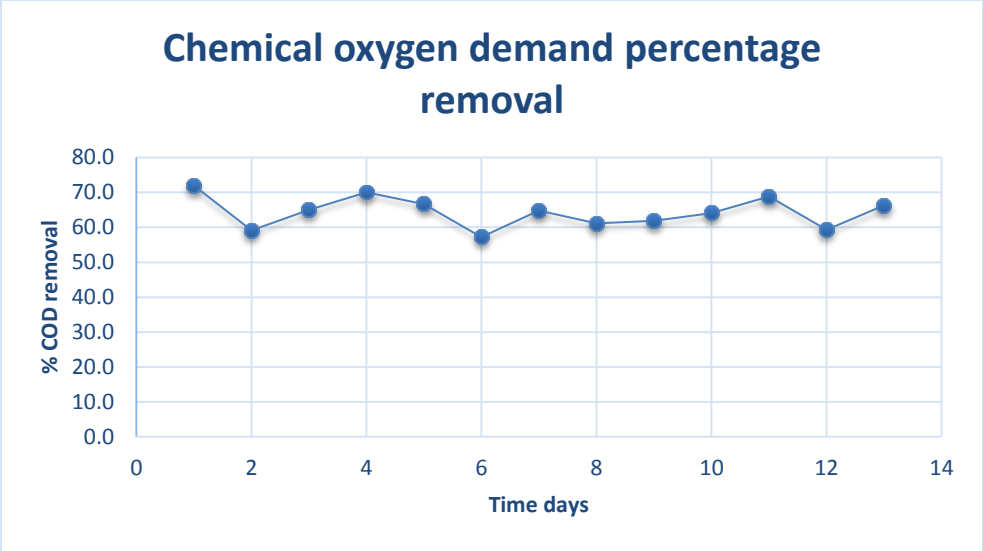


Fig 4.11: The percentage of SCOD removed in first reactor.

As in the first experiment, pH was maintained at around 6.3 ± 0.3 throughout the experiment for both reactors connected in series. In addition to phosphate buffer (100 mM) and sodium bicarbonate (6 mM), 1 mL/ (L of reactor volume) of 1 N NaOH was used to adjust pH when necessary. Maintaining pH as close to neutral as possible will result in preventing any accumulation of protons and acidification of biofilm (Metcalf and Eddy, 2003). Table 4.2 presents pH measurements of influent and effluent of all streams for reactors connected in series.

Table 4.2: pH measurements of both saline water influents and effluents; along with wastewater influents and effluents.

Date	pH SWE1	pH SWE2	pH SWI	pH WWE1	pH WWE2	pH WWI
27-Jan	2.18	1.73				
28-Jan		1.73	8.11	6.55	6.39	8.28
29-Jan		1.7		6.65	6.35	8.36
30-Jan		1.71		6.8	6.65	8.54
31-Jan	2.26	1.8	8.14	6.4	6.35	8.44
2-Feb		1.66		6.46	6.5	
3-Feb	2	1.7		6.33	6.41	8.56
4-Feb		1.77	8.52	6.45	6.34	
5-Feb		1.6		6.12	5.96	8.55
6-Feb	1.73	1.63	8	6	6.35	8.6
7-Feb	1.88	1.72	8.3	6	5.92	8.5
8-Feb		1.62		6.28	6.48	
9-Feb		1.62		6.2	5.8	
10-Feb		1.6		6.17	6.52	8.35
11-Feb		1.6		5.81	6.21	8
12-Feb		1.66		6.8	6.7	8.17
13-Feb	1.75	1.66	8.6	6.7	6.71	8.66
14-Feb		1.68		6.23	6.05	8.25
15-Feb		1.6		6.31	6.57	8.35
16-Feb		1.7		5.92	6.09	8.46

Note: the symbols used in the table were explained in the abbreviation. Number 1 in the symbol relates to reactor 1 (the lead) and number 2 relates to reactor 2 (the Trailing).

Total Dissolved Solid Removal and Anions and Cations Transitioning Patterns

Two reactors connected hydraulically in series were operated for two months and continually generated power while degrading 1.6 g COD /L/day sucrose in the first reactor and 0.6 g COD/L/day in the second reactor. The benefit of the produced electricity resulted in 86% of the salt removed in total. In this experiment, the HRT of saline water was meant to be 2.5 days in

total (30 hrs. in each reactor) like the previous experiment but the salt water was retained less time in each reactor. We observed no precipitations formed in the collecting reservoir used for to recover cathode chamber effluent as the previous experiment however low pH of the cathode chamber plays a role in preventing the formation of precipitations. Figure 4.12 presents the total percentage removal of salt based on TDS.

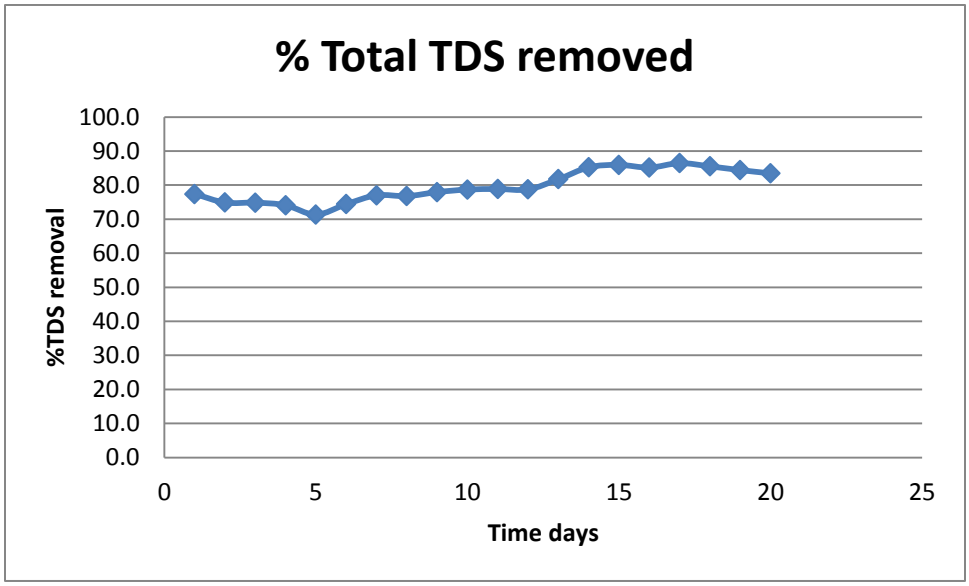


Fig 4.12: Total percentage of the salt removed.

The relocation of anions and cations were captured in this experiment through ion chromatography measurements. Figures 4.13 and 4.14 show initial concentrations of anions and cations; also shows the fate of the migrated anions and cations through reactors' compartments.

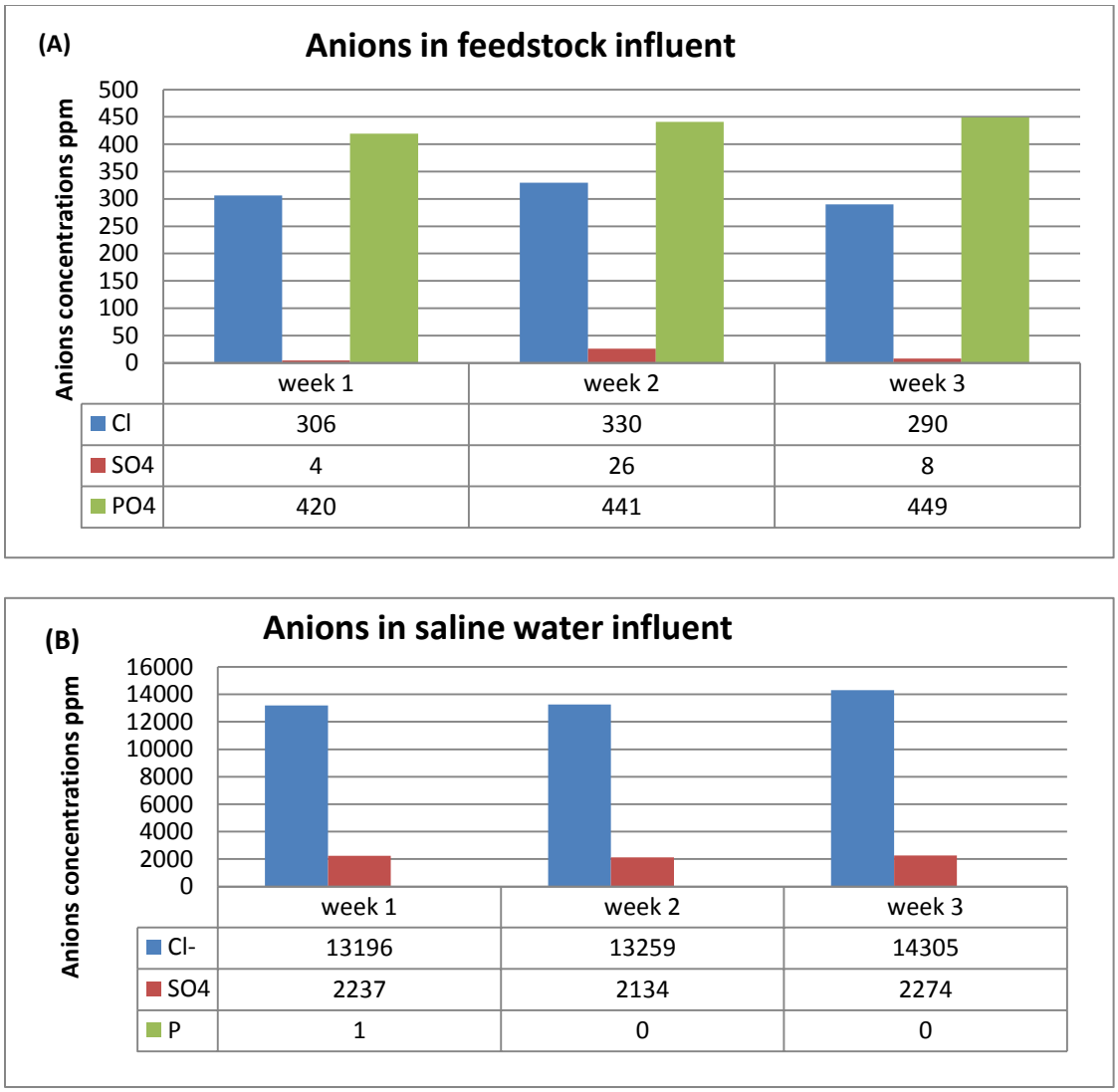
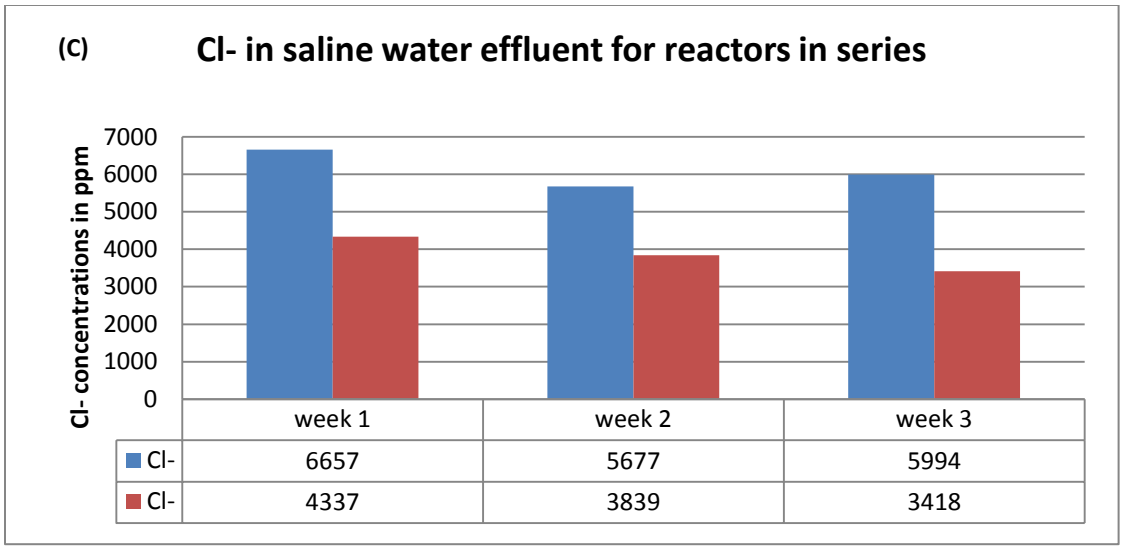
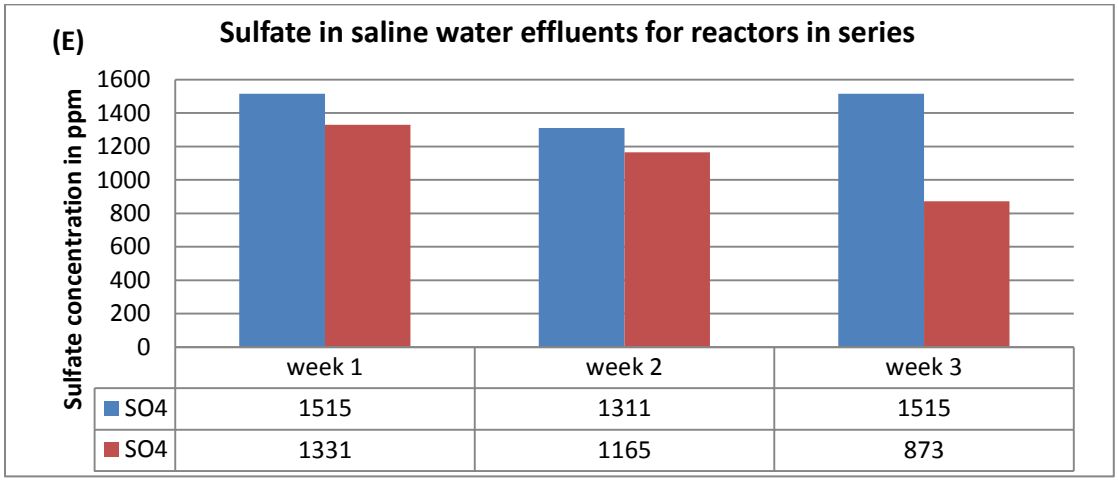


Figure 4.13 Anions concentration in ppm for reactors connected in series for three weeks: (A) feedstock influents; (B) saline water influents; (C) Cl^- conc.in wastewater effluents in reactor 1 in blue and reactor 2 in red; (D) Cl^- in saline water effluents in reactor 1 in blue and reactor 2 in red ; (E) SO4-2 conc. in saline water effluents in reactor 1 in blue and reactor 2 in red ; (F) SO4-2 conc. in wastewater effluents in reactor 1 in blue and reactor 2 in red ; (G) PO4-2 conc. in saline water effluents in reactor 1 in blue and reactor 2 in red and (H) PO4-2 conc. in wastewater effluents in reactor 1 in blue and reactor 2 in red .





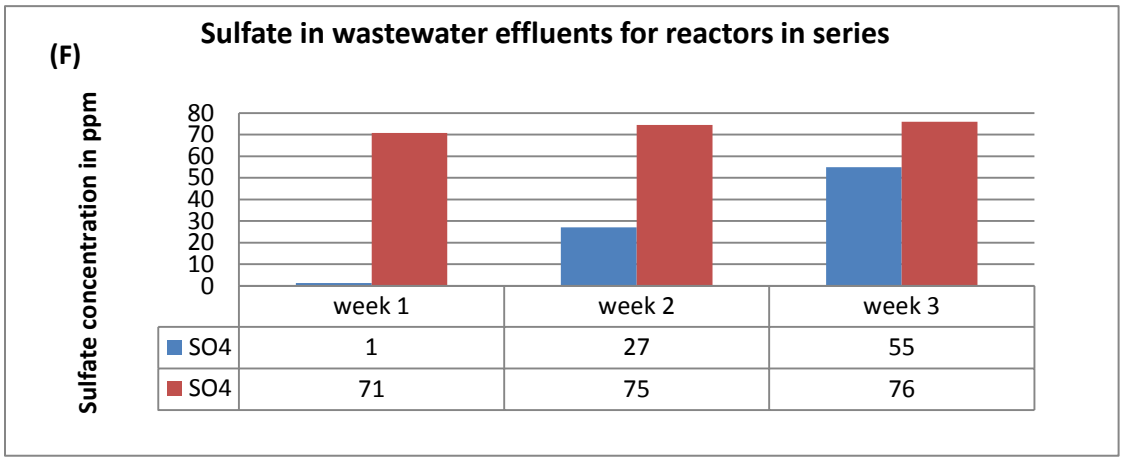
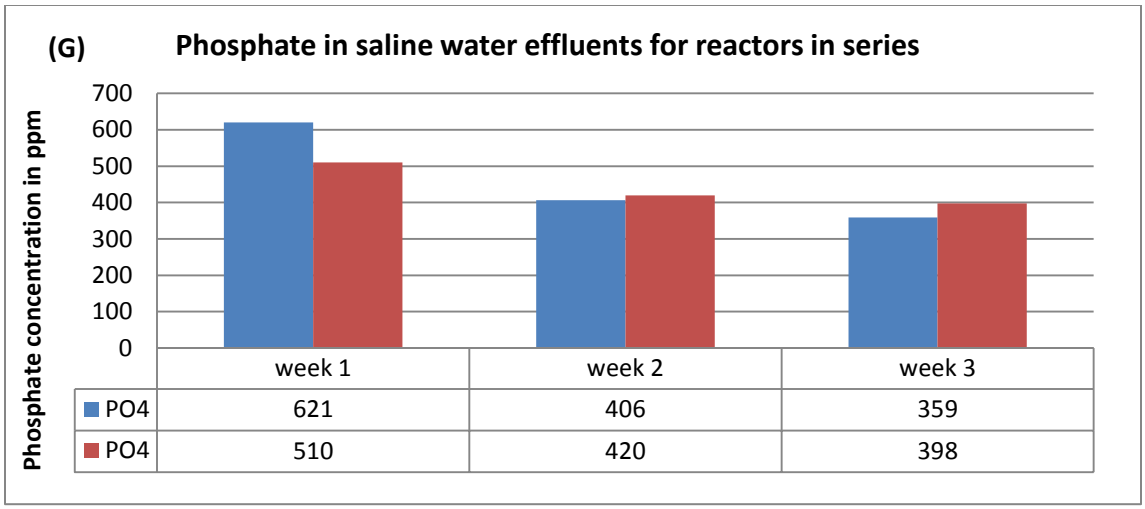
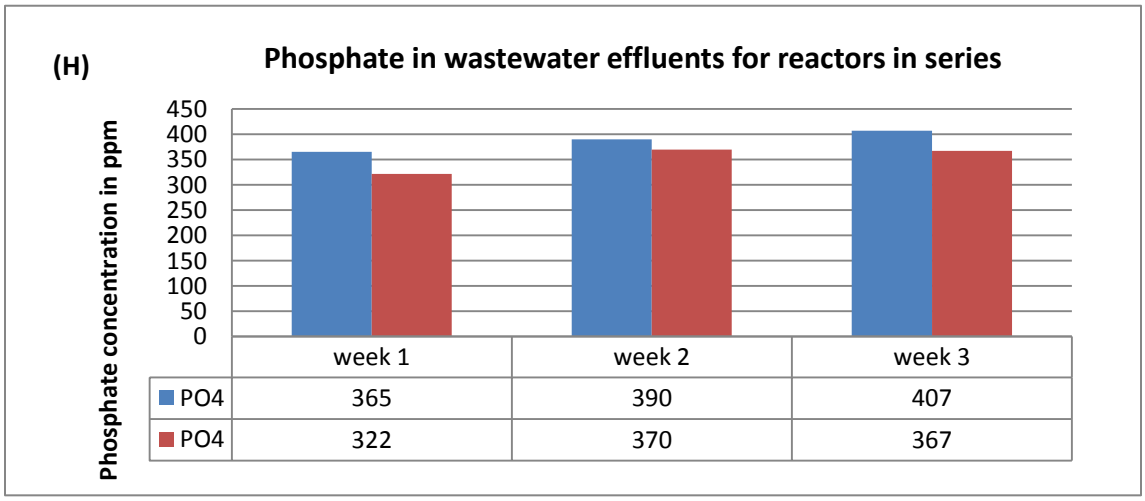


Figure 4.13 Continued





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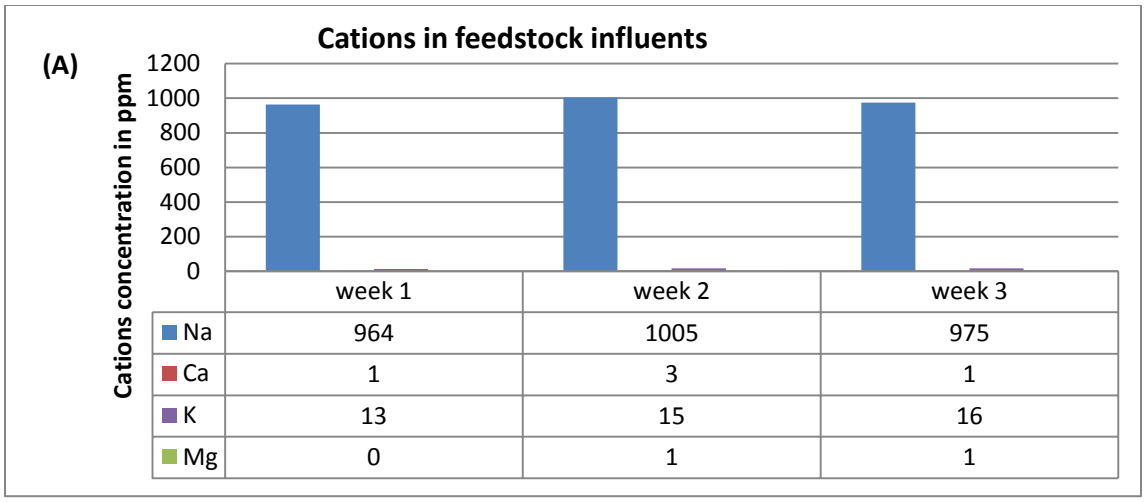


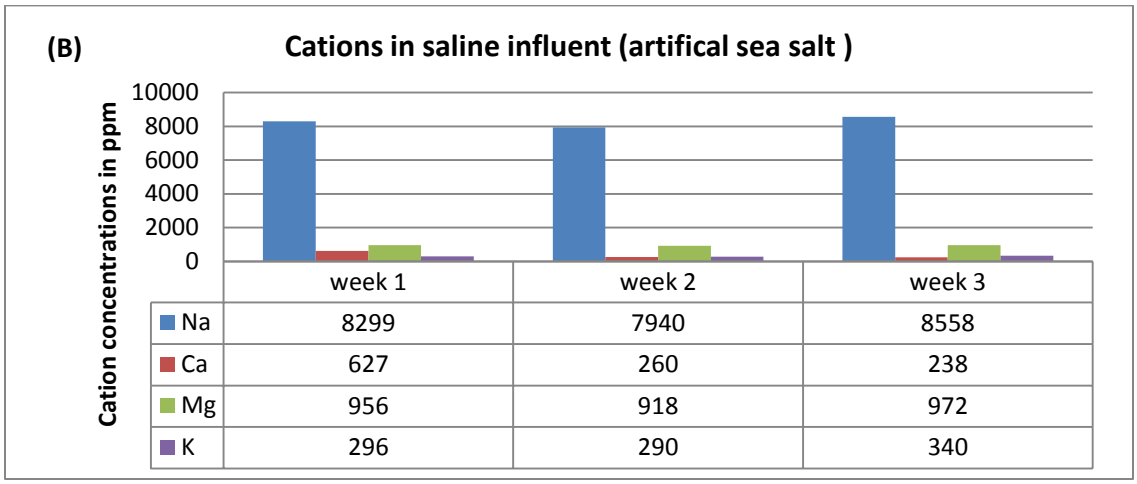
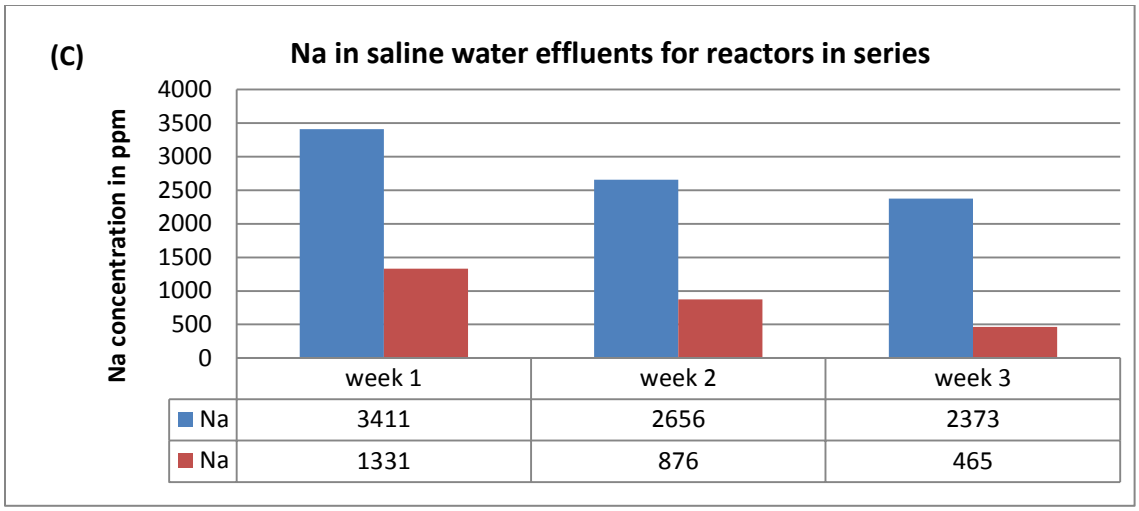
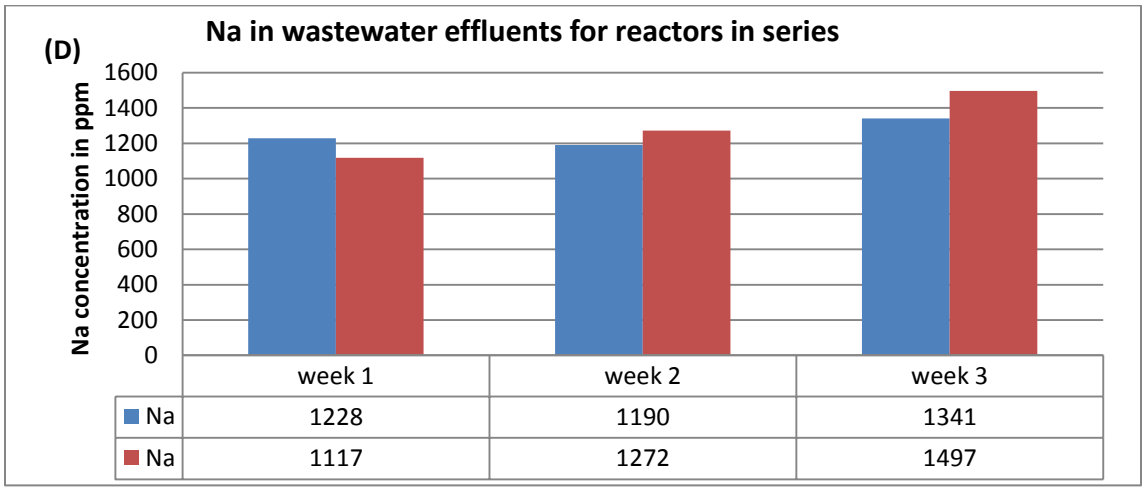


Figure 4.14 Cations concentration in ppm for reactors connected in series for three weeks: (A) feedstock influents; (B) saline water influents; (C) Na+ conc.in saline water effluents in reactor 1 in blue and reactor 2 in red ; (D) Na+ conc. in wastewater effluents in reactor 1 in blue and reactor 2 in red ; (E) Ca+2 conc. in wastewater effluents in reactor 1 in blue and reactor 2 in red ; (F) Ca+2 conc. in saline water effluents in reactor 1 in blue and reactor 2 in red ; (G) Mg+2 conc. in wastewater effluents; (H) Mg+2 conc. in saline water effluents ; (K) K+ conc. in wastewater effluents in reactor 1 in blue and reactor 2 in red and (M) K+ in saline water effluents in reactor 1 in blue and reactor 2 in red.





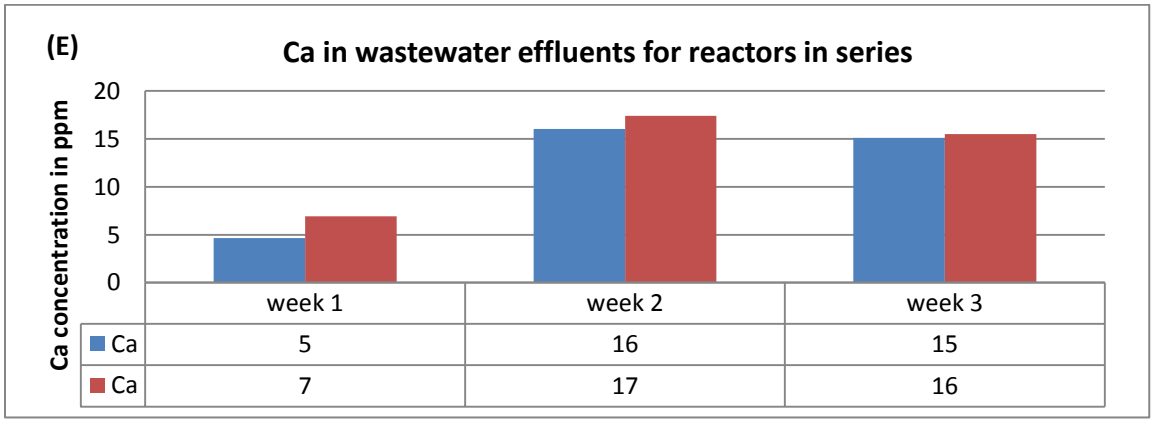
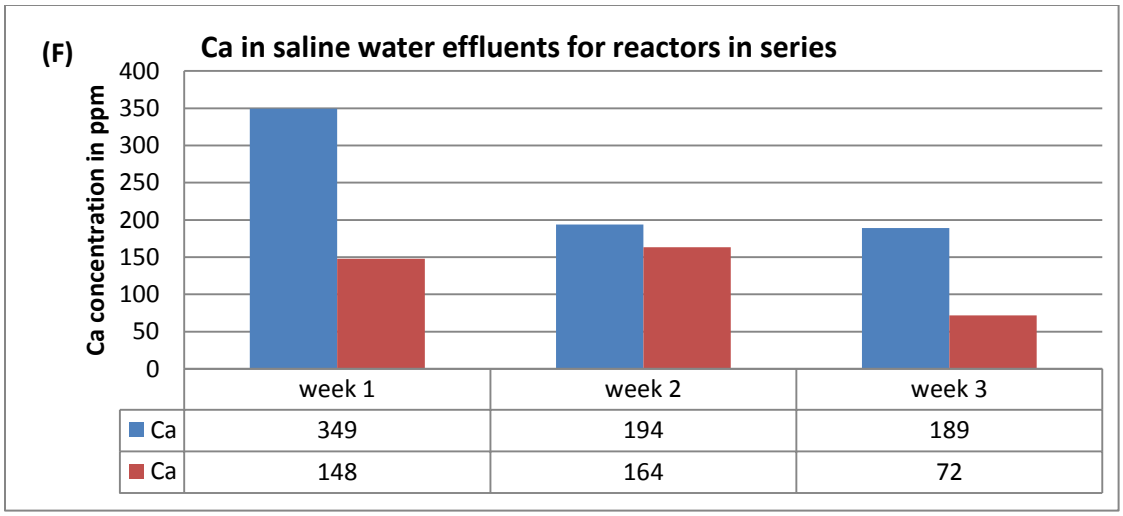
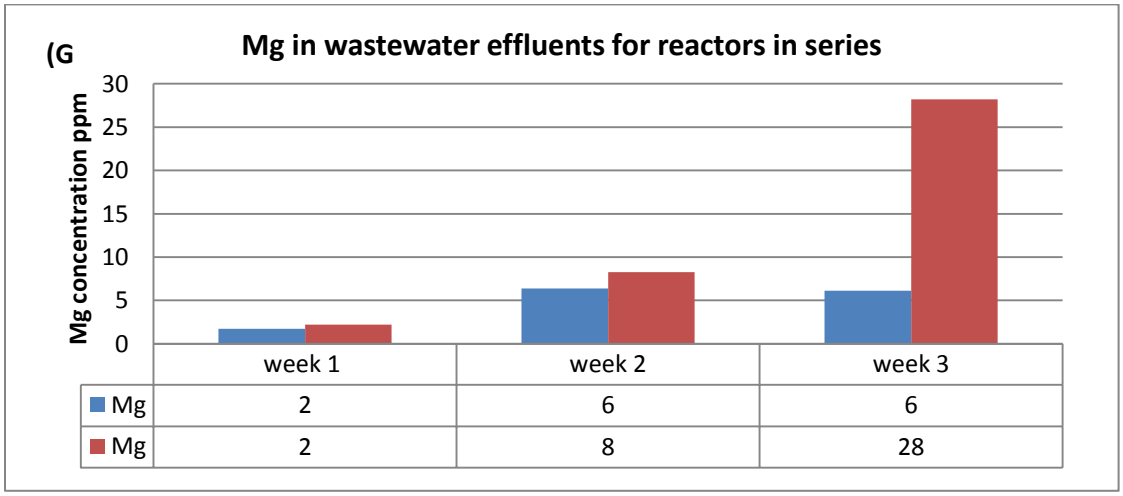


Figure 4.14 Continued





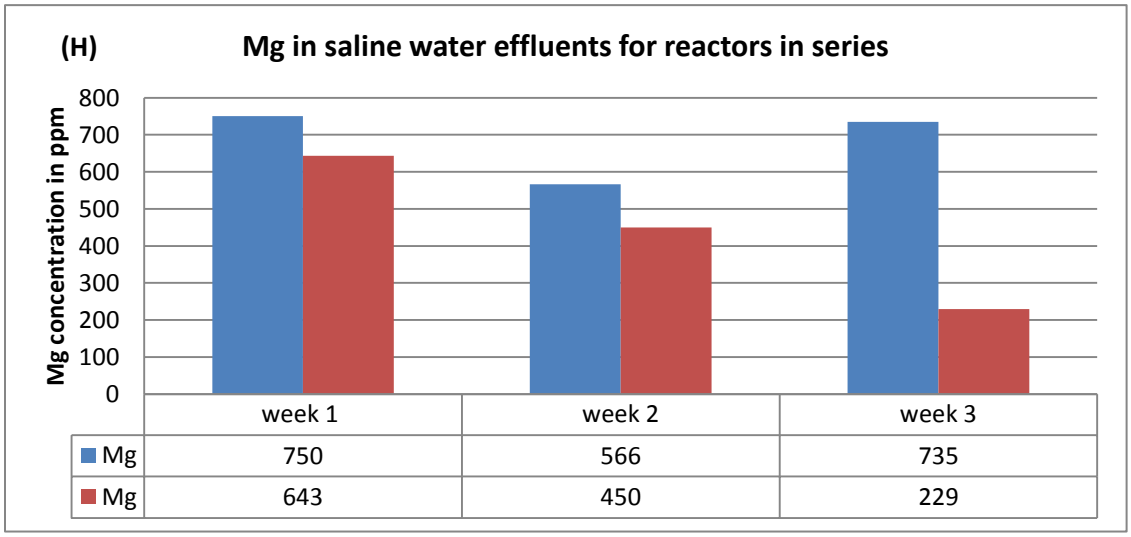
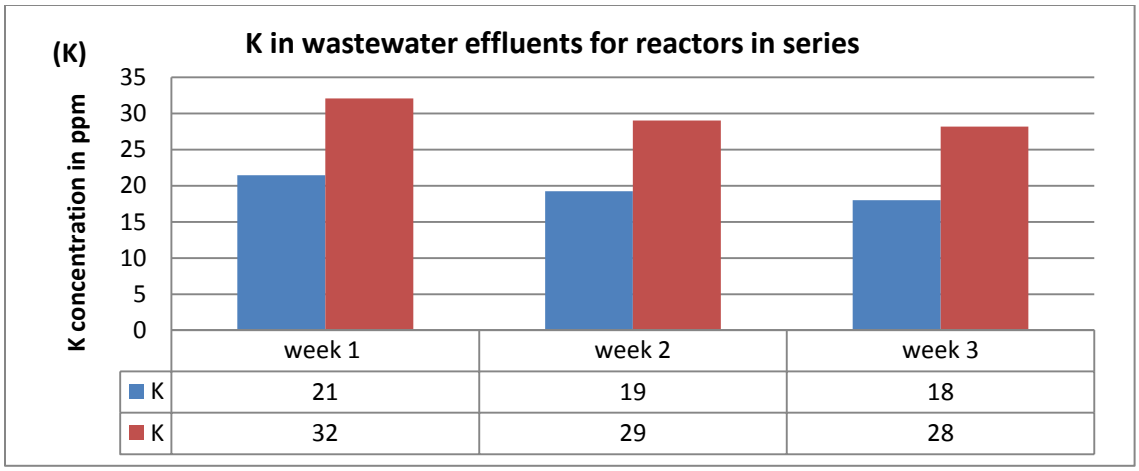


Figure 4.14 Continued



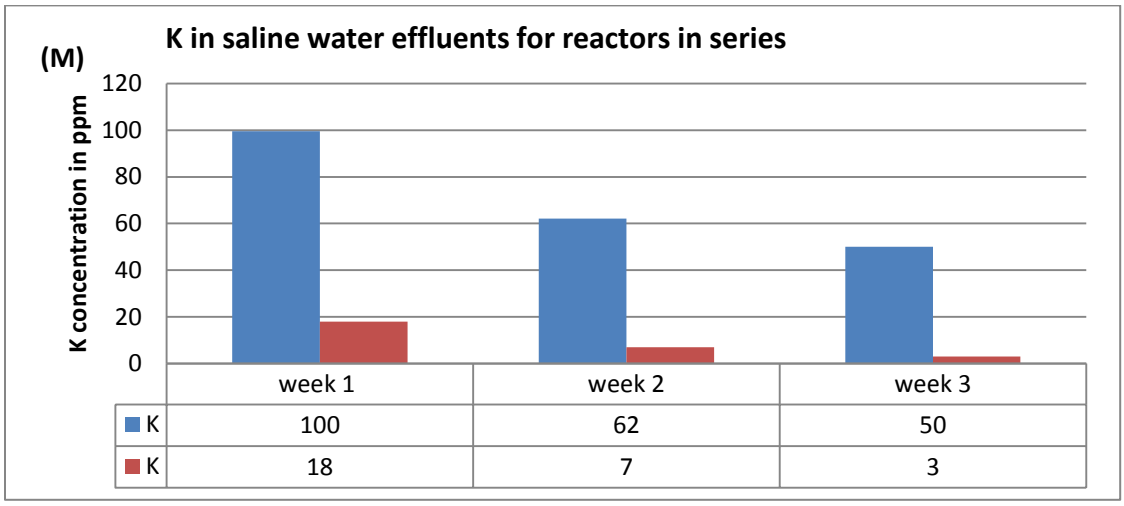


Figure 4.14 Continued

Conducting mass balances is a requirement to describe proper balance of migrated anions and cations in the reactors' chambers. The following equation shows one major anion mass balance as an example and for other anions and cation, the mass balance calculations will be provided in the appendix.

The equations below are a mass balance for chloride, knowing that the flow rate of the anode chamber was 1 mL/min and for the cathode chamber was 0.21 ml/min:

Cl^- in influent stream = Cl^- in effluent stream

Week 1, Reactor 1

0.306 g/mL × 1 mL/min + 13.2 g/mL × 0.21 mL/min = 0.975 g/mL × 1 mL/min + 6.66 g/mL ×0.21 mL/min

3.08 g/ min > 2.37 g/min

Week 1, Reactor 2

0.975 g/mL × 1 mL/min + 6.66 g/mL ×0.21 mL/min = 1.05 mg/L × 1 mL/min + 4.34 g/mL ×0.21 mL/min

2.37 g/min > 1.96 g/min

Week 2, Reactor 1

0.33 g/mL × 1 mL/min + 13.26 g/mL ×0.21 mL/min = 1.04 g/mL × 1 mL/min + 5.68 g/mL ×0.21 mL/min

3.12 g/min > 2.23 g/min

Week 2, Reactor 2

1.04 g/mL × 1 mL/min + 5.68 g/mL ×0.21 mL/min = 1.4 g/mL × 1 mL/min + 3.84 g/mL ×0.21 mL/min

2.23 g/min = 2.21g/min

Week 3, Reactor 1

0.29 g/mL × 1 mL/min + 14.31 g/mL ×0.21 mL/min = 1.1 g/mL × 1 mL/min + 6 g/mL ×0.21 mL/min

3.3 g/min > 2.36 g/min

Week 3, Reactor 2

1.1 g/mL × 1 mL/min + 6 g/mL ×0.21 mL/min = 1.56 g/mL × 1 mL/min + 3.42 g/mL ×0.21 mL/min

2.36 g/min ≈ 2.28 g/min

Through observing the pattern of the migration of chloride in the stacked reactors, it is clear that the lower the concentration of the ion, the better the recovery. Other factors such as molecules diameter can play a role in hindering the relocation of ions to cross the ion exchange membrane (Luo 2012). Table 4.3 presents a mass balance summery for ions (anions and cations) pumped to reactor 1, recovered and then pumped to reactor 2 with percentage difference between influents pumped and effluents recovered.

Table 4.3: A mass balance summary of all ions interred, and recovered from reactors in series.

Ion		Week 1			Week 2			Week 3		
		Inf. g/min	Eff. g/min	% difference	Inf. g/min	Eff. g/min	% difference	Inf. g/min	Eff. g/min	% difference
	Cl^-	3.08	2.37	23	3.12	2.23	29	3.3	2.36	28
		2.37	1.96	17	2.23	2.21	1	2.36	2.28	3
	SO_4^{-2}	0.52	0.32	38	0.5	0.3	40	0.56	0.37	34
		0.32	0.35	-9	0.3	0.32	-7	0.37	0.26	30
	PO_4^{-2}	0.42	0.5	-19	0.44	0.48	-9	0.46	0.49	-7
		0.5	0.43	14	0.48	0.46	4	0.49	0.45	8
	Na^+	2.7	1.95	28	2.7	1.77	34	2.8	1.84	34
		1.95	1.4	28	1.77	1.45	18	1.84	1.6	13
	Ca^{+2}	0.13	0.08	38	0.06	0.06	0	0.05	0.06	-20
		0.08	0.04	50	0.06	0.06	0	0.06	0.03	50
	Mg^{+2}	0.21	0.16	24	0.19	0.13	32	0.2	0.16	20
		0.16	0.14	13	0.13	0.11	15	0.16	0.08	50
	K^+	0.08	0.04	50	0.08	0.03	63	0.09	0.03	67
		0.04	0.03	25	0.03	0.03	0	0.03	0.03	0

Experiment 2 discussion

Two reactors were connected in series and operated for 2 months including the inoculation time. The HRT of the cathode compartment was 2.5 days (30 hrs. in each unit). The new reactors set up removed 86.5% of the sea salt compared to 71% of the sea salt that was removed in the previous experiment when an individual reactor was used (Figure 4.12). Although the goal was to achieve ≈100% salt removal (97% of 20 g/L NaCl was removed in continuous flow stacked cells, 14 mL desalination chamber volume in 2 days, Qu, 2013); the extra 18% of the salt removed in the series setting indicates that connecting units in series might enhance salt removal efficiency (Qu, 2013). Evaluation of the stacked reactors performance in terms of chemical oxygen demand (COD) percentage removal found that they delivered 64.3% ± 4.3 removed in the first unit leaving mostly fermented by products and fatty acids as influent to the second reactor. The second reactor only removed 7.9% ±13.5 of the fermented 1.7 g COD/L/day of sucrose (Fig 4.11). The first reactor performance in this experiment is similar to that of the first experiment (64.9% ± 9.7 COD removed). One conclusion can be obtained from stacked cells is the necessity of optimizing the organic loading rate so that bacteria in the trailing cells will not starve since the trend is for the most organic loading (≈ 70% removal efficiency) of COD will be consumed in the first cell (Qu, 2013). Insufficient food supply significantly influences power generation in these bioelectrochemical devices in which bacteria are the main player to both processes of breaking down organics and supply electrons to the circuit to drive any subsequent designed process or just to recover energy (He, 2005). He (2005) demonstrated that 97% SCOD (sucrose used as substrate) removal efficiency could be achieved in 1 day (anode HRT) and loading rate of 3.4 g COD/L/day; however, the highest power density of 92.0 mW/m^2 was achieved with 2 g COD/L/day and above this rate no further increase in power density was noticed.

To evaluate the reactors in series in terms of Coulumbic Efficiency (CE) or in other words the fraction of electrons from converted organics that end up in the electrical circuit; the calculated

CE of first reactor was 16% and approximately 4% in the second reactor while it was 5.2% in first experiment. 11-17 % was achieved in a continuous flow tubular reactor (Jacobson, 2012). Obviously large portion of the produced electrons were lost and not recovered in the circuit. The loss of CE could be attributed to loss of electrons by alternative electron acceptor in the anode solution such as nitrate. Charge transfer efficiency (one mole of salt removed per each electron) (Jacobson 20112) in both reactors was 54% which explains that some of the produced electrons lost and that could be because of bad wiring (due to corrosion e.g.), ohmic losses or the nature of the substrate used in which the bacteria surpass fermenting the organic to gain energy rather than releasing electrons to the anode as mentioned earlier (Hubertus et. al., 2010). Reactor 1 power density was 61.5 mW/cm^3 while reactor 2 power density was only 8.4 mW/cm^3. Power densities in this experiment are higher than the previous one (6.4 mW/cm^3) and this could be attributed to well acclimated robust biofilm in the anode compartment.

Anodic pH in this experiment was maintained at 6.33 (table 4.2) just like the previous experiment and that was through the buffering action of phosphate and bicarbonate. No extra buffer was added into the second reactor in series indicating that reduction of loading rate assisted in maintaining pH approximately close to neutral level (He, 2005; Qu, 2013).

Migrations of ions from cathode to anode chamber were illustrated in Fig 4.13 and 4.14. Observing the trends of all ions movement shows a significant change between initial concentrations and final concentrations. When conducting a mass balance for chloride as an example of a major ion in the saline water pumped to the reactor (3^{rd} week), we observed that not all chloride were recovered when hitting the first reactor while all the chloride pumped to the second reactor were recovered. The missing amount (1 g/min) might be exchanged/ regenerate the anion exchanged membrane or complexes with other ions and attached on membrane wall (both AEM and/or CEM). This was indicated in the SEM images and EDS analysis conducted. For cations, studies reported that e.g. 84% of Na^+, 0.4% and 0.1 % of Ca^{+2} and Mg^{+2} respectively will be recovered due to the size of the molecules that hindered the transfer through ion exchange

membrane (Luo, 2012). That explains the poor transfer of such multivalent cations in this experiment.

Generally, data obtained in this experiment were better than the previous one since a higher current had generated. We could conclude that developing a robust biofilm on anode electrode is a time dependent process and since bacteria is the main driver of all biochemical processes starting from organic/inorganic biodegradation and ending in delivering electron to the first electron acceptor (anode electrode), then significant attention must be paid to boost this development and that will bear fruit. Monitoring acidification of anolyte solution is of extreme importance to prevent bacterial shut down.

CHAPTER V

CONCLUSIONS

In this novel research, a tubular reactor was efficiently used to treat two complex streams, sucrose in the anode and artificial seawater (Instant Ocean) in the cathode. Two different experiments using MDC reactors along with an effective air breaking system were conducted. In the first experiment conducted, we investigate the usage of bromoethansulphonate (BES) (methanogen bacteria inhibitor) on electricity generation and power using an up flow microbial desalination cells (MDCs). The results revealed a 23.4% increase in power and a better TDS removal (25 % increases in power density reported by He, 2005) in the first two week of the experiment. For no identified reason the control reactor and reactor with BES inhibitor power densities became similar (reactor 1 power density was 2.3 mW/cm^3 and reactor 2 power density was 1.5 mW/cm^3) in the last week of the experiment. The addition of BES inhibitor contributed 6% increase of total dissolved solid removal due to higher power production. The percentage of chemical oxygen demand removed in reactor with inhibitor dropped by 15% due to deactivation of methanogens. Low current produced and accumulations of protons in the cathode compartment caused precipitation of ions on reactor's cell wall and less migration was monitored.

SEM images and EDS elemental analysis exhibit the biofouling and scaling hypothesis that appeared to hinder the migration of some anions like magnesium and calcium and limited the water flux through the membrane due to heavily plated layer of biofilm covering the membrane. On the other hand, low current contributed to accumulation of aggregate - like structures of cations complex on both AEM membrane and CEM membrane facing the saline water.

For the second experiment, when two reactors were connected hydraulically in series, a better salt removal was achieved proving that connecting reactors in series can improve salt removal. 86.5% of the salt concentration (≈ 29 g/L dropped to 3.4 g/L) was removed. Maximum power density calculated for the first reactor (the lead) was 61.5 mW/cm^3 and 8.4 mW/cm^3 for the second reactor (the trailing). Coulombic efficiency for the first reactor was approximately 16% and 4% for the second. The reduction of SCOD by 64% in the first reactor was behind the low power density and Coulombic efficiency (CE). Less organic load in stacked cells can decrease electricity generation due to high competition on food and accumulation of fermented by- products and fatty acid.

The obtained experience from these experiments will boost the development of reactor(s) with optimum performance and integrated treatment of saline and wastewater.

CHAPTER VI

RECOMENDATIONS

The experience acquired conducting these experiments have led to the development of the following recommendations:

- Organic loading rate: Bioelectrochemical systems can only deal with relatively low loading rate (optimum 2 g COD/L/day) at 25^{o}C to drive the maximum power density. This can be considered an advantage over conventional wastewater treatment such as digesters which treat higher load (5 - 25 g COD/L/day) (Rabeay, 2010) only at 35^{o} C and above. When the BES cells are stacked, optimizing this load is a necessity to ensure sufficient food to the trailing cells.
- Acidified anolyte must be avoided to assure steady bacterial performance. Using too much salt buffer neither is practical nor cost effective. Adopting and developing other strategies is recommended such as recycling the anolyte or in other words using stacked cells can mitigate the dilemma to great extent (Qu, 2013).
- Adopting proper way to collect produced gases (air breaking system) is recommended to avoid unexpected incidents of disconnecting tubing assembly e.g.
- Tubular cell with continuous flow has advantages over other configurations in term of practicality. Supporting structures are needed for such set up to avoid membranes deformation and reduction of exchange surface area. Other manufacturing criteria like sealing the membrane required great attention to avoid leakage across membranes.

- It was observed and reported in literature that fermentable organics like sugar can be transferred through membrane creating a good environment to grow bacteria in the cathode chamber. A proper way to disinfect the cathode effluents is necessary to disrupt pathogenic bacteria if available (He, 2005).
- For future work, I would recommend using 3 to 4 cells connected hydraulically in series while optimizing the organic loading rate to boost bacterial performance to get the highest salt removal. I would also recommend operating this set up for 1 to 2 years and monitor the performance of the both AEM and CEM membranes.
- A proposed scenario to operate stacked cell is illustrated below:

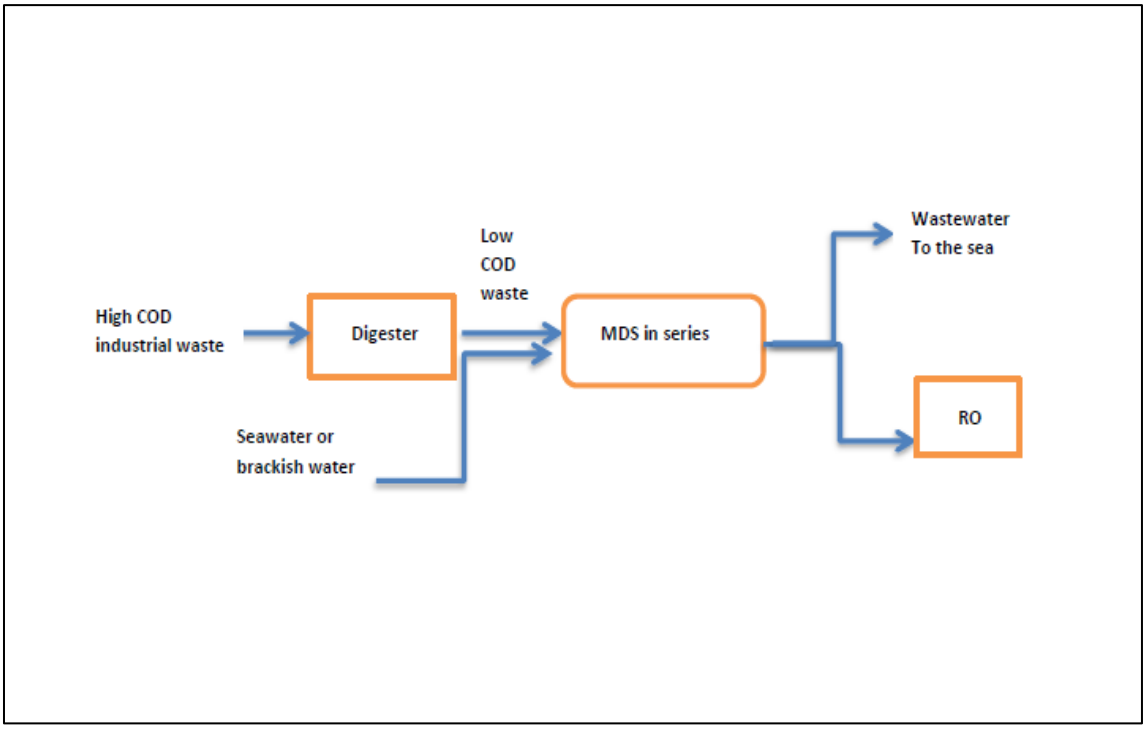


Figure 6.1: A proposed scenario to operate MDC in series with low organic substrate collected from a digester and finally treated the saline effluent with RO and discharge treated wastewater into the sea.

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APPENDICES

- Appendix A: values of % SCOD measured for experiment 1 influents and effluents and experiment 2 influents and effluents.
- Appendix B: values of TDS measured for experiment 1 influents and effluents and experiment 2 influents and effluents.
- Appendix C: values of measured conductivity for experiment 1 saline water influents and effluents.
- Appendix D: ions mass balances equations for experiment 2 along with anions movements in reactor 2, experiment 1.
- Appendix E: SEM images and EDS analysis.

APPENDIX A

Table 1: SCOD measured in reactor 1influent and effluent and reactor 2 influent and effluent (experiment 1).

Date	COD inf. 1 mg/L	COD eff.1 mg/L	% removal	COD inf. 2 mg/L	COD eff. 2 mg/L	% removal
13-Oct	1365	545	60.07	1230	735	40.24
14-Oct	1785	565	68.35	1305	615	52.87
15-Oct	1720	530	69.19	1245	500	59.84
16-Oct	1685	595	64.69	1210	395	67.36
17-Oct	1795	590	67.13	1300	330	74.62
18-Oct	1705	750	56.01	1100	450	59.09
21-Oct	1755	890	49.29	1330	625	53.01
22-Oct		770	55.77		310	75.11
23-Oct		860	50.60		360	71.10
24-Oct		750	56.92		340	72.71
25-Oct		850	51.17		360	71.10
26-Oct		790	54.62		440	64.68
28-Oct		895	48.59		310	75.11
29-Oct		905	48.01		340	72.71
31-Oct		735	57.78		435	65.08
1-Nov		855	50.89		430	65.48
4-Nov		925	46.86		580	53.44
5-Nov		940	46.00		650	47.82
6-Nov		840	51.75		535	57.05
8-Nov	1785	790	55.74	1255	505	59.46

Table 2: SCOD measured of reactor influent and effluent of first and second reactor (experiment 2).

Date	**COD inf. mg/L**	**COD eff. 1 mg/L**	**% removal**	**COD eff. 2 mg/L**	**% removal**
28-Jan	1390	390	71.94	695	
30-Jan	1125	460	59.11	580	
3-Feb	1100	385	65.00	325	15.58
5-Feb	1235	370	70.04	390	
7-Feb	1200	400	66.67	565	
9-Feb	1180	505	57.20	460	8.91
10-Feb	1465	515	64.85	570	
11-Feb	1300	505	61.15	375	25.74
12-Feb	1310	500	61.83	475	5.00
13-Feb	1420	510	64.08	455	10.78
14-Feb	1330	415	68.80	440	
15-Feb	1230	500	59.35	390	22
16-Feb	1365	460	66.30	430	6.52

APPENDIX B

Table 1: TDS measured for reactor influent and both reactor 1 &2 effluents (experiment 1).

Date	TDS eff.1 mg/L	TDS inf mg/L	% removal	TDS eff 2. mg/L	% removal
8-Oct	12.4	26.2	52.67	14.7	43.89
10-Oct	8.57	26.54	67.29	13.5	49.13
11-Oct	7.78	26.54	70.31	13.4	49.51
12-Oct	8.22	26.54	69.03	14.3	46.12
13-Oct	7.7	26.54	70.99	13.88	47.70
14-Oct	8.07	26.54	69.59	14.29	46.16
15-Oct	8.8	26.54	66.84	13.7	48.38
16-Oct	11.01	26.54	58.52	13.35	49.70
17-Oct	14.66	26.54	44.76	13.72	48.30
19-Oct	13.4	26.54	49.51	13.8	48.00
20-Oct	13.36	26.54	49.66	13.9	47.63
21-Oct	12.65	26.54	52.34	13.55	48.94
22-Oct	15.3	26.54	42.35	13.8	48.00
23-Oct	15.75	27.3	40.66	14.1	48.35
24-Oct	15.55	27.3	41.41	14	48.72
25-Oct	15.4	27.3	43.59	16.6	39.19
26-Oct	14.37	27.3	47.36	16	41.39
27-Oct	13.7	27.3	49.82	12.7	53.48
28-Oct	13.7	27.3	49.82	11	59.71
29-Oct	13.15	27.3	51.83	9.8	64.10
30-Oct	12.2	27.3	55.31	9.1	66.67
31-Oct	12	27.3	56.04	7.2	73.63
1-Nov	11.8	29.7	56.78	6.4	78.45
2-Nov	11.9	29.7	56.41	5.5	81.48
3-Nov	12.1	29.7	59.26	5.4	81.82
4-Nov	14	29.7	52.86	6.4	78.45
5-Nov	14.35	29.7	51.68	8.2	72.39
6-Nov	13.15	29.7	55.72	12	59.60
7-Nov	12	29.7	59.60	15	49.49

Table 2: TDS measured for both reactor 1 influent & effluent and reactor 2 effluent (experiment 2 reactors connected in series).

Date	TDS eff.1 mg/L	TDS inf mg/L	% removal	TDS eff 2. mg/L	% total removal
27-Jan	12.91	25.3	49.17	5.74	77.4
28-Jan				6.38	74.88
29-Jan				6.39	74.84
30-Jan				6.58	74.09
31-Jan	13.29		47.68	7.28	71.34
2-Feb				6.5	74.41
3-Feb	12.05		52.56	5.84	77.01
4-Feb				5.9	76.77
5-Feb		24.1		5.6	77.95
6-Feb	11.64		54.17	5.41	78.70
7-Feb	10.73		57.76	5.37	78.86
8-Feb		26.8		5.4	78.74
9-Feb				4.64	81.73
10-Feb				3.75	85.24
11-Feb				3.57	85.94
12-Feb				3.77	85.16
13-Feb	11		56.69	3.44	86.46
14-Feb				3.68	85.51
15-Feb				3.96	84.41
16-Feb				4.2	83.46

APPENDIX C

Table 1: Conductivity measured for saline water influent and reactor 1 & 2 effluents (experiment 1).

Date	Cond. SWI,mS/cm	Cond. SWE2,mS/cm	Cond. SWE2,mS/cm
12-Oct	38	39.64	39.64
13-Oct	38	11.7	20.7
14-Oct	38	10.95	20.2
15-Oct	38	11.82	19.45
16-Oct	38	15.39	19.58
17-Oct	38	20.4	18.52
19-Oct	38	18.63	19.77
20-Oct	38	18.07	20.1
21-Oct	38	17.39	19.7
22-Oct	38	20.8	20.3
23-Oct	39.5	20.3	19.9
24-Oct	39.5	21.3	20.2
25-Oct	39.5	20.5	20.3
26-Oct	39.5	18.92	21.2
27-Oct	39.5	17.55	18.88
28-Oct	39.5	17.6	17.07
29-Oct	39.5	16.86	14.61
30-Oct	39.5	15.91	14.14
31-Oct	39.5	15.88	16.11
1-Nov	41.7	15.47	16.25
2-Nov	41.7	15.42	15.19
3-Nov	41.7	15.23	15.25
4-Nov	41.7	14.23	14.76
5-Nov	41.7	13.19	11.51
6-Nov	41.7	14.2	14.33
7-Nov	43.4	13.91	17.1

APPENDIX D

Mass balance equations calculated for reactors connected in series

SO_4^{-2} in influent stream = SO_4^{-2} in effluent stream

Week 1, Reactor 1

0.045 g/mL × 1 mL/min + 2.24 g/mL × 0.21 mL/min = 0.014 g/mL × 1 mL/min + 1.52 g/mL ×0.21 mL/min

0.52 g/ min > 0.32 g/min

Week 1, Reactor 2

0.014 g/mL × 1 mL/min + 1.52 g/mL ×0.21 = 0.071 g/mL × 1 mL/min + 1.33 g/mL ×0.21 mL/min

0.32 g/min ≈ 0.35 g/min

Week 2, Reactor 1

0.026 g/mL × 1 mL/min + 2.24 g/mL ×0.21 mL/min = 0.027 g/mL × 1 mL/min + 1.31 g/mL ×0.21 mL/min

0.5 g/min > 0.302 g/min

Week 2, Reactor 2

0.027 g/mL × 1 mL/min + 1.31 g/mL ×0.21 = 0.075 g/mL × 1 mL/min + 1.165 g/mL ×0.21 mL/min

0.302 g/min = 0.319 g/min

Week 3, Reactor 1

0.081 g/mL × 1 mL/min + 2.27 g/mL ×0.21 mL/min = 0.055 g/mL × 1 mL/min + 6 g/mL ×1.52 mL/min

0.56 g/min > 0.37 g/min

Week 3, Reactor 2

0.055 g/mL × 1 mL/min + 6 g/mL ×1.52 mL/min = 0.076 g/mL × 1 mL/min + 0.873 g/mL ×0.21 mL/min

0.37 g/min > 0.26 g/min

PO_4^{-2} in influent stream = PO_4^{-2} in effluent stream

Week 1, Reactor 1

0.42 g/mL × 1 mL/min + 0 g/mL × 0.21 mL/min = 0.37 g/mL × 1 mL/min + 0.62 g/mL ×0.21 mL/min

0.42 g/ min < 0.5 g/min

Week 1, Reactor 2

0.37 g/mL × 1 mL/min + 0.62 g/mL ×0.21 mL/min = 0.32 g/mL × 1 mL/min + 0.51 g/mL ×0.21 mL/min

0.5 g/min > 0.43 g/min

Week 2, Reactor 1

0.44 g/mL × 1 mL/min + 0 g/mL ×0.21 mL/min = 0.39 g/mL × 1 mL/min + 0.41 g/mL ×0.21 mL/min

0.44 g/min ≈ 0.48 g/min

Week 2, Reactor 2

0.39 g/mL × 1 mL/min + 0.41 g/mL ×0.21 mL/min = 0.37 g/mL × 1 mL/min + 0.42 g/mL ×0.21 mL/min

0.48 g/min ≈ 0.46g/min

Week 3, Reactor 1

0.45 g/mL × 1 mL/min + 0 g/mL ×0.21 mL/min = 0.41 g/mL × 1 mL/min + 0.36 g/mL ×0.21 mL/min

0.46 g/min ≈ 0.49 g/min

Week 3, Reactor 2

0.41 g/mL × 1 mL/min + 0.36 g/mL ×0.21 mL/min = 0.37 g/mL × 1 mL/min + 0.4 g/mL ×0.21 mL/min

0.49 g/min ≈ 0.45 g/min

Na^+ in influent stream = Na^+ in effluent stream

Week 1, Reactor 1

0.96 g/mL × 1 mL/min + 8.3 g/mL × 0.21 mL/min = 1.23 g/mL × 1 mL/min + 3.41 g/mL ×0.21 mL/min

2.7 g/ min > 1.95 g/min

Week 1, Reactor 2

1.23 g/mL × 1 mL/min + 3.41 g/mL ×0.21 mL/min = 1.12 g/mL × 1 mL/min + 1.33 g/mL ×0.21 mL/min

1.95 g/min > 1.4 g/min

Week 2, Reactor 1

1 g/mL × 1 mL/min + 7.94 g/mL ×0.21 mL/min = 1.2 g/mL × 1 mL/min + 2.7 g/mL ×0.21 mL/min

2.7 g/min > 1.77 g/min

Week 2, Reactor 2

1.2 g/mL × 1 mL/min + 2.7 g/mL ×0.21 mL/min = 1.27 g/mL × 1 mL/min + 0.88 g/mL ×0.21 mL/min

1.77 g/min > 1.45/min

Week 3, Reactor 1

0.98 g/mL × 1 mL/min + 8.6 g/mL ×0.21 mL/min = 1.34 g/mL × 1 mL/min + 2.37 g/mL ×0.21 mL/min

2.8 g/min > 1.84 g/min

Week 3, Reactor 2

1.34 g/mL × 1 mL/min + 2.37 g/mL ×0.21 mL/min = 1.50 g/mL × 1 mL/min + 0.47 g/mL ×0.21 mL/min

1.84 g/min > 1.6 g/min

Ca^{+2} in influent stream = Ca^{+2} in effluent stream

Week 1, Reactor 1

0 g/mL × 1 mL/min + 0.63 g/mL × 0.21 mL/min = 0.005 g/mL × 1 mL/min + 0.35 g/mL ×0.21 mL/min

0.13 g/ min > 0.08 g/min

Week 1, Reactor 2

0.005 g/mL × 1 mL/min + 0.35 g/mL ×0.21 mL/min = 0.007 g/mL × 1 mL/min + 0.15 g/mL ×0.21 mL/min

0.08 g/min > 0.04 g/min

Week 2, Reactor 1

0.003 g/mL × 1 mL/min + 0.26 g/mL ×0.21 mL/min = 0.02 g/mL × 1 mL/min + 0.2 g/mL ×0.21 mL/min

0.06 g/min = 0.06 g/min

Week 2, Reactor 2

0.02 g/mL × 1 mL/min + 0.2 g/mL ×0.21 mL/min = 0.02 g/mL × 1 mL/min + 0.2 g/mL ×0.21 mL/min

0.06 g/min = 0.06g/min

Week 3, Reactor 1

0 g/mL × 1 mL/min + 0.24 g/mL ×0.21 mL/min = 0.02 g/mL × 1 mL/min + 0.2 g/mL ×0.21 mL/min

0.05 g/min ≈ 0.06 g/min

Week 3, Reactor 2

0.02 g/mL × 1 mL/min + 0.2 g/mL ×0.21 mL/min = 0.02 g/mL × 1 mL/min + 0.07 g/mL ×0.21 mL/min

0.06 g/min = 0.03 g/min

Mg^{+2} in influent stream = Mg^{+2} in effluent stream

Week 1, Reactor 1

0 g/mL × 1 mL/min + 1 g/mL × 0.21 mL/min = 0.002 g/mL × 1 mL/min + 0.75 g/mL ×0.21 mL/min

0.21 g/ min > 0.16 g/min

Week 1, Reactor 2

0.002 g/mL × 1 mL/min + 0.75 g/mL ×0.21 mL/min = 0.002 g/mL × 1 mL/min + 0.64 g/mL ×0.21 mL/min

0.16 g/min ≈ 0.14 g/min

Week 2, Reactor 1

0.001 g/mL × 1 mL/min + 0.92 g/mL ×0.21 mL/min = 0.006 g/mL × 1 mL/min + 0.57 g/mL ×0.21 mL/min

0.19 g/min > 0.13 g/min

Week 2, Reactor 2

0.006 g/mL × 1 mL/min + 0.57 g/mL ×0.21 = 0.008 g/mL × 1 mL/min + 0.5 g/mL ×0.21 mL/min

0.13 g/min ≈ 0.11g/min

Week 3, Reactor 1

0 g/mL × 1 mL/min + 0.97 g/mL ×0.21 mL/min = 0.006 g/mL × 1 mL/min + 0.74 g/mL ×0.21 mL/min

0.2 g/min > 0.16 g/min

Week 3, Reactor 2

0.006 g/mL × 1 mL/min + 0.74 g/mL ×0.21 mL/min = 0.03 g/mL × 1 mL/min + 0.22 g/mL ×0.21 mL/min

0.16 g/min > 0.08 g/min

K^+ in influent stream = K^+ in effluent stream

Week 1, Reactor 1

0.013 g/mL × 1 mL/min + 0.3 g/mL × 0.21 mL/min = 0.021 g/mL × 1 mL/min + 0.1 g/mL ×0.21 mL/min

0.08 g/ min > 0.04 g/min

Week 1, Reactor 2

0.021 g/mL × 1 mL/min + 0.1 g/mL ×0.21 mL/min = 0.03 g/mL × 1 mL/min + 0.02 g/mL ×0.21 mL/min

0.04 g/min ≈ 0.03 g/min

Week 2, Reactor 1

0.02 g/mL × 1 mL/min + 0.3 g/mL ×0.21 mL/min = 0.02 g/mL × 1 mL/min + 0.06 g/mL ×0.21 mL/min

0.08 g/min > 0.03 g/min

Week 2, Reactor 2

0.02 g/mL × 1 mL/min + 0.06 g/mL ×0.21 mL/min = 0.03 g/mL × 1 mL/min + 0.007 g/mL ×0.21 mL/min

0.03 g/min = 0.03 g/min

Week 3, Reactor 1

0.02 g/mL × 1 mL/min + 0.34 g/mL ×0.21 mL/min = 0.02 g/mL × 1 mL/min + 0.05 g/mL ×0.21 mL/min

0.09 g/min > 0.03 g/min

Week 3, Reactor 2

0.02 g/mL × 1 mL/min + 0.05 g/mL ×0.21 mL/min = 0.03 g/mL × 1 mL/min + 0.003 g/mL ×0.21 mL/min

0.03 g/min = 0.03 g/min

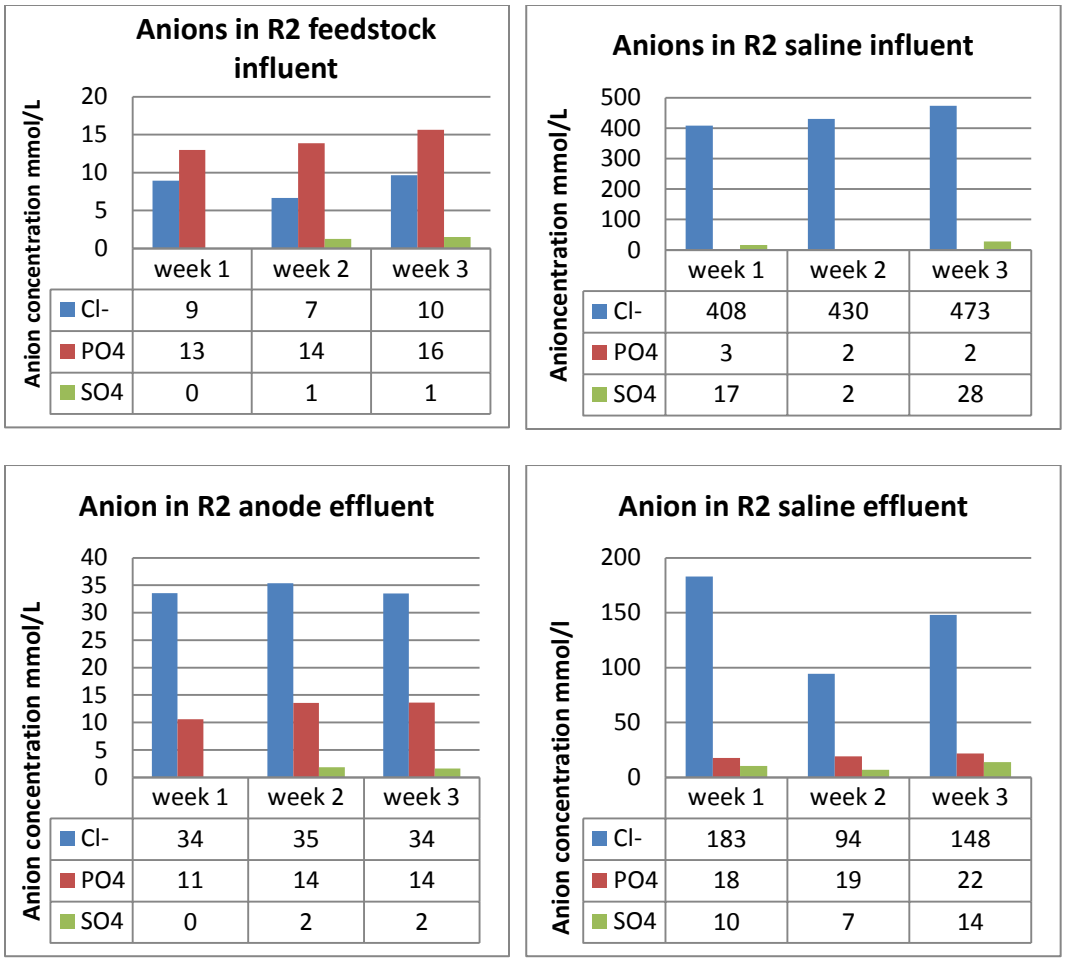


Figure 1: Anions in feedstock influent and effliuent along with saline water influent and effluent for reactor 2, experiment 1.

APPENDIX E

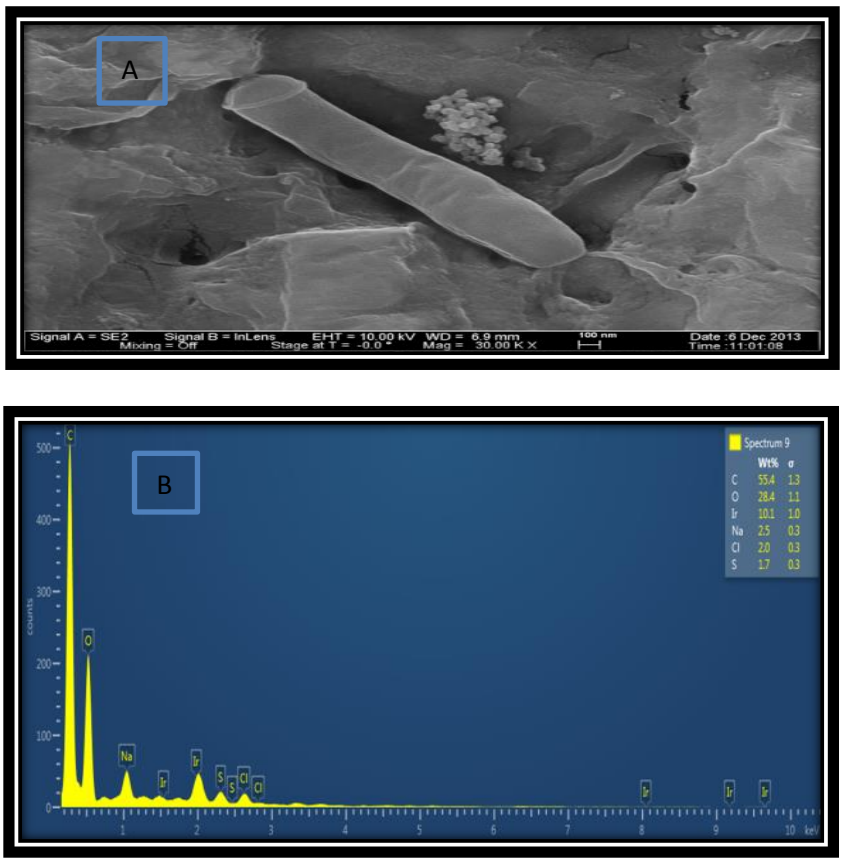
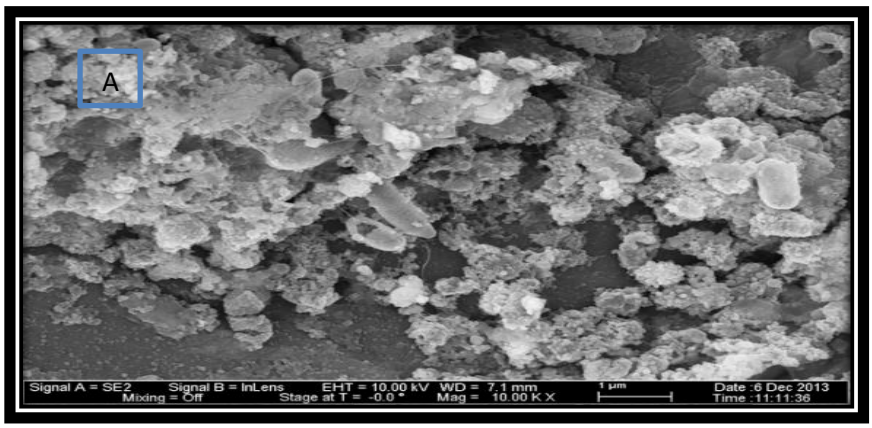


Figure 1: Anion exchange membrane facing biomass; (A) SEM image, (B) elemental analysis.



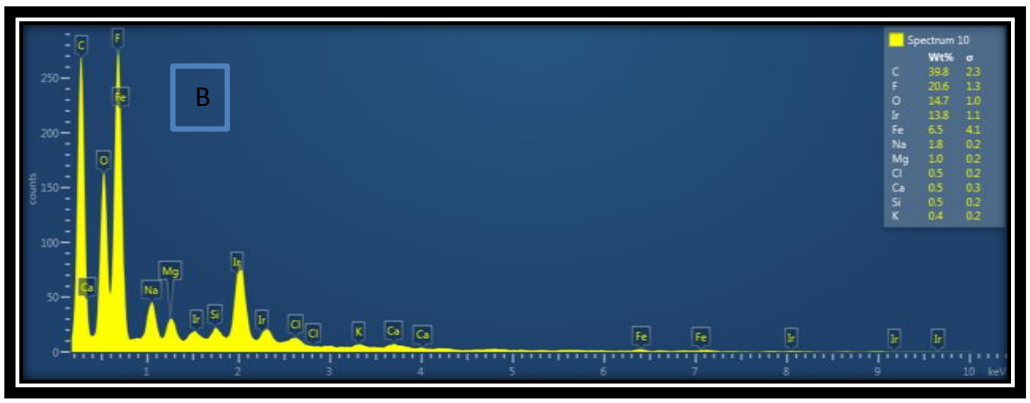


Figure 2: Anion exchange membrane facing saline water; (A) SEM image, (B) elemental analysis.

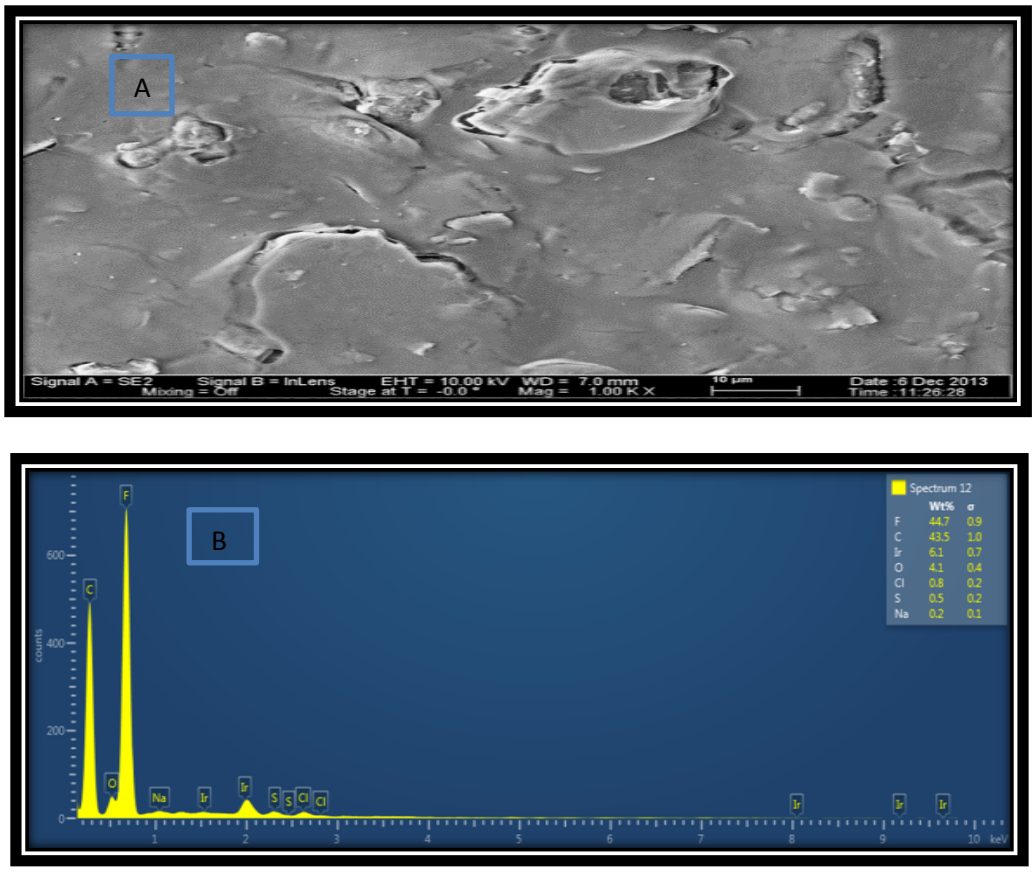


Figure 3: Anion exchange membrane facing biomass; (A) SEM image, (B) elemental analysis.

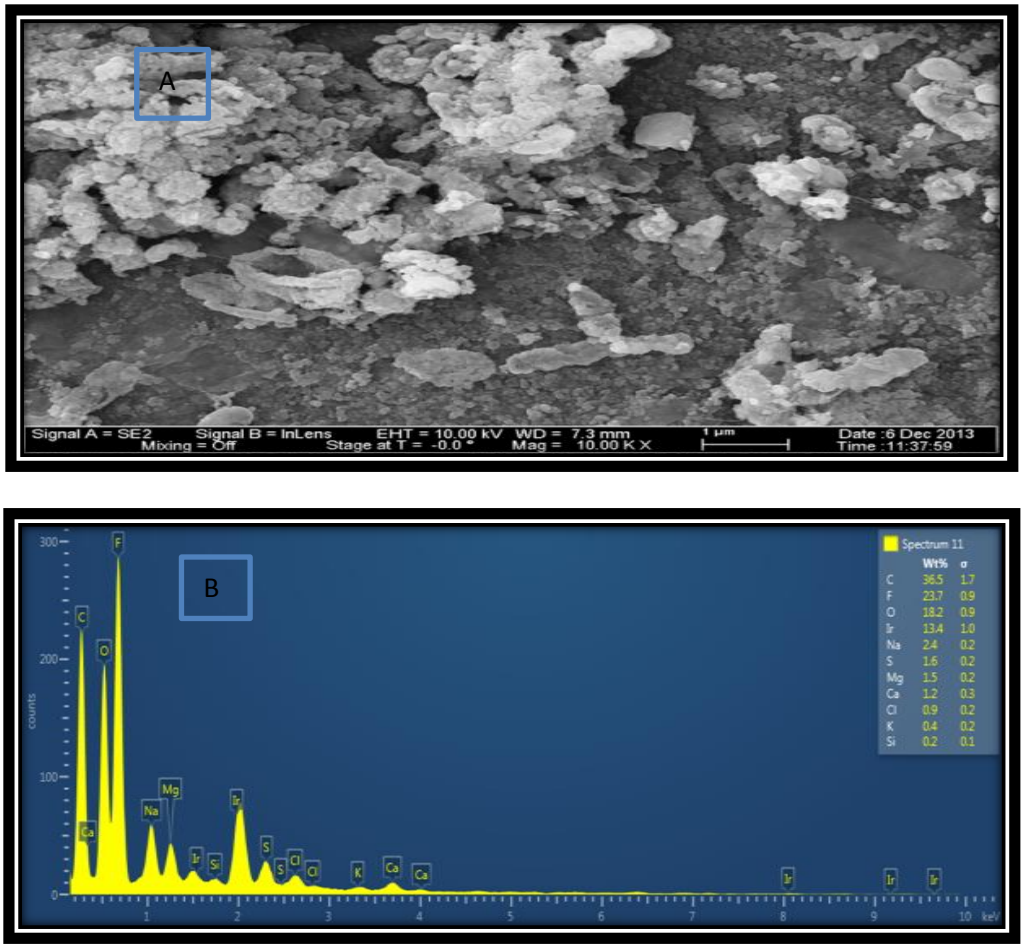
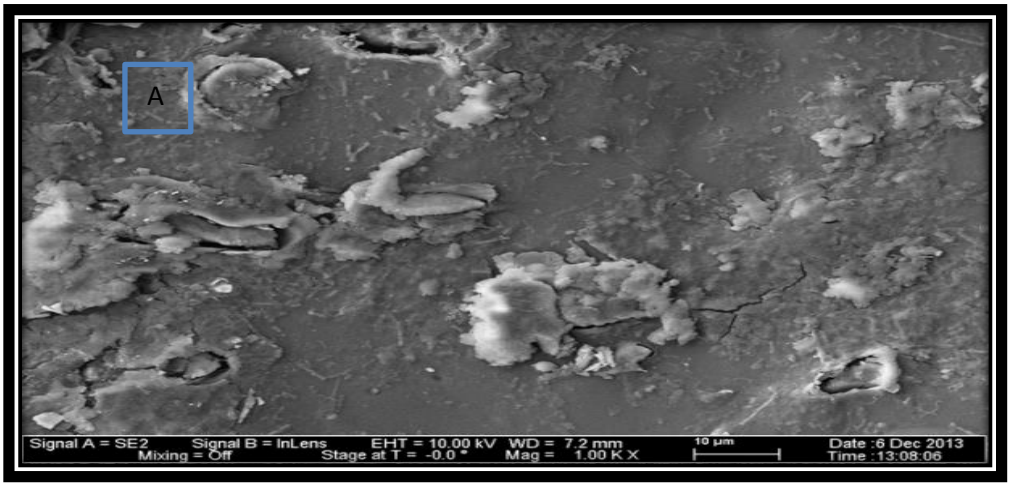


Figure 4: Anion exchange membrane facing saline water; (A) SEM image, (B) elemental analysis.



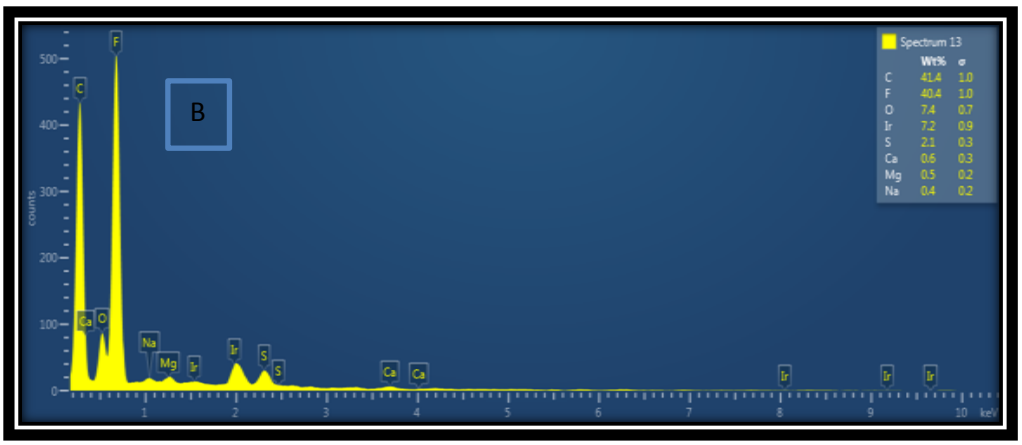
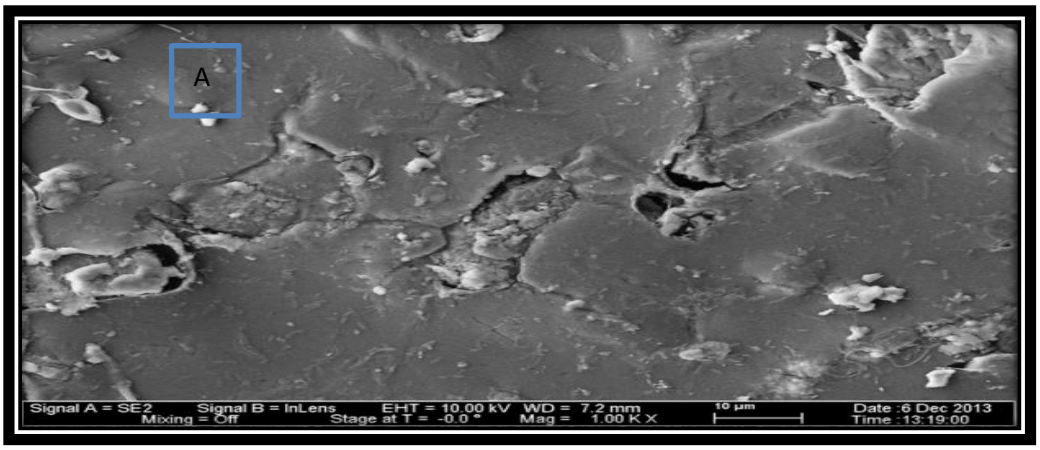


Figure 5: Cation exchange membrane facing saline water; (A) SEM image, (B) elemental analysis.



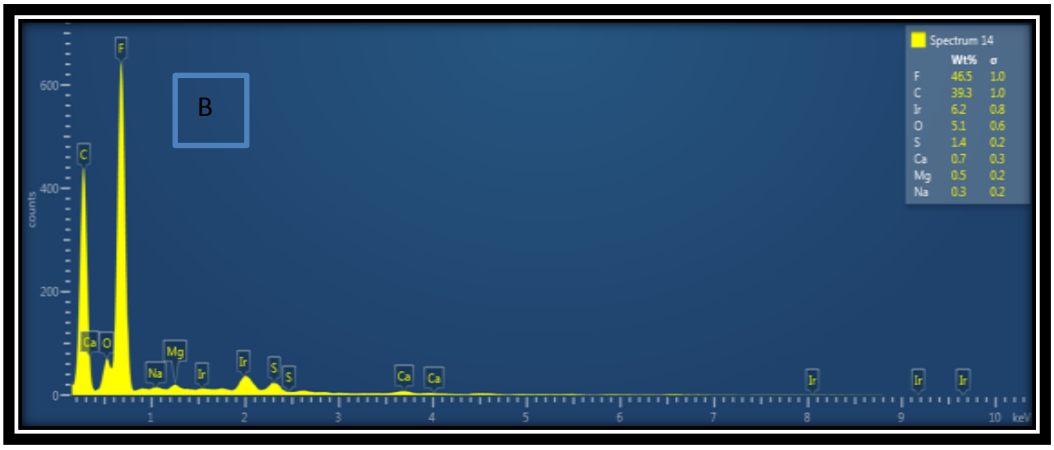


Figure 6: Cation exchange membrane facing Acidified wash; (A) SEM image, (B) elemental analysis.

VITA

Dina Faisal Ahmed Al Azawi

Candidate for the Degree of

Doctor of Philosophy

Thesis: A STUDY EXAMINING MDC UNITS COUPLE TREATING CARBOHYDRATE STREAM WASTE AND ARTIFICIAL SEAWATER.

Major Field: Civil Engineering

Biographical:

Education:

Completed the requirements for the Doctor of Philosophy in Civil Engineering at Oklahoma State University, Stillwater, Oklahoma in May/2014.

Completed the requirements for the Master of Science in Civil Engineering at Al Mustansiryah University/Engineering Collage, Baghdad, Iraq/2000.

Completed the requirements for the Bachelor of Science in Civil Engineering at Al Mustansiryah University/Engineering Collage, Baghdad, Iraq/1991.

Experience:

Site engineer working for National Engineering Consultation Center/Baghdad/Iraq from April 1992 to June 1996
Instructor in the Engineering Collage/Al Mustansiryah University/Environment Engineering Department from June 1996 to July 2007.

Professional Memberships: CHI EPSILON