Shale gas produced water treatment using innovative microbial capacitive desalination water cell

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HIGHLIGHTS

• Actual shale gas produced water was treated with no external energy input.
• Biodegradation of organics generated stable voltages for desalination.
• On average, 36 mg TDS per g activated carbon was removed in 1 h.
• A maximum organic removal rate of 6.4 mg DOC per hour was achieved in the reactor.

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ABSTRACT

The rapid development of unconventional oil and gas production has generated large amounts of wastewater for disposal, raising significant environmental and public health concerns. Treatment and beneficial use of produced water presents many challenges due to its high concentrations of petroleum hydrocarbons and salinity. The objectives of this study were to investigate the feasibility of treating actual shale gas produced water using a bioelectrochemical system integrated with capacitive deionization—a microbial capacitive desalination cell (MCDC). 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 dissolved organic carbon per hour in the reactor, and the MCDC removed 36 mg salt per gram of carbon electrode per hour from produced water. This study is a proof-of-concept that the MCDC can be used to combine organic degradation with desalination of contaminated water without external energy input.

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1. Introduction

Increasing demands on energy and freshwater are two major challenges facing the world. Technological advances in horizontal drilling and hydraulic fracturing have made extraction of oil and gas from unconventional reservoirs economically viable. During the fracturing process, thousands of cubic meters of freshwater are injected into a well at high pressure to fracture the subsurface formations and liberate oil or gas trapped within the geological formations [1–7]. Meanwhile, significant amounts of wastewater generated during oil and gas production, known as produced water, require proper disposal.

Produced water disposal is a major challenge due to high cost, water quality limitations and regulations [8–10]. High concentrations of petroleum hydrocarbons and salts increase the risks of soil and groundwater contamination. Some of the aromatic and polycyclic aromatic hydrocarbons are known carcinogens, and high salt concentrations reduce water quality and potential for beneficial reuse. Development of efficient on-site treatment technologies, including desalination, would not only reduce oil and gas production costs but also conserve freshwater and minimize adverse environmental impacts. 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 [11]. 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 between 0.7–2 kWh and 13.2–22.7 kWh to treat 1 m³ of brackish water and seawater, respectively [12]. Severe scaling and fouling during the
was successfully desalination of produced water requires extensive pretreatment that increases membrane treatment complexity and costs.

Emerging technologies have been studied for produced water treatment, such as membrane distillation (MD) and forward osmosis (FO). MD can treat highly saline water, however, produced water contains volatile compounds that can cross the membrane with water vapor and contaminate the permeate stream. Surfactants, alcohols and other compounds in produced water can also reduce the surface tension and cause wetting of the membrane pores, allowing the feed to flow directly across the hydrophobic membrane unhindered [13,14]. Energy requirements of MD vary widely, but can be an energy-efficient technology if low-grade heat is available [15].

Compared to RO, FO operates under a low hydraulic pressure, which results in less fouling and extends membrane lifetime [16,17]. After treatment, a regeneration process is required to separate the permeate-draw solution mixture. 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 at 64% recovery using 21 kWh of energy per m³ permeate [18]. For FO to be successful in treating highly saline produced water, the draw solution must have a high osmotic pressure, which increases the amount of energy needed for draw solution separation and regeneration [19,20].

In addition to physical and chemical technologies, biological processes have also been studied to remove organic contaminants from saline produced water. Tellez et al. reduced 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 [21]. However, the large footprint, accumulation of sludge and associated costs (aeration, transportation of produced water, disposal of sludge), may hinder the use of conventional activated sludge system as an on-site treatment option. A study by Fakhru’ll-Razi et al. demonstrated membrane bioreactors could successfully remove over 91% of total organic carbon (TOC), and oil and grease from produced water with a TDS of 16.4 g/L [22]. Although the system had a smaller footprint compared to an activated sludge process, a hydraulic retention time of 20 h was required and membrane fouling led to a reactor downtime of 24 h [23].

Recently, a new technology called a microbial desalination cell (MDC) was developed that concurrently generates electrical current, desalinates salt water, and treats wastewater [24–27]. The MDC was derived from a traditional microbial fuel cell (MFC) system, and reactors are constructed by adding a desalination chamber in-between the anode and cathode chambers. A cation exchange membrane (CEM) separates the cathode and desalination chamber, allowing cations to transport from the desalination chamber to the cathode. An anion exchange membrane (AEM) separates the anode and desalination chamber, allowing anions to transport from the middle desalination chamber to the anode. In the anode chamber, exoelectrogenic bacteria transfer electrons liberated from the oxidation of organic matter to the anode during their anaerobic respiration. Electrons then flow through an external circuit to the cathode where terminal electron acceptors, such as oxygen, are reduced. A pH imbalance is created in the anode and cathode chambers with this configuration and limits performance [28,29]. 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 [28]. In the cathode, consumption of free H⁺ increases the pH and causes scaling and warping of the CEM and the electrode [28]. 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 certain reuse applications [30].

A microbial capacitive desalination cell (MCDC), which integrates capacitive deionization (CDI) into the MDC design, has the advantages of using porous electrodes to electrically sorb ions thus preventing salt transport to anode and cathode [30–33]. The challenges of pH imbalance are overcome by using two CEM based assemblies that allow the free transfer of protons across the system and prevent significant pH changes observed in traditional MDCs. Previous work demonstrated the proof-of-concept of MCDCs using synthetic wastewater and ferricyanide as electron acceptors [30,31], which provides an attractive energy positive process for simultaneous removal of salt and organics in produced water. Therefore the aim of this study was to investigate the MCDC’s ability to remove inorganic and organic constituents from actual produced water generated during unconventional natural gas production. This paper focuses on understanding the removal mechanisms of the system by comprehensive water quality characterization and demonstrates that the energy generated by the microbes from the biodegradation of organics in the produced water is sufficient to drive desalination.

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, Colorado, USA, which receives produced 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 compound removal. After removing suspended solids and oil, the effluent TDS concentration was measured at 15,870 ± 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 produced water constituents included chloride (9290 ± 240 mg/L), sodium (5990 ± 80 mg/L), alkalinity (700 ± 8 mg/L as CaCO₃), calcium (240 ± 60 mg/L) and magnesium (30 ± 2 mg/L).

Samples taken from each MDC chamber before and after each run were either analyzed immediately or stored in glass vials at 4 °C prior to analysis. Conductivity and pH were measured using a pH and conductivity meter (HACH Co., CO). Total alkalinity was measured by a HACH alkalinity test kit (HACH Co., CO). Samples were diluted and filtered through a 0.45 μm filter and analyzed for anions and cations using ion chromatography (IC) (Model ICS-90, Dionex, Sunnyvale, CA) and inductively couple plasma optical emission spectroscopy (ICP-OES) (Optima 5300 DV, Perkin Elmer Inc., Waltham, MA), respectively. DOC concentrations were quantified with a TOC analyzer (TOC 500, Shimadzu Corp., Kyoto, Japan). Filtered samples were further analyzed by a spectrophotometer (DU 800 UV Spectrometer, Beckman Coulter, Brea, CA) and a fluorospectrometer (FluoroMax-4, HORIBA Jobin Yvon, Edison, NJ). Fluorescence data were interpreted by a MATLAB script (MathWorks, MA). All samples were diluted to levels suitable for analysis for the different analytical instruments.

2.2. Reactor configuration and operation

The MCDC was comprised of three cubic polycarbonate chambers: anode, desalination and cathode (Fig. 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. A carbon fiber brush
(Gordon Brush, CA), used as the anode electrode, was washed in acetone and heated at 350 °C for 30 min. 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 [34]. The desalination chamber was situated between the anode and cathode and separated by a CEM on either side (CMX-SB, Astom Corporation, Japan). 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 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 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 100 mM anolyte media contained per liter: 1.6 g NaCH₃COO, 0.62 g NH₄Cl, 4.9 g NaH₂PO₄ H₂O, 9.2 g Na₂HPO₄, 0.26 g KCl, 10 mL trace metals and 10 mL vitamin solution. A catholyte media was used that contained, per liter: 9.8 g/L (71 mM) NaH₂PO₄ H₂O and 18.3 g/L (129 mM) Na₂HPO₄. 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.

For this feasibility study, the MCDC was operated in a fed-batch mode. Pretreated produced water was fed into the three chambers for organic removal and desalination (Fig. 1). The anode and cathode chambers were each connected to an external 100 mL reservoir containing produced water and recirculated at 2 mL/min (Master flex, Cole Parmer): the total recirculated volume for each chamber equaled the reservoir volume plus the chamber volume. At the bioanode brush, carbon dioxide, electrons and hydrogen ions are generated 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 Fig. 1) in the desalination chamber where cations are removed via electrosorption. To maintain electroneutrality, anions sorb to the opposing ACC electrode (blue in Fig. 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 h 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 carry-over of salt residuals from previous cycles in desalination chamber, the ACC assemblies were regenerated by short-circuiting the MCDC for 20 min and rinsing the desalination chamber with 100 mL of deionized water. The produced water desalinated during the previous cycle was added back to the desalination chamber for another cycle. This process was repeated for three cycles; after each cycle samples from the anode, desalination and cathode chambers were collected for analyses. 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 3 runs, or 9 cycles (Fig. 2). Each cycle was 1.3 h (3.9 h per run) as a result of exhausted sorption capacities of the ACC assemblies. Stable potentials over 9
successive cycles were observed, with an average peak electrical potential of 0.28, 0.25 and 0.25 V 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.

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 and milliequivalent per gram of ACC (mg and meq/g carbon). Salt removal was highly effective in 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 h 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 5–18 times higher than conventional CDI using activated carbon as electrodes [30,35,36]. Due to additional sorption capacities, the normalized salt removal rate (mg salt removed per cm² of ion exchange membrane surface area per hour) of the MCDC was approximately 1.1–12 times higher than conventional MDC systems [24,28], while having a great advantage of preventing salt to transport to and accumulate in anode and cathode chambers.

When comparing the removal of monovalent to divalent ions, higher amounts of monovalent ions Na⁺ and Cl⁻ were removed than divalent ions Mg²⁺ and Ca²⁺ 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 Ca²⁺ (204, 192 and 162 mg/L) and Mg²⁺ 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. The observed adsorption trend of different ions is similar to previous studies using carbon aerogel CDI to treat brackish water [35,36]. For species having similar initial solution concentration (in terms of molarity), the hydrated radius might determine the electrode’s ion sorption capacity. Monovalent ions such as sodium with smaller hydrated radii (3.58 Å) can easily diffuse into electrode pores and preferentially adsorb over multivalent ions (such as calcium 4.12 Å) 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.

High percent removal of divalent ions, however, was primarily due to their low influent concentrations in the produced water: for Runs 1 and 2, percent removal achieved 80.5% and 73.5% for Ca²⁺, and 71.8% and 65.7% for Mg²⁺, compared to 56.7% and 49.9% for Cl⁻, and 53.8% and 47.8% for Na⁺, respectively. For Run 3, Ca²⁺ removal (59.1%) was the highest followed by removal of Cl⁻ (47.5%), Na⁺ (47.3%) and Mg²⁺ (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 suggest, 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 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 (Fig. 3). 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 brush to the bulk solution in anode chamber over subsequent runs.

In the cathode, a higher percent removal of divalent ions Ca²⁺ (40.7%, 45.8%, 20.5%) and Mg²⁺ (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 would adsorb counter ions—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

Fig. 3. Percent removal of calcium, magnesium, sodium and chloride ions from the anode, desalination and cathode chambers during Runs 1, 2 and 3. Error bars represent the standard deviations of three cycles.

Fig. 4. DOC percent removal for Runs 1, 2 and 3 in the anode, desalination and cathode chambers (operating time for each run is 3.9 h). Removal values calculated from averaged quadruplicate readings. Error bars represent the standard deviation.
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 full wavelength scan, Specific UV Absorbance (SUVA) at 254 nm, and Fluorescent Excitation–Emission Matrix (F–EEM) 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 (Fig. 4). 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 is mostly due to biodegradation in the anode. Although the anodic biofilm was acclimated to produce 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 (Fig. 5). Below 240 nm, absorption of peptide bonds begins to dominate aromatic and disulfide complexes. Previous studies have shown at 200 nm, the protein absorbance can be 20 times higher than at 280 nm [37,38]. 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 (Fig. 5). 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.

Ultraviolet absorbance at 254 nm (UVA254nm) and SUVA of samples (normalized to DOC concentrations) were used to determine the removal of aromatic fractions in the produced water (Fig. 6). SUVA is defined as the UV absorbance of a water sample at 254 nm (UVA254nm) normalized for DOC concentration. SUVA,
strongly correlated with percent aromaticity, therefore, is used as a useful parameter for estimating the dissolved aromatic carbon content (petroleum hydrocarbons) in produced water. Aromatic organics and proteins, such as tyrosine and tryptophan are characteristic compounds that absorb at a wavelength of 254 nm \cite{39}. For UVA_{254nm}, Run 1 performed the best with removal efficiencies of 33.6% and 68.1% in the anode and desalination chambers, respectively; no cathodic DOC removal was observed. For Run 2, the desalination and cathode chambers removed 73.2% and 25.4%, respectively and no anodic removal was observed. For all chambers in Run 3, less than 6% removal was observed.

SUVA and UVA_{254nm} results exhibit a similar removal trend suggesting aromatic compounds in the DOC fraction were removed from produced water samples. The positive removal percentage of SUVA in desalination and cathode chambers further suggest that aromatic petroleum hydrocarbons were preferentially sorbed over other organic contaminants. In the desalination chamber, larger decreases in absorbance were seen in Runs 1 and 2 but, due to ACC saturation, the sorption of aromatics in Run 3 was minimal. In the anode, the high SUVA value from Run 1 implies aromatics were initially removed due to sorption. The negative anodic SUVA percentage removal during the second and third runs suggests that, after the initial sorption capacity exhausted in Run 1, the removal rate of aromatic fractions in DOC was lower than other organic compounds. It indicates the biodegradation rate of aromatics were slower than non-aromatic compounds in the reactor. Previous studies have demonstrated that immobilized microbes can degrade recalcitrant aromatic compounds \cite{40–42}. However, microbial communities in the MCDC converge over successive batch cycles to favor exoelectrogenic organisms \cite{43} that may not be effective in degrading aromatics. Highly saline conditions may make aromatic biodegradation even more difficult for the microbes. Long-term experiments are required to investigate the biodegradability of produced water, in particular aromatic compounds, using an MCDC.

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 Fluorescent Excitation–Emission Matrix (F-EEM) spectroscopy (Fig. 7). F-EEM is a fingerprinting tool that classifies fluorophores based on characteristic excitation and emission properties. Fluorescence regional integration (FRI) is an accepted and an increasingly widely used classification method that divides the F-EEM map into five different zones (I–V), representing a characteristic dissolved organic matter (DOM) fraction: Zones I and II correspond to aromatic proteins, such as tryptophan and tyrosine; Zone III to fulvic acid-like compounds; Zone IV to soluble microbial byproduct-like material; and Zone V humic acid-like organics (Fig. 7) \cite{44,45}. Because the peaks in Fig. 7 may be the result of compounds with multiple fluorescing regions, the F-EEM method is for qualitative comparison and not meant as discrete method for identifying specific molecules \cite{45,46}.

In Fig. 7, excitation–emission peaks observed at 240 nm/360 nm and 280 nm/360 nm correspond to aromatics and extracellular biological organic matter (EBOM), respectively. To compare the characteristic EBOM fractions in produced water, the fluorescence volume was calculated by creating a boundary from 260 to 320 nm (excitation) and 300 to 475 nm (emission) that included fluorescence intensities greater than 0.5. Summated peak volume values for Ex/Em of 280 nm/360 nm were normalized to initial DOC concentration of the produced water samples. Calculations showed change in 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
Fig. 7. Run 1 F-EEM matrices of (A) Anode Initial, (B) Anode Final, (C) Desalination Initial, (D) Desalination Final, (E) Cathode Initial and (F) Cathode Final. Samples were normalized to 5 mg/L DOC. It should be noted that the original DOC concentrations in the samples varied.

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 tend to sorb to activated carbon [47]. Although not fully distinguishable, visual inspection of the peak intensity in Zone II (aromatics) shows a decrease in the desalination and cathode chambers, supporting the decrease in aromatic compounds, which is consistent with the results of UV–vis full wavelength scan and SUVA that aromatic organic carbon was removed from the produced water in MCDC.

Produced water is a mixture of water, salt, natural organic matter, and oil and gas from either thermogenic or biogenic origins. Thermogenic oil and gas is created from the continued burial of algae, wood and small pieces of landmass over millions of years, which are exposed to high pressures and temperatures [48]. In contrast, biogenic oil and gas are derived from anaerobic degradation of organics and plant matter at low depths. High initial fluorescent
protein peaks detected by F-EEM and UV–vis full wavelength scans are consistent with biogenic oil and gas formation of the produced water.

4. Conclusions

In this study we investigated the removal capabilities and mechanisms of a microbial powered system that harnesses the energy stored in the organic compounds to power the treatment of produced water. This proof-of-concept study demonstrated that the 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 processes, in the MCDC. Over 36 mg TDS/g ACC was removed from the desalination chamber in 1 h, demonstrating the desalination efficiency of MCDC is much higher than conventional MDC and CIDI.

For a continuous flow operation, produced water could be treated first at the anode to degrade organics then flow to the cathode where the higher salt concentrations would be beneficial for electron transfer. Finally, the produced water would flow through 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 MDCs could be used as a pretreatment to partially degrade organics 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 impacts 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 produced water desalination, treatment and power generation.
- 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.

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