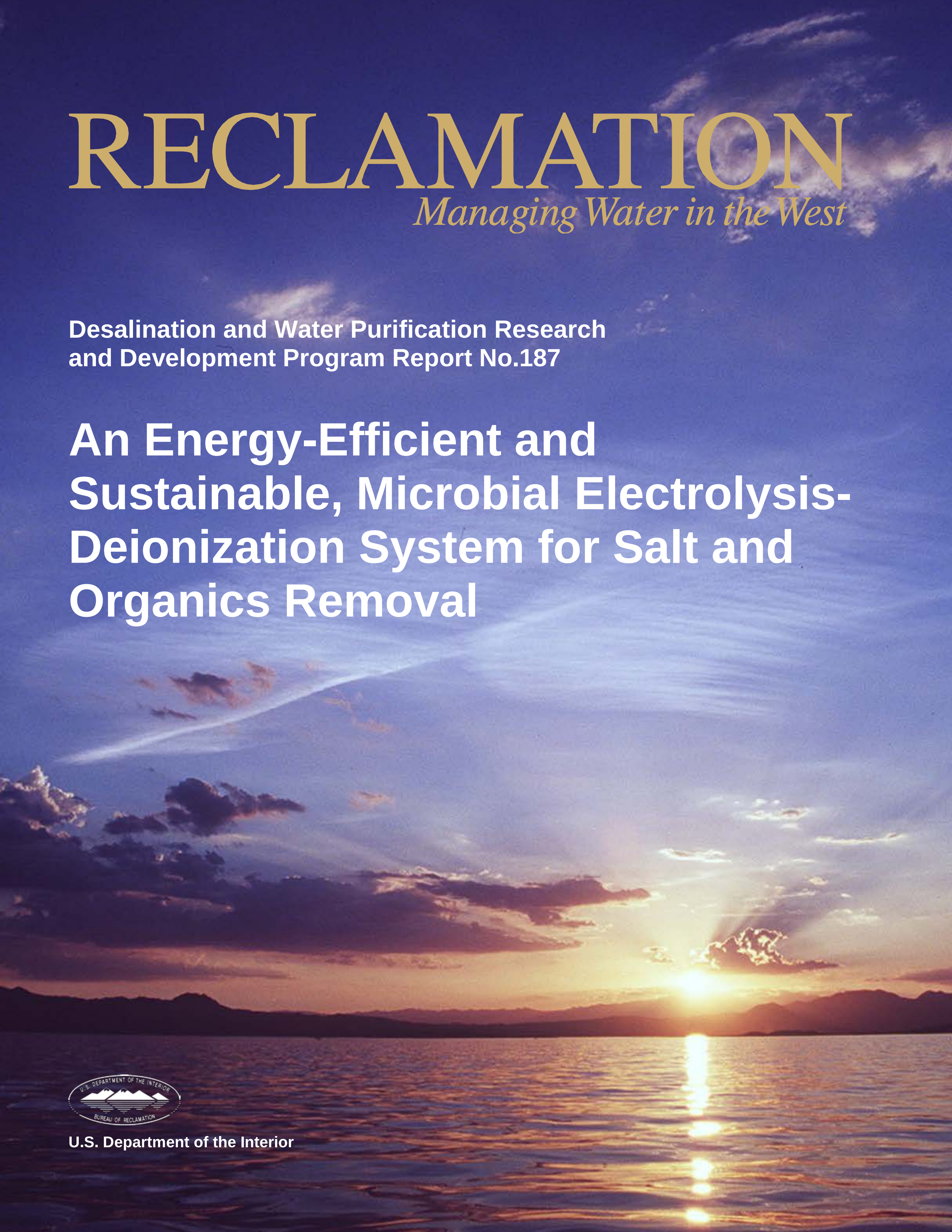

RECLAMATION

Managing Water in the West

Desalination and Water Purification Research
and Development Program Report No.187

An Energy-Efficient and Sustainable, Microbial Electrolysis-Deionization System for Salt and Organics Removal

U.S. Department of the Interior

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14. ABSTRACT A novel process to remove salt and organic contaminants synergistically was developed. The conversion of soluble organic compounds via microbial electrolysis cell (MEC) was coupled to salt removal via capacitive deionization (CDI) providing a proof of principle for synergistic salt and organic removal. Hydrogen was generated by MEC from organic compounds and used to produce renewable electricity via a fuel cell, which was then used to power the CDI cell to achieve deionization. This demonstrated the concept of a microbial electrolysis-deionization system (MEDS) which has potential for energy-efficient desalination.					
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Desalination and Water Purification Research and Development Program Report No. 187

An Energy-Efficient and Sustainable, Microbial Electrolysis-Deionization System for Salt and Organics Removal

Prepared for the Bureau of Reclamation Under Agreement No. R13AC80021

By

Abhijeet P. Borole (PI), R. K. Goud, The University of Tennessee, Knoxville, Tennessee

Robert Campbell (Co-PI), Fred Seamon, CAP Holdings Company

Costas Tsouris, Oak Ridge National Laboratory (No-cost collaborator)

Mission Statements

The U.S. Department of the Interior protects America’s natural resources and heritage, honors our cultures and tribal communities, and supplies the energy to power our future.

The mission of the Bureau of Reclamation is to manage, develop, and protect water and related resources in an environmentally and economically sound manner in the interest of the American public.

Disclaimer

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Acronyms and Abbreviations

BOD	biological oxygen demand
CDI	capacitive deionization
CE	coulombic efficiency
CHC	CAP Holdings Company
COD	chemical oxygen demand
DWPR	Desalination and Water Purification Research
EWP	Removal of TDS using EWP from synthetic water.
KIPT	Kharkov Institute of Physics
LLNL	Lawrence Livermore National Laboratory
MBEST	Monterey Bay Education Science and Technology Center
MEC	microbial electrolysis cell
MEDS	microbial electrolysis-deionization system
MFC	microbial fuel cell
MXC	microbial electrochemical systems
ORNL	Oak Ridge National Laboratory
PEM	polymer electrolyte membrane
Reclamation	Bureau of Reclamation
TDS	total dissolved solids
UTK	University of Tennessee, Knoxville
WSH	West Star Holdings

Measurements

°C	degrees Celsius
A	amps
A/m2	amps per square meter
g/L	grams per liter
g/L-anode reservoir-day	grams per liter per anode reservoir per day
L	liters
L/L day	liter of hydrogen per liter day
L/min	liters per minute
mA	milliamps
mg/g-carbon-hour	milligrams per gram of carbon per hour
mL	milliliters
mL/min	milliliter per minute
mM	millimeter
mS/cm	millisiemens per centimeter
mW/m^2	megawatt hours per square meter
V	volts
W/m^2	watts per square meter

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Executive Summary

The University of Tennessee, Knoxville (UTK) received funding from the Bureau of Reclamation (Reclamation) in September 2013 to investigate a novel salt and organic removal technology. Using microbial electrolysis cell (MEC) technology and salt removal via capacitive deionization (CDI) to remove organic compounds present in produced water was investigated. This project was conducted in collaboration with CAP Holdings Company (CHC), which provided expertise in CDI technology.

Converting soluble organic compounds via MEC was coupled to salt removal via CDI, providing a proof of principle for synergistic salt and organic removal. Hydrogen was generated by MEC from organic compounds and used to produce renewable electricity via a polymer electrolyte membrane (PEM) fuel cell , which was then used to power the CDI cell to achieve deionization.

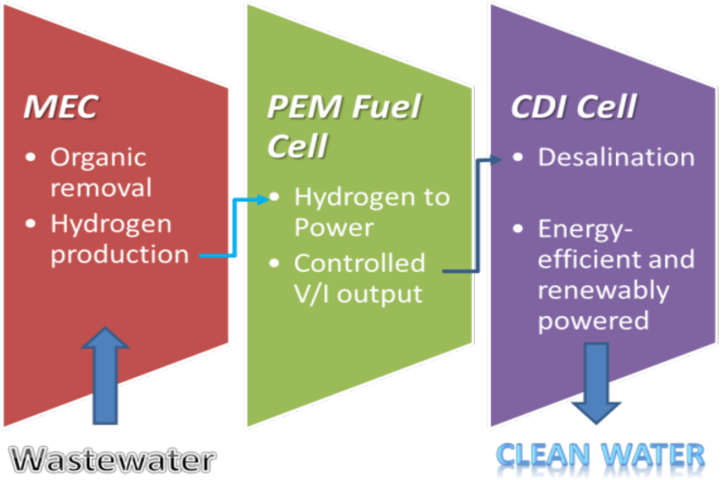

Figure 1. MEDS schematic.

This demonstrated the concept of a microbial electrolysis-deionization system (MEDS) capable of energy-efficient desalination. Demonstration of the MEDS concept opens the door to applying this technology for treatment of fracking water and produced water—resulting in simultaneous salt and organic removal. A patent application is being submitted related to this technology.

CHC has an interest in investigating the feasibility of this technology via field testing and subsequently to develop it for application in the oil and gas industry. We look forward to further collaboration with the Reclamation Desalination and Water Purification Research (DWPR) Program to take this technology to the next step and apply the MEDS system to develop a fracking/produced water and brackish water treatment technology.

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1. Technical Summary

To develop a system for synergistic removal of salts and organics, studying the effect of salt on organic removal was necessary. This was achieved during the first few months of the project. We developed a microbial biofilm catalyst capable of extracting energy from typical organic contaminants (such as acetate) in the presence of salt, and designed and constructed a microbial fuel cell (MFC) harboring the microbial biofilm anode. The MFC performance was measured by current density and power density to quantify the bioenergy production from the organic contaminants. The results indicated tolerance of up to 35 grams per liter (g/L) salt and optimal anode performance at 25 g/L salt concentration. A current density of 4.7 amps per square meter (A/m^2) was obtained with a power density of 650 megawatt hours per square meter (mW/m^2).

Salt removal was investigated using a capacitive deionization method with a mesoporous carbon electrode. We applied voltage from 0.5 to 1.6 volts (V). A salt removal rate of 4.8 milligrams per gram of carbon per hour (mg/g-carbon-hour) was achieved at an applied voltage of 1V. A voltage of 1 V is necessary for effective salt removal, therefore direct use of MFC for power generation was not feasible. Use of a microbial electrolysis cell to generate hydrogen and a polymer electrolyte membrane (PEM) fuel cell stack to generate power with 1 V or higher output was effective in salt removal, achieving a rate of 17.4 mg/g-carbon-hour.

Using the MFC anode evolved for salt tolerance, we developed a microbial electrolysis cell capable of hydrogen production. Conversion of acetate and organic contaminants in produced water to hydrogen was investigated. Production of hydrogen at a rate of 5.1 ± 0.1 L H_2/L-anode-day and a current density of 5.4 ± 0.3 A/m^2 was demonstrated in batch studies at a salt concentration of 25 g/L. Maximum hydrogen production rate of 6.5 ± 0.3 L H_2/L-anode-day was obtained at a salt concentration of 10 g/L. Continuous operation was demonstrated resulting in a hydrogen production rate of 15.7 L H_2/L-anode-day at a current density of 12.7 A/m^2 at a substrate loading of 14.4 g/L-day.

Demonstration of the MEDS concept for integrated salt and organic removal was carried out via a step-by-step approach and included multiple stages of development. First, salt removal via CDI was investigated using electricity generated by an external (non-renewable) power source. This was followed by investigations of salt removal using power generated by a PEM fuel cell. A two-cell stack was used for this purpose. Investigations demonstrating power production using hydrogen generated by an MEC were shown using the PEM fuel cell separately. The final stage included integration of all components:

MEC, fuel cell and CDI cell to show that hydrogen generated from organic waste present in produced water can be used to power a fuel cell, which can be used to operate a CDI cell performing deionization. This integrated system demonstrates the synergy of the MEC and CDI technologies resulting in a completely renewable waste-to-energy powered desalination system, which is a landmark achievement for this project.

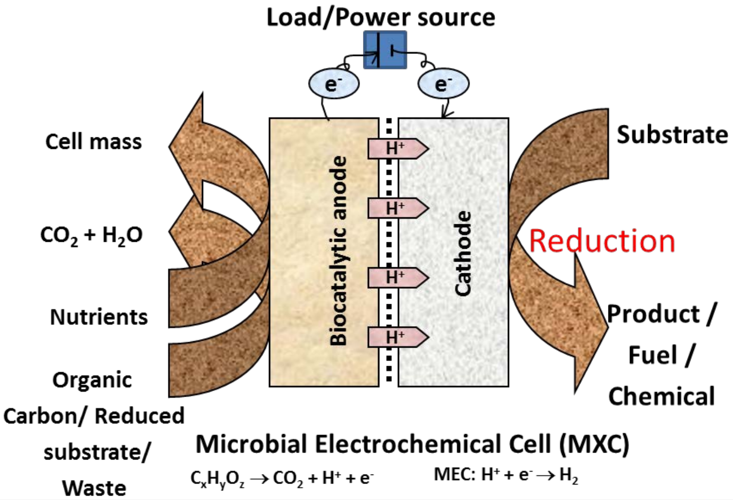
2. Background and Introduction

2.1. Capacitive Deionization (CDI)

The CDI process has been tested for treating various wastewaters, including brackish water for production of reusable water (Sun 2012). The industry collaborator on this project, CAP Holdings Company (CHC) has been working with Oak Ridge National Laboratory (ORNL) and other partners on development of CDI technology for the last decade or so. A flow-through electrode design was previously tested at ORNL, which demonstrated improved capacity and lower energy use compared to previous parallel plate designs. Other technology improvements have also been made in collaboration with Lawrence Livermore National Laboratory (LLNL) (Tsouris, C., et al. 2011) and at companies such as Voltea in the Netherlands.

2.2. Microbial Electrolysis

Microbial electrochemical systems (MXC) integrate microbial catalysts which break down organic matter with electrocatalysts to generate energy or chemicals. Figure 2 shows a representation of an MXC. Operation of the cell using an oxygen-reducing catalyst generates electricity, while use of a proton-reducing catalyst at the cathode results in hydrogen production. The half reactions at the anode and cathode for the hydrogen production process are as follows (using acetic acid as substrate):



Type of BES	Cathode substrate	Product
MFC	Oxygen	Electricity
MEC	Protons	Biohydrogen
BES	Acetate	Ethanol
BES	Oxygen	Hydrogen peroxide

Figure 2. Schematic of a Microbial electrochemical cell (MXC) and potential products

Anode half reaction: $CH_3COOH + 2H_2O \rightarrow 2CO_2 + 8H^+ + 8e^-$ ...1
Cathode half reaction: $8H^+ + 8e^- \rightarrow 4H_2$ …2

The former device is called a microbial fuel cell (MFC), while the latter is a microbial electrolysis cell (MEC). Microbial electrolysis requires external electrical energy in the range of 0.3 to 1.0V to overcome the thermodynamic barrier to generate hydrogen. It is a type of modified electrolysis, where the majority (60-70 percent) of the electrical energy needed to produce electrolytic hydrogen is obtained from an organic chemical source, like organic waste or biological oxygen demand BOD. Thus, although electrical energy is needed for hydrogen production, a 3-4 fold higher energy is generated by using the microbial electrolysis method, while removing the organic matter from the water.

The performance of microbial electrolysis cells has been steadily improving over the last five years. With the coulombic efficiencies and current densities reported recently (Logan 2010, Rozendal et al. 2008, and Sleutels et al. 2012), commercialization of this technology is within reach in the next four to six years. Sleutels et al. (2012) reported that current density of 20 A/m^2 is necessary for commercial consideration of the MEC technology. Anode current densities greater than 20 A/m^2 have been demonstrated in PI’s laboratory for other wastewater streams (Borole et al. 2011a and Ichihashi and Borole 2013). The scale-up of this technology has also been under investigation (Logan 2010, Rozendal et al. 2008, and Sleutels et al. 2012) and is expected to ramp up over the next three years.

Our laboratory has expertise in MEC technology for converting organic matter to hydrogen and holds three patents in the area of microbial fuel cells and electrolysis cells (Borole and Tsouris 2009a and Borole 2010 and 2012). One of the patents is focused on combined salt and organic removal from fuel processing water using a microbial fuel cell (Borole 2009)]. The second patent is on production of electricity and hydrogen from biomass-derived organic acids, phenolic molecules and furan aldehydes (Borole 2010, 2012, 2013a and 2013 b) . Development of the catalyst for efficient conversion of biomass-derived organics was demonstrated for biorefinery wastewater treatment. Conversion of acetic acid, partially oxygenated aromatics, phenolics and various other organics has been demonstrated (Borole 2010 and 2012, Borole et al. 2013c and 2013a).

The potential for hydrogen production from multiple waste streams was estimated and shown to be of significant value to the overall process (Borole and Mielenz 2011).

2.3. Microbial Fuel Cell -Capacitive Deionization System

We have previously reported developing a method to treat salt-containing water by combining MFC and capacitive deionization (CDI) (Borole and Tsouris 2009a and 2009b). The MFC targets reduction in organic contaminants, while the CDI removes salt ions. The MFC generated energy from the organic matter, which was then used for powering the CDI process.

Electricity production from hydrocarbons has been reported via MFC in the literature as well (Morris and Jin 2008). While the CDI process can remove salt ions at an applied voltage of 0.2 to 0.5V, operating the CDI at a voltage of 1V increases salt removal significantly. Operation of the system in MEC mode can generate hydrogen, which can then be used to generate power at 1V using a fuel cell stack. This option also offers better organic removal rates by using external electricity to drive the cathodic reaction and, consequently, the overall conversion process. MEC and, in general, MXCs, thus represent novel systems for removing organic matter and. if used in concert with CDI, can make an efficient system for treatment of water containing salts.

2.4. Technical Approach

This project targeted development of a microbial electrolysis-deionization system (MEDS). A block diagram of an MEDS process is shown in Figure 3. It consists of a coupled microbial electrolysis-fuel cell system to generate electricity from organic waste. The electricity thus generated is used to separate salts via capacitive deionization. The approach is intrinsically energy-efficient due to the components used in the system. Microbial electrolysis has an efficiency of 50-80 percent (Cheng and Logan 2007), fuel cells have an electrical efficiency of 35-60 percent and CDI alone has an efficiency of about 10 percent, but is dramatically improved with energy recovery which uses the charged capacitor of one cycle to energize a subsequent cycle. This energy recovery cycle has been demonstrated at about 80 percent efficiency. The scheme also allows for minimizing external energy input, while simultaneously treating an additional waste, for example by removing organic waste or by simultaneously removing the two pollutants from the same stream (e.g., fracking-derived flow-back/produced water) and thus enabling a new dimension in sustainable desalination.

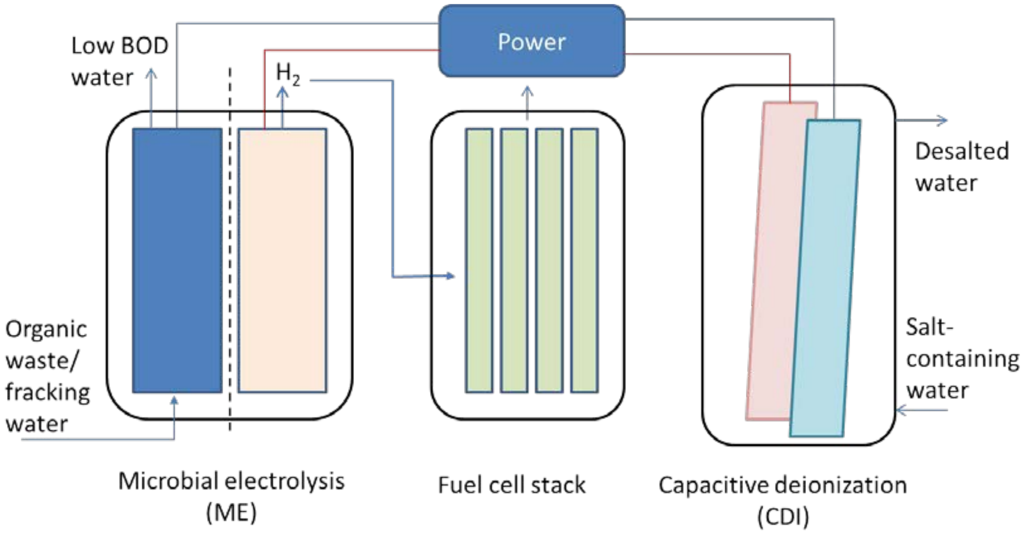


Figure 3. MEDS block diagram.

3. Development of MEDS System Components

The primary components of the MEDS system include microbial electrolysis and capacitive deionization. These components were developed separately as an individual unit using model systems and then integrated to achieve simultaneous salt and organic removal.

3.1. Development Bbioanode for Salt Tolerance

Experimental work on Task 1 was initiated in the first quarter by beginning development of a bioanode. A bioanode biocatalyst was established by formation of an electroactive biofilm on a carbon felt electrode over a period of two weeks. A current density of 2.5 A/m^2 was obtained under continuous operation conditions.

Following the initial two week period, adaptation of the bioanode to various salt concentrations in the feed stream was initiated. The bioanode was subjected to a salt concentration of 10 g/L and 20 g/L. Figure 4 shows the performance of the bioanode under conditions of no salt addition and with 20 g/L salt. The presence of salt enhances current density which has been observed previously. Analysis of the biofilms adapted to no salt and with 20 g/L salt was conducted via cyclic voltammetry. This provided information on the maximum current generated by the biofilms at a poised potential of 0.1 V (vs. Ag/AgCl).

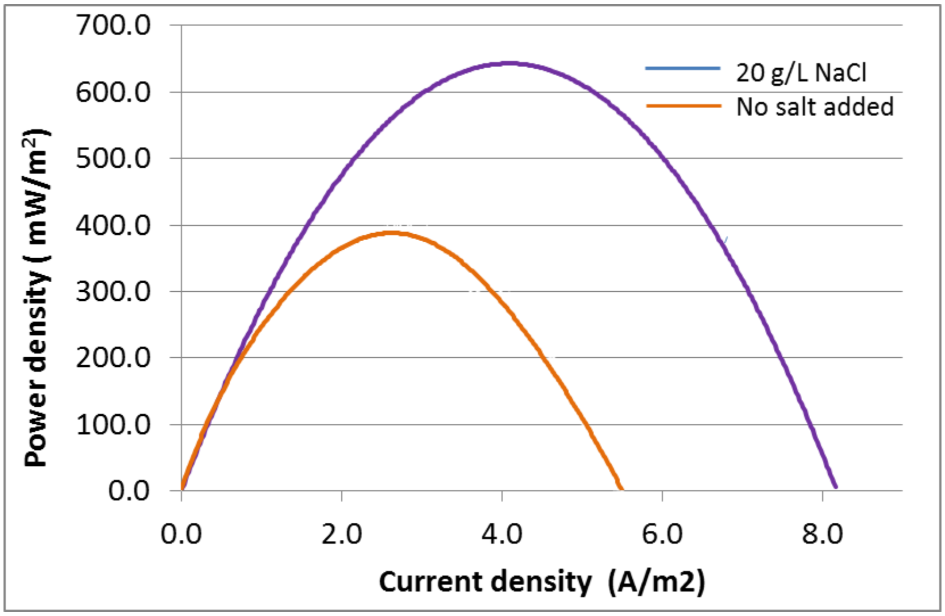


Figure 4. Performance of bioanode with and without added salt (NaCl). Current density of the anode increased from 2.5 to 4 A/m^2 in the presence of salt at 20 g/L.

Figure 5 shows the results from this analysis.The bioanode showed a maximum current density of 2.5 A/m^2 with no salt, and 8 A/m^2 with 20 g/L NaCl in the feed stream. A maximum current density of 2.5 A/m^2 was observed for the bioanode which was subjected to no additional salt. Adding the salt in the feed stream (20 g/L NaCl) increased the maximum current to 8 A/m^2. A microbial sample was collected and stored at -80 degrees Celsius (°C) for microbial characterization.

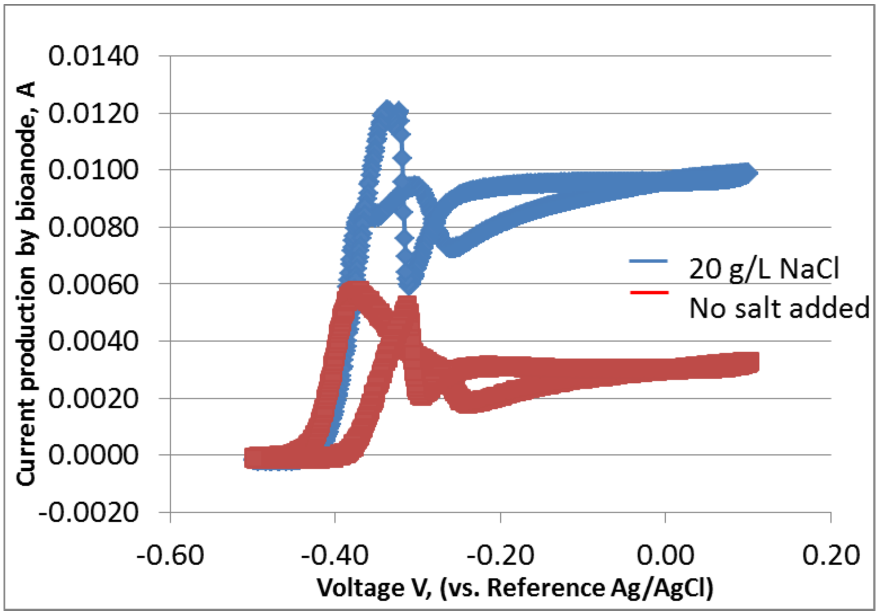


Figure 5. Assessment of bioanode via cyclic voltametry.

After initial enrichment of a microbial biofilm in the bioanode, two parallel bioanode systems were inoculated to enable further enrichment and testing higher salt concentrations, reproducibility of growth and performance.

Performance of the bioanode was further examined from 10 to 45 g/L salt in the aqueous stream as outlined in Task 3 of the proposal. Figure 6 shows the cyclic voltammetry data generated during this experiment. The maximum current produced at each salt concentration is plotted in the Figure 6 inset.The steady state maximum current produced increased from 3.28 mA to 6.13 mA as salt concentration increased from 0 to 25 g/L, while it decreased down to about 3.28 mA at 40 g/L salt concentration. The peak in current observed in the range of -0.3 to -0.5 V cannot usually be sustained and is a result of residual capacitive behavior of electroactive biofilms observed under transient conditions. Figure 6 inset. Shows the effect of salt concentration on stable max current production (at 0.1 V) Highest current density was obtained at a salt concentration of 25 g/L salt concentration; however, increasing the salt concentration beyond this level reduced the current.

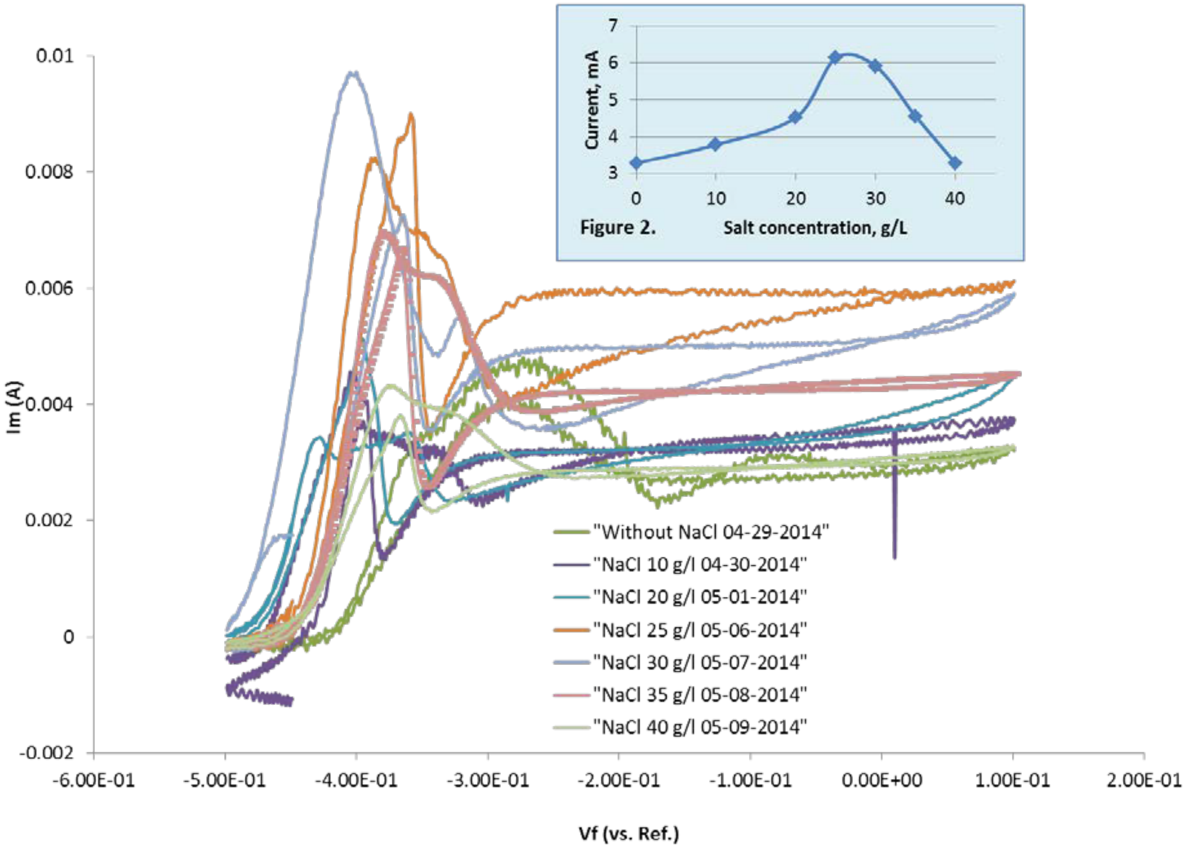


Figure 6. Current production by bioanode at various salt concentrations measured by cyclic voltammetry.

While there was a decrease in performance at higher salt concentrations, the current was no less than what was observed in the absence of salt. A continuous experiment was conducted following this work to determine if the maximum current can be generated continuously. Operation of the bioanode was confirmed over several weeks while continuously generating the maximum of 5.9 mA (equivalent to 4.7 A/m^2 current density) at a salt concentration of 25 g/L. This is an exciting result since it suggests that produced or fracking water with moderate concentration of salt can be used as is, in the system for removal of organics, while simultaneously generating bioenergy.

3.2. Microbial Fuel Cell Assessment

3.2.1. Effect of Salt Concentration

The performance of a MFC for electricity generation using the bioanode developed above was examined at various salt concentrations. Figure 7 shows the power density curves for the bioanode operated MFC.

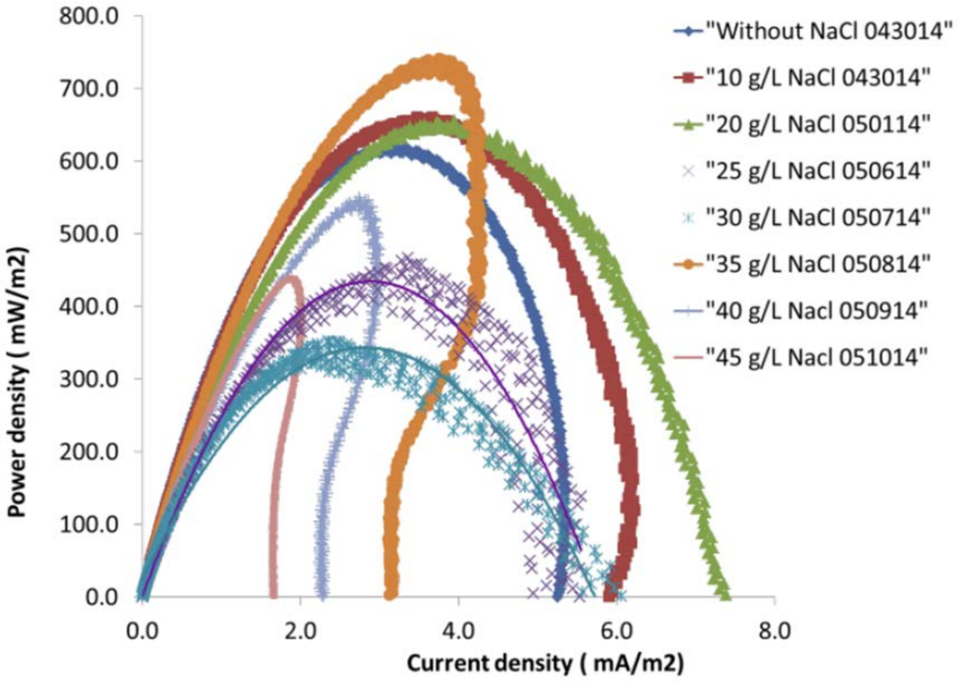


Figure 7. Effect of salt concentration on power generated by MFC. Above 25 g/L, the maximum current produced decreases as observed previously.

3.2.2. Production of Struvite from Wastewater

A different MFC experiment was initiated to study the phosphate to struvite conversion process. The MFC was designed with an alternate cathode to allow removal of struvite crystals from the surface. The MFC was amended with different concentration of phosphate, magnesium, and ammonium to determine the effect on production of the brownish-white crystalline mineral, $NH_4MgPO_4 \cdot 6H_2O$. Production of crystals of struvite was observed using phosphate in the anode medium; however, the presence of phosphate in cathode did not result in formation of crystals. A current density of one A/m^2 was achieved in these experiments. The amount of struvite was not sufficient to allow materials characterization. Further work on increasing the rate of struvite production via use of improved designs and current densities above five A/m^2 may allow analysis and the production rate needed for commercial consideration.

3.3. Microbial Electrolysis Cell Development

The bioanode developed for salt tolerance was tested for hydrogen production by changing the cathode to anaerobic operation and application of an external potential as described in the proposal in Task 2.

3.3.1. Effect of Applied Voltage

MEC was tested by poising the cathode at voltages from 0.7 to 1V to assess current and hydrogen production. Figure 8 shows the chronoamperometry data obtained at various applied potentials. Current densities higher than that obtained with MFC operation were observed. However, testing over a period of 24 hours indicated that the current densities were not sustained at these levels under all conditions. The coulombic efficiency (CE) under MFC operating conditions at 25 g/L salt concentration was greater than 50 percent. These experiments were conducted under batch substrate addition conditions. Previous work has indicated that CE can be increased substantially under continuous substrate addition conditions (Borole et al. 2013b), which would be the case when actual produced water is used.

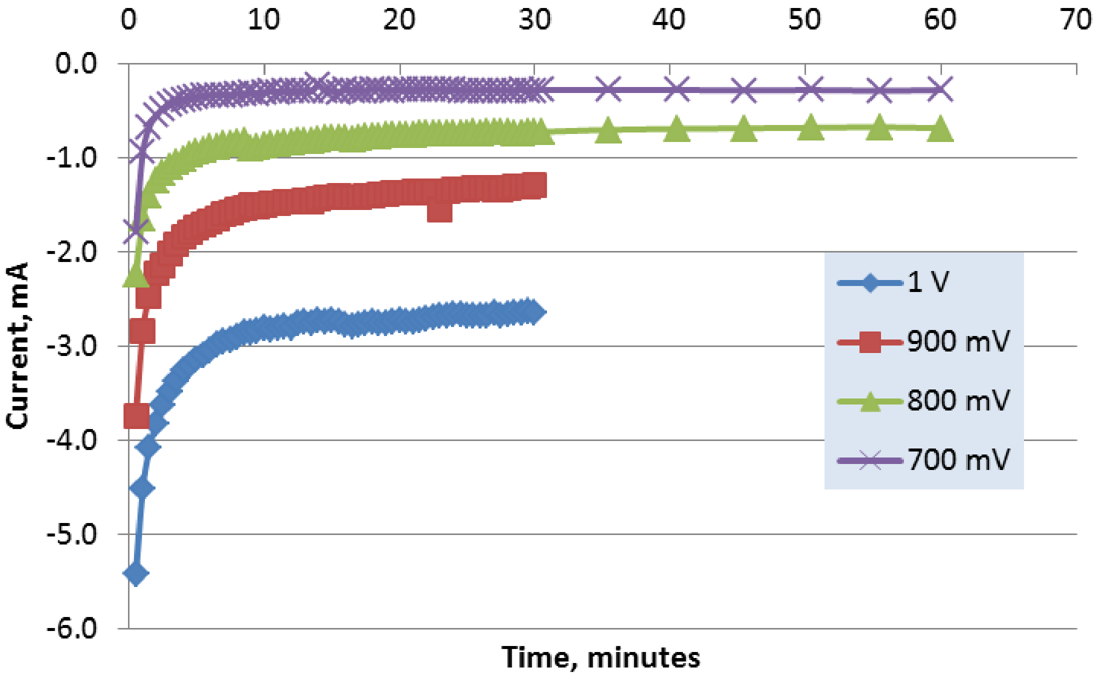


Figure 8. Chronoamperometry assessment of microbial electrolysis system. The data shows current generated by the bioanode to support hydrogen production at cathode in the ME system.

3.3.2. Effect of Anode Poised Potential

We evaluated the effect of additional process variables on hydrogen production and other MEC performance parameters by conducting experiments at 25 g/L salt concentration. Lower salt concentrations were also tested, but these experiments are not reported here. The experiments were conducted by poising the anode at a specific potential vs. an Ag/AgCl reference electrode. In the previous section, the experiments were done by poising the cathode at a certain potential. The change was made after the observation of an adverse effect on bioanode during an MEC experiment, caused by stress on the anode when cathode was poised at a high potential (e.g., 0.8V or higher). Since a cathode poised potential of 0.9 V or higher was needed for hydrogen production using the Pt/C electrode, the MEC operation was unsustainable. Therefore, we studied the alternate method of anode poised potential. Using an anode poised potential was shown to be successful, demonstrating hydrogen production using this method.

The anode was tested at a poised potential from 0.0 V to -0.4V. The typical redox potential of an anode half-cell is about -0.45V vs. Ag/AgCl reference electrode. Thus, poising it at a potential above this potential should result in electron transfer to the cathode. This results in cathode potential becoming negative. As shown in Figure 9, the cathode potential ranged between -1.0 to -0.5V. The larger the difference between the anode and the cathode potential, the larger is the overpotential; however, a minimum threshold potential is necessary for hydrogen production. Theoretically, this is -0.3V for acetate conversion to hydrogen in MEC. Thus, a minimum of - 0.3V needs to be applied to the anode for hydrogen production. Current observed at the various applied potentials were recorded and found to range from -1 to -6 milliamps (mA).

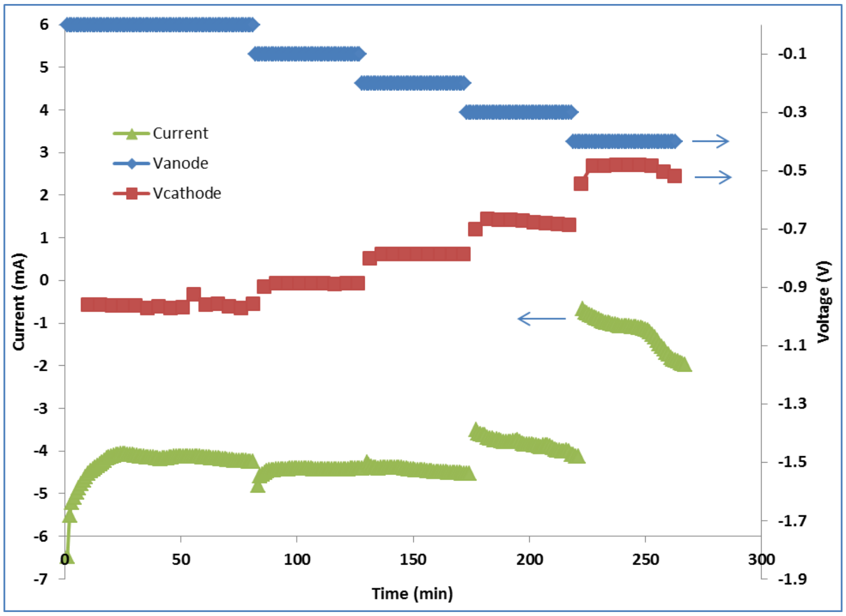


Figure 9. Chronoamperometric analysis of microbial electrolysis system. The data shows current production by the bioanode as well as cathode potential resulting from electron transfer from anode. A potential of -0.3 or higher (anode poised potential) is considered to be sufficient to initiate hydrogen production.

Hydrogen production was measured in a subsequent experiment at a poised potential of -0.2V. This potential was selected based on two criteria. Firstly, it resulted in a cathode potential of - 0.8V, which is known to be sufficient for hydrogen production at cathode. Secondly, it was considered safe for anode operation to avoid redox stress to the biofilm and for maintaining long term viability.

The MEC was operated overnight to measure hydrogen generation at an anode poised potential of -0.2V. The chronoamperometry results are shown in Figure 10. The continuous current production between 5 to 6 mA indicates stability of the MEC operation. Reduction after 16 hours was due to depletion of substrate in anode. Corresponding hydrogen production was measured using an inverted cylinder method. A total of 12 milliliters (mL) was collected over a period of 14 hours. This corresponds to a rate of 1.57 L-H_2/L anode volume-day.

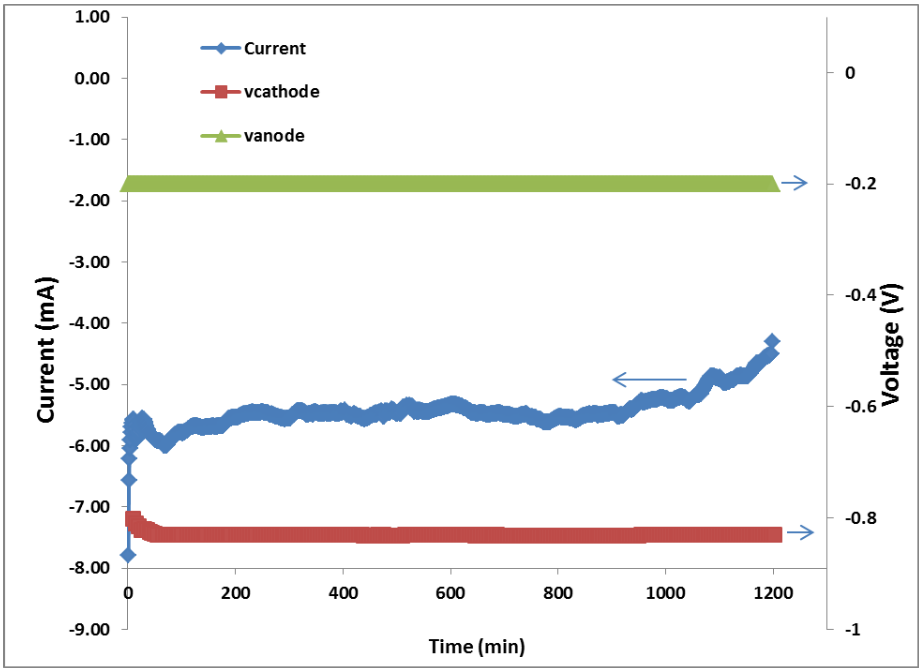


Figure 10. Hydrogen production experiment using an anode poised potential of -0.2V. Hydrogen evolution was observed at the cathode with a total accumulation of 12 mL over a 14 hour period.

3.3.3. Hydrogen Production Under Batch MEC Operation Conditions

After establishing anode operating conditions and demonstrating hydrogen production, we initiated investigations of batch vs. continuous substrate feeding to understand the upper limits of hydrogen productivity.

Experimentation at various salt concentrations indicated that 25 g/L salt was not detrimental to current production in the bioanode. Therefore, salt concentrations up to 25 g/L were tested to assess hydrogen production. An applied potential of -0.2V was used at the anode vs. Ag/AgCl electrode with an acetate concentration of 0.35 g/L. The hydrogen production was studied over a period of 7-14 hours. Figure 11 shows the current production in an MEC for 25 g/L salt concentration compared with no added salt in a duplicated experiment conducted over two consecutive days. The current production and corresponding hydrogen evolution was highest at the beginning of the run and diminished with time at a steady rate. The decay in current may be due to decreasing substrate concentration. It was also observed that the rate of decay of the current and consequently, hydrogen production was not constant at all salt concentrations. As observed in Figure 11, the presence of salt enabled continued production of hydrogen for a longer period compared to the MEC without salt. The current production decreased below 1 mA for the MEC with no salt shortly after 10 hours, while current production continued well beyond 14 hours for the MEC employing salty water.

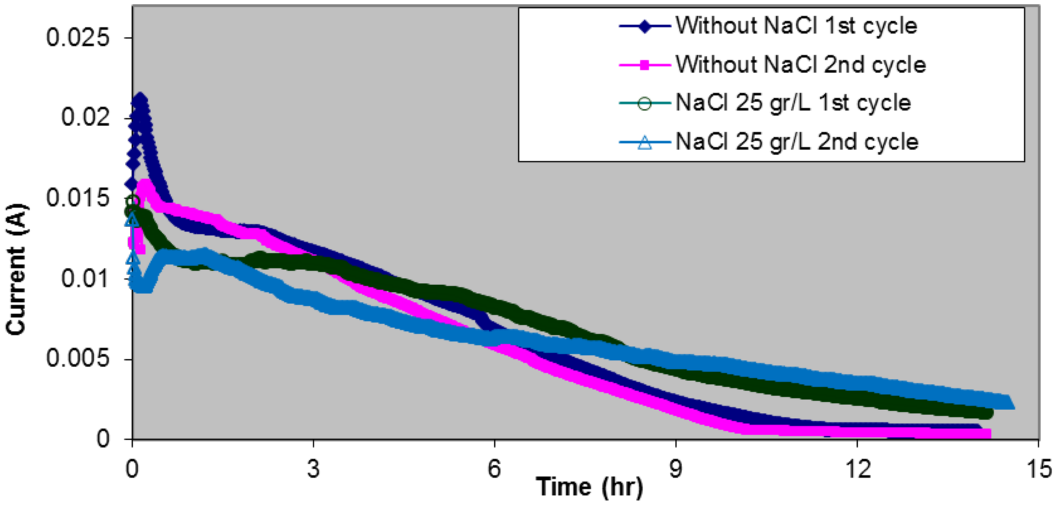


Figure 11. Chronoamperometric analysis of MEC during hydrogen production at 0 and 25 g/L salt concentration.

A plot of the rate of decay of current vs. salt concentration is shown in Figure 12. The slope of the straight portion of the current vs. time profile was used to obtain this plot. This shows that salt helps to maintain current and hydrogen production at higher rate. It is interesting to note that the current production at the beginning of the experiment was not a function of the salt concentration. This may be due to the fact that the pH of the cathode at time 0 is neutral, while as the reaction proceeds, cathode pH increases and reaches above 11.5 within 2 to 3 hours. The beneficial effect of salt only comes into play after this initial period, when pH polarization increases and charge balancing is required.

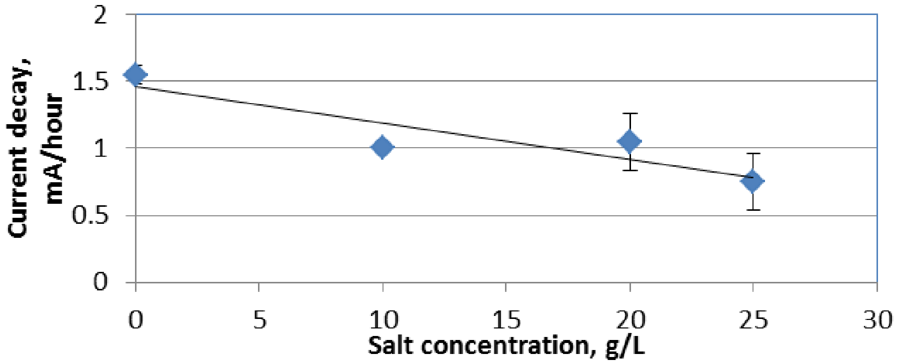


Figure 12. Rate of decay of current production in an MEC as a function of salt concentration.

3.3.4. MEC Performance and Conversion Efficiency.

Hydrogen production was measured via an inverted-flask set up displacing water to collect the gas. Table 1 shows the amount of hydrogen collected after a period of 14 hours at various salt concentrations.

Table 1. MEC performance data for 14-hour tests using acetate as model organic substrate at varying salt concentrations.

Salt concentration g/L	Current density, A/m2	Hydrogen gas collected, mL	Rate of hydrogen production, L H2/L-anode-day	Overall efficiency, %
0	5.0	44	5.7	27.6
	4.5	33	4.3	28.3
10	5.8	48	6.2	37.5
	5.8	52	6.7	34.7
20	5.4	40	5.2	27.3
	4.3	36	4.6	19.2
25	5.4	40	5.2	27.3
	5.0	39	5.0	24.3

The results indicated that hydrogen production was higher at 10 g/L salt concentration compared to no salt MEC as well as to higher salt concentrations. A deeper look at the performance parameters for the MEC shows that this was due to the higher overall conversion efficiency at 10 g/L salt concentration. It is not clear why the efficiency was highest at this salt concentration. The overall efficiency is made up of two components: the Coulombic efficiency and cathodic efficiency. These two efficiencies are plotted individually in Figure 13 and Figure 14. The salt does seem to have mostly beneficial effect on the hydrogen production process. It may have detrimental effect at higher salt concentrations, but based on previous work, this limit seems to be above 30 g/L salt concentration.

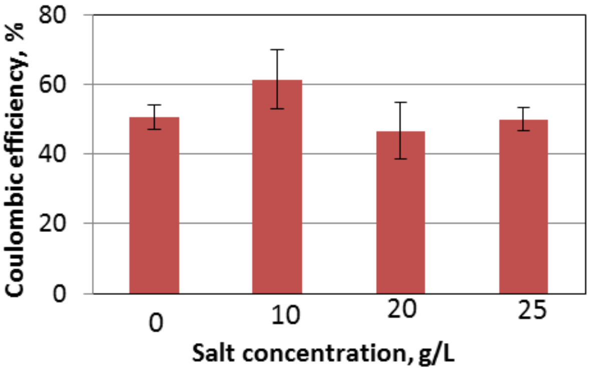


Figure 13. Effect of salt concentration on Coulombic efficiency. This is a measure of the fraction of electrons extracted from acetate as current.

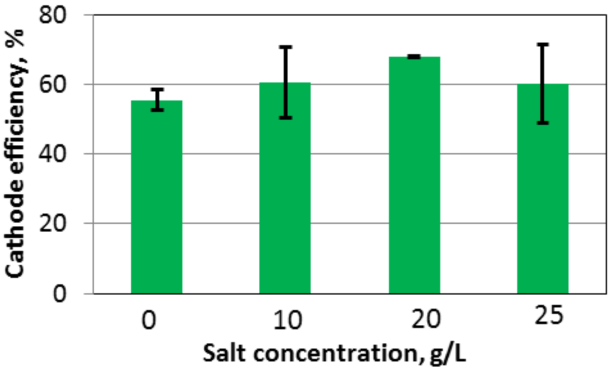


Figure 14. Effect of salt concentration no hydrogen production at the cathode. This is a measure of the efficiency of conversion of current into hydrogen by the cathode.

We also conducted experiments were also conducted with MEC over shorter time durations (6-8 hours). This revealed that the rate of hydrogen production was much higher during the initial period of the operation (by 50-90 percent). A maximum rate of hydrogen production of 9 liters of hydrogen per liter day (L/L-day) was observed during a

7-hour run using 10 g/L salt concentration, which also demonstrated a higher average current density of 7.3 A/m^2.

3.3.5. Effect of Continuous Loading on MEC Performance

A continuous process of MEC operation was designed and studied in the laboratory to understand how produced water processing can be achieved in the field. The effect of substrate loading was studied to determine dynamic response of hydrogen production in an MEC. Figure 15 shows the increase in current associated with hydrogen production when the substrate loading was increased from 0.05 to 0.35 grams per liter per anode reservoir per day (g/L-day).

A reverse experiment was carried where the substrate loading was reduced over time to see the effect of loading rate on current production. A proportionate decrease was observed with concomitant reduction in hydrogen production (Figure 16).

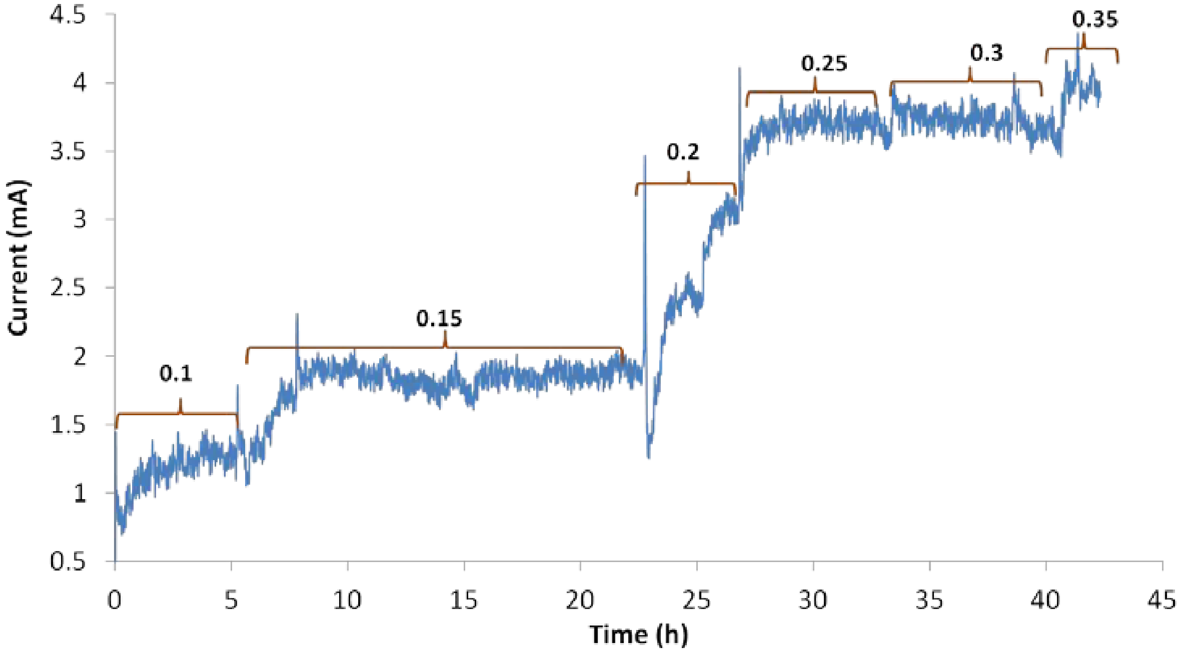


Figure 15. Effect of substrate loading on current production during operation of MEC for hydrogen production.

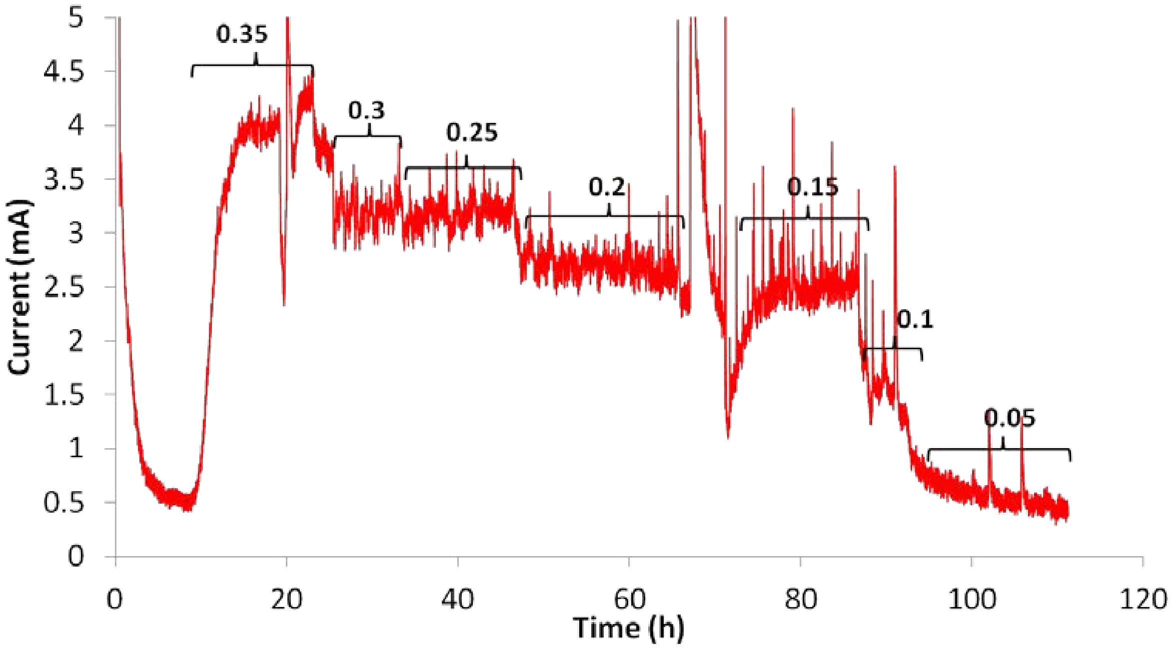


Figure 16. Effect of descending substrate loading rate on current production during operation of MEC for hydrogen production.

The duration of the second experiment was also increased to enable consistency in measurement, since considerable noise was observed in electrical current measurements. This noise was determined due to the distance between anode and reference electrode. Due to the compact nature of the anode of the MEC systems used here, the reference electrode could not be placed inside the anode. Thus, the closest location it could be placed was downstream from the anode in the recirculation loop. While this was always in hydraulic contact with the anode, production of gas bubbles in the line and fluctuations due to liquid flow and pumping inconsistencies resulted in the noise.

To ascertain stability of MEC operation, longer term experiments were conducted. The substrate loading was increased to 2 g/L-anode reservoir-day and the system was operated over a period of 24-48 hours. The anode reservoir volume was 200 mL while the anode volume was 16 mL with porosity of 0.83. Figure 17 shows the reproducibility of the current production at a given substrate loading. To improve productivity of hydrogen from the MEC, we conducted hydrogen measurement experiments to test the limits of the MEC system. Results from three replicate runs with a constant substrate loading of 2 g/L-anode reservoir-day showed consistent average current production from the anode. The drop in current after the first 24 hours was identified as due to drop in pH of the anode from using a recirculation flow loop. In a real application, recirculation may not be necessary since the low concentrations present in the wastewater or produced water can be handled by the anode.

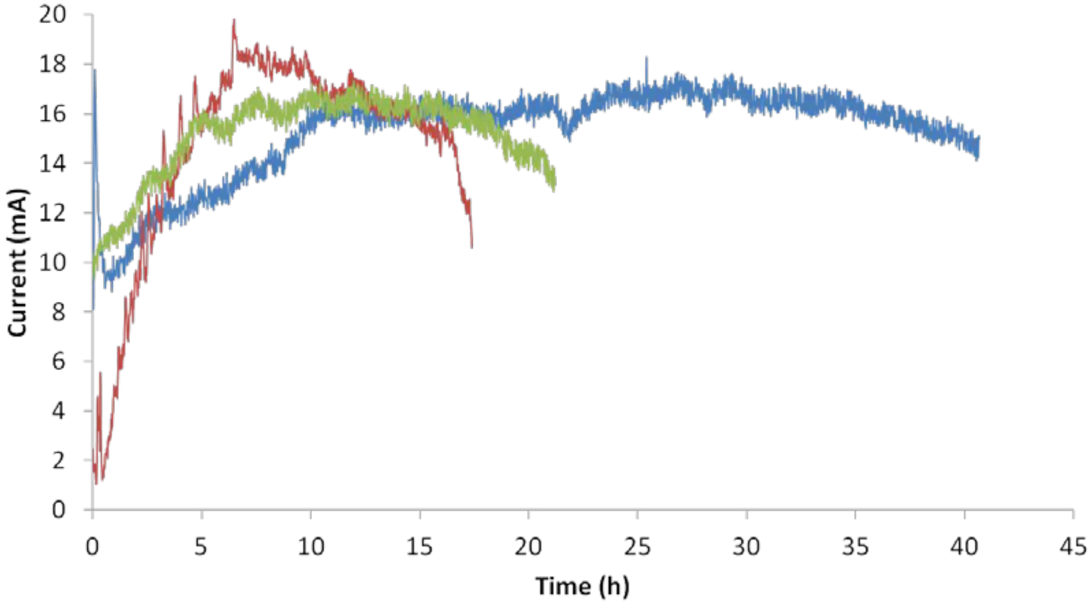


Figure 17. Results from three replicate runs with a constant substrate loading of 2 g/L-anode reservoir-day.

Figure 18 shows the current production profile during the experiment. Hhydrogen accumulation was measured simultaneously with current measurements and is shown in Table 2.

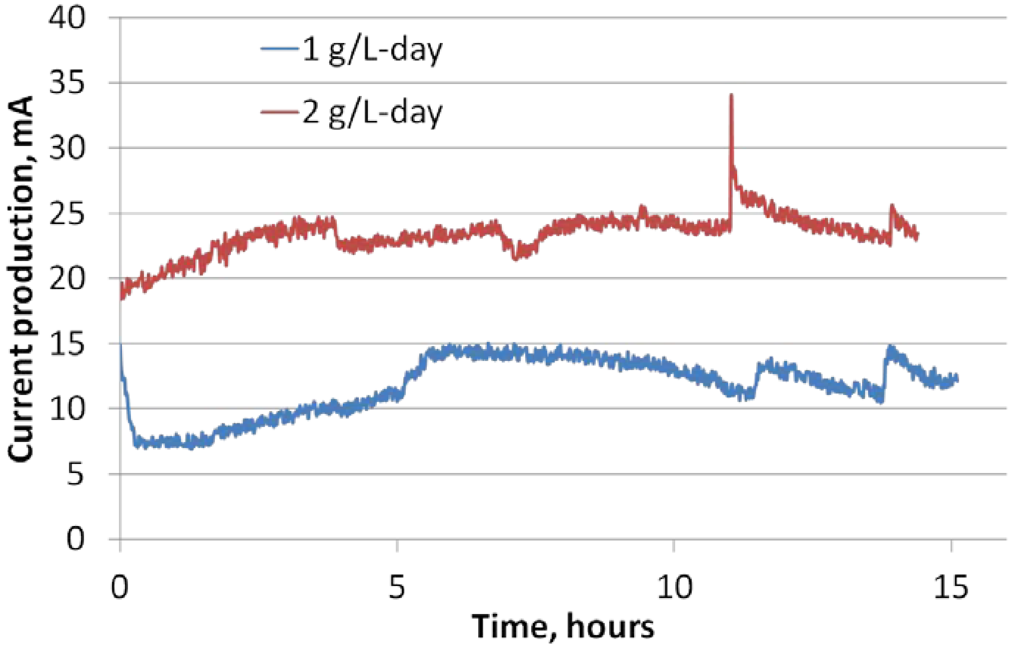


Figure 18. Current production profiles during hydrogen accumulation experiment.

Table 2. Characteristics of MEC Performance At Different Substrate Loading

Substrate loading rate, g/L-anode reservoir-day	Time	Observed average current, mA	Observed H_2 production, mL	CE, %	H_2 % recovery	L-H_2/L-anode-day	A/m^2
1 g/L-day	15 hours	11.72	60	80.6	65.8	7.2	9.0
2 g/L-day	30 hours	16	260	57.9	75.1	15.7	12.7

3.4. Capacitive Deionization

CHC conducted experiments to study the salt removal using electrosorption in collaboration with their partners, Kharkov Institute of Physics (KIPT) and others. The capacitive deionization (CDI) unit was tested using synthetic water as well as real water sample obtained from various ground water sources in Ukraine and municipal water sources with high levels of calcium.

The set-up is shown in Figure 19. The cell volume is 2.1 liters (L), and the flow rate used was 1 liters per minute (L/min).

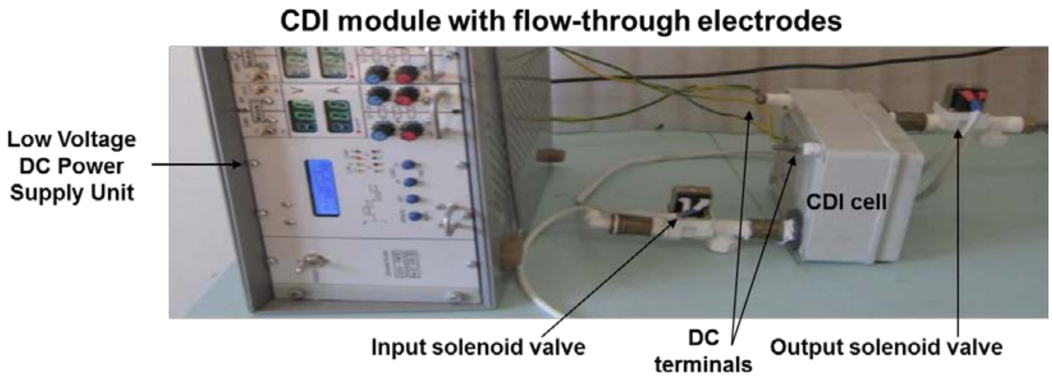


Figure 19. Capacitive Deionization (CDI) cell set-up.

The schematic in Figure 20 demonstrates the recycled water nature of the testing whereby the deionized water is collected and reused in a closed loop to allow long test cycles during which the extracted hydrated ions collect within the electrodes. Instrumentation allows the measurement of adsorption rate, electrical conductivity, and electrodynamic parameters of multiple charge-discharge cycles. Figure 20 indicates that the cell is a “flow through” configuration. A wide variety of electrode materials were tested with the best results achieved using carbon fiber cloth (Busofit) with a proprietary metallization process held within a spot welded titanium frame. Cells have been in operation for up to six months. Best adsorption rates and regeneration percentages are being obtained in a constant current mode of operation for each cell.

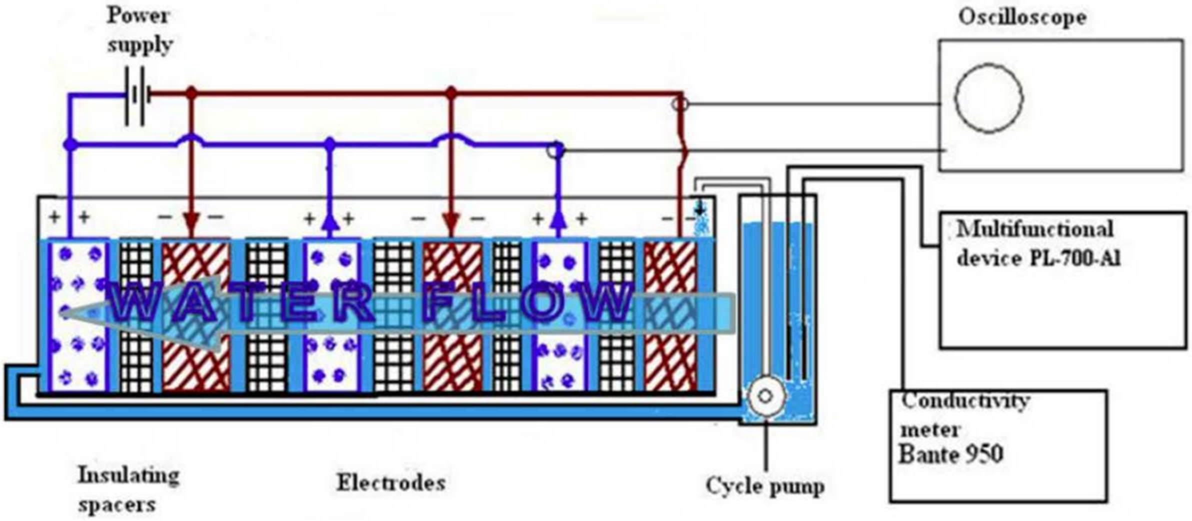


Figure 20. Flow schematic and electrical diagram of the CDI cell.

Removal of TDS and calcium ions from synthetic water was studied and is shown in Figure 21 and Figure 22. Reduction of Ca^{++} from 210 mg/L to 150 mg/L was observed, and a TDS reduction from 700 to 410 mg/L was demonstrated.

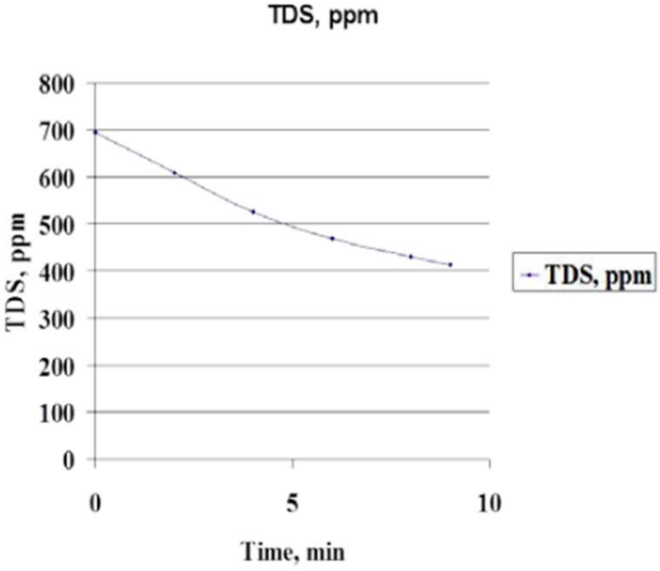


Figure 21. Removal of calcium ions from synthetic water at an applied current of 5 amps (A).

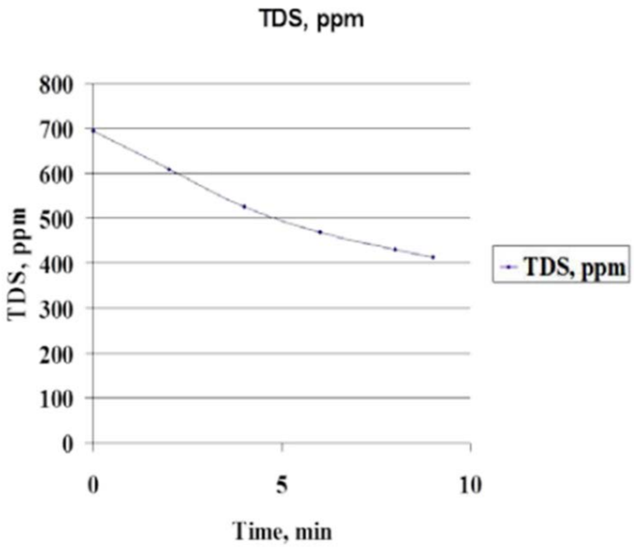


Figure 22.Removal of total dissolved solids (TDS) from synthetic water.

The effect of ionic charge on its removal was studied and determined to be directly proportionality (Figure 23). The removal of monovalent Na^+ was twice that of divalent Ca^{++}.

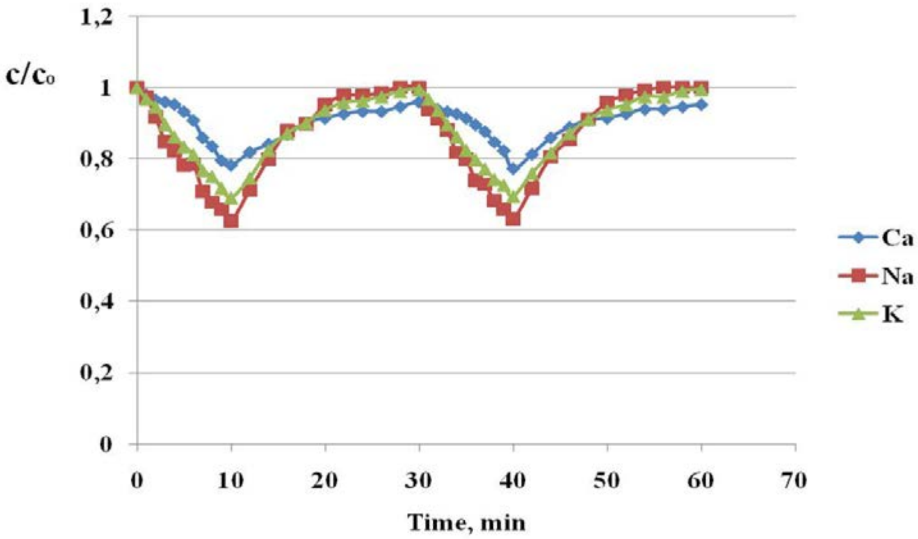


Figure 23. Effect of ionic charge/valence on its removal from synthetic solutions of 5 millimeter (mM) chloride salt.

We also studied the effect of initial total dissolved solids (TDS) concentration. Even at low TDS concentrations, high rate of removal, similar to that at an initial concentration of 900 mg/L was observed as shown in Figure 24. Changes in polarity of the electrode did not significantly affect removal.

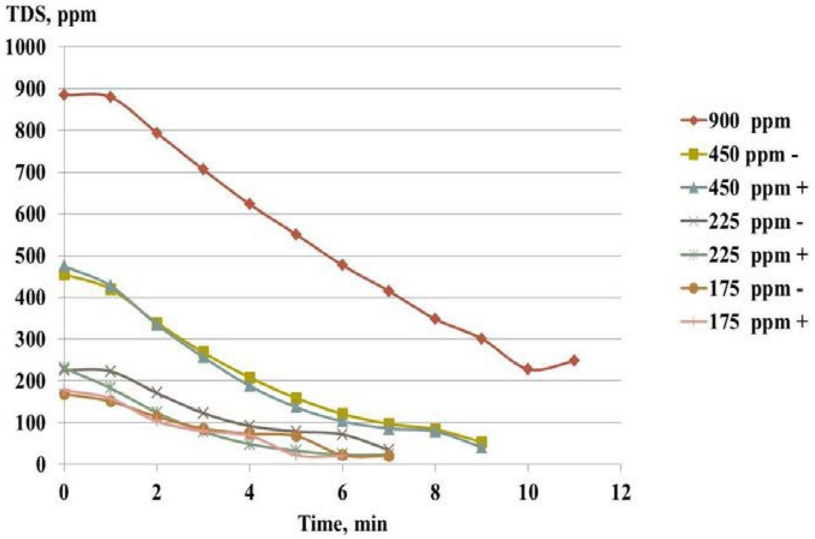


Figure 24. Effect of concentration and polarity (reversal of electrode) on removal.

Removal of ions from real water sample is shown in **Figure 25** and **Figure 26**. A drop in TDS from 490 to 180 was observed at a flow rate of 1.1 L/min and a current of 10 A. Removal of all ions was observed as shown in **Figure 27**.

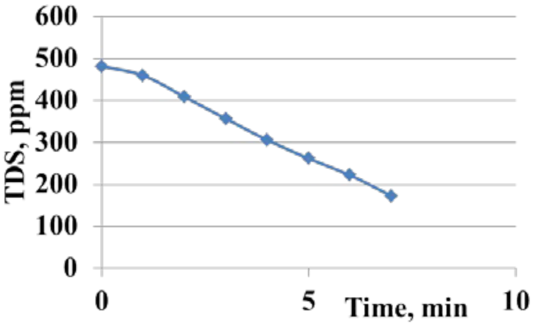


Figure 25. . Removal of TDS from real water at an applied current of 10 A.

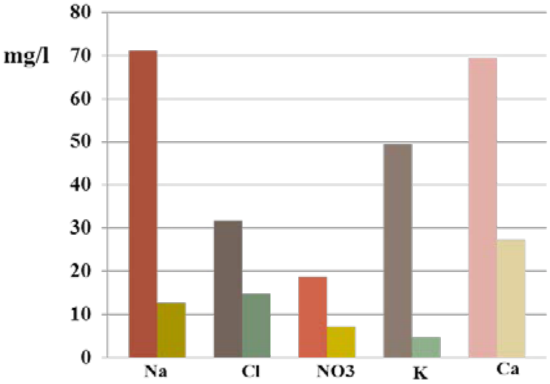


Figure 26. Composition of ions in water before and after treatment.

3.4.1. CDI Testing for Nitrate Removal

Work at CHC included testing removal of nitrate in collaboration with KIPT. Field testing of CDI units was focused on nitrate removal from ground waters as shown in Figure 27.

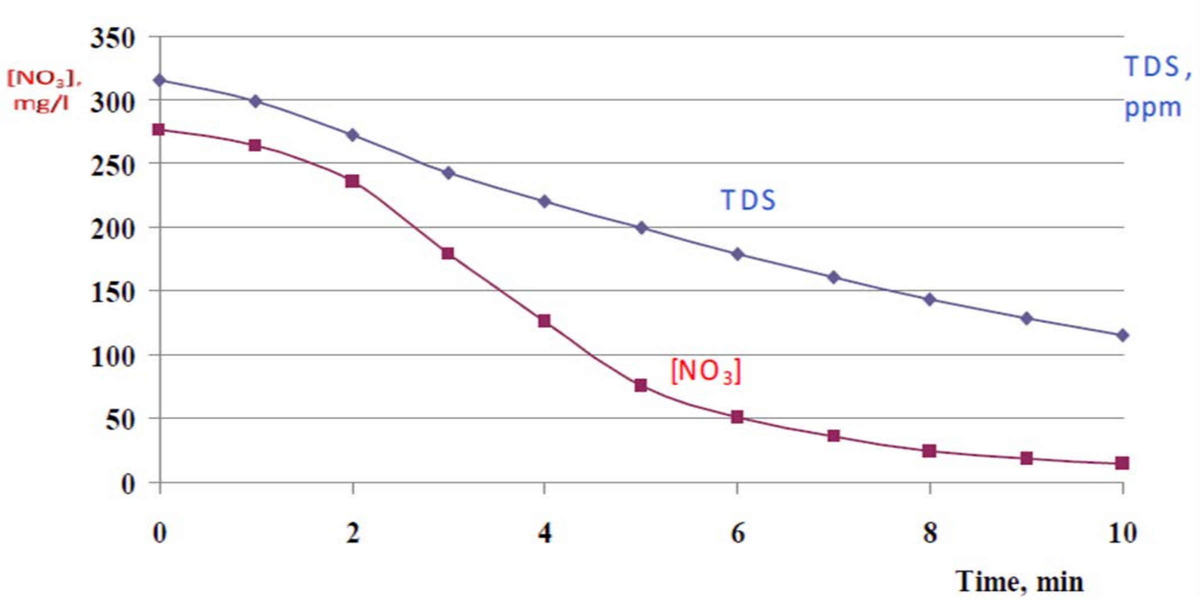


Figure 27. Removal of nitrate from groundwater using electrosorption (CDI) cell.

Adsorption rates using the KIPT set up improved to 15.3 milligrams per gram (mg/g) of functionalized carbon in the electrode, which is the highest performance reported in literature.

CHC has also investigated methods for functionalizing the nano-carbon electrodes to enhance selective removal of selected hydrated ions (focus now is on arsenic and boron). Experiments for understanding energy recovery from regenerating units were also conceptualized and tested at CHC. CHC currently estimates up to 60 percent energy recovery from parallel cell configurations.

3.4.2. CDI Testing for Removing Common Salts

In addition to the work at CHC and KIPT, work on Task 6 was also conducted at UTK to enable its integration with MEC located at UT, using a CDI cell (Figure 28). Figure 29shows the deionization profiles using a CDI shown in Figure 28. The complete setup is shown in Figure 30. The CDI cell contains a mesoporous carbon electrode developed by CHC in a previous collaboration with ORNL. The tests enabled reproduction of results obtained previously by CHC and ORNL. The results are shown in Table 3. This data was collected for use as a basis for deionization experiments using fuel cell power and then MEC derived hydrogen, which was planned as the fuel for a fuel cell stack.

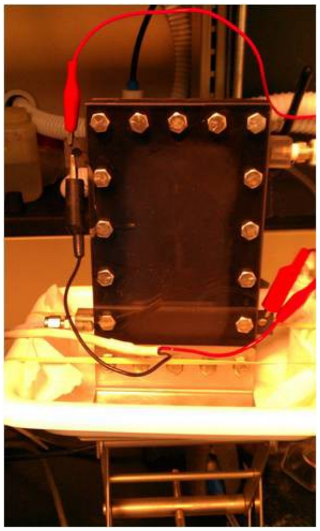


Figure 28. CDI cell used for testing fuel cell stack and other power sources.

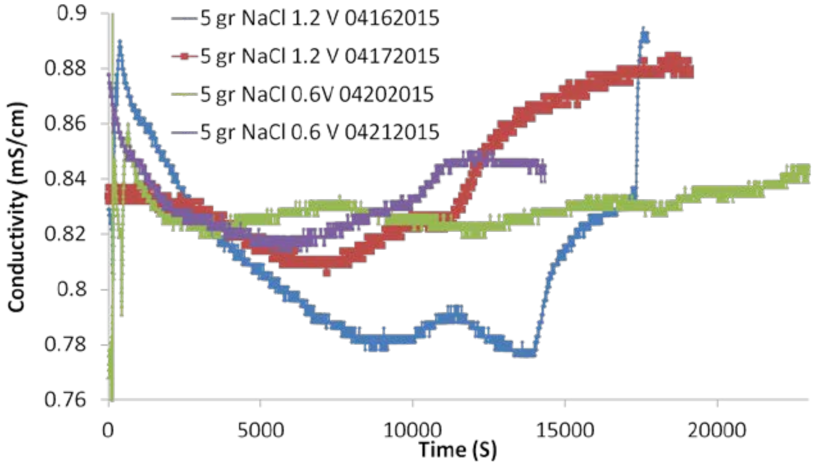


Figure 29. Deionization and desorption cycles at 1.2 and 0.6 V applied voltage using CDI cell.

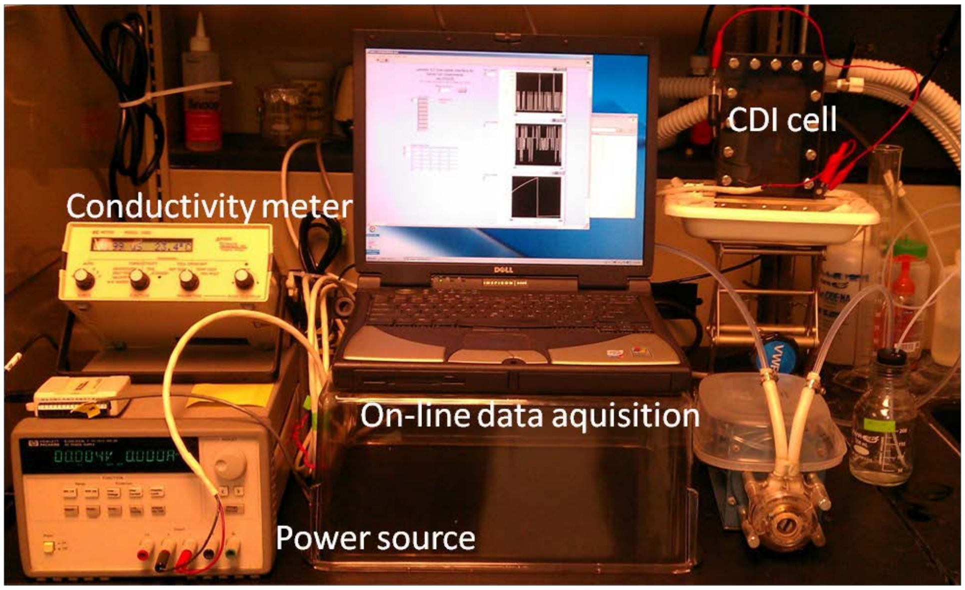


Figure 30. Complete system used for testing CDI cell using an external power source to obtain baseline data for deionization.

Table 3. Results from Capacitive Deionozation Experiments Using a Power Source and CDI Cell at an Applied Voltage of 1 V.

Run #	H2 flow rate, mL/min	Waste-water flow rate, mL/min	Initial conductivity	Final conductivity	Total salt removal, g	Salt removal rate, (mg/g-carbon-hour
1	5	9	9.34	8.39	0.060	5.7
2	5	9	9.28	8.62	0.042	3.9

The simplified system consisting primarily of a power source and CDI cell is shown in Figure 31.

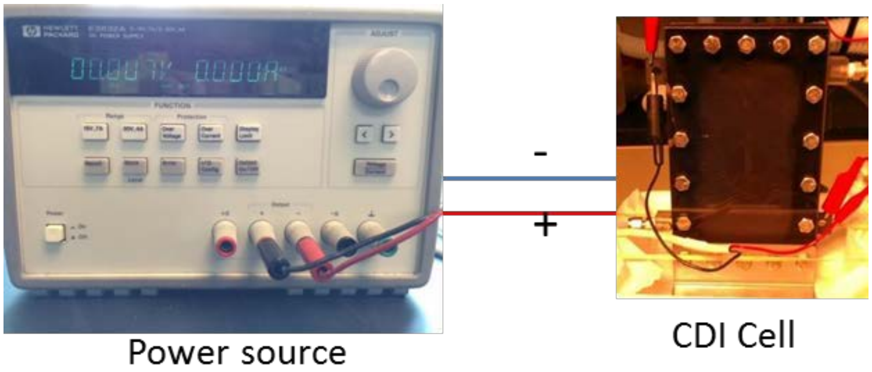


Figure 31. Set-up for CDI cell operation using a power source. The current output was measured using a PC and the conductivity was measured using an in-line conductivity cell.

3.5. Fuel Cell Testing

Prior to investigating the effect of fuel cell power on salt removal it was important to understand the power output of the fuel cell. Experiments were done to characterize the fuel cell at various hydrogen flow rates. Figure 32 shows a power density curve for the PEMFC at a hydrogen flow rate of 1 milliliter per minute (mL/min). The two-cell stack generated a current density of 40 A/m^2 at the maximum power density point corresponding to 45 watts per square meter (W/m^2). The power output increased as hydrogen flow rate increased as shown in Figure 33.

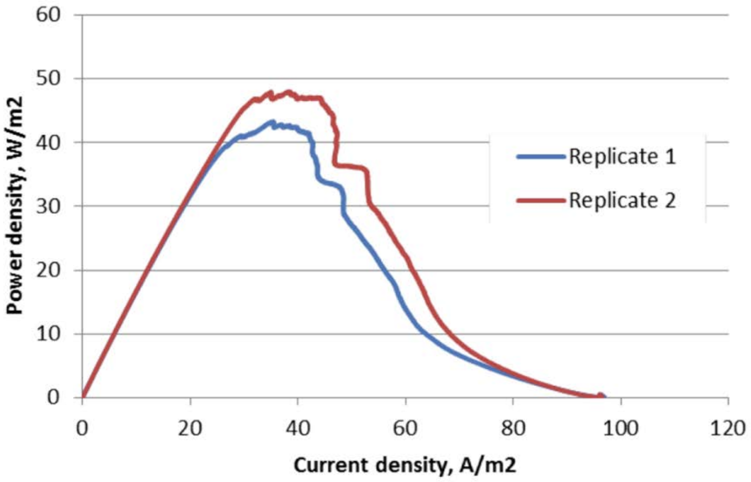


Figure 32. Power density of fuel cell at a hydrogen flow rate of 1 mL/min.

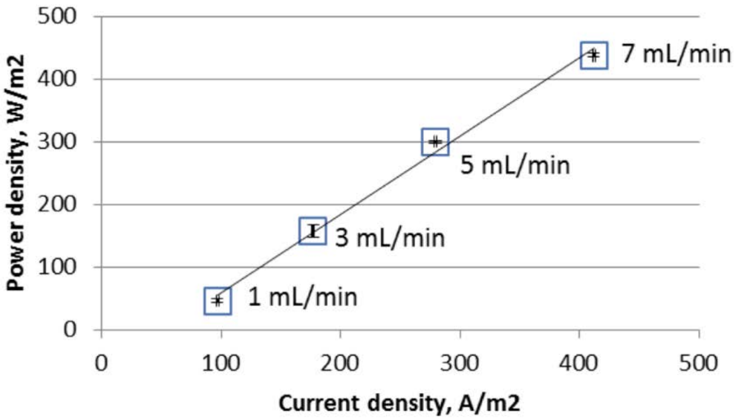


Figure 33. Effect of hydrogen supply rate on power and current output. The data points show error bars and an average for two replicates.

4. Development of Integrated MEDS System

The proposed MEDS system includes three main components the MEC, fuel cell and the CDI cell. Performance of each of the components was tested and reported in sections above. These components were put together to demonstrate integrated operation and simultaneous salt and organic removal.

4.1. Salt Removal via PEM Fuel Cell Generated Power

The effect of applied voltage on CDI cell to achieve salt removal revealed that a voltage of 1.2 volts was necessary for deionization. Experiments were conducted using a hydrogen-powered fuel cell to operate the CDI cell. A 2-cell stack polymer electrolyte membrane (PEM) fuel cell was used. The open circuit voltage generated by this cell stack was 1.7V. The CDI cell was set up as a load on the fuel cell which reduced its initial voltage output. The voltage was measured using a data acquisition system developed in-house for a previous project. The change in conductivity was measured using in-line cell and a conductivity meter and the data was recorded continuously using the acquisition system. The experiment was conducted using a salt concentration of 5 g/L, which had a conductivity of about 9 millisiemens per centimeter (mS/cm). The salt-containing water was recirculated through the CDI cell until saturation of the cell was achieved.

4.1.1. Effect of Fuel Cell Power Output

Previous experiments using electrical power source have shown that an applied voltage of 1.2V was necessary and represented a key factor in determining the rate of deionization. Recent experiments at CHC have shown that current also plays a significant role in determining the rate of deionization. The effect of the power generated by the fuel cell on the CDI cell was studied to understand the effect of current and voltage generated by the fuel cell. A hydrogen generator was used to produce the hydrogen needed for the PEM fuel cell in the first set of experiments. A renewable source of hydrogen was investigated later on, as described further in the report. Figure 34 shows a system using the hydrogen generator.

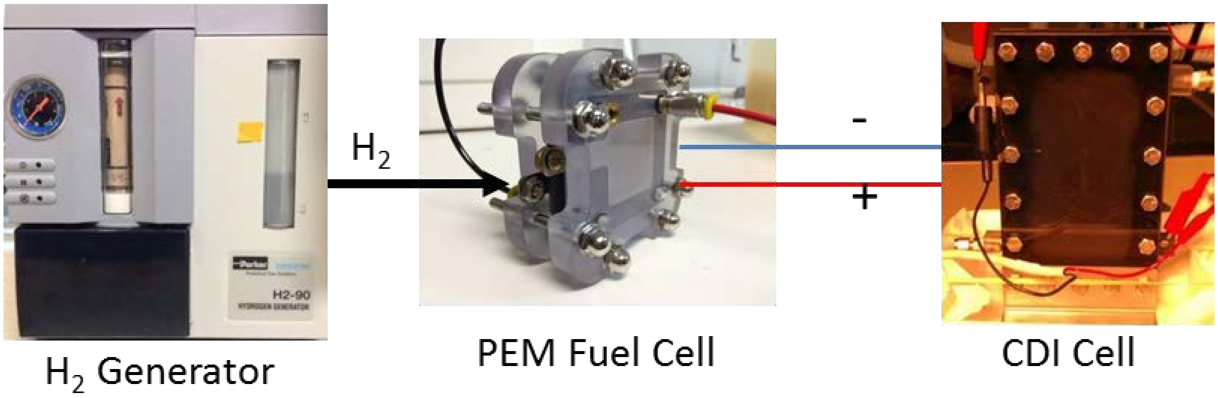


Figure 34. A fuel cell using hydrogen produced by a commercial hydrogen generator connected to a CDI cell.

The power produced by the fuel cell was applied to the CDI cell for deionization. As the hydrogen flow rate was increased, the current increased, increasing the rate of salt removal.

Figure 35a shows a plot of conductivity vs. time and Figure 35c shows the corresponding applied voltage, which is essentially the voltage of the fuel cell under load. The rate of increase in voltage with time signifies a reduction in load with time. As the salt is removed, the amount of power required to run the CDI cell decreases, causing the voltage of the cell to rise until it reaches a steady value.

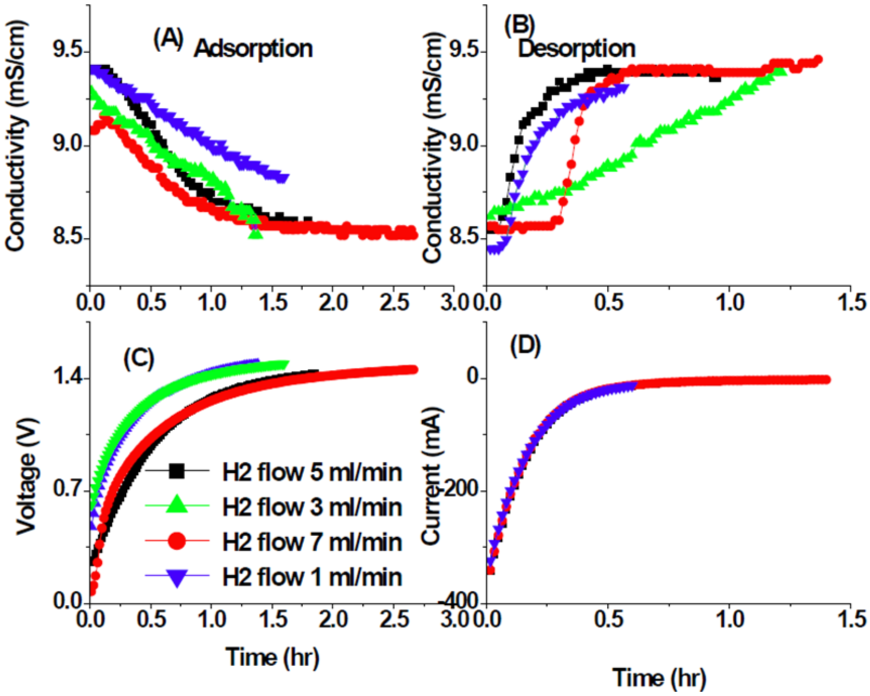


Figure 35. Deionization of water containing 5 g/L NaCl using CDI powered by a fuel cell.

Figure 35b and Figure 35d show the changes in conductivity and current during the desorption cycle. The results show an initial current production of 300 milliamps (mA). This device thus also works as an energy storage device or as a capacitor where the recovered current may be used to powering peripheral equipment.

A study of the effect of hydrogen flow rate on the two parameters indicated that rate of salt removal increased with the hydrogen flow rate. The amount of salt removal is also function of the electrode surface area used in the CDI cell. In the cell used here, a mesoporous carbon layered over carbon plate was used for anode and cathode, which were separated by the spacing of ~6 mm. The electrode material had a surface area of 600 m^2/g and total weight of the mesoporous carbon electrode used in the construction of the cell was 9.65 g. This resulted in a salt removal rate of 17.4 mg/g carbon-hour. The rate of deionization obtained in the experiment using the PEM fuel cell was slightly higher than that reported previously (15.2 mg/g-carbon-hour) for the cell using an external power source and a voltage of 1.2V (Tsouris et al. 2011). The higher rate may be due to the higher voltage (1.5V) resulting from the use of fuel cell as the source of power.

4.1.2. Effect of Water Flow Rate

The rate of deionization is also affected by the flow rate of contaminated water flowing through the CDI cell. This effect was examined by changing the recirculation rate of salt-contaminated water from 5 to 18 mL/min. Figure 36a shows that a flow rate of 9 mL/min was optimal for salt removal. The corresponding voltage profile is shown in Figure 36c. A higher flow rate/ lower retention time may result in channeling through the cell, resulting in lower rate of deionization. The lower flow rate, on the other hand, may be causing stagnation in the cell causing less salt removal in a given time period.

Figure 36(b and d) also shows the behavior of the cell during the desorption cycle. This was primarily performed to regenerate the CDI cell for next operation. However, an interesting observation was made during this experiment: we found that 9 mL/min was not optimal for salt desorption from the electrodes. This requires further testing, but the results show that a slower flow rate may be better for desorption.

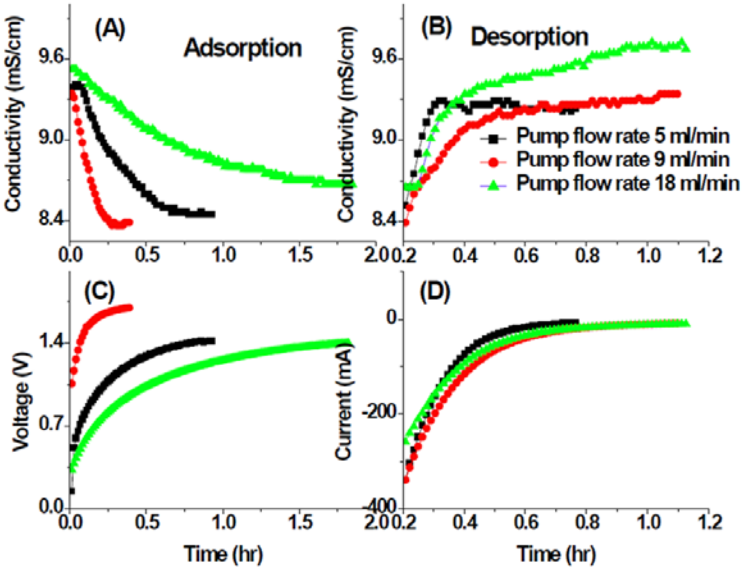


Figure 36. Effect of water flow rate on salt removal and desorption.

4.2. Power Integration of MEDS and PEM Fuel Cell

4.2.1. Power Production Using MEC-Derived Hydrogen

The hydrogen produced by a MEC can contain small amounts of nitrogen, since the system is made anaerobic using nitrogen as a purge gas. Furthermore, any impurities in the hydrogen gas can contribute to changes in power output when used as the fuel source in a PEM fuel cell.To test these factors, the PEMFC was operated using MEC-derived hydrogen. The power can then be used to run the CDI cell as seen in an example system in Figure 37.

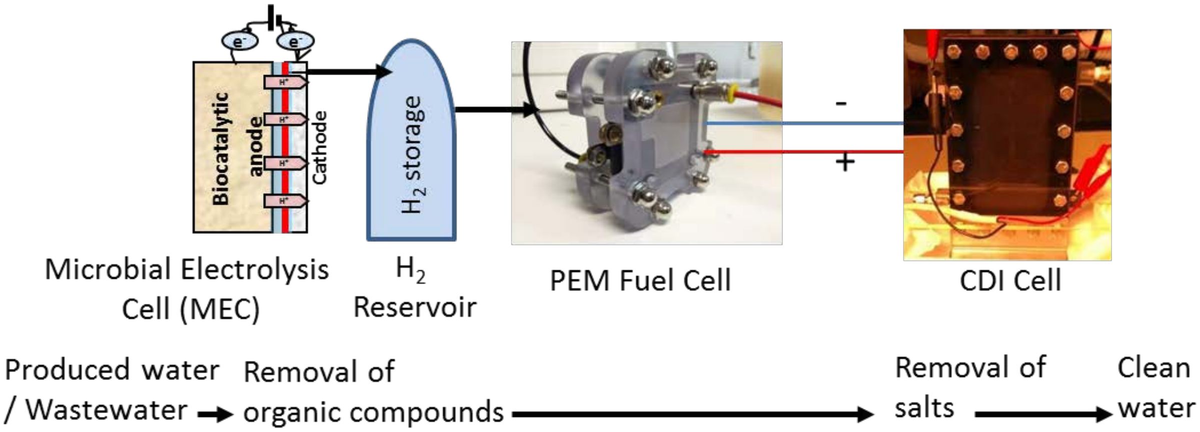


Figure 37. An integrated MEC-PEMFC-CDI cell, capable of using organic waste or wastewater to generate energy to drive salt removal.

4.2.2. Power Generation Using MEC-Derived Hydrogen.

To test the effect of hydrogen quality on power production by a PEM fuel cell, we carried out initial experiments. A simulated produced water containing acetic acid as the organic contaminant was used to generate hydrogen in an MEC. The MEC set up is shown in Figure 38.

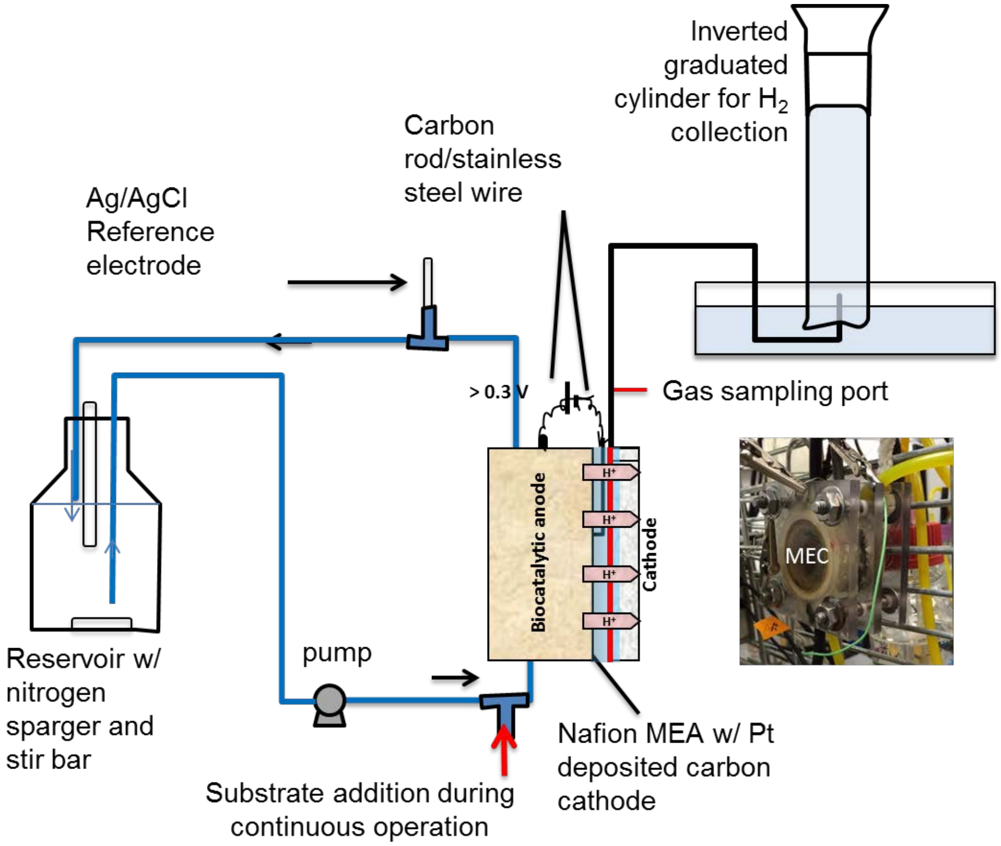


Figure 38. MEC experimental set-up.

The hydrogen collection system was a simple inverted cylinder containing water and hydrogen was collected in the cylinder by water displacement. This hydrogen was then utilized for fuel cell testing. Figure 39 shows the comparison of salt removal using the MEC-derived hydrogen and that produced from a commercial hydrogen generator. The result shows that the MEC-derived hydrogen works very similar to the hydrogen generator system. This shows that the hydrogen produced by the MEC does not have any detrimental effects on the fuel cell or the CDI operation. Analysis of the gas generated by MEC showed the hydrogen content to be greater than 80 percent with no hydrogen sulfide or other harmful contaminants. This further demonstrates the suitability of EC technology for powering the CDI cell for salt removal.

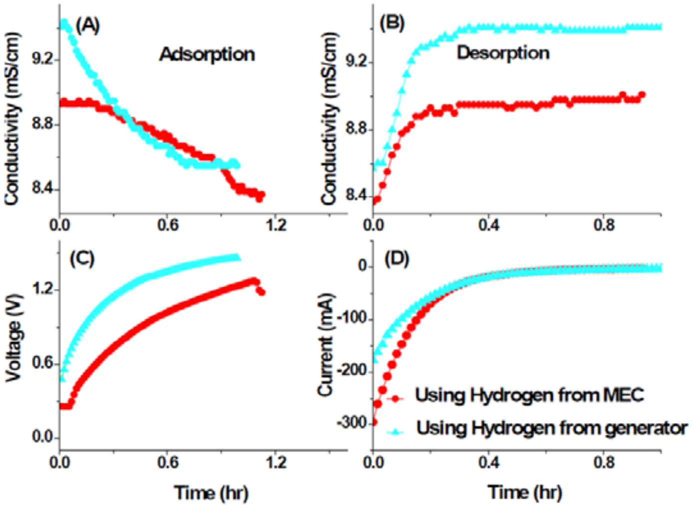


Figure 39. Comparison of deionization using MEC-derived hydrogen with that produced by a hydrogen generator.

4.3. Facilities for Field Testing and Prep Work for the MEDS System

CHC continues its business and technology sponsorship development with West Star Holdings (WSH), Nevada, to bring opportunities to test the MEDS technology for use in areas of mine waste water remediation and oil/gas waste water treatment. CHC and WSH have seen sufficient business opportunity as to form a joint venture, WestCap Technologies, that is now underway to capture technology sponsorships in these fields of use of the MEDS technology.
CHC has completed occupancy of the Monterey Bay Education Science and Technology Center (MBEST) facilities (CHC is leasing this laboratory and test facility from the University of California), and will continue to work on integration of the CDI and Power Supply using support from Kharkov Institute of Technology (KIPT).

CHC is also working with the University of California, California State University and others to identify student interns and other technical support personnel to support the MEDS system development at MBEST.

5. Testing Produced Water:

The results reported above were obtained using simulated produced water containing acetic acid as a representative organic compound and NaCl as the representative salt. After gaining a good understanding of the conversion of acetic acid to hydrogen and salt removal using CDI, we conducted experiments with produced water obtained from a gas field in Colorado. The purpose of these experiments was to demonstrate the utility of the MEDS system with real, field-derived contaminated water.

5.1. Organic Removal and Deionization Using Fracking and Brackish Water

The first task in the testing of produced water was to determine the MEC anode biocatalyst's activity towards hydrogen production using the produced water. We observed that the biocatalyst developed using acetic acid as the substrate had a low initial activity with produced water as the substrate. However, after an acclimation period of a week, significant increase in activity was observed (Figure 40).

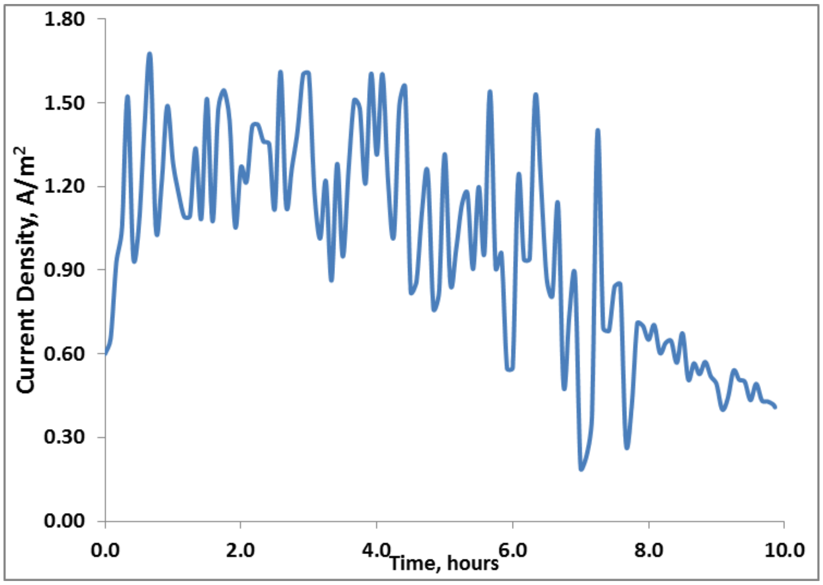


Figure 40. Current density observed from organics present in produced water in MEC via chronoamperometry. The organic concentration in this batch study was 0.05 g/L of COD, obtained by diluting produced water with synthetic MFC medium.

Produced water was tested to determine activity of the MEC anode developed using acetic acid as the primary energy source. Since produced water contains many other organic compounds, it was necessary to acclimate the anode microbial consortium to the produced water. The chemical oxygen demand (COD) of the produced water was measured to be 2.8 g/L. Figure 40 shows the current production during a 10-hour run carried out using diluted produced water. The hydrogen production was also measured over the 10-hour period. The current production and corresponding hydrogen evolution were high at the beginning of the run (first 4 hours). After this time period, a gradual drop was observed, potentially due to depletion of substrate.

Table 4 shows MEC performance and the amount of hydrogen collected in the 10-hour period. The organic concentration in this batch study was 0.05 g/L of COD, obtained by diluting produced water with synthetic MFC medium. The initial conductivity of the produced water with synthetic MFC medium measured experimentally was 7.5 mS/cm. The desired starting concentration for this combined salt and organic removal study was achieved by diluting the produced water (9.5 mL) with synthetic MFC medium (190.5 mL). This resulted in a COD concentration of the mixture of 0.05 g/L. After the 10-hour run, the conductivity dropped slightly to 7.37 mS/cm and the COD was reduced by 24 percent.

Table 4. MEC performance During Treatment Of Produced Water At A Concentration of 0.08 g/L COD.

Average Current	H_2 generated	CE,	H_2 recovery	COD removal
1.23 mA	6.29 mL	46%	57.6%	24 %

A second experiment was carried out to study organic as well as salt removal from the produced water. In order to allow comparison of the results with model system studies described in Section 4.2, the concentration of the salt in the produced water was reduced by dilution. The conductivity of the produced water measured experimentally as 8.1 mS/cm. This was equivalent to 4.2 g/L using NaCl as the salt. Since produced water contains several different salts besides NaCl, this concentration is only an approximation of the total salts present in produced water. The desired starting concentration for this combined salt and organic removal study was achieved by diluting the produced water with distilled water in a 40:60 mixture. This resulted in a COD concentration of the mixture of 0.83 g/L.

The diluted produced water was used to study the removal of COD in an MEC with simultaneous hydrogen production. Figure 41 shows the current density over a 73-hour run. The produced water was diluted to a COD of 0.83 g/L with distilled water to reach a target salt concentration for comparison with model system studies. The increase in current density after 45 hours was due to adjustment of pH to 7.2. As this sample had a higher concentration of organics, the current production lasted longer than the first experiment. However, since this sample was generated by diluting the produce water with distilled water and not the nutrient medium, the current generated was lower.

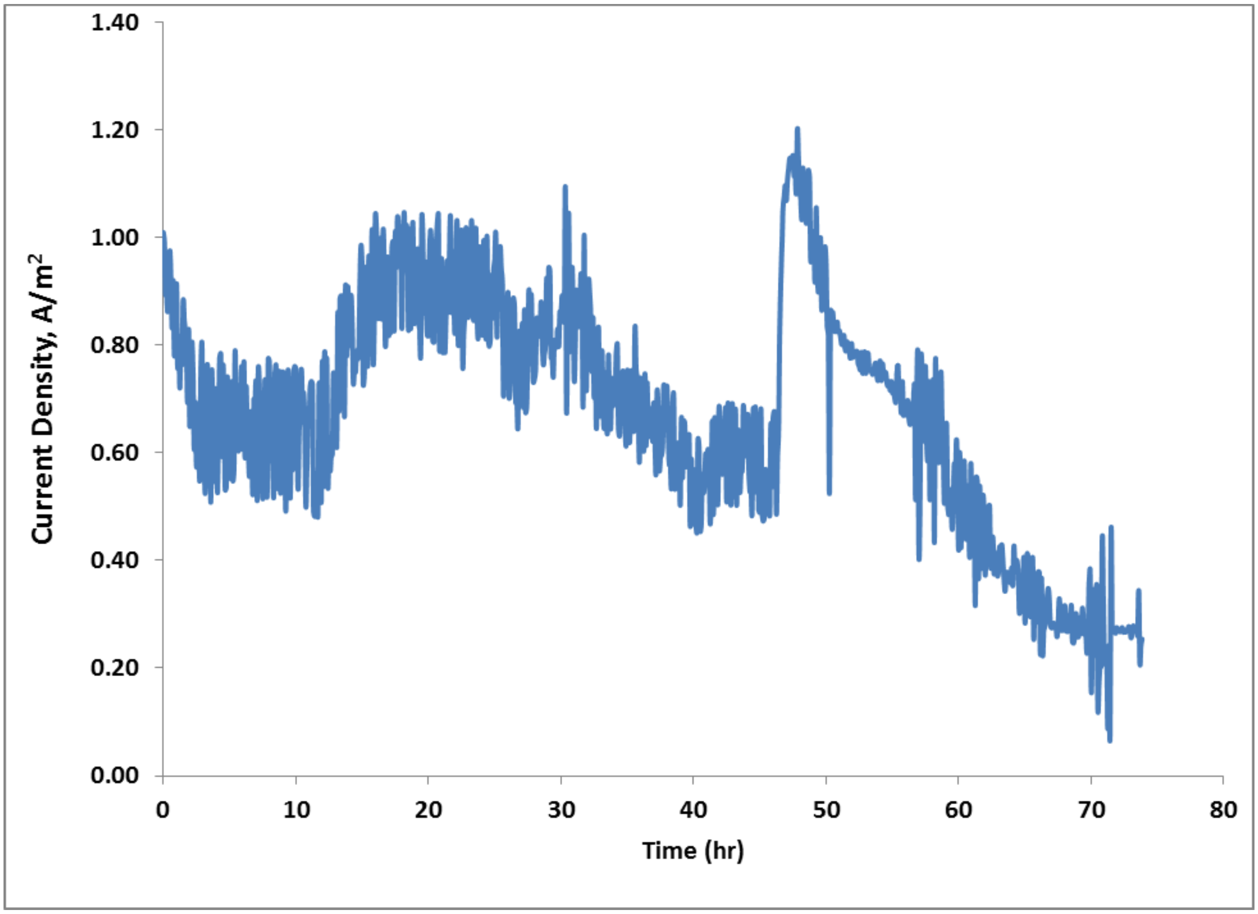


Figure 41. MEC performance during treatment of produced water.

Nevertheless, the current production was sustained for a period of 45 hours at an average current density of 0.7 A/m^2. The slow drop in current after first 20 hours was potentially due to a gradual reduction in pH. An adjustment of the pH to 7.2 after 45 hours resulted in a steep increase in the current density (1.2 A/m^2). The subsequent reduction in current was more rapid than the reduction from 20 to 45 hours, potentially due to the faster loss of buffering capacity. The implications of this observation for treatment of produced water are important. Although the drop in pH is a concern for application of this method for treatment of produced water, the salt concentration of the undiluted produced water will be higher (by about 2.5 times), and compensate for the negative effects of the reduction in pH. Thus, the presence of salts in produced water might be advantageous in this case. Initial and final conductivity, COD and pH of the samples collected from the MEC was measured and used to determine contaminant removal efficiency.

The implications of this observation for treatment of produced water are important: the presence of salts in produced water might be advantageous in this case.

Table 5 shows the amount of hydrogen collected after 73 hours and the efficiencies of conversion of the organics to hydrogen.

Table 5. MEC performance during treatment of produced water at a concentration of 0.83 g/L COD.

Substrate loading rate Batch run	**Duration of run**	**Observed average current**	**Observed H_2 production**	**CE**	**H_2 recovery**	**L-H_2/L-anode-day**	**A/m^2**
0.83 g/L-day	73.7 hour	0.84 **mA**	21 **mL**	14.2**%**	11.58**%**	0.5	0.7

The COD removal from the diluted produced water used in this experiment was about 55 percent. A maximum current density of 5.8 A/m^2 was obtained at an organic concentration of 0.35 g/L in the model system studies (using acetic acid as substrate, Section 3.3.3. *Hydrogen Production Under Batch MEC Operation Conditions*). The current density obtained with produced water is about 12 percent of that obtained using the model substrate, because the concentration of substrates available for exoelectrogenic organisms to produce current is much lower. The other organic compounds present in the produced water have to be broken down to substrates that the exoelectrogens can use, such as acetic acid. This takes time and may require a different group of organisms. Sustained production of current for 45 hours indicates that such microorganisms may be present in the anode biofilm, however, not at a level high enough for rapid release of acetic acid. The current and hydrogen production rates obtained during this MEC experiment were consequently low. The anode biocatalyst was not optimized for treatment of produced water. Enrichment of the bioanode and further acclimation is necessary to obtain better conversion rates and efficiencies. It is expected that up to an order of magnitude improvement can be achieved via the biocatalyst optimization process (Borole et al. 2011b) which will enable rates of conversion and efficiencies approaching those observed with acetic acid reported in Section 4. *Development of Integrated MEDS System.* Additionally, the process parameters have not been optimized for produced water treatment. This can bring additional improvements in the rate of hydrogen production and COD removal rates.

The experiment described in this section was primarily aimed at obtaining proof of principle for MEC treatment of produced water, which has been accomplished. The MEC effluent generated from this run (partially treated produced water) was then used to test salt removal in a CDI cell to demonstrate a synergistic application.

5.2. Salt Removal from Produced Water

We conducted an experiment using MEC effluent (produced water diluted to 40 percent) which was subjected to removal of organics for a period of 73 hours in MEC. Produced water treated in a MEC was used for this deionization experiment to demonstrate salt removal using power generated from a PEMFC using MEC- derived hydrogen. The conductivity of the effluent was 6.9 mS/cm, which corresponded to a salt concentration of 3.7 g/L. The salt concentration was determined from the linear relationship between salt concentration and conductivity. The salt-containing water was recirculated through a CDI cell until the electrodes were saurated, as shown in Figure 42a. An integrated PEM fuel cell-CDI was used in the experiment. The power produced by the fuel cell was applied to the CDI cell for deionization. A hydrogen flow rate of 5 mL/min was used in the experiment. This resulted in a salt removal rate of 2.4 mg/g-carbon-hour using the 40 percent produced water mixture. This rate is lower than the experiments using synthetic wastewater, since the conditions have not been optimized for application to produced water.

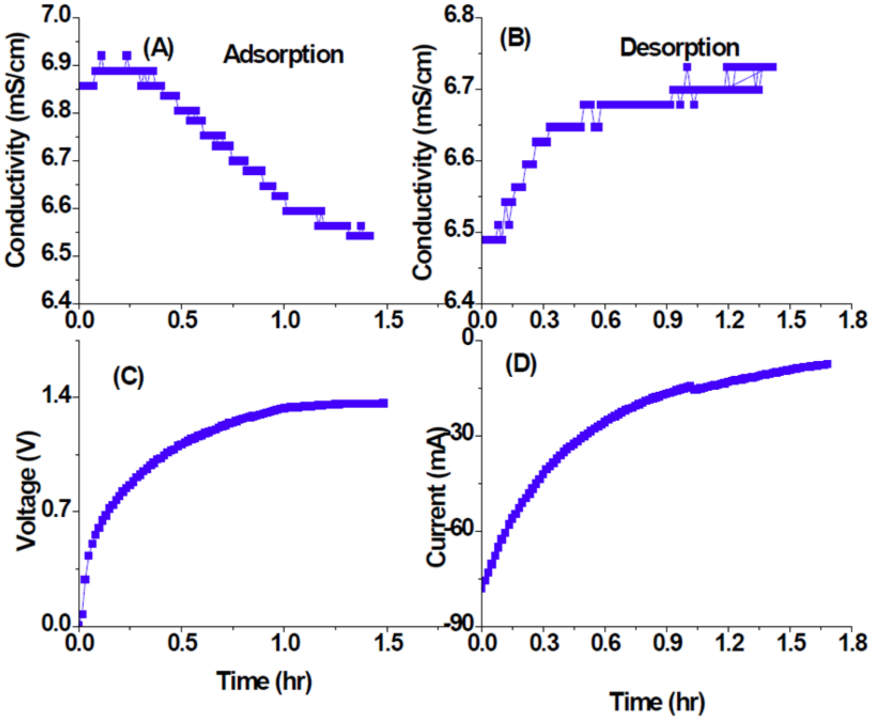


Figure 42. Deionization of produced water in a CDI cell using an integrated MEC-PEM fuel cell-CDI cell system.

Figure 42c shows the voltage changes during the experiment. The voltage applied to the CDI cell increased from 0 to 1.6V during the run, as the deionization process reached saturation over the 90-minute period. Desorption of the CDI unit was conducted immediately after the adsorption phase by applying a cell voltage of 0V. The produced water sample took longer time for desorption than the sample with NaCl salts. This suggests that adsorption and desorption capacity changes with the nature of the wastewater.

6. Conclusions

The project successfully demonstrated an efficient waste-to-energy powered, synergistic technology for simultaneous salt and organic removal, which can be applied to treatment of produced water and fracking water. Removal of salt and organic contaminants was first demonstrated using a model system using acetic acid as organic contaminant and NaCl as the salt contaminant. A hydrogen productivity of 15.7 L-H_2/L-day was obtained corresponding to a current density of 57.9 percent using the model system. A salt removal rate of 17.4 mg/g carbon-hour was obtained using the model system. The application of the microbial electrolysis desalination system was demonstrated for produced water by removal of organics in MEC producing hydrogen and use of hydrogen as an energy source for salt removal via a PEM fuel cell-CDI cell combination.

CHC now believes the most immediate commercial application may be the removal of organics, nitrates, arsenic, and other contaminates from ground water near agricultural activities (especially in the Salinas Valley of California). The treated water could supplement much needed potable water sources in that area, and many other drought struck agricultural areas of the West. The treatment of produced and fracking waters continues to be a primary target for application of this technology.

7. Publications

1. Borole, A. P., 2014. Bioelectrochemical Systems for Treatment of Salt and BOD in Fracking Water. 29th Annual Water Reuse Symposium. Dallas, Texas.

2. Goud, R. K. and A. P. Borole, In Prep. "Effect of salt on hydrogen production from produced water using microbial electrolysis." Environmental Science: Water Research & Technology. Manuscript in preparation.

3. Goud, R. K. and A. P. Borole, In Prep. "An integrated microbial electrolysis-desalination process for practical treatment of salt-impacted waters." Desalination. Manuscript in preparation.

4. Goud, R. and A. P. Borole, 2014. Microbial fuel cell for harnessing sustainable energy from wastewaters containing high salt concentrations or produced water. AIChE Annual Meeting. Research Frontiers of Water Sustainability. Atlanta, Georgia.

5. Goud, R. K. and A. P. Borole, 2014. Developing microbial lectrochemical systems for treatment of produced water. ORNL Annual Postdoctoral Symposium. Oak Ridge, Tennessee.

8. References

Borole, A.P., 2010. Microbial fuel cell with improved anode. US Patent 7,695,834. 2010. UT- Battelle: USA.

Borole, A.P., 2012. Microbial fuel cell treatment of ethanol fermentation process water. U.P. Office, Editor. 2012, UT-Battelle, LLC: USA.

Borole, A.P. et al., 2011b. Electroactive biofilms: Current status and future research needs. Energy Environ. Sci., 2011. 4: p. 4813-4834.

Borole, A.P. et al., 2013a. Controlling accumulation of fermentation inhibitors in biorefinery water recycle using microbial fuel cells. Biotechnol. Biofuels, 2009. 2(1): p. 7.

Borole, A.P. et al., 2013b. Improving power production from acetate-fed microbial fuel cells via enrichment of exoelectrogenic organisms in continuous flow systems. Biochem. Eng. J., 2009. 48: p. 71-80.

Borole, A.P., et al., 2013. Efficient conversion of biomass-derived wastewater organics at high coulombic efficiency and current density. Bioresource Technol., manuscript in preparation.

Borole, A.P., C. Hamilton, and S. Schell, 2013c. Conversion of residual organics in corn stover- derived biorefinery stream to bioenergy via microbial fuel cells. Environ Sci Technol., 2013. 47(1): p. 642-8.

Borole, A.P., C.Y. Hamilton, and T.A. Vishnivetskaya, 2011a. Enhancement in energy conversion efficiency and current density of 3-dimensional MFC anodes using pre-enriched consortium and continuous supply of electron donors. . Bioresour. Technol., 2011. 102(8): p. 5098-5104.

Borole, A.P. and J. Mielenz, 2011. Estimating hydrogen production potential in biorefineries using microbial electrolysis cell technology Intl J. Hydrogen Energy, 36(22): p. 14787-14795.

Borole, A.P. and C. Tsouris, 2009a. Microbial Fuel Cell Treatment of Fuel Process Wastewater, Application Serial No. 12/366709.

Borole, A.P. and C. Tsouris, 2009b. Use of microbial fuel cells for produced water treatment., in AIChE Annual Meeting. Nashville, Tennessee.

Cheng, S. and B.E. Logan, 2007. Sustainable and efficient biohydrogen production via electrohydrogenesis. Proc. Natl. Acad. Sci., 2007. 104(47): p. 18871-18873.

Ichihashi, O. and A.P. Borole, Optimizing current density and coulombic efficiency via controlled electro-active biofilm growth. manuscript in preparation, 2013.

Logan, B.E., 2010. Scaling up microbial fuel cells and other bioelectrochemical systems. Appl. Microbiol. Biotechnol., 2010. 85: p. 1665-1671.

Morris, J.M. and S. Jin, 2008. Feasibility of using microbial fuel cell technology for bioremediation of hydrocarbons in groundwater. Journal of Environmental Science and Health Part a-Toxic/Hazardous Substances & Environmental Engineering, 2008. 43(1): p. 18-23.

Rozendal, R.A., et al., 2008. Towards practical implementation of bioelectrochemical wastewater treatment. Trends Biotechnol., 2008. 26(8): p. 450-459.

Sleutels, T., et al., 2012. Bioelectrochemical Systems: An Outlook for Practical Applications. Chemsuschem, 2012. 5(6): p. 1012-1019.

Sun, X., 2012. Large scale electrosorption system for waste water recovery: Practice and electrochemical aspects, in The 221st Electrochemical Society Meeting. 2012.

Tsouris, C. et al., 2011. Increasing Ion Sorption and Desorption Rates of Conductive Electrodes,U. PTO, Editor.

Tsouris, C. et al., 2011. Mesoporous Carbon for Capacitive Deionization of Saline Water. Environ. Sci. Technol. 45(23): p. 10243-10249.