

Microbial Fuel Cell with Multiple Cathode Chambers to Treat Oily, Salty and Nitrate Contaminated Wastewaters

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Abstract

The overall objective of this study was to develop and design new integrated microbial fuel cells (MFC) to not only rapidly treat the wastewaters that have high levels of oil, salts and nitrates on a continuous parallel process but also produce electricity and also commercially valuable by-products. Simulated industrial wastewater samples were used in this study. The new multi chamber MFC was used to rapidly treat the pretreated wastewater for the following reasons: (1) produced biosurfactant in the anode chamber while treating the oily wastewater using bacteria; (2) reduce the nitrate (NaNO_3) concentrations in the cathode chamber using algae and solar energy and also recover algae oil (lipids) and recycle the algae (3) reduce the salt (NaCl) content in the cathode chamber and (4) produced electricity while treating the wastewaters in parallel process configuration. Effects of solar energy (temperature range 66°F to 82°F), waste concentrations (5% oil; up to 50 g/L salt; 5 g/L nitrate) and pH (range 5 to 9) on the total removal and rate of removal of waste materials and algae growth were investigated and quantified. Also the new integrated MFC configuration can be easily adopted in the field sites not only to treat wastewater but also produce commercially valuable by-products. Also the solar energy (increase in temperature) enhanced the algae growth and also salt and nitrate removal in the cathode chamber.

Introduction

Technological advances have led to unprecedented growth in unconventional oil and gas extraction in the U.S. over past few decades. There is an urgent need for developing low cost and effective treatment methods for flowback and produced water (FPW) that can be easily adopted in the field under varying geological formations. In Texas alone there are over 280,000 active wells. Water management has emerged as a critical issue in the development of these inland gas reservoirs, where hydraulic fracturing is used to liberate the gas. Each well may require as much as 2 to 12 million gallons of water. Following hydraulic fracturing, large volumes of water containing very high concentrations of total dissolved solids (TDS) and oil return to the surface. The TDS concentration in this wastewater, also known as “flowback,” can reach 2 to 5 times that of sea water. Also there are many chemical and petroleum products manufacturing companies that

need to recycle the wastewater. Wastewaters that contain high TDS levels are challenging and costly to treat and currently used technologies such as electro-coagulation (EC) and dissolved air floatation (DAF) have many limitations. Economical production of shale gas resources will require creative management of flowback to ensure protection of groundwater and surface water resources. With global concerns over the use of fresh water for hydraulic fracturing and industrial processes, novel water management strategies and developing rapid treatment technologies will be very valuable (Angelakis et al. 2018; UNESCO 2017;. US AID 2008;

(i) Why Select MFC? It has been shown that treating wastewater (TDS with oil and suspended solids) from hydraulic fracturing is a challenge due the complex nature of the wastewater no single treatment method such as electro-coagulation (EC) or dissolved air flotation (DAF) could be used. Hence there is need to develop a comprehensive treatment systems that will handled the types of wastes encountered in the wastewater. The uniqueness of MFC is that it has bio-electrochemical oxidation process in the anode chamber and reducing electrochemical process in the cathode chamber removes the dissolved salts. In the anode chamber, based on the type of oil in the wastewater and the bacteria introduced during the pretreatment process, biologically produced coagulating agents and biosurfactants will be produced that will enhance the rapid removal of the fine suspended solids and part of the dissolved solids in the wastewater. The treated water from the anode chamber (with the suspended solids removed) will be introduced to the cathode chamber where dissolved solids will be removed (by precipitation) based on reduction reactions. Based on the quality of the treated wastewater from the cathode chamber, the water can be recycled for use in hydraulic fracturing. The combined processes in the MFC will also produce electricity to partly sustain the wastewater treatment operations. The potential of recycling the wastewater and producing electricity makes the MFC concept very attractive.

(ii) Is Pretreatment and Post treatment of Wastewater Needed? The wastewater (flowback fluid) has high levels of suspended solids, dissolved solids (order of 100,000 ppm) and oil (API 2010). Before introducing the wastewater to MFC treatment, pretreatment will be necessary to condition the wastewater so that it can be treated rapidly in the MFC. The TDS content can be rapidly reduced by pretreatment where dissolve metals and chlorides can be rapidly precipitated and removed. Filtering the large suspended solids, adding used vegetable oil and bacteria (*Serratia* organisms and mixed cultures) to enhance the biological activities in the anode chamber will have to be investigated based on the composition of the wastewater. The used vegetable oil will be considered as one of the additive to condition the wastewater for the following reasons: (1) it has been demonstrated that biosurfactant can be produced in the anode chamber using the bacteria available at the UH research laboratory and also it enhanced the electricity production (2) biosurfactant produced from this process has the ability to **solubilize/mobilize** DNAPLs; (3) biosurfactant can also be used as a **coagulating agent** to rapidly remove some of the fine suspended particles; (4) biosurfactant can be **biodegraded** in a reasonable time period and is non-toxic. Based on a recent study, performance of the treated wastewater from the MFC can be substantially improved with post treatment for more enhanced hydraulic fracturing fluid that can be recycled.

(iii) What is New? Currently used wastewater treatment technologies (EC and DAF) have limitations in not only treating the wastewater but also recycling the treated wastewater. The proposed pretreatment will rapidly reduce the metal and chloride contents in the wastewater. The

integrated new MFC is unique in its ability to oxidize the oily waste in the anode chamber producing bioflocclulants to rapidly precipitate the suspended solids (fine particles) and in the cathode chamber reduce and precipitate the remaining metals in the dissolved solids. At the same time bioelectricity is produce to power the electrical appliances to totally or partly control the operation. Post treatment will enhance the fracturing performance of the treated wastewater.

2. Objectives

The overall objective of this study is to develop an environmentally sustainable **Real-time Monitoring Multiple Cathode and Anode Microbial Fuel Cell Configuration integrated** with **solar energy** to not only rapidly treatment the various types of wastewaters but also to recycle and reuse the treated wastewaters (oily, acidic and salty) by the industries. Also production of biosurfactant (anode chamber) and algae fuel (cathode chambers) will have market value. Taking advantage of the oxidation and reduction conditions in the anode and cathode chambers respectively in the MFC, the study will develop a well-integrated approach to recycle various types of wastewaters in four TASKS. The specific objectives of this study are as follows:

- (1) **Real-Time Monitoring**: New two probe method has been developed for real-time monitor changes in the fluids and solids and patterned in the U.S. recently (Vipulanandan 2020 and 2021). This method uses alternative current (A.C.) to identify the critical electrical properties of the fluids in the anode and cathode chambers.
- (2) **Pretreatment**: Remove the proppants and other suspended particles by rapidly filtering. Rapidly remove the dissolved salts by precipitating the metals and chlorides using an innovative additive developed recently.
- (3) **Optimize the MFC: The multiple cathode chambers** MFC configuration will be developed to rapidly treat and recycle the wastewaters.
 - (a) Optimize the cathode chambers (outside tanks) architecture to treat various types of wastewaters to remove the remaining dissolved solids efficiently. It will also accelerate the degradation of nitrates and chlorides in the wastewater with the algae growth enhanced using solar energy.
 - (b) Optimize the anode chamber (inside tank) architecture to not only extract maximum electrons during the biological production of bioflocclulants/biosurfactants from oil but also accelerate the coagulation and precipitation of the fine suspended solid particles.

3. Materials and Methods

Materials

Based on past experiences, literature reviews and some of the changes in the national rules and regulations the materials that were selected for this study are summarized in Table 1.

Table 1. Summary of Materials and Other Variables

Parameters	Materials and Processing/Testing Conditions
Electrode Configuration	Carbon brushes (shape and size), LCR meter
Anode Chamber Architecture	Pretreated waste water, Used vegetable oil, Bacteria, Temperature, Anaerobic and Volume
Cathode Chambers and New Bridges	Types and concentrations of wastewaters, pH, Volume, Algae (acidic and basic) and Solar energy, Polymer Grouts
Wastewaters	Oily and salty wastewaters (chloride and nitrate), Total suspended and dissolved solids, pH = 4 to 9
Pretreatment	Filters, additives, used-vegetable oil, bacteria (<i>Serratia</i> organisms and mixed cultures), algae (acidic and basic)
Post treatment	Biosurfactant produce in the anode chamber will be used for algae fuel extraction

Methods

It is important to identify the critical electrical properties of the wastewater with bacteria and algae to do the monitoring.

LCR Meter

The LCR meter (measures the inductance (L), capacitance (C) and resistance (R)) with the alternative (AC) current frequency varying from 20 Hz to 300 kHz and using the two probes (flexible wires) were used. This LCR device had a least count of $1 \mu\Omega$ for the electrical impedance (resistance, capacitance and inductance) in the frequency range of 20 Hz to 300 kHz. Based on the impedance (z) – frequency (f) response it was determined that the wastewaters were a resistive material. Hence the resistance was measured at 300 kHz using the two probe method during the testing.

Resistivity

Two Different methods were used in this study to measure the electrical resistivity of water and wastewaters. To assure the repeatability of the measurements, the initial resistivity was measured at least three times for each cement slurry and the average resistivity is reported. The electrical resistivity of the cement slurries were measured using the conductivity probe and digital resistivity meter.

(a).Conductivity Probe

Commercially available conductivity probe was used to measure the conductivity (inverse of resistivity) of the slurries. In the case of cement, this meter was used during the initial curing of the cement. The conductivity measuring range was from $0.1 \mu\text{S/cm}$ to 100 mS/cm , representing a resistivity of $0.1\Omega\cdot\text{m}$ to $10,000 \Omega\cdot\text{m}$.

(b).Digital Resistivity Meter

Digital resistivity meter (used in the oil industry) was used measure the resistivity of fluids, slurries and semi-solids directly. The resistivity range for this device was $2.5 \Omega\cdot\text{m}$ to $10000 \Omega\cdot\text{m}$. The conductivity probe and the digital electrical resistivity device were calibrated using

commercially available calibration solutions.

Chloride and Nitrate Probes

Both chloride and nitrate probes were calibrated and used to monitor the concentrations during the treatment processes.

4. Results, Analyses and Discussions

The objectives will be achieved in four TASKS. The major test variables to be investigated are summarized in Table 1.

REAL-TIME MONITORING

The new two probe (flexible wires) method (Vipulanandan Patent Number 10,690,586) was used to characterize the entire MFC system using AC with less than 1 volt and the frequency was varied from 20 Hz to 300 kHz (LCR Meter). The new method will separate out the effects of the cathodes and anodes from the fluids in the chambers. The new method will also quantify the conditions of the anodes and the cathodes real-time (Vipulanandan 2020 and 2021). Also conductivity, salt content (NaCl and NaNO₃) and pH were measured and compared with the impedance –frequency responses.

It is very important to real-time monitor the conditions of the wastewaters that needs to be treated and also the treatment processes and recycled water in the field. At present the field monitoring is done using probes which only give the water quality at a point. Wastewaters are transported through pipelined and channels and it is important to monitor the conditions along the length and also stored in tanks and reservoirs and it is important to determine the conditions with depth (vertical) and also laterally (horizontally). The recently developed 2-probe method has the potential for monitoring all these configurations.

Material (Wastewater) Characterization

It is important to identify the critical electrical property that can be used to monitor the wastewaters and recycled waters (treated waters) in the field during various treatments and applications. The electrical impedance-frequency response using the two probes and alternative current (AC) was used to identify critical electrical property such as inductance, capacitance (permittivity), resistance (resistivity) or a combination for the water, wastewaters and recycled waters.

Vipulanandan Impedance Model

Equivalent Circuits

Identification of the most appropriate equivalent circuit to represent the two probe contacts and the electrical properties of the testing materials (water and wastewaters) is essential to further understand its properties. In this study, an equivalent circuit to represent the water and wastewater were required for better characterization through the analyses of the Impedance Spectroscopy (IS) data (Vipulanandan 2020 and 2021).

(a). Waste water with 5% Clay

The test results of the water and wastewaters (5% suspended clays) tested in this study is shown in Figure 1. The equivalent electrical circuit is shown in Figure 2, which includes the two contacts and the bulk material (water or wastewater). This is also referred as CASE 2 in the literature. The resistances at 300 kHz for the water with 5% kaolinite and 5% bentonite were 2640 Ω, 2500 Ω and 1870 Ω respectively.

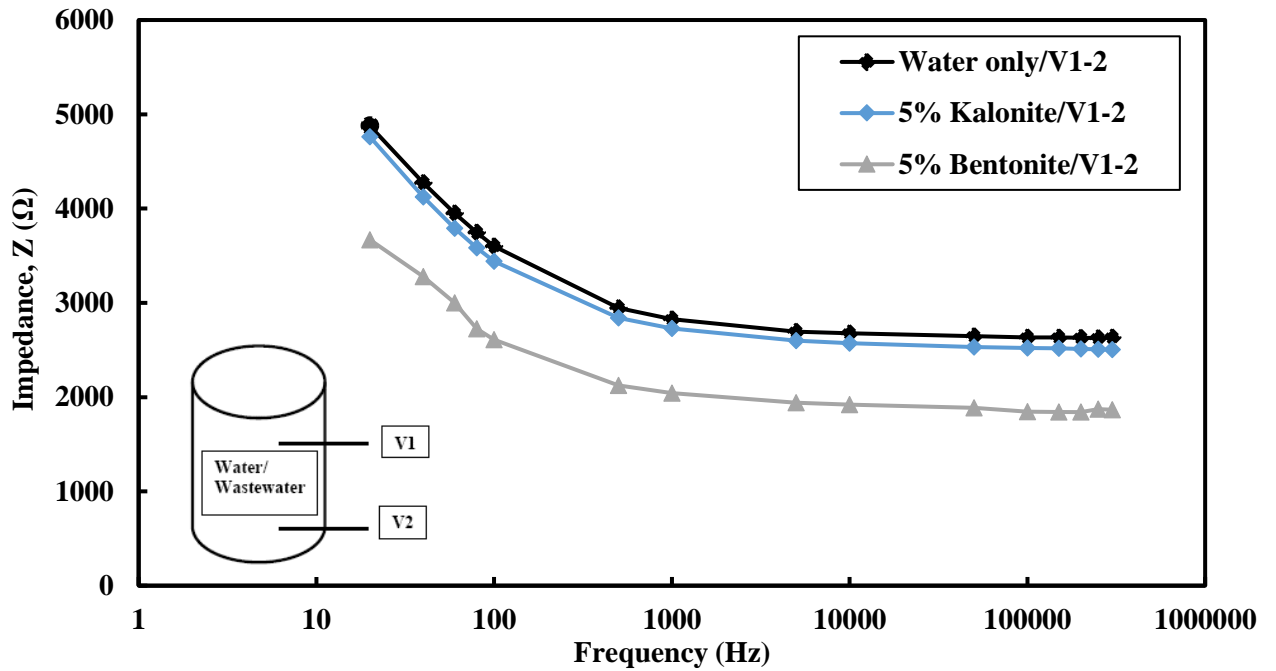


Figure 1. Impedance – Frequency Responses of Water and Wastewaters with 5% Clay

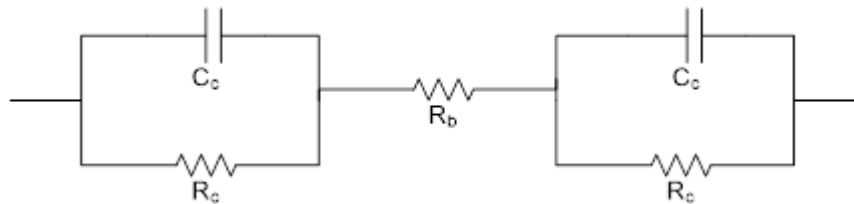


Figure 2. Equivalent Electrical Circuit Representing the Water with Clay Using the 2- Probe Monitoring.

CASE-2: Special Bulk Material - Resistance Only

The total impedance of the equivalent circuit for CASE-2 (Z_2) is as follows (Figure 2):

$$Z_2(\sigma) = R_b(\sigma) + \frac{2R_c(\sigma)}{1 + \omega^2 R_c^2 C_c^2} - j \frac{2\omega R_c^2 C_c(\sigma)}{1 + \omega^2 R_c^2 C_c^2} \tag{1}$$

$$= R_2 + j X_2 \tag{2}$$

The term R_2 in Eqn. (2) represents the real part of the impedance (Z_{real} of Z_2) and X_2 represents the imaginary part of the impedance (Z_2). When the frequency of the applied signal was very low, $\omega \rightarrow 0$, $Z_2 = R_2 = R_b + 2R_c$, and when it is very high, $\omega \rightarrow \infty$, $Z_2 = R_2 = R_b$ and X_2 will be equal to zero. In CASE-2, if the impedance is measured at very high frequency it will measure the resistance (R_b) in the material and eliminates the effects of the contacts and also it is frequency independent. This becomes another unique advancement in measurement and also monitoring since the resistance is independent of the very high frequency of measurement. In this study, resistance will be measured using the LCR meter and will be correlated to resistivity (material property) measured using the conductivity probe and digital resistivity meter.

(b). Waste water with 5% bacteria (*Serratia* organisms)

In the anode chamber bacteria was used to treat the oily wastewaters. It is important to determine the critical electrical property to monitor the process during the treatment of the waste waters. Using the LCR meter with the two probes placed vertically at 2 inches part (Fig. 1 insert) was used to monitor the waste water with 2% bacteria used in this study. The impedance frequency response is show in Figure 3, and it clearly indicated CASE 2 as observed for the clay contaminated wastewater. Also the resistance at 300 kHz was 640 Ω .

(c). Waste water with 5% normal algae (*Micractinium pusillum*)

In the cathode chamber normal algae was used to treat the salty (hydraulic fracturing fluids and Industries) wastewater. It is important to determine the critical electrical property to monitor the process during the treatment of the waste waters. Using the LCR meter with the two probes placed vertically at 2 inches part (Fig. 1 insert) was used to monitor the waste water with 2% normal algae used in this study. The impedance frequency response is show in Figure 4, and it clearly indicated CASE 2 as observed for the clay contaminated wastewater. Also the resistance at 300 kHz was about 41 Ω .

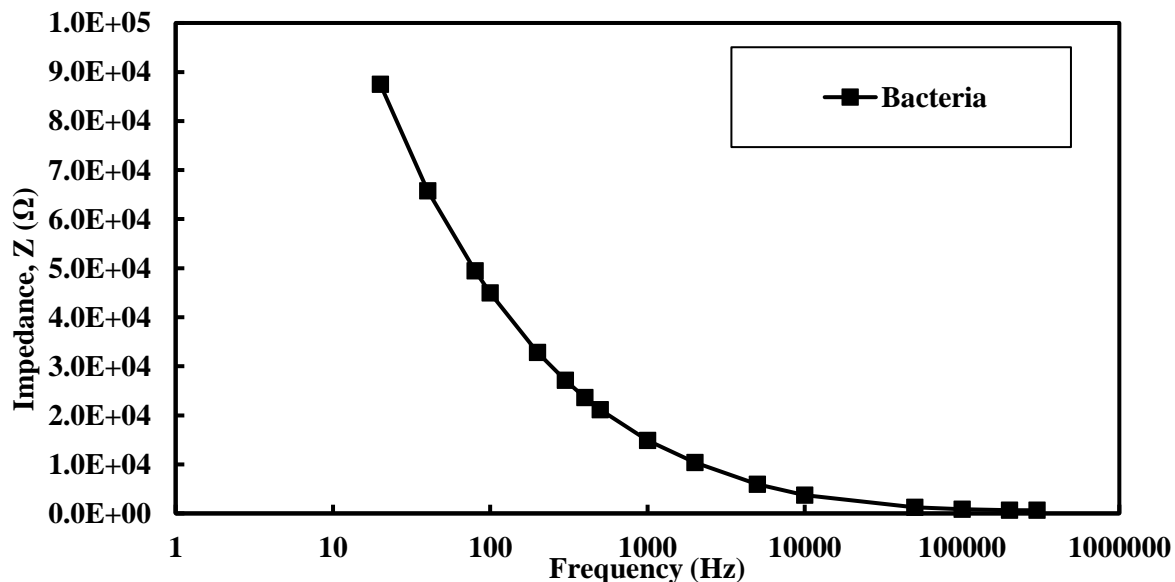


Figure 3. Impedance – Frequency Responses of Wastewaters with 2% Bacteria

(d). Waste water with 5% acidic algae (Lamar University)

In the cathode chamber acidic algae was used to treat the sodium nitrate (fertilizers and chemical industries) contaminated wastewaters. It is important to determine the critical electrical property to monitor the process during the treatment of the waste waters. Using the LCR meter with the two probes placed vertically at 2 inches part (Fig. 1 insert) was used to monitor the waste water with 2% bacteria used in this study. The impedance frequency response is show in Figure 4, and it clearly indicated CASE 2 as observed for the clay contaminated wastewater. Also the resistance at 300 kHz was about 410 Ω.

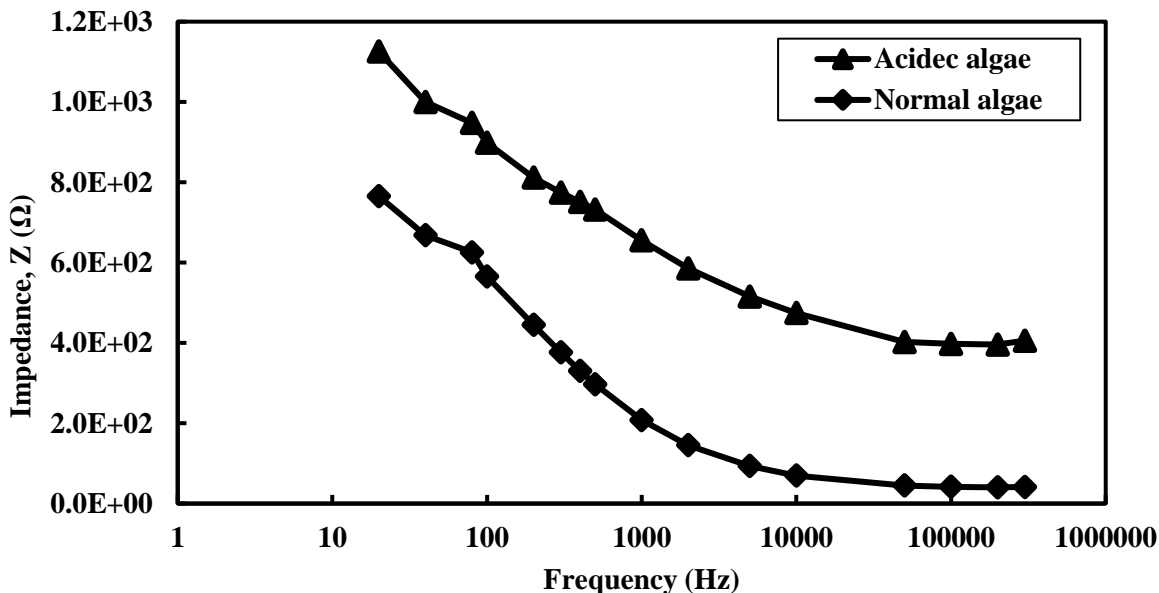


Figure 4. Impedance – Frequency Responses of Wastewaters with 2%Algae

Property Correlations with Resistivity

(a). Clay Content

The suspended solids, especially clay particles are one of the challenges in treating the hydraulic fracking wastewaters, industrial wastewaters and also flood waters. It is also important to quantify the sensitivity of resistivity to the amount and also the type of clays in the wastewaters. In the petroleum products and chemical products manufacturing industries kaolinite clay is used and the wastewaters are impacted by the kaolinite clay. Bentonite clays are encountered in hydraulic fracturing wastewaters. In this study the effect of kaolinite clay contamination was compared to the bentonite clay (sodium montmorillonite) contamination and also investigate the sensitivity of resistivity to detect the clay contamination. It is also important to quantify the changes using reliable models as shown in Figure 5.

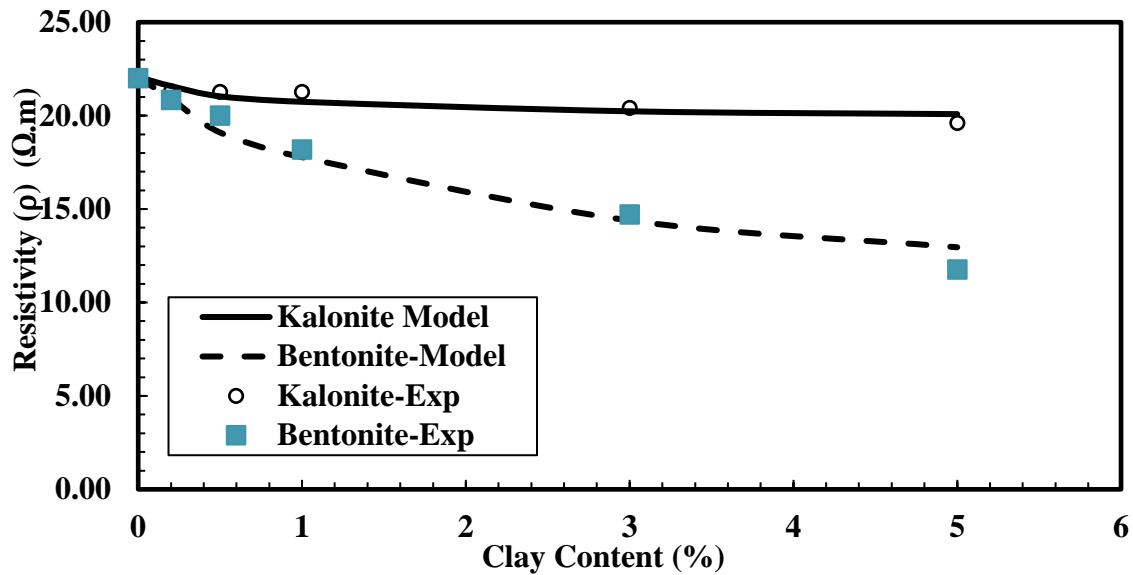


Figure 5. Variation of Resistivity of Wastewaters with up to 5% Bentonite and Kaolinite Clay Contents

Vipulanandan Correlation Model

It will be of interest to evaluate the effects of type and clay contents on the wastewaters. Hence, it will be important select the appropriate model to develop the correlations. Based on experiences, Vipulanandan Correlation model with the three parameters was selected and the relationship is as follows:

$$\rho = \rho_0 + \frac{x}{A + B * x} \tag{3}$$

Where x is the independent variable (example contaminated clay content) and ρ (Ωm) is the dependent variable (resistivity). Parameters ρ₀ (Ωm), A (%/Ωm) and B (Ωm)⁻¹ are related to the waste water compositions and testing environments (temperature, pressure and others). This model can represent both linear and nonlinear correlations. Also model parameters A and B can be positive or negative based on the correlation. This model is unique, since it has limited values for Y when x= 0 and x = ∞.

Kaolinite Clay: The changes in resistivity with the kaolinite clay content in the wastewater is shown in Figure 5. The resistivity of the water used in this study was 22.1 Ωm. With the kaolinite clay contamination the resistivity decreased. With 1% kaolinite clay, the resistivity of the wastewater decreased to 21.28 Ωm, the decrease in resistivity was -0.82 Ωm a -3.71% decrease. With 3% kaolinite clay, the resistivity of the wastewater decreased to 20.41 Ωm, the decrease in resistivity was -1.69 Ωm a -7.65% decrease. With 5% kaolinite clay, the resistivity of the wastewater decreased to 19.61 Ωm, the decrease in resistivity was -2.49 Ωm a -11.27% decrease. The percentage change in resistivity was more than double the percentage kaolinite clay content clearly indicates the sensitivity of resistivity to detect the kaolinite clay contamination. The model parameters with the statistical parameters (root mean square error (RMSE) and coefficient of determination (R²)) are summarized in Table 2.

Bentonite Clay: The changes in resistivity with the bentonite clay content in the wastewater is shown in Figure 5. The resistivity of the water used in this study was 22.1 Ωm . With the bentonite clay contamination the resistivity decreased. With 1% bentonite clay, the resistivity of the wastewater decreased to 18.18 Ωm , the decrease in resistivity was -3.92 Ωm a -17.74% decrease. This change was about 5 times (500%) higher than the change with 1% kaolinite clay contamination. With 3% bentonite clay, the resistivity of the wastewater decreased to 14.71 Ωm , the decrease in resistivity was -7.39 Ωm a -33.44% decrease. This change was about 4 times (400%) higher than the change with 3% kaolinite clay contamination. With 5% bentonite clay, the resistivity of the wastewater decreased to 12.96 Ωm , the decrease in resistivity was -9.14 Ωm a -41.36% decrease. This change was about 3.5 times (350%) higher than the change with 5% kaolinite clay contamination. The percentage change in resistivity was more than more than 8 times (800%) the percentage bentonite clay content clearly indicates the sensitivity of resistivity to detect the bentonite clay contamination. The model parameters with the statistical parameters (root mean square error (RMSE) and coefficient of determination (R^2)) are summarized in Table 2. The model parameters are also sensitive to the type of clay contamination.

Table 2 Correlation Model Parameters for Resistivity and Type of Contaminated Clay

Contaminate Clay Type	A (%/ Ωm)	B (Ωm) ⁻¹	ρ_0 (Ωm)	R^2	RMSE (Ωm)
Kaolinite	-0.30	-0.44	22.10	0.85	0.31
Bentonite	-0.15	-0.08	22.10	0.87	0.05

(b). Bactria Content

With the increase in bacteria content from 10 g/L (1%) to 1000 g/L (100%), 100% increase in the bacteria content, the resistivity of the wastewater solution increased from 5.7 Ωm to 22.8 Ωm , about 300% increase as shown in Figure 6. This clearly indicates the sensitivity of resistivity to the bacteria content. Also with the increase in bacteria content the pH of the solution reduced from 7.63 to 5.29, about a 31% reduction. This percentage change also clearly indicates the sensitivity of resistivity compared to the pH.

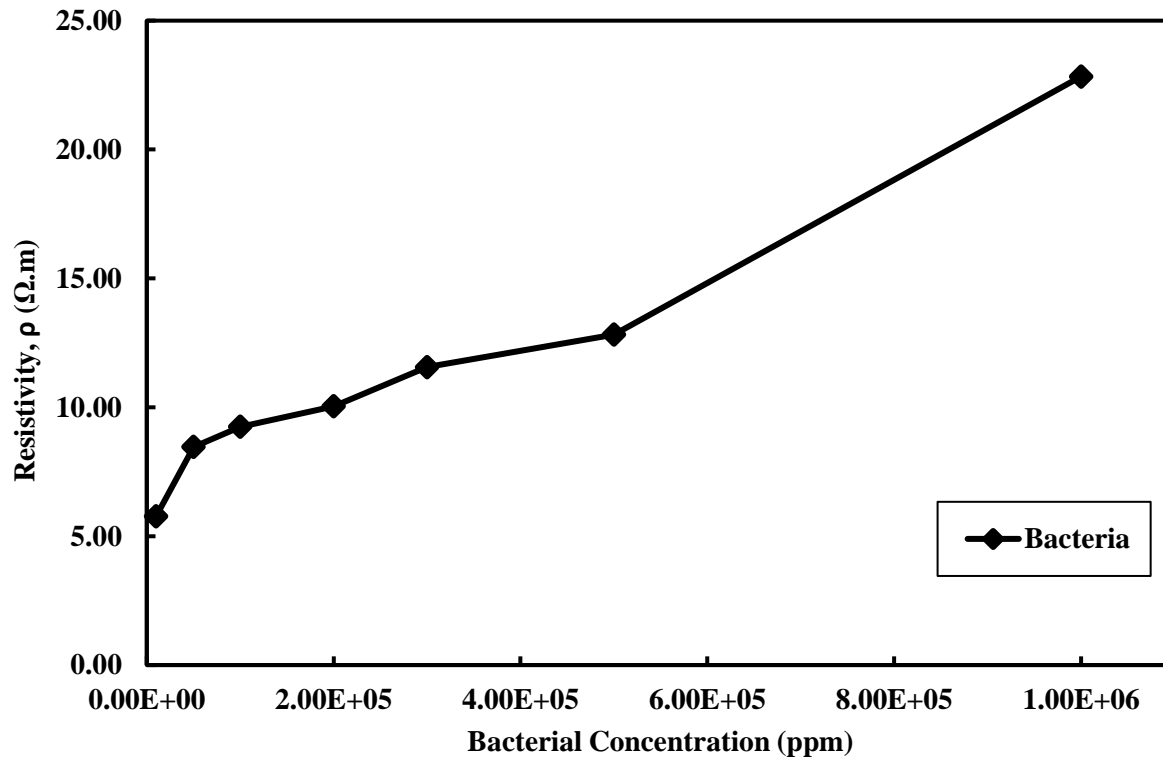


Figure 6. Variation of Resistivity of Wastewaters with up to 10% Bacteria Contents

(c). Normal Algae (*Microactinium pusillum*) Content

With the increase in algae content from 10 g/L (1%) to 1000 g/L (100%), 100% increase in the normal algae content, the resistivity of the wastewater solution decreased from 16.2 Ωm to 2.8 Ωm , about 83% decrease as shown in Figure 7. This clearly indicates the sensitivity of resistivity to the normal algae content and the trend was opposite to the bacteria. Also with the increase in normal algae content the pH of the solution reduced from 6.34 to 5.78, 8.8% reduction. This percentage change also clearly indicates the sensitivity of resistivity compared to the pH.

(d). Acidic Algae Content

With the increase in algae content from 10 g/L (1%) to 1000 g/L (100%), 100% increase in the normal algae content, the resistivity of the wastewater solution decreased from 12.3 Ωm to 0.25 Ωm , about 98% decrease as shown in Figure 7. This clearly indicates the sensitivity of resistivity to the acidic algae content and the trend was opposite to the bacteria. Also with the increase in acidic algae content the pH of the solution reduced from 7.01 to 4.31, 39% reduction. This percentage change also clearly indicates the sensitivity of resistivity compared to the pH.

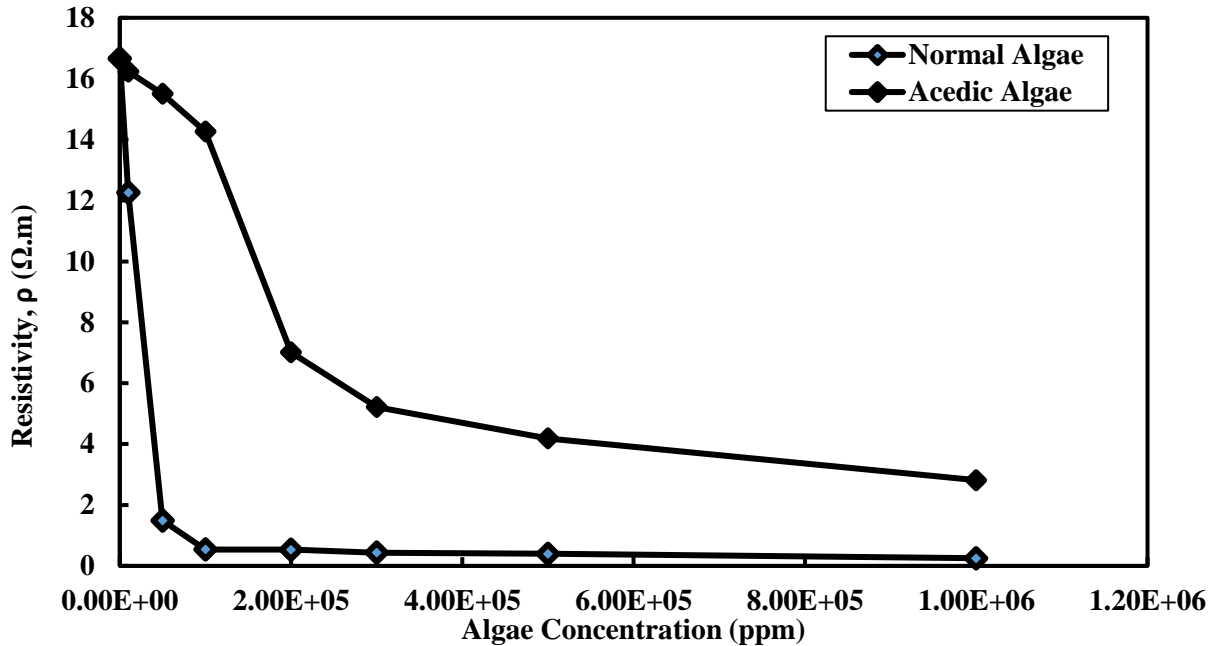


Figure 7. Variation of Resistivity of Wastewaters with up to 100% Normal and Acidic Algae Contents

(e). Salt Solutions

(i). NaCl Solution

With the increase in NaCl content from 10 g/L (1%) to 1000 g/L (100%), 100% increase in the NaCl content, the resistivity of the wastewater solution decreased from 0.22 Ωm to 0.064 Ωm, about 71% decrease as shown in Figure 8. Also with the increase in normal NaCl content the pH of the solution increased from 6.30 to 6.78, 7.1% increase. This percentage change also clearly indicated the sensitivity of resistivity compared to the pH.

(i). NaNO₃ Solution

With the increase in NaNO₃ content from 10 g/L (1%) to 500 g/L (50%), 50% increase in the NaNO₃ content, the resistivity of the wastewater solution increased from 0.081 Ωm to 0.147 Ωm, about 81% increase as shown in Figure 9. Also with the increase in normal NaNO₃ content the pH of the solution increased from 7.43 to 6.99, 5.9% decrease. This percentage change also clearly indicated the sensitivity of resistivity compared to the pH. All the trends were just the opposite of what was measured for the NaCl solution.

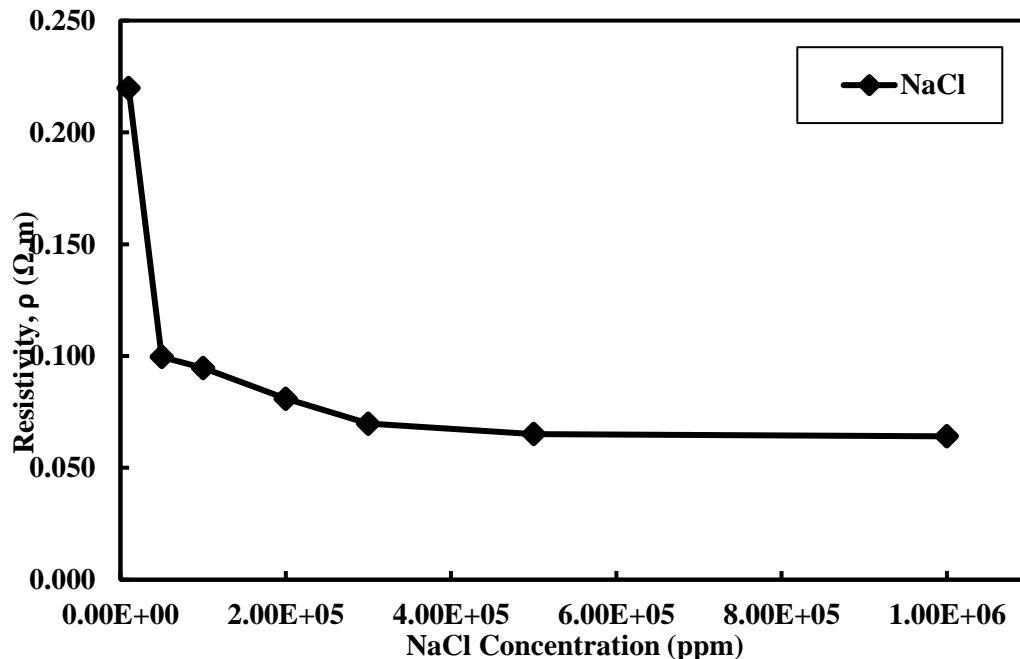


Figure 8. Variation of Resistivity of Wastewaters with up to 1000 g/L (100%) NaCl Contents

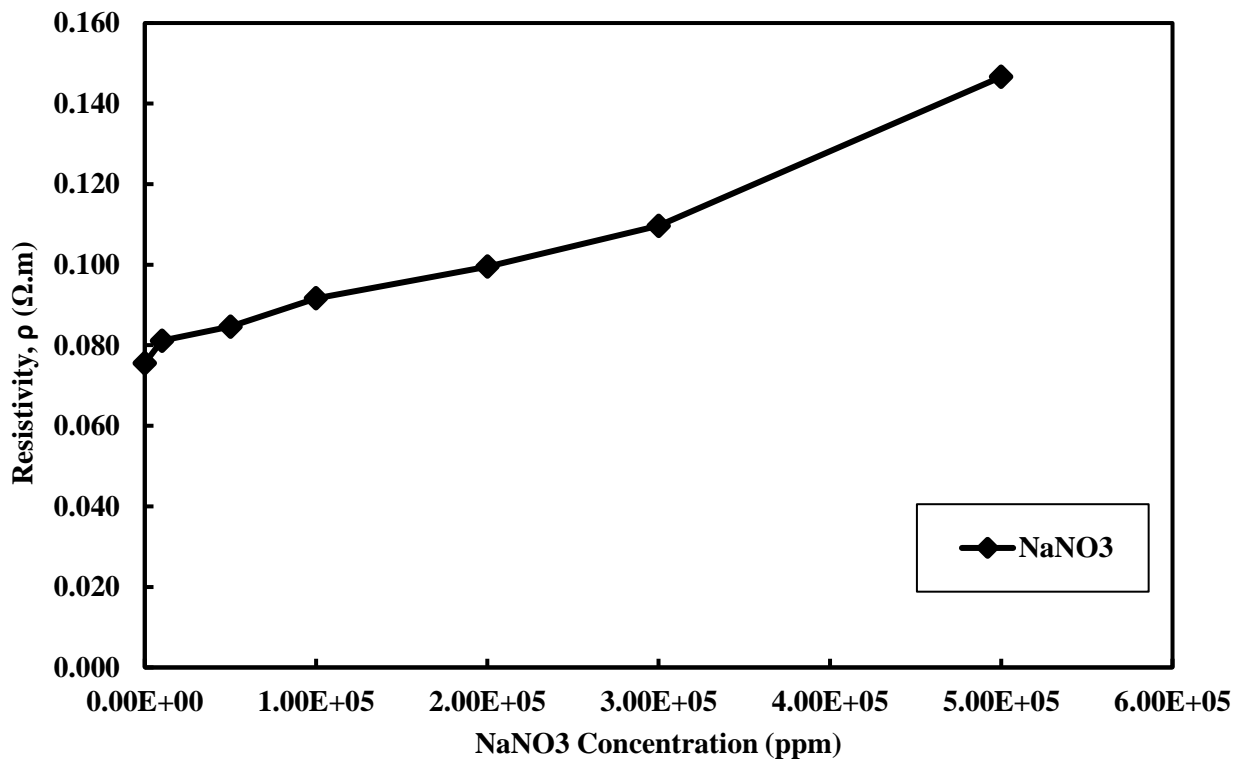
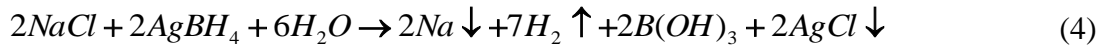


Figure 9. Variation of Resistivity of Wastewaters with up to 500 g/L (50%) NaNO₃ Contents

PRETREATMENT

Methods to condition the wastewaters before introducing them into the anode chamber was investigated. In this study borohydrate was used to remove the NaCl salt . Additive, silver borohydrate (AgBH_4) was used to precipitate the metal (Na) and chloride as follows:



The Na was precipitated with AgCl so that these were removed with large size suspended proppant solids (sand diameter greater than 0.5 mm) using filters and used vegetable oil (no more than 1%) and bacteria (*Serratia* organisms and mixed cultures) were added to accelerate the biological activities in the anode chamber (Liu and Vipulanandan 2017). Also the pH of the wastewater was adjusted to be in the range of 6 to 8.

DEVELOPMENT OF NEW MFC

New **multiple cathode and anode chamber MFC** will be further developed to treat the oil contaminated salt water received from pretreatment and monitored using the new nondestructive 2 probe electrical method. This configuration will be easy to adopt in the field as treatment ponds on the surface or parallel pipelines buried in the ground. Also this MFC can be adopted as mobile units in trucks. Several multi chamber MFC has been built as shown in Figure 10 with four probe (2 vertical and 2 horizontal) in each chamber for monitoring.

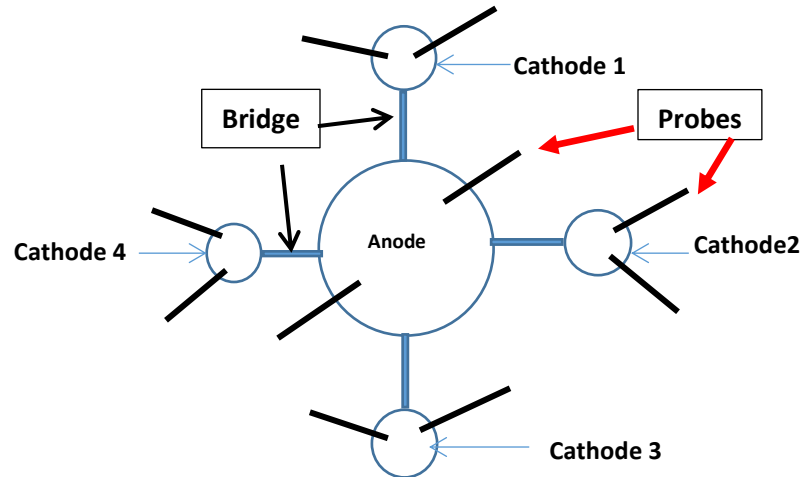


Figure 10. Multi Chambers (Five) MFC with the Monitoring Probes

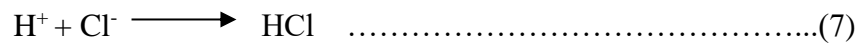
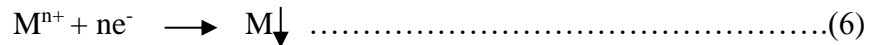
The multi chamber MFC had one anode chamber connected to four cathode chambers for rapid treatment of wastewaters. In this study, 1000 mL anode solution and 250 mL cathode solution in the cathode chambers with varying concentration of salt solutions were investigated with different polymer grout bridge materials. Instead of using the cation exchange membrane, polymer gels were used in the bridge separating the anode chamber from the cathode chambers. Currently

the multi chamber configuration is being checked for leakage of water and being monitored for resistance changes using the LCR meter. Carbon fiber brushes are being used as anode and cathode electrodes. Anode electrode was externally connected to the cathode electrodes using 15 kΩ external resistance.

Anode treatment: convert oil waste into bioflocculant and flocculation of the suspended solid



Cathode treatment: reduce the dissolved solids (metal ions M^{n+}) to become precipitates:



In order to further develop efficient MFC systems, various configurations for the cathode chamber including **acrylamide grout bridges** instead of cation exchange membrane (CEM) were investigated (Table 1). As electrons and protons are transported to the cathode chambers of MFC, the e^- released from electrode of cathode can be used to reduce the dissolved metals in the solution. The reduction process of contaminants (Eqn. 6 & 7) in the cathode can be due to the gain of electron or gain of hydrogen. Based on the composition of the wastewaters two types of reduction reactions also enhanced by the acclimated algae (*Micractinium pusillum* (normal algae) and acidic algae) growth under solar energy that in the cathode chambers.

One study was focused on treating the oil waste in the anode chamber and treating 4.5 g/L of NaCl wastewater in one cathode chamber (#3) with the normal algae and 1.2 g/L NaNO_3 wastewater in another cathode chamber (#4) with the acidic algae. In cathode chambers #1 and #2 only water was used to compare the results. Also 4 probes (anode probes) were used in the anode chamber and each probe was connected to the 4 cathode chambers separately. Also impedance-frequency responses of each cathode chamber with the corresponding anode probe were tested.

Impedance-frequency Responses

It is important to characterize the anode and cathode chambers independently to identify the critical electrical parameter to monitor.

Connection 1-1 (Cathode #1 (water) and Anode #1 (oily waste))

The impedance –frequency response is shown in Figure 11 where the probes were the anode and the cathode. The response is CASE 2 indicating resistivity will be the critical electrical parameter to monitor. Also the impedance curve is relatively flat compared to Figure 3, indicating that the two probes are very efficient with very low resistance. Also the impedance curve reduced with time indicating good flow of electricity. The bulk resistance at 300 kHz reduced from 3770 Ω to 3500 Ω in one month, a 7.2% reduction.

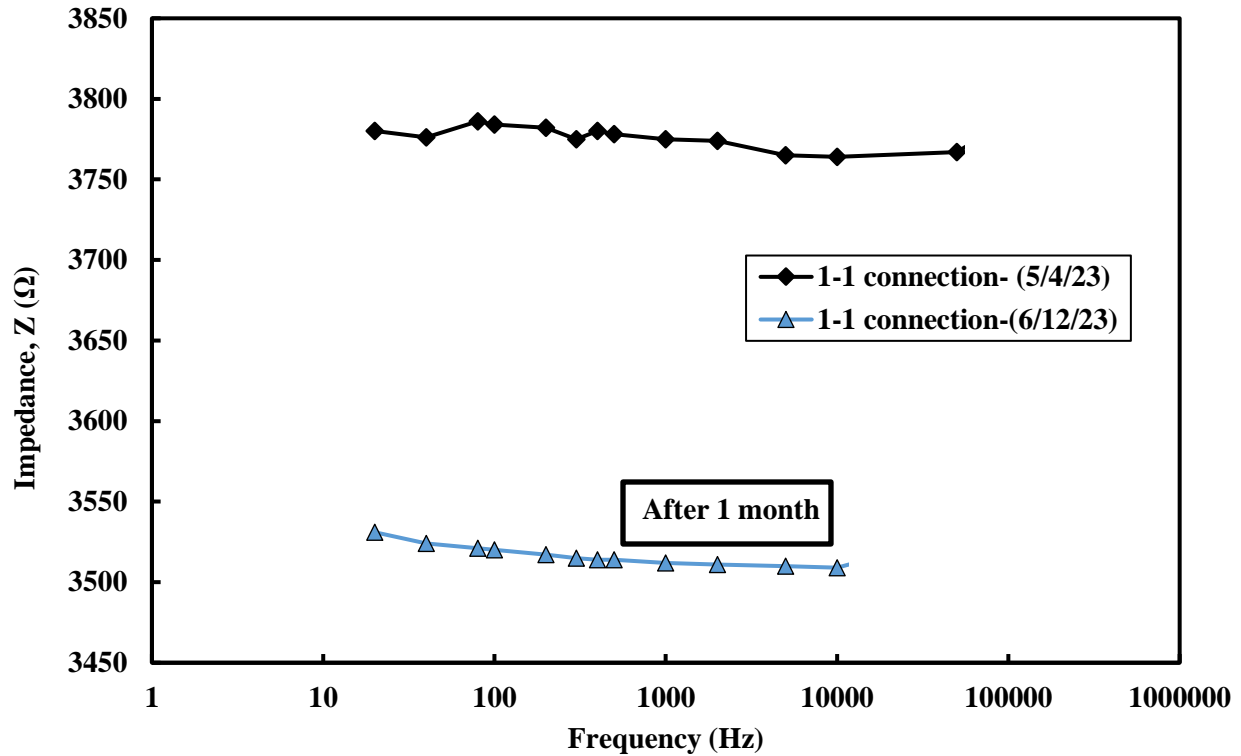


Figure 11. Impedance-frequency Response of Anode #1 and Cathode#1 Connection

Connection 2-2 (Cathode #2 (water) and Anode #2 (oily waste))

The impedance –frequency response is shown in Figure 12 where the probes were the anode and the cathode. The response is CASE 2 indicating resistivity will be the critical electrical parameter to monitor. Also the impedance curve is relatively flat compared to Figure 3, indicating that the two probes are very efficient with very low resistance. Also the impedance curve reduced with time indicating good flow of electricity. The bulk resistance at 300 kHz reduced from 4130 Ω to 3980 Ω in one month, a 3.6% reduction.

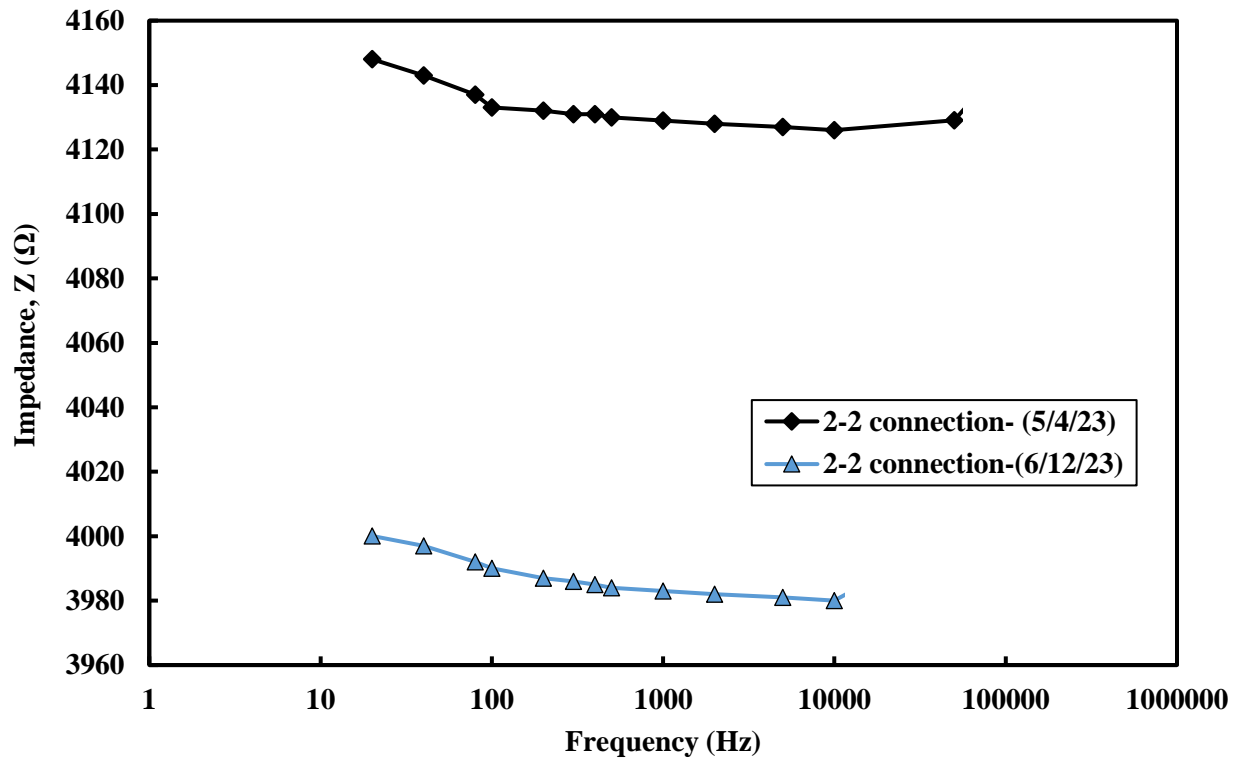


Figure 12. Impedance-frequency Response of Anode #2 and Cathode#2 Connection

Connection 3-3 (Cathode #3 (NaCl wastewater with normal algae) and Anode #3 (oily waste))

The impedance –frequency response is shown in Figure 13 where the two probes were the anode and the cathode in 4.5 g/L NaCl with normal algae . The response is CASE 2 indicating resistivity will be the critical electrical parameter to monitor. Also the impedance curve is relatively flat compared to Figure 3, indicating that the two probes are very efficient with very low resistance. Also the impedance curve reduced with time indicating good flow of electricity. The bulk resistance at 300 kHz reduced from 4200 Ω to 1390 Ω in one month, a 67% reduction.

Connection 4-4 (Cathode #4 (NaNO₃ wastewater with acidic algae) and Anode #4 (oily waste))

The impedance –frequency response is shown in Figure 14 where the two probes were the anode and the cathode in 1.2 g/L NaNO₃ with acidic algae. The response is CASE 2 indicating resistivity will be the critical electrical parameter to monitor. Also the impedance curve is relatively flat compared to Figure 3, indicating that the two probes are very efficient with very low resistance. Also the impedance curve reduced with time indicating good flow of electricity. The bulk resistance at 300 kHz reduced from 4550 Ω to 2570 Ω in one month, a 43.5% reduction.

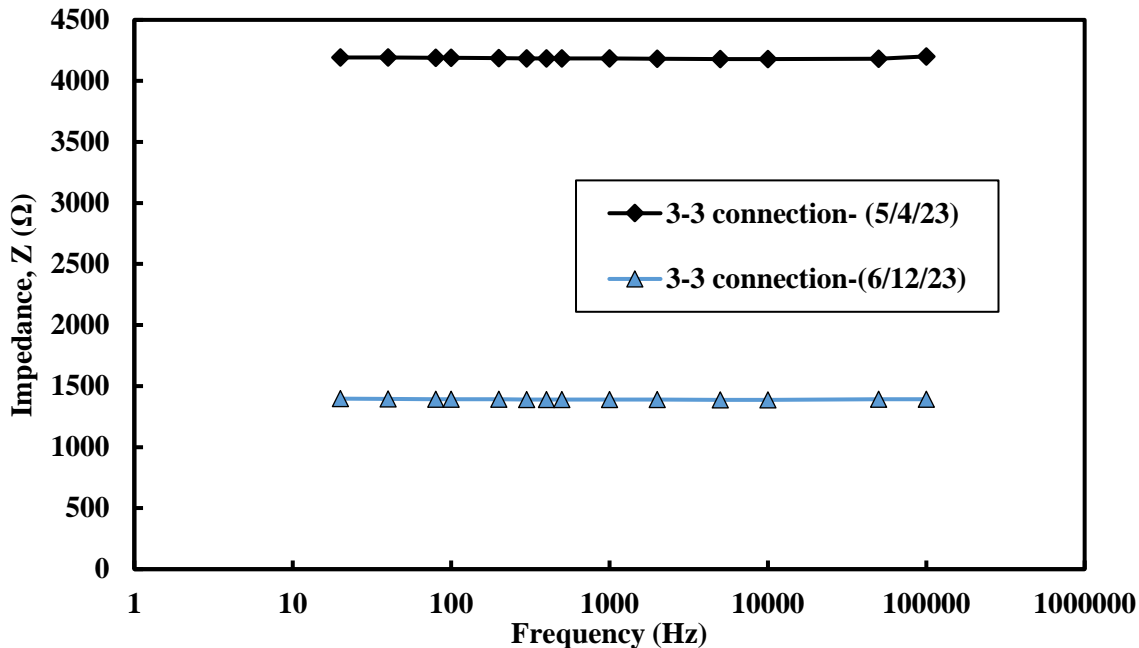


Figure 13. Impedance-frequency Response of Anode #3 (in oil waste) and Cathode#3 (in 4.5 g/L NaCl with normal algae) Connection

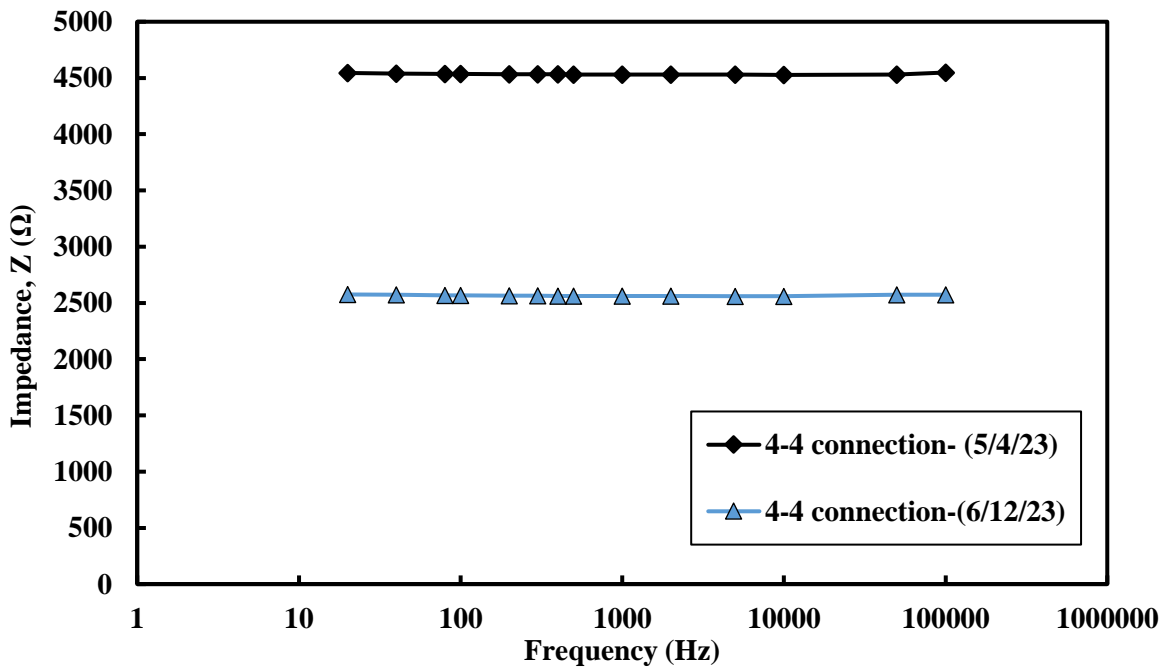


Figure 14. Impedance-frequency Response of Anode #4 (in oil waste) and Cathode#4 (in 1.2 g/L NaNO₃ with acidic algae) Connection

Current Flow

Connection 1-1

The current flow was 0.0048 mA and it remained constant over 40 days of measurements.

Connection 2-2

The current flow was 0.0031 mA and it remained constant over 40 days of measurements.

Connection 3-3 (Cathode #3 (NaCl wastewater with normal algae) and Anode #3 (oily waste))

The current flow increased from 0.0007 mA to 0.0193 mA in 40 days, over 2,650% increase as shown in Figure 15. So the normal algae activity in cathode chamber #3 with 4.5 g/L NaCl solution was very effective in increasing the current flow. Also the current flow is 5 to 6 times higher than the Connection 1-1 and Connection 2-2 respectively

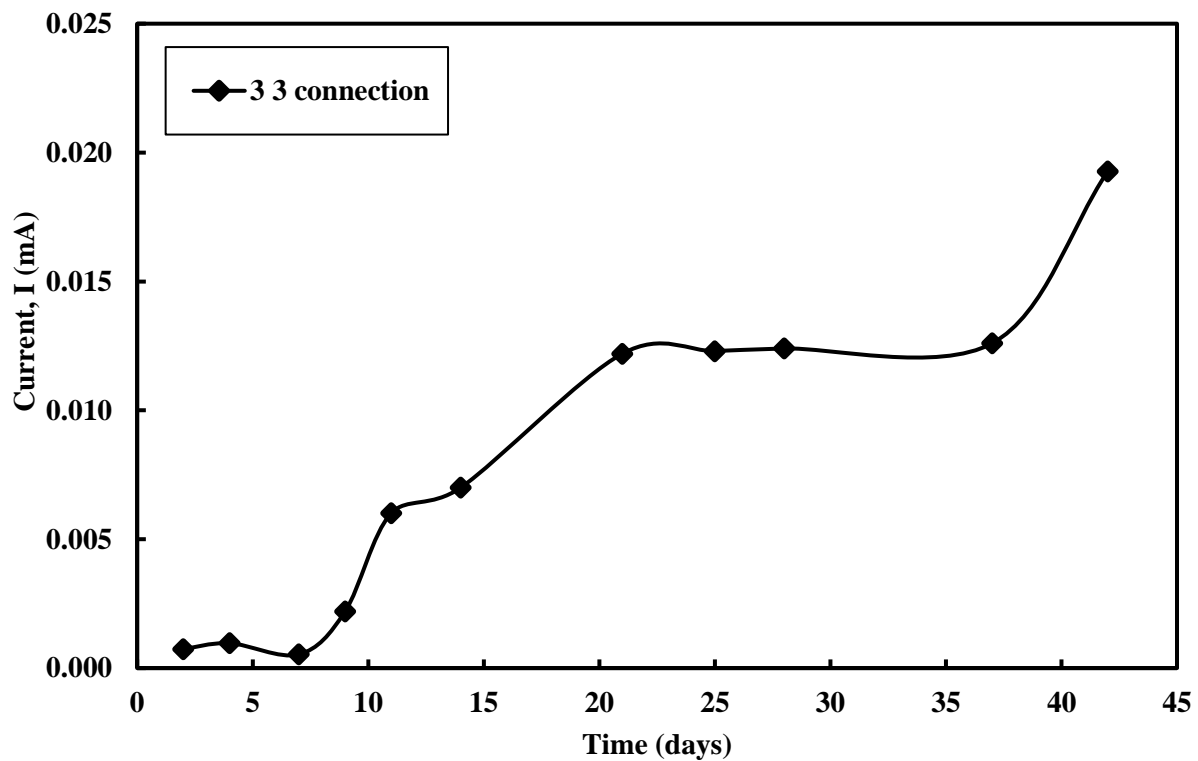


Figure 15. Bioelectrical Current Production from Anode #3 (in oil waste) and Cathode#3 (in 4.5 g/L NaCl with normal algae) Connection

Connection 4-4 (Cathode #4 (NaNO₃ wastewater with acidic algae) and Anode #4 (oily waste))

The current flow increased from 0.0035 mA to 0.0077 mA in 40 days, over 120% increase as shown in Figure 16. So the acidic algae activity in cathode chamber #4 with 1.2 g/L NaNO₃ solution was

very effective in increasing the current flow. Also the current flow was close to 2 times higher than the Connection 1-1 and Connection 2-2.

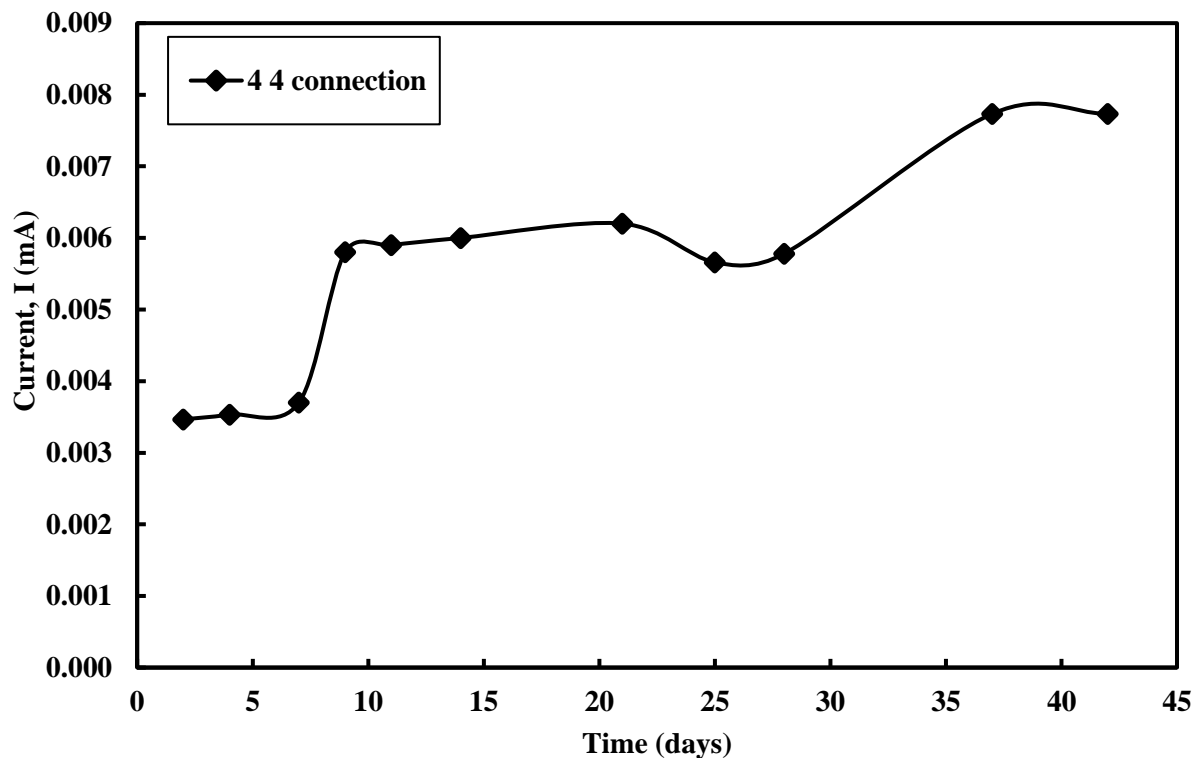


Figure 16. Bioelectrical Current Production from Anode #4 (in oil waste) and Cathode#4 (in 1.2 g/L NaNO₃ with acidic algae) Connection

Salt Removal in the Cathode Chambers

(i). Cathode Chamber #3 (NaCl removal)

The NaCl concentration in the cathode chamber #3 with the normal algae reduced from 4500 ppm to 2263 ppm in 30 days, close to 50% reduction as shown in Figure 17. Normal algae was very effective in removing the NaCl in the cathode chamber and also increasing the current flow.

(ii). Cathode Chamber #4 (NaNO₃ removal)

The NaNO₃ concentration in the cathode chamber #4 with the acidic algae reduced from 1200 ppm to 640 ppm in 30 days, close to 47% reduction as shown in Figure 17. Acidic algae was effective in removing the NaNO₃ in the cathode chamber and also increasing the current flow.

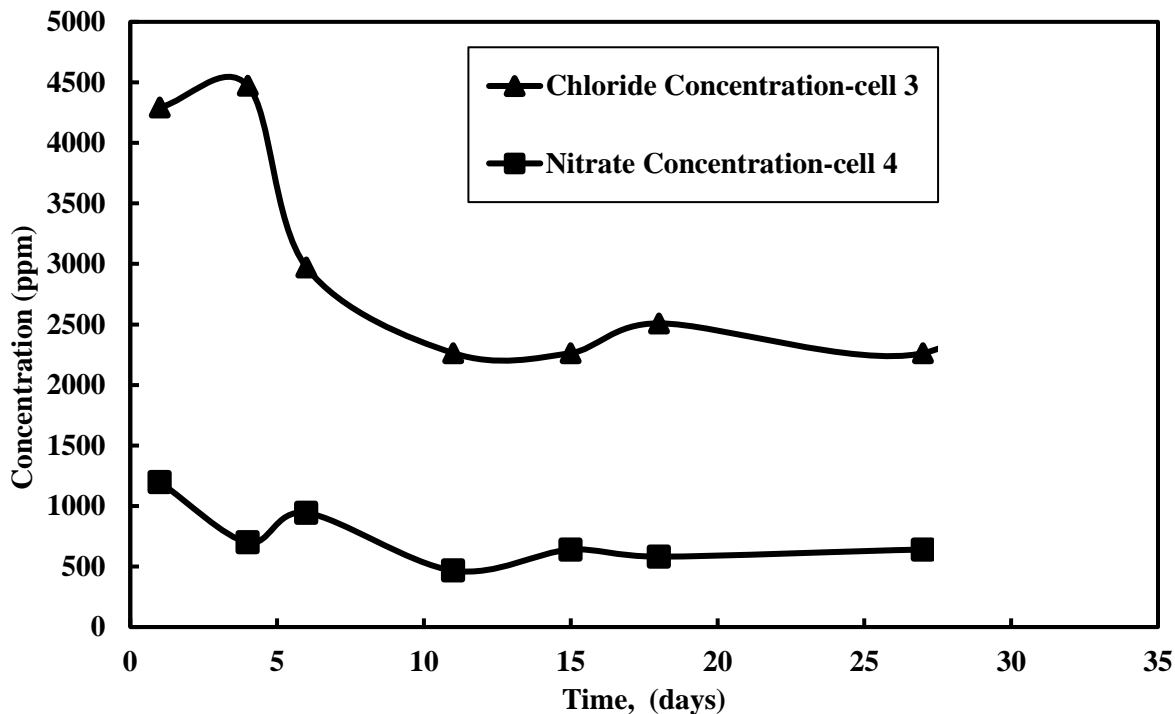


Figure 17. Removal of NaCl and NaNO₃ in the Cathode Chambers with the Algae

CONCLUSIONS

Based on the experimental studies and analyses of the data following conclusions are advanced.

- (1). New fluid characterization method using the electrical impedance-frequency responses the water and waste water with various contaminants, bacteria and algae were characterized. Based on the responses, critical electrical property to monitor was identified.
- (2). The two probe method using alternative current (AC) and 1 volt was effective in real-time monitoring the contaminated wastewaters and also the MFC treatment process.
- (3). The pretreatment of wastewater using silver borohydrate in removing NaCl was very effective.
- (4). The multi-chamber microbial fuel cell (MFC) was very effective in treating oily wastewaters, salty wastewaters, producing bioelectricity and also producing by-products such as biosurfactant and algae fuel. Also the two probe method was very effective in real-time monitoring the treatment processes.
- (5). The MFC treatment method was very cost effective.

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