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Mustard tuber wastewater treatment and simultaneous electricity generation using microbial fuel cells

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HIGHLIGHTS

- Mustard tuber wastewater was used as fuel in microbial fuel cells.
- Correlation between primary clarifier effluent and R_{int} was concluded.
- Comparatively, S1 was the most appropriate fuel for electricity generation.
- Microbial fuel cells were capable of resisting load shock.

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ABSTRACT

Mustard tuber wastewater (MTWW) was utilized as fuel in the typical dual-chamber microbial fuel cells (MFCs) to recover bio-energy and to obtain effluent treatment simultaneously. The whole experiment was divided into four phases characterized by increasing contents of primary clarifier effluent (PCE). Results showed substrate1, with which MFC generated a maximum power density of 246 mW/m^2, was the most appropriate fuel in terms of power recovery and the internal resistance and columbic efficiency were 121 Ω and 67.7 ± 1%, respectively. When feeding MFCs with substrate4, 85 ± 0% of COD could be removed, which was the highest COD removal, however, the power retrieve efficiency was much lower. Interestingly, significantly negative correlation ($P < 0.01$, F-test) between contents of PCE and maximum cell voltages and positive correlation between the contents and internal resistances were found. It was the complexity and colloidal particulates present in PCE that gradually increased internal resistance and accordingly decreased power-generating performance.

1. Introduction

Fuling Mustard Tuber (FMT), one of the three most famous pickles worldwide, is produced from *Brassica juncea* after three main steps in proper order: dehydration, pickling with salt and elutriation. During the production of FMT, a large volume of Mustard Tuber Wastewater (MTWW), characterized by high-strength and high-salinity as well (Chai and Kang, 2012), is discharged. Currently, anaerobic process was taken as pretreatment for the effluent, and was commonly followed by aerobic and/or physicochemical technology so as to satisfy stringent discharge standards (Chai and Kang, 2012). Nonetheless, aerobic treatment not only consumed energy up to 500–600 Wh/m^3, which took up to 50% of operating costs, but generated around 0.4 kg of excess sludge per kg of oxidized COD and its handling could account up to 50% of the total operating costs (Rabaey and Verstraete, 2005; McCarty et al., 2011). On the other hand, a theoretical energy of 3.86 kWh could be recovered as oxidizing per kg COD (McCarty et al., 2011). Specifically, when real wastewater was used as fuel in Microbial Fuel Cells (MFCs), 0.22–0.30 kWh/kgCOD of electrical energy could be recovered (Cusick et al., 2010; Kaewkannetra et al., 2011). Therefore, it is desirable to extract energy in the form of biogas or bioelectricity from wastewater, especially high-strength effluent (e.g., MTWW), which could definitely offset partial running costs of sewage treatment.

MFCs, an emerging technology, have been gaining increasingly wide attention as it could, utilizing exoelectrogenic bacteria as bio-catalyst, produce electric energy directly from anaerobic oxidation of organic matters present in wastewater (Logan et al., 2006; Ge et al., 2012; Cheng and Logan, 2011). Various types of wastewater have been explored as fuel in MFCs such as domestic wastewater (Min and Logan, 2004; Ge et al., 2012), sewage sludge (Zhang et al., 2012; Fischer et al., 2011), swine wastewater (Min et al., 2005; Ichihashi and Hirooka, 2012), steroidal drug industrial effluent (Li and Ni, 2011; Liu et al., 2012), urine (Kuntke et al., 2012), landfill leachate (Puig et al., 2011), potato-processing wastewater (Durruty et al., 2012), and all these wastewater have

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Table 1
Characteristic of PCE and ARE.

Samples	PCE[a]	ARE[b]
COD (mg/L)	287	3065
TN (mg/L)	197.5	92.3
TP (mg/L)	44.9	26.9
Salinity (NaCl, g/L)	21.1	20.1
Conductivity (mS/cm)	37.7	35.6
Chlorides (g/L)	10.1	9.96
pH	4.57	7.24

[a] PCE-primary clarifier effluent.
[b] ARE-anaerobic reactor effluent.

been demonstrated as feasible substrate. Nonetheless, to broaden MFCs' industrial applications, it is really worth investigating other effluents which could be perfectly used as fuel in bioelectric devices and gain simultaneous energy recovery and wastewater purification.

Among challenges MFCs facing towards real-world applications, the low value of electricity density, typically no more than 0.5 W/m^2, is the primary one (Logan and Rabaey, 2012; Ahn and Logan, 2010), even lower power densities have been reported (Li and Ni, 2011; Mohanakrishna et al., 2010; Liu et al., 2011), which was attributed to complexity of substrates, lower solution conductivity and diminished buffer capacities (Logan and Rabaey, 2012). As for solution conductivity, Liu et al. (2005) observed increased power output from 720 mW/m^2 to 1330 mW/m^2 by adding NaCl which resulted in an increase in solution ionic strength. Studies conducted by Lefebvre et al. (2012) also demonstrated decrease in internal resistance and consequent enhancement of maximum power production when 20 g/L of NaCl was added. However, in both these studies sodium acetate was utilized as anolyte and additional NaCl was needed to improve conductivity, and so far little research on feeding anode with real wastewater with natural high-salinity has been performed. Meanwhile, it has been proved MFCs can benefit from high NaCl concentration up to 20 g/L, while the further increase would cause significantly detrimental effects on overall performance (Lefebvre et al., 2012). The suggested optimal NaCl content is the very salinity of MTWW (Table 1; Table 2). Therefore it is attractive to use MTWW as fuel in MFCs when the overall characteristics: optimum salinity, sufficient and readily biodegradable organic matters, are taken into account.

The objectives of this study were to examine feasibility and bio-electricity generation performance of using MTWW as fuel in typical dual-chamber MFCs, to investigate removal efficiency of organic compounds and to analyze effects of substrate on internal resistance. It was hoped that study findings could provide ideas for anolyte-selecting and treatment of MTWW as well.

2. Methods

2.1. Wastewater collection

MTWW was taken from the wastewater treatment plant in a mustard tuber factory, located in Fuling, Chongqing. Samples, collected at two sites: Primary Clarifier Effluent (PCE) and Anaerobic Reactor Effluent (ARE), were kept in a refrigerator at 4 °C. Detailed information of PCE and ARE could be found in Table 1.

2.2. MFC construction

Two set of identical dual-chamber, cubic-shaped MFCs were constructed with Plexiglas to perform experiments in duplicate. Both the anodic chamber and the cathodic one with same dimensions: 5 cm × 5.5 cm × 6 cm, had working volumes of 150 mL and the two compartments were separated by a Cation Exchange Membrane (CEM, Ultrex CMI7000, Membranes International Inc., USA) with a cross-sectional area of 33 cm^2. At top of chambers, there were three ports for discharging gas, replacing substrates and inserting Ag/AgCl reference electrodes (RE-1C, Jiangfen Tech Co., Jiangsu, China), and introducing electrodes. All ports were sealed with rubber stoppers during operation. Non-wet proof carbon cloth (Hesen Carbon Material Co., Shanghai, China) with a projected surface area of 40.5 cm^2 (4.5 cm × 4.5 cm × 2,×2 means two sides of a piece of carbon cloth) was used as anode and cathode as well. The electrodes were introduced with titanium wire and connected to an external resistor (0–9999.9 Ω), completing a close circuit. Magnetic stirring was applied to diminish substrate gradient.

2.3. MFC start-up and operation

For start-up, Substrate1 (S1, Table 2) was used as both substrate and inocula. Phosphate (100 mM) buffered ferricyanide (100 mM) was used as catholyte in both reactors at all operation phases to minimize the effects of cathode on system performance. Electrolytes were replaced with fresh ones when voltage across a fixed external load dropped below 50 mV, completing a whole cycle of power generation. When reproducible voltage and comparable cycle duration were obtained at least for 3 cycles, a successful acclimation was reached. The whole study was divided into four phases during which all substrate used was sterilized to minimize the effects of extra microorganism present in MTWW on electricity generation and organic matter degradation. When shifting Phase1 (P1, S1) to Phase2 (P2, S2), then to Phase3 (P3, S3) and finally to Phase4 (P4, S4), a new acclimation should be obtained again before assessing current production performance (Sleutels et al., 2011). All mixed MTWW (S1, S2 and S3) and S4 were directly used as fuel without any adjustment except adjusting pH to ~7 with 1 M HCl or 1 M NaOH. Due to the fact that a mere 1–3 drops of HCl or NaOH was used, the conductivity of anolytes would hardly be affected (Table 1; Table 2). Therefore, the addition of HCl or NaOH was not taken into account when reporting the conductivity of anolytes. All experiment was conducted in fed-batch mode at 25 ± 2 °C and all tests were performed in duplicate.

2.4. Electrochemical analysis and calculations

Cell voltage (V) across the external resistance of 500 Ω (unless stated otherwise) was monitored every 2 min using a Data

Table 2
Characteristics of substrate used during different operation phases[a].

Operation phase	P1 (S1)	P2 (S2)	P3 (S3)	P4 (S4)
Composition (ARE:PCE)	9:1	7:3	1:1	0:1
COD (mg/L)	550 ± 46	972 ± 57	1561 ± 13	2968 ± 218
Salinity (NaCl, g/L)	20.1 ± 0.2	20.9 ± 0.4	20.7 ± 0	21.1 ± 0.1
Conductivity (mS/cm)	35.9 ± 0	36.0 ± 0.6	37.0 ± 0.1	37.7 ± 0.3
pH[b]	7.05 ± 0	7.05 ± 0	7.04 ± 0.1	7.08 ± 0

[a] All data in the table was expressed as mean ± standard deviation (two samples).
[b] Adjusting to around 7 with HCl or NaOH.