TO: Texas Hazardous Waste Research Center

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SUBJECT: Annual Progress Report

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PROJECT TITLE:

Accelerated Treatment and Recycling of Hydraulic Fracturing Wastewater Using the Microbial Fuel Cell (MFC)

PROJECT PERIOD: September 1, 2013 to July 15, 2015

DATE: September 15, 2014

Project Description

Development of unconventional, onshore natural gas resources in deep shale is rapidly expanding in Texas (Eagle Ford, Barnett, Haynesville-Bossier) and many parts of the U.S. (Marcellus, Fayetteville, Niobrara) to meet the energy needs. In the U.S. about 35,000 well are hydraulically fractured annually (API 2010). Water management has emerged as a critical issue in the development of these inland gas reservoirs, where hydraulic fracturing is used to liberate the gas. Each well may require as much as 2 to 12 million gallons of water. Following hydraulic fracturing, large volumes of water containing very high concentrations of total dissolved solids (TDS) and oil return to the surface. The TDS concentration in this wastewater, also known as "flowback," can reach 5 times that of sea water. Wastewaters that contain high TDS levels are challenging and costly to treat and currently used technologies such as electro-coagulation (EC) and dissolved air floatation (DAF) have many limitations. Economical production of shale gas resources will require creative management of flowback to ensure protection of groundwater and surface water resources. Currently, deep-well injection is the primary means of management. However, in many areas where shale gas production will be abundant, deep-well injection sites are not available. With global concerns over the quality and quantity of fresh water, novel water management strategies and treatment technologies that will enable environmentally sustainable and economically feasible natural gas extraction will be critical for the development of this vast energy source.

Microbial Fuel Cell

Microbial fuel cell (MFC) technology represents the newest approach for not only enhancing the treatment of wastewater produced from various industries but also generating bioelectricity. In the anode chamber, the bio-electrochemical oxidation reactions that produce electrons and bioflocculants will greatly enhance the performance of MFC. The bio-electrochemical reactions in the anode chamber will be an enhanced version of the EC. In the cathode chamber reduction reactions will be used to rapidly precipitate and/or float (using micro bubbles) the dissolve metals from the waste and also degrade various other environmental pollutants from the flowback wastewater from hydraulic fracturing. Hence the cathode treatment will be somewhat similar to the DAF. Hence MFC can be considered as an integrated and enhanced operation of EC and DAF in parallel. When the treated water meets the environmental requirements it can be recycled and used for hydraulic fracturing. Hence MFCs should be developed for applications in the areas where wastewater from hydraulic fracturing has become a challenge.

(i) Why Select MFC? It has been shown that treating wastewater from hydraulic fracturing is a challenge due the complex nature of the wastewater and no single treatment method such as electro-coagulation (EC) or dissolved air flotation (DAF) could be used. Hence there is need to develop a comprehensive treatment systems that will handled the types of wastes encountered in the wastewater. The uniqueness of MFC is that it has bio-electrochemical oxidation process in the anode chamber and reducing electrochemical process in the cathode chamber. In the anode chamber, based on the type of oil in the wastewater and the bacteria introduced during the pretreatment process, biologically produced coagulating agents and biosurfactants will be produced that will enhance the rapid removal of the fine suspended solids and part of the dissolved solids in the wastewater. In this study anode chamber will be designed as the primary treatment unit to treat the wastewater. The treated water from the anode chamber (with the suspended solids removed) will be introduced to the cathode chamber (secondary treatment unit) where dissolved solids will be removed (by precipitation and/or air floation) based on

reduction reactions. Based on the quality of the treated wastewater from the cathode chamber, the water can be recycled for use in hydraulic fracturing. The combined processes in the MFC will produce electricity to partly sustain the wastewater treatment operations. The potential of recycling the wastewater and producing electricity makes the MFC concept very attractive.

(ii) Is Pretreatment of Wastewater Needed? The composition of the waste water from hydraulic fracturing varies tremendously based on the composition of the fluids used for fracturing and type of rock formation. The wastewater has high levels of suspended solids, dissolved solids (order of 100,000 ppm) and oil (API 2-10). Before introducing the wastewater to MFC treatment, pretreatment will be necessary to condition the wastewater so that it can be treated rapidly in the anode chamber. Filtering the large suspended solids, adding used vegetable oil and bacteria (*Serratia organisms and mixed cultures*) to enhance the biological activities in the anode chamber will have to be investigated based on the composition of the wastewater.

(iii) What is New? Currently used wastewater treatment technologies have limitations in not only treating the waste but also recycling the treated waste water. The MFC is unique in its ability to oxidize the oily waste in the anode chamber producing bioflocculants to rapidly precipitate the suspended solids (fine particles) and dissolved solids and in the cathode chamber reduce and precipitate the metals in the dissolved solids. Oxidized and reduced wastewater in the MFC (integrated EC and DAF) will have the ability to be reused for hydraulic fracturing. At the same time bioelectricity is produce to power the electrical appliances to totally or partly control the operation.

Objectives

The overall objective of this study is to develop an environmentally sustainable Microbial Fuel Cell technology to not only rapidly treatment the wastewater from hydraulic fracturing but also to recycle and reuse the treated water. Taking advantage of the oxidation and reduction conditions in the anode and cathode chambers respectively, the study will develop a free standing MFC to do the entire treatment. The schematic diagram of the proposed MFC treatment with the necessary inputs and outputs are shown in Fig. 1. The specific objectives of this study are as follows:

(1) Condition the wastewater with the necessary pretreatment to enhance the bio-electrochemical activities in the anode chamber.

(2) Optimize the anode chamber (primary treatment tank) architecture to not only extract maximum electrons during the biological production of bioflocculants/biosurfactants from oil but also accelerate the coagulation and precipitation of the fine suspended solid particles.

(3) Optimize the cathode chamber (secondary treatment tank) architecture to treat contaminated water to remove the total dissolved solids efficiently. It will also accelerate the degradation of remaining oil, other organics and nitrates in the wastewater.

(4) optimize the total MFC configuration (coupling the appropriate anode and cathode) to handle various types of wastewater. Also Impedance Spectroscopy (IS) will be used to quantify the electrical resistances at the electrodes and bulk resistances of the solutions before, during and after treatment. The objectives will be achieved in four TASKs and completed in two years.

Methodology

The stated objectives will be achieved in four TASKS. The major test variables to be investigated are summarized in Table 1. Both laboratory (Table 1) and field samples will be used.

TASK 1. PRETREATMENT

It will be important to condition the waste water before introducing it into the anode chamber. Large size suspended solids (diameter greater than 0.5 mm) will be filtered and used vegetable oil (no more than 1%) and bacteria (*Serratia organisms and mixed cultures*) will be added to accelerate the biological activities in the anode chamber. Also the pH of the wastewater will be adjusted to be in the range of 6 to 8.

Table 1. Summary of Possible Materials and Other Variables

Parameters	Materials and Processing/Testing Conditions
Electrodes	Metals (stainless steel, Al, composites), Graphite
Electrode Configurations	Circular or rectangle rods, Perforated sheets, Flexible nets , cloth, paper, coil
Anode Chamber Architecture (Primary)	Pretreated waste water (including field samples), Used vegetable oil, Bacteria, Temperature, Anaerobic, Aerobic, Chamber shape and configuration
Cathode Chamber Architecture (Secondary)	Types and concentrations of treated wastewater, pH, Temperature, Additives (Biosurfactant), , Chamber shape and configuration
Wastewater	Suspended solids, Total dissolved solids (up to 100,000 mg/L), pH = 5 to 9 (API, 2010; Gregory et al. 2011)
Pretreatment	Filters, used-vegetable oil, bacteria (*Serratia organisms and mixed cultures*), algae (Deng et al. 2003)

TASK 2. DEVELOPMENT OF ANODE CHAMBER (Oxidation Reaction)

Pretreated wastewater will be first treated in the anode chamber to remove the suspended solids. There will be biotransformation of the oil waste and used-vegetable oil with the help of the bacteria in the anode chamber. Methods to accelerate the production of bioflocculants/biosurfactants will be investigated. Number of issues (including the addition of used-vegetable oil) will be investigated to develop a comprehensive anode chamber with (1) relatively low electrical resistance; (2) high bioflocculants/biosurfactants production and (3) rate of precipitation of the suspended solids and part of the dissolved solids.

(i) Electrode Materials: The requirements for an anode material are: highly conductive, non-corrosive, high specific surface area and easy to scaled to larger sizes. Various materials (Table 1) will be used as electrodes to reduce the biofilm resistance and increase the production of electrons. Also various shapes and configurations (rod, paper, cloth, coil) will be investigated.

(ii) Anode Solution: Main organic source for the bacteria (*Serratia organisms and mixed cultures*) with and without algae is the oil waste from the wastewater and the added used-vegetable oil. In order to enhance the biological activities mineral salts such as 0.1%, K_2HPO_4, 0.05% KH_2PO_4, 0.01% KCl, 0.05% $MgSO_4$ and 0.2% $NaNO_3$ 0.2% will be added (Liu and Vipulanandan 2013). Based on the amount of electrical current (I), power (W) and bioflocullant/biosurfactant production, the volume of used-vegetable oil will be varied.

(iii) H+ Removal: The performance of the anode chamber will be very much affected by the rate of removal of H+ produced in the chamber. Various configurations from salt bridges to membranes will be used in this study.

(iv) Measurements (a) Electrical: Open circuit voltage will be measured at regular intervals by connecting the True RMS multi meter directly with the anode electrode and cathode electrode of the MFC. When the open circuit voltage reaches a stable value, closed circuit voltage and current (I) will be measured using the multi-meter with varying external resistors.

(b) Others: pH and the oxidation reduction potential (ORP) of the fermentation liquid in the anode will be measured using the pH-ORP meter at constant intervals.

(c) Bacteria and Algae: The bacterial growth will be monitored using the UV-Vis spectrophotometer by determining the Optical density (OD) at 600 nm. Algae growth will be determined at 680 nm. At least three samples will be used.

(d) Suspended and Dissolved Solids: Rate and total removal of the suspended and dissolved solids will be monitored. Samples from the anode chamber will be collected and analyzed using ion chromatography (IC), conductivity and atomic absorption (AA) spectroscopy.

TASK 3. DEVELOPMENT OF CATHOD CHAMBERS (Reduction Reactions)

In order to develop efficient MFC systems, optimized system developed in TASK 2 will be used as the anode chamber with various configurations for the cathode chamber. The wastewater that was treated in the anode chamber will be introduced into the cathode chamber for further treatment and rapidly remove the remaining dissolved solids.

(i) Electrode Materials Various materials (Table 1) will be used as electrodes to reduce the resistance and increase the degradation of the contaminants. Also various shapes and configurations (rod, coil) will be investigated.

(ii) Cathode Solutions: Wastewater after the primary treatment in the anode chamber will be used. Based on the types of contaminants in the wastewater, conditioning of the wastewater will be investigated.

(iii) Additives: Use of surfactants (to produce micro-bubbles), other solutions (bioflocculants/biosurfactants) or pumping air to enhance the removal of dissolved solids will be investigated.

(iv)Total Dissolved Solids: Rate and total removal of the dissolved solids will be used to optimize the cathode chamber operations. Methods such as conductivity, ion chromatography and atomic absorption spectroscopy will be used to analyze the treated wastewater.

(v) Treated Wastewater: Quality of the treated water will be tested for suspended solids and dissolved solids. Treated wastewater form the cathode chamber will be reusable for hydraulic fracturing if the TDS is less than 500 mg/L (API 2010).

Summary: At least three cathode chamber configurations with up to 70,000 mg/L of TDS will be investigated to determine the optimum configuration based on removal of dissolved solids and other contaminants.

Accomplishments/Problems

Based on the literature review, representative samples were prepared for preliminary testing. The salt content in the samples were varied up to 100 g/L with clay content of 10%.

Task 1: The waste water was filtered using various types of filtering materials. The filters and the clay were effective in removing part of the salt in the waste water. Also new methods to characterize the waste water are being investigated. This approach can be adopted in the field to determine the level of contamination in the water..

Task 2: Several MFC tests are being performed to improve the performance of the anode side of the MFC. Initial tests were performed with the selected waste water by adding 1% used vegetable oil as the anode solution. The surface tension dropped to 32 mN/m after 200 hours during the testing period, which indicated the production of biosurfactant in MFC. During the study the power density achieved was increased by 5 times from 0.30 to 1.5 $\mu W/m^2$ and the internal resistance has been reduced by over 70% from the original resistance. Also the salt bridge gel was replaced by a low permeability grout (low cost) and it reduced the internal resistance. Several more tests are planned for the coming year.

Task 3: High inner resistance is a significant issue that reduces the performance of microbial fuel cell (MFC). Polarization resistance of cathode is one major factor composed the inner resistance of the MFC. Different catalysts have been applied to the surface of the cathode

electrode to reduce its polarization resistance. Pt is the most commonly used catalyst. As its cost is high, lots of cost-effective catalysts were developed. Cobalt oxide, lead dioxide, activated carbon nanofibers, carbon black, nickel nanoparticles (NPs), iron phthalocyanine, and copper-phthalocyanine have all been reported as cathode catalyst). In this study, Ni NPs was used as cathode catalyst. Ni is one kind of transition metal, and use of transition metal as catalyst in fuel cells has been reported.

Power density was compared for MFC with or without Ni NPs on the cathode surface during 6 days operation with 1 kΩ external resistance (Fig.1). A maximum power density of 0.07 mW/m^2 was achieved during the third day with Ni NPs on the cathode surface. However a maximum of 0.005 mW/m^2 power density was produced from the control of carbon cathode. This showed the catalyst capacity of Ni NPs to enhance the power production of the MFC. The maximum power density of the cathode with Ni NPs was 0.32 mW/m^2 by changing the external resistance to 9.5 kΩ. As the maximum power density was obtained when the external resistance of the MFC equals to its inner resistance, the inner resistance of this MFC was 9.5 kΩ. Results also showed that maximum of 0.17 V CCV was obtained for the MFC when applying 9.5 kΩ external resistances.

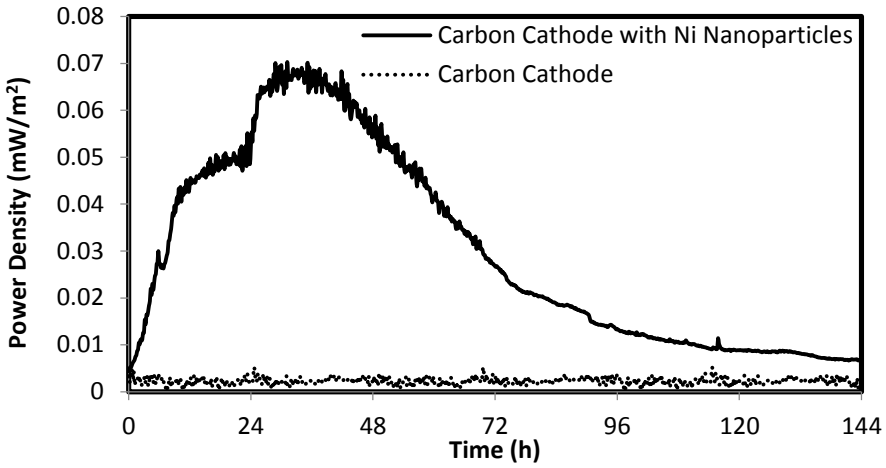

Fig.1 Power Density Change with Time of Microbial Fuel Cell with or without Ni Nanoparticles on Cathode Surface

Ni NPs on the cathode surface enhanced the power density of the MFC to 0.07 mW/m^2 with 1 kΩ external resistance. By changing the external resistance to 9.5 kΩ, the power density was further enhanced to 0.32 mW/m^2 in this study.

Future Work

More tests are planned to further enhance the performance of the MFC by modifying the anode chamber and cathode chamber configurations. Also waste waters with various amounts of salt (Table 1) will be tested to demonstrate the performance of MFC in accelerated treatment and recycling of hydraulic fracturing waste water.

List of Publications and Presentations

Preparing an abstract to submit to the next CIGMAT Conference on March 6, 2015.