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Coupling bioelectricity generation and oil sands tailings treatment using microbial fuel cells

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HIGHLIGHTS

- Dual-chambered MFCs using MFT and OSPW as inoculum were constructed.
- Electricity was generated with maximum power density of 392 ± 15 mW/m^2.
- The presence of vitamins and minerals did not facilitate the electrical production.
- 27.8% of total COD, 81.8% of soluble COD, and 32.9% of total acid extractable organics were removed.
- There was a high removal efficiency for most of the eight heavy metals analyzed in MFT and OSPW.

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ABSTRACT

In this study, four dual-chambered microbial fuel cells (MFC1-4) were constructed and filled with different ratios of mature fine tailings and oil sands process-affected water to test the feasibility of MFCs to simultaneously generate electricity and treat oil sands tailings. After 800 h of operation, the maximum voltage was observed in MFC4 at 0.726 V with 1.2 kΩ external resistance loaded. The maximum power density reached 392 ± 15 mW/m^2 during the 1700 h of MFC4 operation. With continuous electricity generation, MFC4 removed 27.8% of the total COD, 81.8% of the soluble COD and 32.9% of the total acid extractable organics. Moreover, effective removal of eight heavy metals, includes 97.8% of ^{78}Se, 96.8% of Ba, 94.7% of ^{88}Sr, 81.3% for ^{66}Zn, 77.1% of ^{95}Mo, 66.9% of ^{63}Cu, 44.9% of ^{53}Cr and 32.5% of Pb, was achieved.

1. Introduction

The Athabasca oil sands in northern Alberta, Canada, contain an estimated 1.8 trillion barrels of recoverable bitumen and represent one of the largest oil deposits in the world. Large volumes of water are used to extract bitumen and this process produces oil sands tailings consisting of water, sand, silt, clay and residual bitumen. The tailings are stored on-site in large settling basins, where solids settle into a thick slurry of mature fine tailings (MFT), capped by a layer of clarified oil sands process-affected water (OSPW). Currently, there are more than 170 km^2 of tailings ponds, containing 840 million m^3 of fine tailings, in the northern Alberta oil sands region (Siddique et al., 2011).

Oil sands production has become increasingly controversial in Canada because of health and environmental concerns, and increased international media attention has resulted (Jordaan, 2012). One major issue is that OSPW in tailings ponds contains solid and dissolved inorganic and organic components, some of which are toxic to aquatic and terrestrial organisms. Notably, naphthenic acids (NAs) in OSPW are an important toxic component (Headley et al., 2009). To reduce the toxicity and environmental impact of OSPW, remediation strategies have been employed; for instance, ozonation was shown capable of oxidizing more than 95% of the NAs in wastewater, attenuating their toxicity toward both *Vibrio fischeri* and *Chironomus dilutus* (Scott et al., 2008). However, chemical oxidation for complete mineralization is generally expensive because the oxidation intermediates formed during treatment tend to be increasingly resistant to complete chemical degradation thus extending treatment times and energy consumption. Nanofiltration can successfully remove more than 95% of NAs and divalent cations from OSPW (Kim et al., 2011; Peng et al., 2004), however, fouling caused by suspended solids can decrease the filtration membrane's permeate flux and lifespan and limit its practical application. Petroleum coke, a by-product of bitumen upgrading, at dosages 20–30.1 wt.% in an adsorption process can remove 91–94% of total organic acids (Gamal El-Din et al., 2011; Zubot et al., 2012; Small et al., 2012). This strategy was limited however, by a long residency time (6–8 months) for the adsorption

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Table 1
Configuration and electrical generation of microbial fuel cells.

	Configuration of MFCs						Cell voltage
	Anode	Cathode	External resistance	Membrane	Anolyte	Catholyte	
MFC1	Carbon cloth	Carbon cloth coated with Pt	1200 Ω	Cation exchange membrane (CMI-7000S)	20% OSPW + 80% media[a]+20 mM NaAc	50 mM $K_3Fe(CN)_6$ in 50 mM PBS	0.058 V
MFC2					100% OSPW + 20 mM NaAc		0.173 V
MFC3					10% MFT + 90% media[a] + 20 mM NaAc		0.063 V
MFC4					10% MFT + 90% OSPW + 20 mM NaAc		0.726 V

[a] Bacterial growth media: 4.4 g KH_2PO_4, 3.4 g $K_2HPO_4{\cdot}3H_2O$, 1.5 g NH_4Cl, 0.1 g $MgCl_6{\cdot}6H_2O$, 0.1 g $CaCl_2{\cdot}2H_2O$, 0.1 g KCl, trace metals and vitamins in 1 L H_2O.

and the petroleum coke's release of significant amounts of sulfur (~7 wt.%) and trace metals including vanadium, zirconium, barium, strontium, nickel, lanthanum, molybdenum, neodymium, cobalt, and zinc (Zubot et al., 2012).

Microbial fuel cells (MFCs) are bioreactors that use microorganisms, usually bacteria, to oxidize organic substrates and generate electrical energy during the transfer of electrons to an electron acceptor. Although monoculture MFCs containing *Shewanella* spp. or *Geobacter* spp. have been widely studied, MFCs inoculated with mixed bacterial communities have been shown to be more stable, robust and productive because of nutrient adaptability and resistance to stressors (Holmes et al., 2004). MFCs containing mixed bacterial communities have been used for wastewater treatment, to convert energy within wastewater organic matter into electrical energy. Laboratory-scale MFCs have been studied for treating a wide range of wastewaters, including domestic wastewater (Liu et al., 2004), food processing wastewater (Oh and Logan, 2005), beer brewery wastewater (Wen et al., 2009), swine wastewater (Zhuang et al., 2012), composite vegetable waste (Venkata Mohan et al., 2010), palm oil mill effluent (Cheng et al., 2010), and molasses wastewater (Zhong et al., 2011) among others.

The fast development of the Athabasca oil sands industry demands new techniques to reduce its operating costs while also addressing its treatment of oil sands tailings to avert environmental concerns. As MFCs have been used for treating wastewaters from other sources, they are promising for treatment of OSPW. Diverse microbes were found to exist in oil fields which may be indigenous or introduced during water-flooding for secondary recovery of oil. In agreement with this, a diverse bacterial community was found in MFT samples from Athabasca's oil sands with the majority (~55%) of sequences showing relation to *Proteobacteria*, including some presumptive nitrate-, iron-, or sulfate-reducing, and hydrocarbon-degrading genera (e.g., *Thauera*, *Rhodoferax*, and *Desulfatibacillum*). The rest of the microbial community was composed of *Firmicutes* and other groups including the *Bacteroidetes*, *Chloroflexi*, *Spirochaetes*, and *Acholeplasma* (Penner and Foght, 2010). This diversity of microbes in oil sands tailings provides an opportunity for testing the feasibility of simultaneous electrical energy generation and tailings water treatment using MFCs. To our knowledge, this is the first report of applying MFCs in the oil sands industry. In this study, various two-chambered MFCs were constructed and inoculated with mixtures of MFT and OSPW, with and without bacterial growth media, in order to produce energy and thus reduce chemical oxygen demand (COD) and the concentrations of acid extractable organics and heavy metals without extra energy input.

2. Methods

2.1. Source of MFT and OSPW

Samples of oil sands MFT were taken from the 10 m standpipe at the Department of Civil and Environmental Engineering, University of Alberta (Jeeravipoolvarn et al., 2009), which was filled in 1982 with MFT from a 25-m depth in Syncrude's Mildred Lake tailings pond (Jeeravipoolvarn et al., 2009). The OSPW samples were collected into 20 L plastic buckets from Syncrude's Mildred Lake tailings pond in June 2011, and these buckets were transported to the University of Alberta and stored at 4 °C until use.

2.2. MFC construction and operation

Four dual-chambered MFCs (MFC1-4) were constructed with anode and cathode chambers separated by a cation exchange membrane (CMI-7000S, Membrane International Inc., Ringwood, USA) (Table 1). The anodes consisted of 5 cm × 5 cm carbon cloth (Fuel Cell Earth, MA, United States) and the cathodes of 5 cm × 5 cm platinum-coated carbon cloth (Fuel Cell Earth, MA, United States). Nickel–chromium wires were used to connect the electrodes to external resistors. The total volumes of anolyte and catholyte in each MFC were 160 mL. The anode chambers of MFC1 and 2 were inoculated with either 20% (v/v) OSPW and 80% (v/v) bacterial growth media (MFC1) or 100% OSPW (MFC2). The anode chambers of MFC3 and 4 were inoculated with 10% (v/v) MFT and with either 90% (v/v) bacterial growth media (MFC3) or 90% (v/v) OSPW (MFC4). The bacterial growth media was prepared by adding 4.4 g KH_2PO_4, 3.4 g $K_2HPO_4{\cdot}3H_2O$, 1.5 g NH_4Cl, 0.1 g $MgCl_6{\cdot}6H_2O$, 0.1 g $CaCl_2{\cdot}2H_2O$, 0.1 g KCl, trace metals and vitamins in 1 L H_2O. Concentrated sodium acetate stock solution was added to the anode chamber of each MFC (20 mM final concentration) as an additional carbon source. Fifty mM $K_3[Fe(CN)_6]$ in 50 mM KH_2PO_4–K_2HPO_4 buffer was used as the catholyte. The MFCs were operated in batch mode at a constant room temperature of 21 ± 0.5 °C.

2.3. Electrical production

The voltages generated in the MFCs were measured every 20 min using a data acquisition system (Model 2700, Keithley Instruments, OH, Unites States). Sodium acetate was resupplied to a 20 mM concentration into the anolyte when the voltage dropped below 30 mV. The MCF which showed the highest voltage generation was chosen for further analysis of its power generation and water treatment performance.

A polarization curve that characterizes the cell voltage generation as a function of current density is one of the most common methods to evaluate the performance of MFCs. To obtain the polarization curve, different external resistances (open circuit to 50 Ω) were applied for 20 min. Current, I, was calculated according to $I = E/\mathrm{Rex}$, where E is the voltage and Rex is the external resistance. Power, P, was calculated according to $P = I^2/\mathrm{Rex}$. Current density and power density were determined by normalizing the current and power to the surface area of electrodes (25 cm^2).