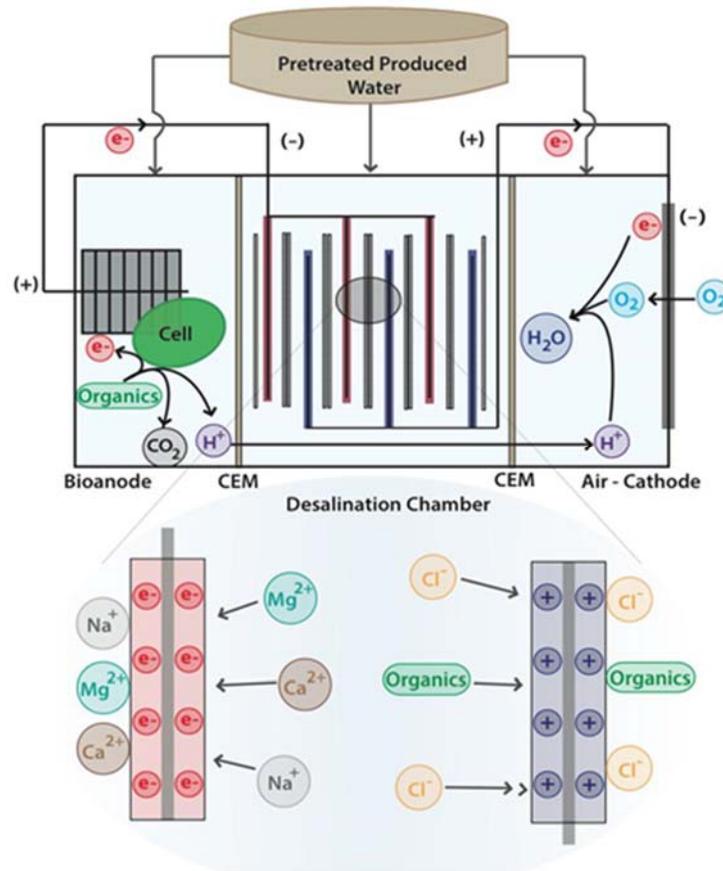


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Self-Sustaining Produced Water Treatment for Concurrent Renewable Energy Production, Desalination and Organic Removal

WRRRI Technical Completion Report No. 373

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Schematic of the microbial capacitive deionization cell (MCDC)

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SELF-SUSTAINING PRODUCED WATER TREATMENT FOR CONCURRENT
RENEWABLE ENERGY PRODUCTION, DESALINATION AND ORGANIC REMOVAL

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ABSTRACT

Management of produced water generated during oil and natural gas exploration and production is a significant challenge. Produced water contains contaminants such as petroleum hydrocarbons, salts, and chemical additives. The water is considered hazardous waste and must be treated or disposed safely. In this project we developed an innovative microbial capacitive deionization cell (MCDC) to simultaneously remove organic substances and salts from produced water so the treated water can be potentially recycled and reused. Moreover, compared to other energy intensive systems, MCDC uses bacteria to convert biodegradable pollutants into direct electricity, which offsets operation energy use or supplies additional energy for other systems.

In this study the MCDC was comprised of three chambers - anode, desalination, and cathode, each with internal volumes of 23, 12, and 27 mL, respectively. Produced water treated by the MCDC had total dissolved solids concentration of 15,900 mg/L and dissolved organic carbon (DOC) concentration of 230 mg/L. Microbial degradation of organic compounds in the anode generated an electric potential that drove the desalination of produced water. Sorption and biodegradation resulted in a combined organic removal rate of 6.4 mg DOC per hour in the reactor, and the MCDC removed 36 mg salt per gram of carbon electrode per hour from produced water. This study demonstrated that MCDC could be used to combine organic degradation and desalination of contaminated water without external energy input.

Keywords: microbial fuel cell; desalination; capacitive deionization; produced water treatment; organic removal; bioelectrochemical processes

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1. BACKGROUND, JUSTIFICATION, AND OBJECTIVES

Increasing demands on energy and freshwater are two major challenges facing the world. To sustain population growth and economic development, energy production has been increased, much of which is derived from fossil fuels. Substantial amounts of freshwater are used by the petroleum industry for oil and gas exploration and production (Hickenbottom et al., 2013; IOGCC and ALL, 2006; Veil et al., 2004; Xu et al., 2008a). Meanwhile, large amounts of wastewater are generated over the life of a well, including drilling wastewater, hydraulic fracturing flowback water, and produced water, the latter being the largest waste stream generated as a byproduct during the oil and gas production (Clark and Veil, 2009). The quantity of produced water is expected to rise with increasing energy demand.

Produced water disposal is a major challenge due to high cost, water quality limitations, and regulations (Drewes et al., 2009). Currently, deep well injection is the most common method for inland disposal, followed by evaporation. Although produced water disposal has been federally regulated since the 1930s, the rapid increase in unconventional drilling has prompted more stringent disposal regulations in the U.S. (McCurdy, 2013; Nicot et al., 2011). As a consequence, on-site treatment and reuse of produced water are becoming more attractive methods than disposal. The development of efficient and sustainable on-site treatment technologies would not only reduce production costs but also conserve freshwater and minimize adverse environmental impacts.

One such technology is desalination. Industrial scale thermal evaporation techniques, such as General Electric's steam-assisted gravity drainage, consume 15.9 - 17.2 kWh to treat 1 m³ of water (Heins and McNeill, 2007). The energy demand of membrane desalination technologies, such as reverse osmosis (RO), electrodialysis, and electrodialysis reversal is highly dependent upon the salinity level of feedwater, varying in the range of 0.7 - 2 kWh and 13.2 - 22.7 kWh to treat 1 m³ of water from brackish water and seawater, respectively (Xu et al., 2009). The salinity of produced water varies greatly from hundreds mg/L to over 250,000 mg/L. Severe scaling and fouling during the

treatment of produced water requires extensive pretreatment, increasing the treatment complexity and costs.

Emerging technologies have been studied for produced water treatment, such as membrane distillation (MD) and forward osmosis (FO). While MD can treat highly saline water, there are disadvantages when treating produced water. Produced water contains volatile organic compounds, which, in an MD system, can cross the membrane with the water vapor, contaminating the permeate stream. Surfactants, alcohols, and other compounds can also reduce the surface tension and cause wetting of the membrane pores, allowing the feed to flow directly across the hydrophobic membrane unhindered (El-Bourawi et al., 2006; Lawson and Lloyd, 1997). A recent review by Camacho and others (2013) summarized thermal energy needs of MD, which ranged from approximately 5 to 810 kWh/m³ (with the high energy demand for treating seawater), while electrical requirements were below 1.75 kWh/m³.

Compared to RO, FO operates under a low hydraulic pressure, resulting in lower operating costs, less fouling, and longer membrane lifetime (Cath et al., 2006; Mi and Elimelech, 2010). After treatment, the permeate-draw solution mixture must be separated by a regeneration process. Recently, a pilot scale FO was able to desalinate produced water with an initial total dissolved solids (TDS) concentration of 73,000 mg/L to less than 300 mg/L with 64% recovery using 21 kWh of energy per m³ permeate (McGinnis et al., 2013). The challenges of using FO to treat highly saline produced water include the requirement of a draw solution with very high osmotic pressure, and energy requirements for draw solution separation and regeneration (McCutcheon et al., 2005; Shaffer et al., 2013).

In addition to physical and chemical processes, biological processes have also been studied to remove organic contaminants from saline produced water. Tellez and others (2002) were able to reduce oil, grease and chemical oxygen demand (COD) by more than 97% using activated sludge at a pilot scale level to treat produced water with TDS of 35,000 mg/L. However, the large footprint, including the accumulation of sludge, and associated costs (aeration, transportation of produced water, disposal of sludge), may hinder the use of a conventional activated sludge system as an on-site treatment option.

A study by Fakhru'l-Razi and others (2010) demonstrated that membrane bioreactors could successfully remove over 91% of total organic carbon (TOC) as well as oil and grease from produced water with TDS of 16.4 g/L. Although the system had a smaller footprint compared to an activated sludge process, a hydraulic retention time of 20 hours was required and membrane fouling led to frequent cleaning (Pendashteh et al., 2011).

Recently, a new technology called a microbial desalination cell (MDC) was developed that concurrently generates electrical current, desalinates salt water, and treats wastewater (Cao et al., 2009; Jacobson et al., 2011; Luo et al., 2010; Luo et al., 2012b). The MDC was derived from a traditional microbial fuel cell (MFC) system, and reactors are constructed by adding a desalination chamber between the anode and cathode chambers. A cation exchange membrane (CEM) separates the cathode and desalination chamber, allowing cations to flow from the desalination chamber to the cathode. An anion exchange membrane (AEM) separates the anode and desalination chamber, allowing anions to flow from the middle desalination chamber to the anode. In the anode chamber, exoelectrogenic bacteria transfer electrons produced from the oxidation of organic matter to the anode during their anaerobic respiration. The electrons then flow through an external circuit to the cathode where terminal electron acceptors, such as oxygen, are reduced. A limitation of this configuration is the pH imbalance created in the anode and cathode chambers (Luo et al., 2012a; Qu et al., 2012). H^+ ions generated from the oxidation of organic matter in the anode chamber are blocked by the AEM between the anode and desalination chambers, decreasing the pH, creating unfavorable conditions for the microbes, and decreasing power output (Luo et al., 2012a). In the cathode, consumption of free H^+ increases the pH and causes scaling and warping of the CEM and the electrode (Luo et al., 2012a). Recirculation of the anolyte and catholyte has been shown to remedy pH imbalances, but the resulting anolyte and catholyte solutions become concentrated with salt from the desalination chamber, rendering them inappropriate for reuse applications (Forrestal et al., 2012b).

A microbial capacitive desalination cell (MCDC), which integrates capacitive deionization (CDI) into the MDC design, has the advantages of using electrodes to

electrically sorb ions while overcoming the challenges of pH imbalance and preventing salt transport to anode and cathode (Feng et al., 2013; Forrestal et al., 2012a; Forrestal et al., 2012b; Yuan et al., 2012). Previous work demonstrated the proof-of-concept of MCDCs using synthetic wastewater and ferricyanide as electron acceptors (Forrestal et al., 2012a; Forrestal et al., 2012b), which provides an attractive energy positive process for simultaneous removal of salt and organics in produced water. Thus the aim of this study was to investigate the MCDC's capacity to remove inorganic and organic constituents from actual produced water generated during unconventional natural gas production. This study focused on understanding the removal mechanisms of the system by comprehensive water quality characterization, and demonstrating that MCDC could generate sustainable electrical potential by utilizing the refractory organic matter in produced water.

The results of this project have been published in the *Journal of Hazardous Materials*. This report summarizes the major findings of the research. Please refer to the figures, tables, and other detailed information in the recently published paper:

Stoll Z.A., Forrestal, C., Ren, Z. and Xu, P. (2015). Shale Gas Produced Water Treatment Using Innovative Microbial Capacitive Desalination Cell. *Journal of Hazardous Materials*, 283, 847-855.

Additional publications related to the research topic are published in:

Stoll, Z.A, Dolfing, J, Ren, Z., Xu, P. (2016). Interplay of anode, cathode and current in microbial fuel cells: implications for wastewater treatment. *Energy Technology*, 4(5), 583-592.

Stoll, Z.A., Ma, Z., Trivedi, C.B., Spear, J.R., Xu, P. (2016) Sacrificing power for more cost-effective treatment: A techno-economic approach for engineering microbial fuel cells. *Chemosphere*, 161, 10-18.

2. MATERIALS AND METHODS

2.1 Produced Water Quality

Produced water samples were collected from the effluent of a wastewater treatment plant (WWTP) in Piceance Basin, which receives produced water and hydraulic fracturing flowback water generated during shale gas exploration and production. The raw produced water was pretreated at the WWTP through a series of processes including initial solids separation and oil removal, hydrocyclones for solid removal, further oil-water separation, dissolved air flotation, and air stripping for volatile organic compound removal. After removing suspended solids and oil, the effluent TDS concentration was measured at $15,870 \pm 290$ mg/L and the COD concentration ranged from 800 to 1100 mg/L. The pH, conductivity, and dissolved organic carbon (DOC) were measured at 7.8 ± 0.2 , 25 ± 0.15 mS/cm, and 230 ± 4 mg/L, respectively. The major ions of the produced water included chloride ($9,290 \pm 240$ mg/L), sodium ($5,990 \pm 80$ mg/L), alkalinity (700 ± 8 mg/L as CaCO_3), calcium (240 ± 60 mg/L), and magnesium (30 ± 2 mg/L).

After the WWTP treatment, the water could be used for well drilling and hydraulic fracturing that have less stringent water quality requirements. For other potential beneficial use applications such as agricultural irrigation and stream-flow augmentation, the high content of salt and organic matter in the produced water must be further reduced.

Samples taken from each MCDC chamber before and after each run were either analyzed immediately or stored in glass vials at 4°C prior to analysis in terms of conductivity, pH, total alkalinity, anions, cations, DOC, UV-VIS spectrophotometry, and fluorescence spectroscopy (emission excitation matrices). Duplicate samples were analyzed to monitor the analytical errors.

2.2 Reactor Configuration and Operation

The MCDC was comprised of three cubic polycarbonate chambers: anode, desalination and cathode (Figure 1). Each chamber had a 3 cm diameter hole cut out. The widths of

the anode, desalination, and cathode chambers were 4.0, 1.5 and 4.0 cm yielding internal volumes of 23, 12 and 27 mL, respectively. The effective volume in anode chamber was slightly smaller than the cathode chamber because of the volume taken by a carbon fiber brush. The carbon fiber brush (Gordon Brush, CA), used as the anode electrode, was washed in acetone and heated at 350°C for 30 minutes to remove the remaining impurities during carbon fiber manufacturing and activate the adsorption sites. The 7 cm² air-cathode was coated with 0.5 mg/cm² Pt/C (10%) and four polytetrafluoroethylene diffusion layers on 30% Teflon coated carbon cloth. The desalination chamber was situated between the anode and cathode and separated by a CEM on either side (CMX-SB, Astom Corporation, Japan).

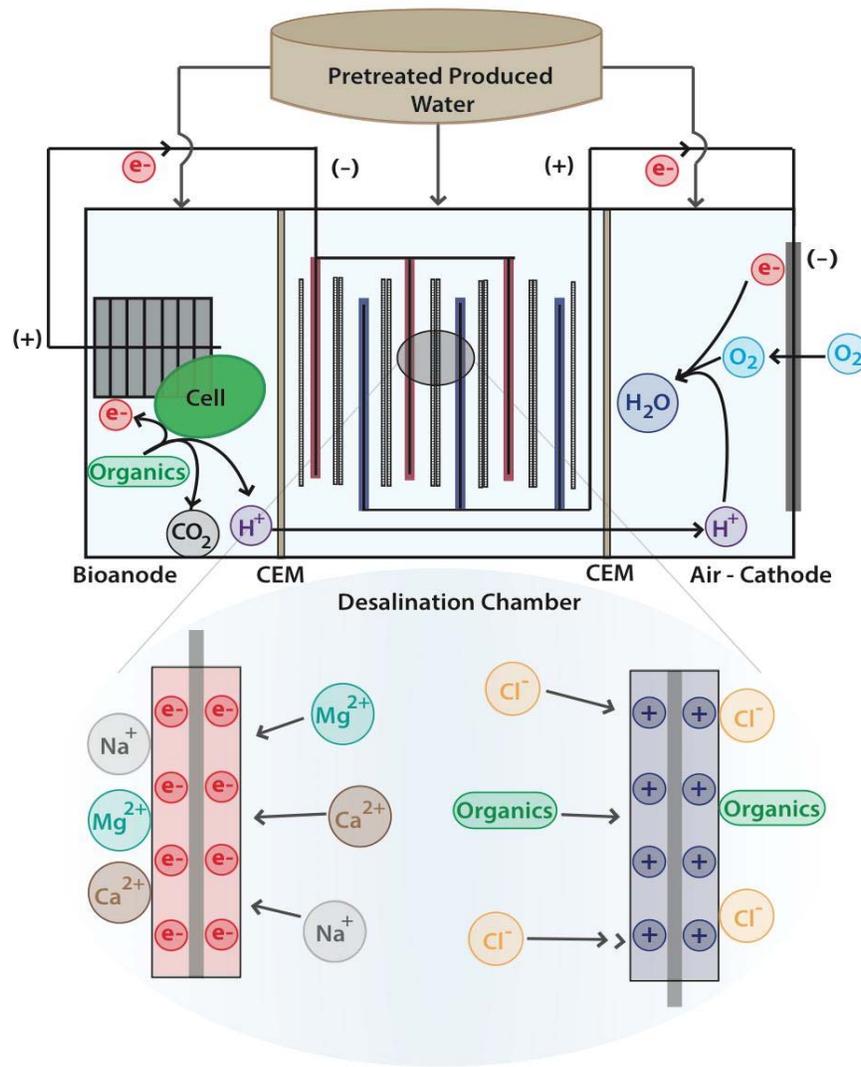


Figure 1. Schematic of the MCDC treatment

The CDI module in the desalination chamber was comprised of two identical electrode sets (positive and negative), each with three electrodes. The central component of each electrode consisted of a flat, circular, 2.5 cm² Ni/Cu current collector (McMaster Carr, IL) with a 2.5 cm² piece of activated carbon cloth (ACC) on both faces (Chemviron Carbon, UK). A 3.0 cm² piece of fine mesh spacer was placed outside each ACC to provide sufficient distance between each electrode and prevent short-circuiting. In total, six Ni/Cu current collectors, twelve pieces of ACC (0.06 g each), and twelve spacers were used. For the external circuit, one piece of titanium wire connected the anode electrode to the positive CDI electrode and another piece connected the negative CDI electrode to the cathode electrode.

The anode brush electrode was acclimated in two steps prior to the experiment. In the first step, the electrode was acclimated in the two-chamber MFC in a simple fed-batch manner for a fast growth of exoelectrogenic microbes. Activated sludge (13 mL) obtained from a local municipal WWTP was mixed with 10 mL of anolyte growth media and used to condition the brush. The first acclimation step was complete when the reactors demonstrated a repeatable voltage profile. In the second step, the MFC was converted to the MCDC by inserting the desalination chamber, with a CEM at both ends, between the anode and cathode chambers. The anode was gradually transitioned from the 100 mM acetate media to 100% produced water. The desalination and cathode chambers were also filled with only produced water.

The MCDC was operated in a fed-batch mode. Pretreated produced water was fed into the three chambers for organic removal and desalination. The anode and cathode chambers were each connected to an external 100 mL reservoir containing produced water and recirculated at 2 mL/min (Masterflex, Cole Parmer): the total recirculated volume for each chamber equaled the reservoir volume plus the chamber volume. Carbon dioxide, electrons, and hydrogen ions are generated at the bioanode brush from the microbial oxidation of organic matter in produced water. Electrons travel from the positively charged brush to the negatively charged ACC electrode (red in Figure 1) in the desalination chamber where cations are removed via electrosorption. To maintain electroneutrality, anions sorb to the opposing ACC electrode (blue in Figure 1) and “push” electrons towards the cathode, resulting in a positively and negatively charged

ACC electrode and cathode, respectively. Electrons are accepted in the cathode and participate in the oxidation-reduction reactions of oxygen to water. Hydrogen ions generated in the anode migrate across both CEMs to the cathode.

A total of three separate runs were conducted, Run 1, 2 and 3, each consisting of 3 cycles. Based on preliminary work, each cycle was capped at 1.3 hours because approximately 90% of the electrosorption occurred within the first hour of operation. At the end of each cycle, the produced water in the desalination chamber was completely removed and stored for the next cycle. To avoid the carryover of salt residuals from previous cycles in the desalination chamber, the ACC assemblies were cleaned by short-circuiting the MCDC and rinsing it with deionized water. The voltage of MCDC was measured continuously using a Keithley 2300 data acquisition system; and the electrical potential between the electrode assemblies in MCDC was monitored by a programmable multimeter (Amprobe, WA).

3. RESULTS AND DISCUSSION

3.1 Reactor Electrical Production

The reactor potential was monitored over three runs, or nine cycles. Stable potentials over nine successive cycles were observed, with an average peak electrical potential of 0.28, 0.25 and 0.25 Volts for Runs 1, 2, and 3, indicating the reactor's ability to maintain a potential by degrading the organic matter in the shale gas produced water. The peak electrical potential generated was lower than typical municipal wastewater and other wastewater that contain higher fractions of easily biodegradable organic matter. But as discussed later in this report, the electrical potential gradient generated from biodegrading recalcitrant organic matter in produced water was sufficient to separate salts in MCDC.

3.2 Salt Removal

Desalination efficiency of the MCDC was evaluated based on ion removal in the anode, desalination, and cathode chambers. Efficiencies were calculated in terms of percent removal and sorbed ions in mg or milliequivalent per gram of ACC (mg or meq/g carbon).

Salt removal was highly effective in the desalination chamber, removing more than 70%, 65% and 64% of TDS in Runs 1, 2, and 3, respectively. In all three runs, an average of 36 mg TDS/g ACC (9.74 meq/g C) was removed per hour. Although the MCDC required regeneration of every 1.3 hours due to the small amount of ACC packed in the desalination chamber (0.72 g in total), the salt sorption capacity of the MCDC was 5 to 18 times higher than in conventional CDI using activated carbon as electrodes (Forrestal et al., 2012b; Gabelich et al., 2002; Xu et al., 2008b).

When comparing the removal of monovalent to divalent ions, higher amounts of monovalent ions Na^+ and Cl^- were removed than divalent ions Mg^{2+} and Ca^{2+} in the desalination chamber. For Runs 1, 2, and 3, more Cl^- ions (5481, 5124 and 4853 mg/L) and Na^+ ions (3374, 3076 and 2935 mg/L) were removed in desalination chamber

compared to Ca^{2+} (204, 192 and 162 mg/L) and Mg^{2+} ions (20.9, 20.5 and 15.6 mg/L). Competitive transport and adsorption in the desalination chamber is affected by a number of factors, including the ionic concentration, hydrated ionic radius, ionic charge, and diffusivity in the carbon cloth electrodes as well as in the boundary layer. For ion species having similar initial solution concentration (in terms of molarity), the hydrated radius might determine the resulting sorption capacity of carbon electrodes. Monovalent ions such as sodium with smaller hydrated radii (3.58Å) can easily diffuse into electrode pores and preferentially adsorb over multivalent ions (such as calcium 3.58Å) on a molar basis. In a competitive multi-ionic solution, high sodium concentration in the produced water further contributed to the high molar or mass removal of sodium over divalent ions.

However, a high percent removal of divalent ions was primarily due to their low influent concentrations in the produced water: for Runs 1 and 2, percent removal achieved was 80.5% and 73.5% for Ca^{2+} , and 71.8% and 65.7% for Mg^{2+} , compared to 56.7% and 49.9% for Cl^- , and 53.8% and 47.8% for Na^+ , respectively. For Run 3, Ca^{2+} removal (59.1%) was the highest followed by removal of Cl^- (47.5%), Na^+ (47.3%) and Mg^{2+} (47.2%). Saturation of ACC assemblies, or decreasing reactor potentials and unfavorable concentration gradients could limit ion removal. The decrease in salt removal and mass balance over successive cycles suggests that, despite regenerating the CDI assemblies after each run, a small fraction of ions remained trapped in the ACC assemblies.

Activated carbon contains many micropores and macropores that increase the specific surface area. During regeneration, the ions sorbed in the larger macropores can desorb and diffuse back to the bulk solution faster than the ions sorbed within the small micropores, decreasing the effective surface area over subsequent runs.

In the anode chamber, less than 10% of salt was removed for all runs. For Run 3, the salt removal efficiencies were much lower than in Run 1 and 2; 2.93% sodium was removed, magnesium had no change, while 5.20% calcium and 2.91% chloride ions were accumulated. Preferential removal of cations can be explained by the CEM separating the anode and desalination chambers. Cations initially in the anode would be able to migrate across the CEM and sorb to the ACC assembly in the desalination chamber, whereas anions would be attracted to the positively charged carbon-brush anode. In

addition to anions, organics and other negatively charged electroactive species would sorb to the anode brush. Because no anodic (or cathodic) regeneration was performed, accumulation of these compounds over the duration of the experiment would decrease the effective sorption sites of the brush electrode and reduce ion removal efficiency, or even leach from the anode back to the bulk solution in anode chamber over subsequent runs. In the cathode, a higher percent removal of divalent ions Ca^{2+} (40.7%, 45.8%, 20.5%) and Mg^{2+} (16.4%, 18.0%, 2.9%) was observed for Run 1, 2, and 3 compared to monovalent ions Na^+ (4.0%, -0.8%, 4.4%) and Cl^- (4.3%, -0.1%, 1.3%). Removal of Na^+ in Run 2 and Cl^- in Runs 2 and 3 was negligible because the percent removal was close to the standard deviation.

The reactor configuration explains why cations were selected over anions. The cathode contains a negatively charged carbon cloth electrode and is separated from the desalination chamber by a CEM. Negatively charged sorption sites on the cathode have adsorbed counter ions, namely, cations. With the gradual saturation of cations in the electrode pores over time, the effective surface area and sorption capacity of cathode decreased. Chloride removal was negligible because the CEM retained anions within the cathode chamber and no sorption sites were available on the negatively charged cathode for chloride. Small amount of salts, however, would be able to diffuse through the CEM due to a large localized concentration gradient between the desalination chamber, ACC assemblies, and catholyte. The diffusion could overcome electrical repulsion and drive a small fraction of Cl^- across the CEM where it could sorb to the ACC.

3.3 Organic Removal in MCDC

3.3.1 Organic Removal in Terms of DOC

To better understand the MCDC capabilities of removing organics, DOC analysis, UV-Vis absorption spectroscopy and fluorescence spectroscopy were used to characterize the organic fraction in the produced water.

The anode chamber removed an average of 3.6, 2.1 and 2.0 mg DOC/h, corresponding to a 27.5, 18.6 and 16.3% removal in Runs 1, 2, and 3, respectively. The initial higher DOC

removal in Run 1 can be attributed to the sorption capacity of the carbon brush. The removal of organics in Runs 2 and 3 was mostly due to biodegradation in the anode. Although the anodic biofilm was acclimated to the produced water prior to the experiment, more research is needed on long-term exposure of exoelectrogenic microbes to produced water under an electric load. For Runs 1 and 2, the desalination chamber removed 2.4 and 1.5 mg DOC/h (24.9 and 14.9%), and the cathode chamber 2.3 and 2.0 mg DOC/h (21.6 and 20.5%), respectively. However, in Run 3, the desalination chamber accumulated 0.4 mg DOC/h (4.1%) and no removal was observed in the cathode chamber. This is most likely due to the accumulation of electroactive compounds in the ACC assemblies and the cathode from the previous two runs.

3.3.2 Organic Removal in Terms of UV-Vis Absorbance

UV-Vis full wavelength scans from 190 to 800 nm were conducted to further characterize the fraction of dissolved organic matter in produced water. Below 240 nm, absorption of peptide bonds begins to dominate aromatic and disulfide complexes. In this study, a major peak at 225 nm was observed for all produced water samples except the desalination final, for which the peak intensity was reduced by more than 3.5 times. The results of UV-Vis full wavelength scans demonstrated the removal of aromatic and peptide contaminants (with wavelength between 190 and 240 nm) from produced water in desalination chamber, mostly due to sorption of these compounds to the ACCs. In addition to organic matter, the produced water contained approximately 26 mg/L nitrate, which also contributed to the absorption at 220 nm. Nitrate was removed by 45% in desalination chamber.

3.3.3 Characterization of Organic Fractions in Produced Water with F-EEM

The removal of dissolved organics in shale gas produced water was further characterized by fluorescence spectroscopy (excitation-emission matrices, F-EEM). F-EEM showed that the change in extracellular biological organic matter (EBOM) peak volume (final minus initial) increased 28.9% in the anode, decreased 95.5% in the desalination chamber and decreased 18.5% in the cathode. Anodic accumulation of EBOM is consistent with biological growth. Conversely, dead cells that detached from the anode, underwent apoptosis and were solubilized would also cause an increase in EBOM and

could explain the decrease in anodic performance. Sorption of EBOM in the desalination and cathode chambers is anticipated since proteins and phenols tend to sorb to activated carbon.

3.4 Use of Inexpensive Carbon Materials as Anode

Graphite brush used in this study is a standard material widely used in microbial fuel cells (MFCs) research. Although a graphite brush is highly effective as an anode, it is expensive. We conducted additional experiments to evaluate two new anode materials - hard carbon felt and carbon foam - against graphite brush to determine if using inexpensive materials with less than ideal properties can achieve more cost-effective treatment than high-cost, high-performing materials. Although the carbon felt generated 14% less power and 15% less anodic current during treatment of domestic wastewater, the power output to electrode cost (W/\$) was 2 times greater than graphite brush. 16S rRNA sequencing showed the microbial community compositions were not statistically different on graphite brush, carbon felt, and carbon foam while organic removal rates were nearly identical for all materials. Our results demonstrate that high-performing materials may not be necessary when treating real wastewater and that inexpensive materials are capable of achieving more cost-effective treatment despite generating less power (Stoll et al, 2016a, b).

4. CONCLUSIONS AND RECOMMENDATIONS

In this study, we investigated the removal capabilities and mechanisms of a microbial powered system that harnesses the energy stored in organic compounds to power the treatment of produced water. This study demonstrated that shale gas produced water contained sufficient biodegradable organic matter to run the MCDC, generating an electrical potential of 0.25-0.28 V for desalination. In the anode, removal of DOC and aromatics was due to biodegradation and sorption, and the microbial community was able to generate a consistent potential over the life of the experiment. Salt was mostly removed by electrosorption, a reversible process, in the MCDC. Over 36 mg TDS/g ACC was removed from the desalination chamber in one hour, demonstrating the desalination efficiency of MCDC is much higher than conventional MDC and CDI.

For a continuous flow operation, produced water could be treated first at the anode to degrade organics and then flow to the cathode where the higher salt concentrations would be beneficial for electron transfer. Finally, the produced water would flow through the desalination chamber for salt removal. Multiple-stage MCDC (sequential operation) is needed to remove organics and salts to meet the water quality requirement for beneficial use of produced water. Or MCDCs could be used as a pretreatment to degrade organics partially and desalinate water to reduce fouling and scaling potential for the following desalination process. While the purpose of this study was to evaluate the feasibility of treating actual produced water with an MCDC, more research is required to understand:

- Produced water characteristics and specific organic compounds removed in MCDC;
- Long-term impact of highly saline produced water and refractory organic contaminants on the microbial community, membranes, electrode assemblies, and overall performance. This information will aid reactor optimization for desalination, treatment, and power generation of produced water.
- Fluctuation of electrical potential generated during the MCDC operation as a function of substrate concentration in produced water. The substrate concentration

determines the theoretical amount of electrons that can be generated and therefore controls the desalination efficiency. Also, the organic concentrations would vary under real-life conditions.

- Therefore, reactor configuration and operation under the sequential MCDC operation scheme must account for substrate fluctuations so that the effluent meets the treatment standards.
- Factors affecting the MCDC regeneration process. Regeneration must be optimized before the MCDC can be implemented on a larger scale.
- Define the applicable range of produced water regarding salinity and organic concentration. The salinity and COD concentration of produced water used in this study were around 16,000 mg/L and 1000 mg/L, respectively. MCDC may not be cost-effective to treat highly saline produced water because the electrode materials will be saturated faster by salt adsorption and require frequent regeneration. In addition, the produced water should contain adequate amount of biodegradable organic carbon to sustain the growth of exoelectrogenic bacteria.

Due to the expansion of oil and gas exploration and production in Permian Basin and San Juan Basin in New Mexico, the produced water volume continues to increase significantly. In addition, with the oil and gas boom millions of gallons of fresh water are needed for well drilling and hydraulic fracturing. At the same time, a prolonged drought has seriously restricted the water available for agriculture, municipal, and industrial uses. Given this situation, it would clearly be desirable to find a way to remediate the increasing supply of produced water to help mitigate the worsening scarcity of fresh water. Our research attempts to address this problem by identifying processes that can desalinate and remove organic contaminants from produced water in an economical way. In particular, we have found that the MCDC process has the potential to achieve this goal by exploiting the electrochemical energy in the contaminants to produce electric power to drive the cleansing reactions. Therefore, MCDC provides attractive application potentials for onsite produced water treatment in the form of multi-function infrastructure without external energy input.

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