



Treating refinery wastewaters in microbial fuel cells using separator electrode assembly or spaced electrode configurations



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HIGHLIGHTS

- Using RW in MFCs produced relatively good power with high organics removal.
- RW had lower power than the DW due to poorer biodegradability/toxicity of RW.
- Oxygen crossover was more important for organics removal in the RW than the DW.
- Organics removals were improved in MFCs compared to previous MEC results for RW.
- SEA had lower organics removals as a result of reduced oxygen intrusion.

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ABSTRACT

The effectiveness of refinery wastewater (RW) treatment using air–cathode, microbial fuel cells (MFCs) was examined relative to previous tests based on completely anaerobic microbial electrolysis cells (MECs). MFCs were configured with separator electrode assembly (SEA) or spaced electrode (SPA) configurations to measure power production and relative impacts of oxygen crossover on organics removal. The SEA configuration produced a higher maximum power density ($280 \pm 6 \text{ mW/m}^2$; $16.3 \pm 0.4 \text{ W/m}^3$) than the SPA arrangement ($255 \pm 2 \text{ mW/m}^2$) due to lower internal resistance. Power production in both configurations was lower than that obtained with the domestic wastewater (positive control) due to less favorable (more positive) anode potentials, indicating poorer biodegradability of the RW. MFCs with RW achieved up to 84% total COD removal, 73% soluble COD removal and 92% HBOD removal. These removals were higher than those previously obtained in mini-MEC tests, as oxygen crossover from the cathode enhanced degradation in MFCs compared to MECs.

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1. Introduction

A microbial fuel cell (MFC) is a microbial electrochemical technology (MET) that is being investigated to recover energy from wastewater in the form of electricity (Logan et al., 2006; Logan and Rabaey, 2012; Rabaey and Verstraete, 2005; Rozendal et al., 2008). The potential advantages of MFCs compared to traditional technologies such as activated sludge are reduced operational costs, due to passive oxygen diffusion to the cathode (no wastewater aeration), reduced sludge production, and electricity production. Tremendous advances have been made in recent years in increasing power densities by improving reactor configurations and developing new electrode materials. The use of inexpensive materials, such as activated carbon cathodes and graphite fiber brush anodes, has substantially decreased the cost of MFC electrodes (Dong et al., 2012; Logan et al., 2007; F. Zhang et al., 2009), which could enable cost-effective systems at larger scales.

Although many different types of wastewaters have been used to produce electricity in MFCs, performance has substantially varied depending on the specific wastewater and reactor configuration (Ahn and Logan, 2013; Feng et al., 2008; Lu et al., 2009; Pant et al., 2010; Puig et al., 2011; Sun et al., 2009). Treatability studies are therefore needed to evaluate a specific wastewater in an MFC in terms of power generation and the extent of organics removal. Mini microbial electrolysis cells (mini-MECs) were recently proposed as a method to rapidly evaluate wastewaters for current generation and chemical oxygen demand (COD) removal (Call and Logan, 2011), and have been used to examine treatment efficiencies (COD removal) and current generation of different types of wastewaters (Ivanov et al., 2013; Ren et al., 2013). The mini-MEC is a completely anaerobic test as both electrodes are sealed in the same gas-tight vial.

Recently, mini-MECs were used to evaluate treatability of six different refinery wastewaters (RWs) (Ren et al., 2013). The best correlation between the organics removal and current production with different RWs was found to be between the headspace biochemical oxygen demand (HBOD) removal and total recovered

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coulombs in one cycle. The de-oiled RW samples produced good current densities and organics removals in the mini-MEC tests. However, there is often less COD removal in an MEC compared to an MFC test (Cusick et al., 2010). COD removal in an MEC occurs under completely anaerobic conditions, while dissolved oxygen is used in a biochemical oxygen demand test. COD removal in MFCs therefore occurs both through anaerobic processes (by exoelectrogenic microorganisms on the anode) and aerobic degradation sustained by oxygen crossover through the cathode (Cusick et al., 2010). Dissolved oxygen can be important for biodegradation of certain organic compounds, particularly those derived from oil and fossil fuels which are relatively recalcitrant under anoxic conditions. In addition, hydrogen gas is produced at the cathode in MECs, and the oxidation of hydrogen could increase current production and compete with organic matter as an electron donor for exoelectrogenic microbes (Call and Logan, 2011). For these different reasons, the extent of COD removal can vary between MECs and MFCs, and therefore treatability in an MFC could be quite different from that obtained in an MEC.

Power produced in an MFC is a function of both solution chemistry and reactor configuration, as these can alter internal resistance. For example, adding a phosphate buffer (50 mM) into a brewery wastewater increased power production by 136% (Feng et al., 2008). However, the use of phosphate buffers or making wastewaters more saline by adding salt to increase solution conductivities are not sustainable approaches for improving power production. Internal resistance due to low solution conductivity can partly be overcome by changing the reactor configuration, for example by reducing electrode spacing. Separators (placed between the anode and cathode) are used with very closely spaced electrodes to avoid direct electrode contact. The use of separator electrode assembly (SEA) MFC designs can reduce internal resistance compared to more widely spaced electrode (SPA) designs (Zhang et al., 2013; Zhang et al., 2009). However, the separator reduces overall oxygen transfer into the anode chamber, which could affect overall COD removal. The effect of the SEA and SPA designs on the rate and extent of COD removal with wastewaters which contain organics that are only slowly degraded under anoxic conditions, such as refinery wastewaters, has not been previously examined.

In this study, the power production and organics removal of a refinery wastewater (RW) sample were compared with a domestic wastewater (DW) sample in MFCs using either the SEA (separator) or the SPA (no separator) configuration. A de-oiled RW sample that showed good performance and organics removal (58% COD removal and 61% HBOD removal) in mini-MECs was selected for testing in the MFCs. Domestic wastewater (DW) was also examined here using the two different MFC configurations as a positive control. COD removal (72%) and HBOD removal (>90%) for the DW sample were higher in the mini-MECs than those obtained using the RW (Ren et al., 2013), indicating its improved biodegradability. The use of the RW and DW samples therefore provided a good contrast in performance of the two different MFC configurations for wastewaters that differed in terms of biodegradability, current generation, and COD removal efficiencies in mini-MECs. In order to investigate if there was cathode degradation with the wastewaters in these two MFC configurations, used cathodes were tested in the electrochemical cell to evaluate the extent of degradation during MFC operation.

2. Methods

2.1. Wastewater samples

Refinery wastewater (RW) samples were collected from a refinery facility in Hawaii, placed on ice in coolers, and delivered to the

Pennsylvania State University within three days. Upon arrival, the samples were stored at 4 °C. The RW samples were obtained from the effluent of an oil–water separator at the refinery [previously identified as DOW3 (Ren et al., 2013)], so that most of the oil phase and suspended solids were removed prior to MFC and HBOD tests. Domestic wastewater (DW) samples were obtained from the primary clarifier effluent at the Pennsylvania State University wastewater treatment plant. Fresh DW samples were obtained every one to two weeks and stored at 4 °C. Although wastewaters may have slightly changed during storage, the influent CODs remained relatively constant during all tests.

2.2. MFC construction and operation

MFCs were single-chamber, cubic-shaped reactors with a cylindrical anode chamber 2 cm long and 3 cm in diameter (Liu and Logan, 2004). The empty bed volume was 13 mL. The anodes were graphite fiber brushes (PANEX 35 50 K, Zoltek, total bristle surface area of ~ 0.056 m²) that were pre-treated at 450 °C for 30 min. Reference electrodes (Bioanalytical Systems, Inc., RE-5B; +0.209 V versus a standard hydrogen electrode, SHE) were inserted through the hole in the middle of the chamber, with the frit ~ 3 mm away from the brush edge. Cathodes were made of carbon cloth as previously described (Cheng et al., 2006), with a diffusion layer made of PTFE on the air facing side, and a Pt catalyst layer (Pt loading of 0.5 mg/cm²) on the solution side.

MFCs were constructed with either the SPA or SEA configurations (Fig. S1). The cathode in the SPA MFC was placed 1.5 cm away from the anode brush core, which removed the possibility of a direct electrical contact between electrodes. The cathode in the SEA MFC was placed 0.5 cm away from the anode brush core, with two layers of a porous cloth separator (DuPont Sontara, style 8864; also known as Amplitude ProZorb Wipers) to prevent electrode short circuiting. All the reactors were initially inoculated and acclimated to DW with the external resistance of 1000 Ω (2–3 weeks), and then half the reactors were switched to the RW samples. This acclimation procedure was previously shown to be an effective method for reactor acclimation and operation with mini-MECs (Ren et al., 2013). During MFC operations, the RW was always used as received without any addition of the DW. With each type of wastewater and configuration, MFCs were operated in fed-batch mode, in duplicate, at 30 °C. The wastewater was replenished when the voltage dropped to less than 30 mV.

2.3. Calculations and measurements

Voltage (U) across the external resistor in the MFC circuit was measured at 20 min intervals using a data acquisition system (2700, Keithley Instrument, OH) connected to a personal computer. Current ($I = U/R$) and power ($P = IU$) were normalized by the projected surface area of the cathode (7 cm²). Anode potentials were measured respect to the reference electrode, and the cathode potentials were calculated based on the anode potentials and the whole cell voltages. Polarization tests were performed using the multi-cycle method (a different resistance for each complete fed batch cycle), in order to obtain the treatment efficiencies at different current conditions, and to minimize the possibility of power overshoot (Watson and Logan, 2011). All the reactors were left open circuit for a cycle, and then the external resistances were varied from 5000 Ω to 250 Ω (DW) or 5000–300 Ω (RW) in a decreasing order over successive fed-batch cycles. Small resistances were repeated for two cycles, while large resistances (>1000 Ω) were tested for only one cycle to avoid changes of wastewater characteristics during storage over the duration of the multi-cycle tests. Coulombic efficiencies (CEs) were calculated as the ratio of recovered coulombs to the theoretical amount of

coulombs that could be produced from organic matter oxidation based on the change of total COD (Logan et al., 2006).

Chemical oxygen demand (COD) was measured using a standard method (method 5220, HACH COD system, HACH Company, Loveland, Co.) (APHA, 1998). For total COD (tCOD) measurements, samples were taken after shaking. For soluble COD (sCOD) measurements, samples were filtered through 0.45 μm pore diameter syringe filters (polyvinylidenedifluoride, PVDF, 25 mm size, Restek Corporation). Biological oxygen demand was determined using a three-day, non-dilution HBOD test at 20 °C as previously described (Logan and Patnaik, 1997). In the test to determine the HBOD of the RW, DW was added as a bacterial seed at ratios of 0%, 25%, 50%, 75% and 100% (v/v). Conductivity and pH were measured using a probe (SevenMulti, Mettler-Toledo International, Inc.). HBOD, tCOD, sCOD, pH and conductivity analyses were performed when samples arrived, before the multi-cycle polarization tests, and at the end of each batch cycle to determine the treatment efficiencies of the MFC system. The HBOD measurements of the effluent were performed without any added bacterial seed.

2.4. Electrochemical tests

Cyclic voltammetry (CV) was used to electrochemically characterize the anode biofilm activities with a potentiostat (VMP3; BioLogic, USA). All tests were conducted using MFCs with the anode as the working electrode and the cathode as the counter electrode. The anode potentials were scanned from -0.49 V to $+0.31\text{ V}$ (vs SHE) at a slow scan rate of 1 mV/s .

Electrochemical impedance spectroscopy (EIS) tests were performed with the whole cell to understand how internal resistance components varied for the SEA and SPA configurations. Impedance measurements were conducted at whole cell voltage of 0.3 V , over a frequency range of 100 kHz to 5 mHz with a sinusoidal perturbation of 10 mV amplitude. Spectra were fitted to an equivalent circuit (Fig. S2) to obtain the solution (or solution/separator) resistance R_s and the reaction resistance R_{rxn} . To simplify circuit analysis, two time constants (RQ components) were used in the equivalent circuit to roughly estimate the impedance associated with the charge transfer/diffusion resistance of both the anode and the cathode (He et al., 2006). The reaction resistance was calculated as the sum of $R1$ and $R2$ in the equivalent circuit.

Used cathodes were characterized with potentiostatic polarization using the potentiostat to compare the performance degradation of cathodes that were previously used with the two different wastewaters, in the presence and absence of a separator. After two months of operation, cathodes were taken out of the reactors and gently cleaned by flushing with deionized water. The cathodes were then placed in an electrochemical cell, which consisted of a working electrode (air cathode with 7 cm^2 projected surface area), an Ag/AgCl reference electrode, and a Pt mesh counter electrode. In order to have consistent solution conductivities with the RW samples, 25 mM phosphate buffer (conductivity 3.7 mS/cm) was used in electrochemical tests. A different potential was set ($0.5\text{--}0\text{ V}$ versus SHE, in 0.05 V increments) for 1 h for the first two points to allow for electrode stabilization, and at 30 min intervals thereafter. Current values were recorded over time using the potentiostat, and the steady state current density (normalized by the cathode projected surface area) was plotted as a function of the potential.

3. Results and discussion

3.1. Wastewater characteristics

The RW sample had a tCOD of $970 \pm 6\text{ mg/L}$ and sCOD of $530 \pm 6\text{ mg/L}$. The HBOD measured using only RW (no additional

seed) was only $13 \pm 1\text{ mg/L}$, suggesting an insufficient bacterial seed in the wastewater relative to aerobic biodegradability. Addition of DW to the RW to provide the necessary microorganisms (25% v/v, DW/RW) increased the HBOD of the RW to $220 \pm 8\text{ mg/L}$ (after subtraction of the DW HBOD). Further increases in the proportion of the DW in the RW increased the HBOD to $290 \pm 5\text{ mg/L}$ (75% v/v), suggesting also toxicity of some components of the RW in these oxygen-based biodegradability tests (Fig. S3). The RW sample had a pH of 9.0, close to the threshold of pH (around 10) that anode bacteria can tolerate in MFCs (He et al., 2008). This was much higher than the DW samples, which had a nearly neutral pH of 7.4. RW samples had a much higher conductivity (3.7 mS/cm) than DW samples (1.7 mS/cm), which should provide more favorable conditions for power generation as higher conductivities can produce lower internal resistances. The CODs and HBOD of the RW sample used in these MFC tests were lower than that used in previous mini-MEC tests (tCOD $1050\text{--}1310\text{ mg/L}$, sCOD $480\text{--}840\text{ mg/L}$, HBOD $470\text{--}640\text{ mg/L}$, Table S1), but the pH and conductivities were similar for both tests.

The DW samples had tCODs ranging from 400 to 500 mg/L and sCODs of $200\text{--}250\text{ mg/L}$ during the MFC acclimation period. The DW samples obtained for polarization tests, however, had a much higher tCOD of $800 \pm 4\text{ mg/L}$, a sCOD of $430 \pm 0\text{ mg/L}$, and a HBOD of $320 \pm 10\text{ mg/L}$. Previous tests in mini-MECs were conducted using DW samples with a tCOD = $350\text{--}450\text{ mg/L}$, a sCOD = $170\text{--}250\text{ mg/L}$ and a HBOD = $200\text{--}260\text{ mg/L}$ (Ren et al., 2013).

3.2. Power production

The RW and DW samples were examined for power production in MFCs constructed with SPA or SEA configurations. With the SPA (1.5 cm electrode spacing), the RW produced a maximum power density of $255 \pm 2\text{ mW/m}^2$, compared to $310 \pm 50\text{ mW/m}^2$ with the DW. This slightly poorer performance with the RW than the DW was consistent with previous mini-MEC tests based on peak current densities, as the RW samples produced a smaller current density (1.14 A/m^2) than the DW samples (1.85 A/m^2). Maximum power densities increased for both the RW and the DW by using the SEA setup, with the DW sample producing a higher power density of $360 \pm 10\text{ mW/m}^2$ than the RW sample ($280 \pm 6\text{ mW/m}^2$) (Fig. 1A). There was a slightly larger (16%) increase in power density when using the DW in the SEA configuration compared to the SPA, than that obtained with the RW in the SEA compared to the SPA configuration (10%). This larger increase was likely due to the lower conductivity of the DW than the RW, making the reduction in solution resistance when moving the electrodes closer more important relative to decreasing the total internal resistance.

The lower power densities (both configurations) of the RW sample, compared to the DW samples, were mainly due to the poorer anode performance. Although the RW sample had only slightly lower HBOD (290 mg/L with sufficient bacteria seed) than the DW (320 mg/L), reactors fed with the RW had more positive anode potentials than those of the DW samples at similar current densities (Fig. 1B), resulting in lower power densities. This more positive anode potential indicated the poorer biodegradability of the RW, likely due to possible toxicity of the components in the RW to exoelectrogenic microorganisms (inferred from the HBOD dilution test results with DW), and possibly a negative impact of high pH on the anode kinetics (Gil et al., 2003). Although the RW had twice the conductivity of the DW sample, the favorable effect of high solution conductivity was insufficient to offset the poorer biodegradability of the RW. The DW samples used for these comparisons to RW samples had only slightly smaller tCOD and sCOD, making it unlikely that the COD concentration was the primary reason for differences in power production. Therefore, the key issue for

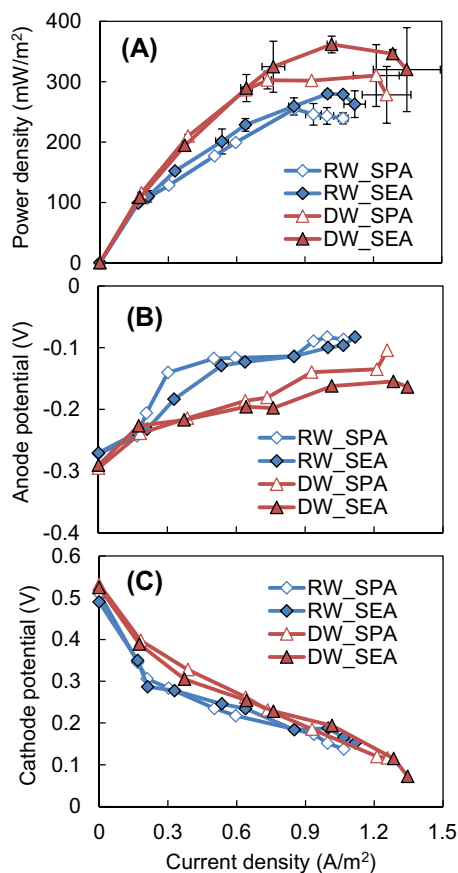


Fig. 1. (A) Power production, (B) anode potentials and (C) cathode potentials obtained from multi-cycle polarization tests, for reactors fed with the RW or the DW, using the SPA or the SEA configuration.

higher power output for the DW sample was the biodegradability of the wastewater, rather than the conductivity of the wastewater.

The cathode performance in the MFCs with the RW were also reduced compared to those of the DW in the low current density range, although they were similar for all reactors in the higher current density range (Fig. 1C). These differences in cathode performance could have resulted from the differences in sample pHs and conductivities (Wang et al., 2011, 2003). The higher pH of the RW sample is more thermodynamically unfavorable for oxygen reduction than the neutral pH of the DW samples. However, the higher solution conductivity (lower solution resistance) of the RW samples should reduce solution resistance and could improve cathode catalyst performance (Wang et al., 2011).

3.3. Coulombic efficiencies

For tests with the RW samples, CEs increased with current density from 6% to 11% in the SPA configuration. When using the SEA configuration, CEs were slightly larger, ranging from 8% to 14% for the RW (Fig. 2A). Reactors fed with the DW similarly showed a trend of an increase in CE with current density. Reactors fed with the DW had CEs of 17–34% with the SPA configuration, which increased to as much as 30–49% with the SEA configuration (Fig. 2A). The larger CEs with the SEA setup were due to the use of separator which reduced the oxygen intrusion into the anode chamber and prolonged the cycle. For both the RW and the DW samples, the SEA configuration had a much longer cycle time but similar peak voltages with those of the SPA (Fig. S4), resulting in a larger CE with the SEA configuration than the SPA. These results

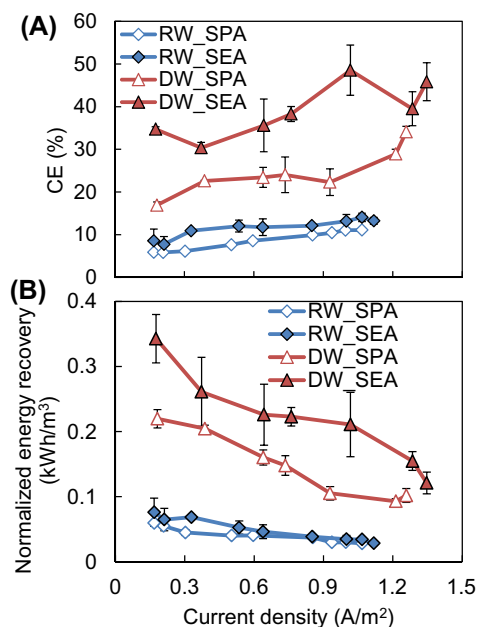


Fig. 2. (A) CEs, (B) energy recoveries (normalized to the reactor volume, i.e. treated wastewater volume) varied with the peak current density produced during the batch cycle (i.e. the external resistance), for reactors fed with the RW or the DW, using the SPA or the SEA configuration.

were consistent with previous studies that the use of separators enhanced CEs (Chen et al., 2013; Fan et al., 2007).

The lower CEs of the RW compared to the DW were likely due to the poorer biodegradability of the RW than the DW. Comparing the voltage–time profiles, the RW had slightly lower peak voltages than that of the DW using the same configuration, but the cycle time with the RW was much reduced compared to that of the DW (Fig. S4). The easily biodegradable organic matter in the RW that was favorable for electricity production resulted in only ~20% lower maximum power densities that those of the DW. However, the fraction of easily biodegradable material in the RW was very small, resulting in CEs that were 65–70% lower than those of the DW.

3.4. Energy recovery

The RW sample produced a maximum normalized energy recovery of 0.08 kW h/m³ (an external resistance of 5000 Ω) in fed-batch tests. The energy recovery from one batch cycle was reduced to 0.03 kW h/m³ when the external resistance was decreased (i.e. increased current density). The SEA configuration did not produce a higher energy recovery than the SPA configuration for the RW, but the SEA did improve energy recoveries with DW samples. MFC tests with DW and the SEA configuration had an energy recovery of up to 0.34 kW h/m³, compared to 0.22 kW h/m³ with the SPA configuration (Fig. 2B). Overall, energy recoveries were much lower with RW than DW samples, mainly due to both the reduced power production (Fig. 1A) and the much shorter cycle time with the RW (Fig. S4).

3.5. Organics removals

The SPA and SEA configurations produced differences in RW treatment efficiencies. Using the SPA configuration and an external resistance of 5000 Ω, RW treatment efficiencies were 84% for tCOD removal, 73% for sCOD removal and 92% for HBOD removal, compared to 79% (tCOD), 70% (sCOD) and 90% (HBOD) with the SEA

configuration. When the external resistance was reduced, the treatment efficiencies were affected by both the enhanced anaerobic oxidation for electricity production, and the decreased aerobic oxidation due to the decreased oxygen intrusion amount as a result of reduced cycle time (Fig. S4). With an external resistance of 2000 Ω , RW treatment efficiencies reached the maximum removals of 86% for tCOD, 78% for sCOD and 92% for HBOD with the SPA configuration, while the SEA had a decreased removal of 63% (tCOD), 60% (sCOD) and 74% (HBOD) (Fig. 3A–C). This better treatment of the SPA configuration compared to the SEA was due to the lack of a separator, which allowed more oxygen transfer into the anode chamber and therefore enhanced aerobic COD removal. The removal efficiencies obtained here using the MFCs were higher than those obtained in the mini-MEC tests (58% tCOD removal, 46% sCOD removal and 61% HBOD removal) with closed circuit, as oxygen intrusion from the cathode enhanced the aerobic organics degradation in MFCs.

Increasing the current density showed a generally increased normalized removal rate for the RW, with a maximum of 0.95 kg tCOD/m³-d for the SPA and 0.84 kg tCOD/m³-d for the SEA (Fig. 3D), indicating the positive effect of current production on organics removal. However, the removal efficiencies were lower at high current density range for both the SPA and the SEA configurations (minimum: 63% tCOD, 62% sCOD, 79% HBOD removals for the SPA; 57% tCOD, 57% sCOD, 67% HBOD removals for the SEA; Fig. 3A–C), mainly due to the dominant negative effect of the reduced cycle time and thus decreased amount of oxygen intrusion over time at higher current densities. This suggested that for RW treatment in MFCs, aerobic oxidization due to oxygen intrusion played a more important role than the anaerobic oxidization (for electricity production). Although the removal rate was higher with a larger current density, the retention time needed to be longer for the SEA than the SPA in order to achieve a good overall removal.

The SPA configuration also improved organics removals relative to the SEA configuration with the DW, but less difference between two configurations was observed for the DW compared to the RW. The DW samples generally had higher organics removal efficiencies than RW samples tested in the same MFC configuration, indicating the greater biodegradability of DW. The maximum removals

were 90% for tCOD, 85% sCOD and 95% for HBOD with the SPA, compared to 87% (tCOD), 80% (sCOD) and 92% (HBOD) with the SEA configuration (Fig. 3A–C). More oxygen intrusion with the SPA did not appreciably change HBOD removals with the DW, compared to a larger difference in HBOD removals observed for the RW (Fig. 3C). This different effect of oxygen availability on HBOD removals for the RW and the DW indicated oxygen less of a factor in organics biodegradability of the DW compared to the RW.

At open circuit conditions, there was less COD removal due to the absence of current generation, although organics were removed due to oxygen transfer through the cathode (Liu et al., 2004). Organics removals in the SPA with the RW were 72% for tCOD, 70% for sCOD and 78% for HBOD, compared to removals of tCOD 59%, sCOD 53% and HBOD 73% with the SEA configuration (Fig. 3A–C). Organic matter removal based on HBODs increased by 7% with the SPA compared to the SEA configuration. This change was smaller than that observed in terms of tCOD and sCOD (22–32%), suggesting that oxygen enhanced the degradation of more refractory compounds in the RW. Compared with mini-MEC under open circuit conditions, where organics removals were only about 30–40%, the removal efficiencies of MFCs at open circuit were much higher, indicating that oxygen intrusion from cathodes substantially increased organics removals in MFCs.

3.6. Effluent pH and conductivity

Effluent pH generally decreased with the peak current density measured in tests using either RW or DW samples. For tests with RW samples, effluent pH decreased from 7.3 with current generation to ~6.7 for both configurations with closed circuits (Fig. 4A). With an open circuit the effluent pH was 7.3, compared to the influent pH of 9. This decrease in pH at open circuit was likely due to the fermentation of organic matter and accumulation of volatile fatty acids. For reactors fed with DW, effluent pH similarly decreased with increasing current densities, from 7.1 to 6.0 with a closed circuit (Fig. 4A). At open circuit, the effluent pH (~7.4) was similar to that of the influent pH of the DW.

The reactor configuration used (SEA or SPA) did not affect changes in solution conductivity. For reactors fed with the RW,

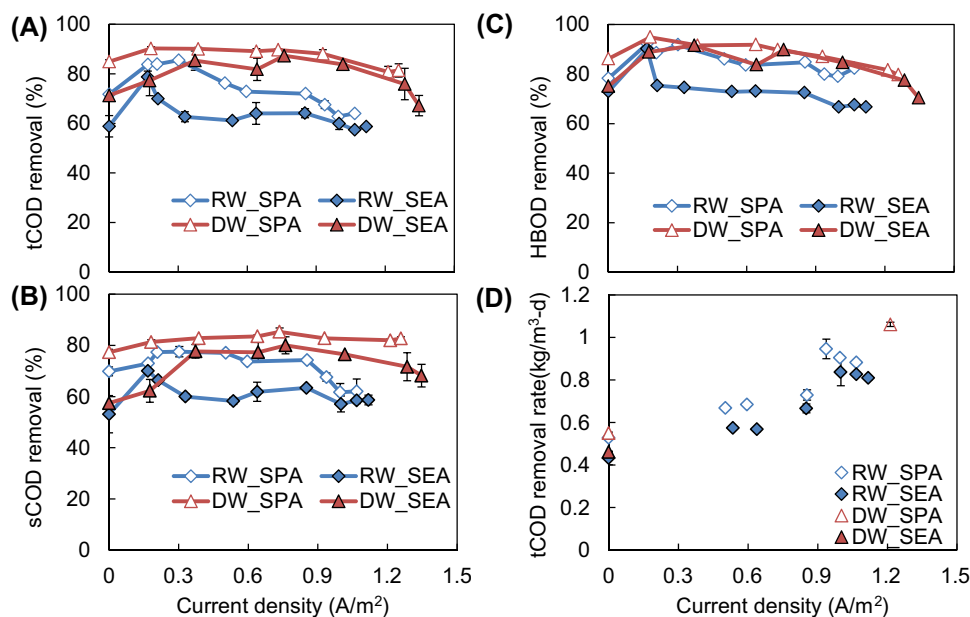


Fig. 3. Changes of (A) tCOD removal (%), (B) sCOD removal (%), (C) HBOD removal (%) and (D) normalized tCOD removal rate (kg/m³-d) with the peak current density produced during the batch cycle (i.e. the external resistance), for reactors fed with the RW or the DW, using the SPA or the SEA configuration. Points at zero current were open circuit controls. [For (D) normalized tCOD removal rate, only points with similar cycle time at a given current density were shown here.]

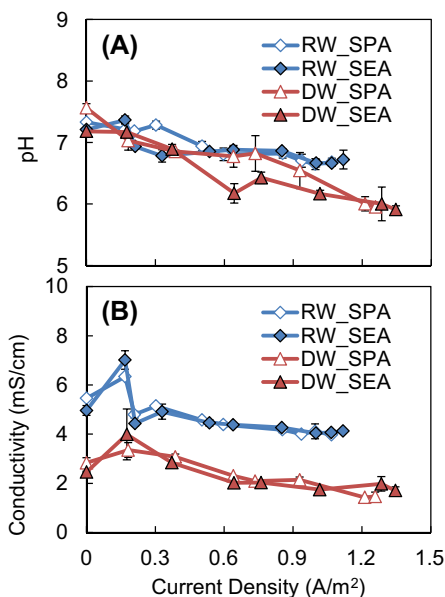


Fig. 4. Effluent (A) pH and (B) conductivity varied with the peak current density produced during the batch cycle (i.e. the external resistance), for reactors fed with the RW or the DW, using the SPA or the SEA configuration. Points at zero current were open circuit controls.

effluent conductivity decreased from ~ 6.6 to ~ 4.0 mS/cm with increasing current density, compared to ~ 5 mS/cm at open circuit. With the DW, conductivities similarly decreased from 4.0 to 1.5 mS/cm as current density increased, compared to ~ 2.6 mS/cm at open circuit (Fig. 4B). The initial increase in conductivity was likely due to fermentation, which results in the production of small molecular weight organic acids (Yang et al., 2013). With increasing current densities, these organic acid compounds would be oxidized faster for electricity production, resulting in the decreasing trend in conductivity with increasing current density.

3.7. Electrochemical characterization

Anodic cyclic voltammetry (CV) was conducted to directly compare anode biofilm performance with the different wastewaters. For both SEA and SPA configurations, reactors fed with the RW had lower peak current densities in CV tests than those fed DW, despite the much higher solution conductivity with the RW (Fig. 5). The reactors fed with the RW also showed a smaller potential range of activities in the first derivative CV plots (Fig. S5). These results showed that reactors fed with the RW had poorer anode activities than those with the DW, which was consistent with the more positive anode potentials of the RW during the polarization tests.

Electrochemical impedance spectroscopy (EIS) was conducted to identify the solution (or solution/separator) resistances (R_s) and reaction resistances (R_{rxn}) for the two different MFC configurations with the different wastewaters. In the SPA configuration, reactors fed with the RW showed a much smaller R_s of 39Ω compared to that of 95Ω with the DW, consistent with higher solution conductivity of the RW samples. However, the R_{rxn} with the RW was much larger (1420Ω) than that of the DW (230Ω) (Fig. 6), suggesting slower reaction kinetics with this substrate. The EIS data showed that the better solution conductivity (smaller R_s) of the RW sample did not offset the negative effects relative to poorer biodegradability. When the SEA configuration was used, the R_s decreased to 7Ω with the RW, and 22Ω with the DW. This decrease in R_s showed that any resistance due to the separator was

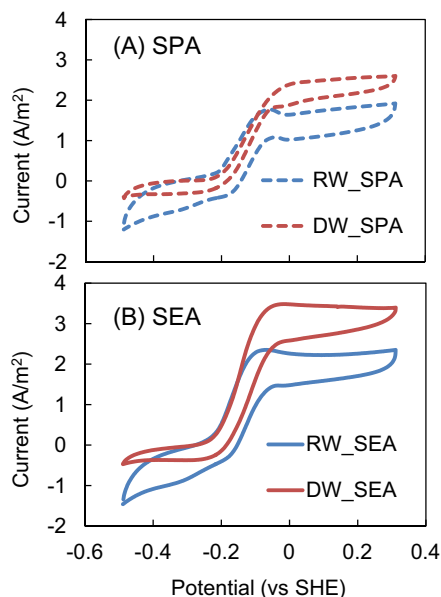


Fig. 5. Comparisons of anode CVs for reactors fed with the DW or the RW in (A) the SPA and (B) the SEA configuration, with a slow scan rate of 1 mV/s.

therefore offset by a larger decrease in solution resistance. The R_{rxn} also decreased slightly to 1230Ω for the RW solution, and to 195Ω for the DW sample (Fig. 6). These overall decreased internal resistances with the SEA configuration were consistent with the higher power densities obtained using the SEA configuration compared to the SPA configuration in the MFC tests.

3.8. Cathode degradation over time with different wastewaters

After two months of operation, previously used cathodes were tested in the electrochemical cell to examine them for relative degradation in performance with the different wastewaters, and relative to the absence or presence of the separator. For the same

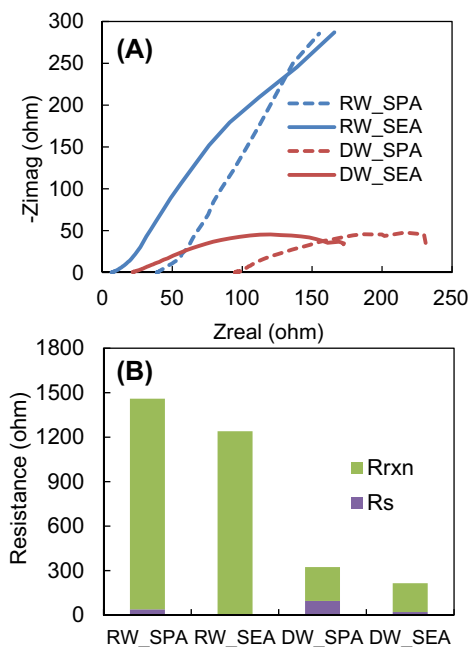


Fig. 6. (A) Nyquist plots of impedance spectra at whole cell voltage of 0.3 V. (B) Component analysis of the whole cell impedance for reactors fed with the RW or the DW, using the SPA or the SEA configuration.

type of wastewater, cathodes previously placed in the SEA configuration had better performance (larger current density at a given potential, i.e. smaller degradation) than those in the SPA configuration (Fig. S6). The better performance indicated that the separator protected the cathode from fouling by avoiding its direct exposure to the solution, which limited substrate availability for microbes on the cathode surface and reduced the biofilm growth. Cathodes from the RW reactors had less performance degradation than those with the DW (Fig. S6), likely because of less cathode biofilm growth in the RW, resulting in less cathode biofouling in tests with RW.

4. Conclusion

Using the RW in an MFC enabled a maximum power density of 280 mW/m², a maximum energy recovery of 0.08 kW h/m³, and high organics removals (up to 86% tCOD, 78% sCOD and 92% HBOD). RW treatment efficiencies were higher in MFCs compared to those obtained in previous mini-MEC tests due to oxygen crossover from the cathode. The SPA MFC had higher organics removals than the SEA, with larger differences observed for the RW than the DW, as oxygen was more important for the organics removal in the RW that was less readily biodegradable than the DW.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.biortech.2013.10.103>.

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