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Microbial fuel cell type biosensor for specific volatile fatty acids using acclimated bacterial communities

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ABSTRACT

Volatile fatty acid (VFA) concentration is one of the most important parameters for monitoring bio-processes such as anaerobic digestion and microbial fuel cells. In this study the correlation between VFA concentration and current/voltage responses and electrochemical properties by using the MFC technology was evaluated. The discrimination between different species of VFA by using two methods i.e., coulombic efficiency and cyclic voltammetry was investigated. Columbic efficiency gave a slow response of greater than 20 h, particularly at concentration levels of 20 mg l^{-1}. By using cyclic voltammetry to measure the oxidation peak at a consistent scan rate showed linear correlation to VFA concentration and peak current produced, up to <40 mg l^{-1}) in a rapid response time of 1–2 min. The results presented showed good correlations between the individual VFA species concentration and charge, and also current generated. A MFC based biosensor array was produced capable of measuring individual acetate, propionate and butyrate concentrations with sensitivity down to 5 mg l^{-1} and up to 40 mg l^{-1}.

1. Introduction

Volatile fatty acids (VFAs), particularly acetate, butyrate and propionate, are important intermediate compounds in the metabolic pathways of fermentation and methanogenesis. VFAs are also important products and contaminants in anaerobic processes in more dilute environments such as still water, sewer systems and primary wastewater and also as substrates in bioelectrochemical systems (BESs) (Kim et al., 2010). VFAs can be inhibitory and indicative of microbial stress if present in high concentrations (Ahring et al., 1995; Siegert and Banks, 2005). Their accumulation results in a decrease of pH, and can ultimately lead to a failure of such biochemical processes in a digester. VFA concentrations can indicate COD removal performance in aerobic, BES or other effluent polishing processes, and monitoring is therefore a useful optimisation and control tool. Concentrations of individual VFAs have often been proposed as measured variables in the control of AD (Perrier and Dochain, 1993; Steyer et al., 2002).

Off-line monitoring of VFAs has been widely used; however delays in measurement time have been inevitable and thus feedback control might have difficulties in preventing a rapid system failure. Only a few reports exist on the development of on-line VFA monitoring systems for individual VFA species, typically by GC (Slater et al., 1990) or HPLC (Zumbusch et al., 1994). Maricou and colleagues have showed that VFAs can be detected in the headspace of liquid samples in the range of ppmv (Maricou et al., 1998). Only a limited number of biosensors and other sensors for VFAs have been reported in the literature to date (Rajashekhara et al., 2006; Yano et al., 1997).

MFCs have been considered as biosensors in previous studies (Chang et al., 2005; Gil et al., 2003; Kumlanghan et al., 2007), where microorganisms in the anode compartment act as biocatalyst and the electrodes and proton exchange membrane (optional) serve as a transducer. The signal is conveniently presented directly as an electrical response of a range and power appropriate for integration through signal conditioning (if necessary) to processing devices. In comparison with other existing sensors (i.e. pH, temperature, and gas flow metres) in AD, MFC biosensors work as small bioreactors with high selectivity (Spanjers and van Lier, 2006) and exhibit long term stability (Gil et al., 2003), thus they may not need catalyst replacement. An MFC based biosensor was reported in 1997 (Yano et al., 1997) where pure culture *Clostridium butyricum* was positioned as the anode biocatalyst to transfer electrons using hydrogen as an electron acceptor. This would allow low cost systems based on existing electronic devices to be developed. These characteristics have ensured that MFC biosensors have received significant attention over the past decade. Chang et al. (2004) were the first to use MFCs for BOD analysis within the linear range of organic contaminant up to 100 mg/ml. The accuracy was further enhanced by the inhibition of other competitive electron acceptors (Chang et al., 2005). A packed bed MFC biosensor using a carbon cloth anode was developed to

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further increase the linear range to 350 mg BOD/l. Besides the mixed culture used as the biocatalyst sensing element, pure culture *Geobacter sulfurreducens* was employed in a packed bed MFC (Tront et al., 2008), in which the system was used for the measurement of acetate concentration and microbial respiration. All these studies focus on the performance of the sensor itself, but not particularly on individual components of the organic contaminants.

In this paper we sought to find a correlation between VFA concentration and the current/voltage responses and electrochemical properties. We also investigated means to discriminate between different species of VFA by using two methods i.e. coulombic efficiency and cyclic voltammetry. We have monitored the oxidation and reduction peaks on CVs from each VFA enriched MFC at different VFA concentrations. The oxidation peak obtained from cyclic voltammetry showed linearity between the VFA concentration and peak current produced at a consistent scan rate. Also, distinctive shapes/patterns of the CVs suggest that they can be used in the speciation of VFAs as well as their quantification. We also sought to enhance the degradation of recalcitrant fermentation end products such as propionate and butyrate using these bioelectrochemical systems hypothesising that the syntrophic relationship between acetogens and methanogens can be replaced by an electrode reaction. This manner of syntropism bioelectrochemically could be very useful in enhancing the sensor's discriminatory response to these recalcitrant products in developing whole cell based VFA sensors.

2. Materials and methods

2.1. MFC configuration and operation

The H-type MFCs were constructed by combining two modified glass bottles (250 ml) with clamp connections between them. The anode electrode was made of carbon paper (TGPH-120 Toray carbon paper, E-tek, 2.5 cm × 4.5 cm). The same size of cathode electrode containing platinum (0.35 mg/cm^2; 10% Pt; E-tek, NJ) was placed in the cathode compartment which was filled with 250 ml of phosphate buffer (50 mM, pH 7.0) prepared as previously described (Kim et al., 2010)and was continuously aerated. Both compartments were separated by a cation exchange membrane (CMI-7000, Membrane International Inc.) and both electrodes were connected to an external resistance (1000 Ω). Three MFC reactors were inoculated with 20 ml anaerobic digester sludge (Cogs Moors wastewater treatment plant, Wales, UK), 230 ml phosphate buffer and VFAs (acetate, butyrate, and propionate, 40 mM each for acclimation). MFCs were operated in a fed batch mode by conducting a batch mode test until the voltage decreased to a low value (< 10 mV) and then replacing the feed solution in the anode chamber. Sodium acetate, sodium butyrate and sodium propionate (Sigma-Aldrich, MO) were used as the sole carbon and energy source for bacteria. The inoculation and cell transfers were conducted in an anaerobic glove box (Coy Scientific Products, MI). All MFC reactor chambers were mixed using a magnetic stirrer in a temperature controlled chamber (30 °C).

2.2. Chemical and electrochemical analyses

The voltage and current across the load were monitored using a virtual instrument based data logging system (National Instruments, LabVIEW™) connected to an analogue input on the I/O card. The power output measurements were determined using potentiodynamic polarisation (scan rate 10 mV s^{-1}) using a Solartron Electrochemical Interface (Farnborough, UK) controlled by a dedicated software (CorrWare 2™, Scribner Associate Inc., NC). Acetate, butyrate and propionate were measured using a Perkin-Elmer head space gas chromatograph (Model number HS40XL, Perkins-Elmer, Waltham, Massachusetts, USA) in conjunction with a flame ionisation detector (FID) and a Nukol free fatty acid phase (FFAP) column (30 m × 0.32 mm) (Supleco) running at 190 °C and 14 psi with nitrogen as a carrier gas according to the method by (Cruwys et al., 2002). Cyclic voltammetry (PC 4/750 potentiostat, Gamry) was carried out to characterise the oxidation–reduction reaction of VFAs on the anode biofilm. The current response at an electrode surface to a specific range of potentials was measured at a fixed scan rate. A conventional three-electrode system was employed with the anode as the working electrode, the cathode (2.5 cm^2, 0.35 mg/cm^2; 10% Pt; E-Tek, NJ) as the counter electrode, and an Ag/AgCl reference electrode. The potentials were shifted from −650 to +650 mV at a scan rate of 50 mV/s while monitoring the current response. Peaks were observed in the range of −600 to 0 mV.

2.3. Calculations

Current (I) and power ($P=IV$) were calculated as described in the previous report (Min et al., 2005). The coulombic efficiency was calculated as, CE (%) = (C_p/C_{Ti})100, where C_p is the total Coulombs calculated by integrating the current over time. C_{Ti} is the theoretical accumulated charge (Coulombs) that can be produced from each substrate respectively, calculated as, $C_{Ti} = Fb_iS_i/M_i$, where F is Faraday's constant (96,485 C/mol e), b_i is the number of moles of electrons produced per mole of substrate ($b_a=8$, $b_p=12$, and $b_b=20$, for acetate, butyrate and propionate respectively), S_i is the substrate concentration, and M_i is the molecular weight of the substrate ($M_a=82$, $M_p=96$, and $M_b=110$).

2.4. Molecular analysis

Anode electrode samples (1 cm^2) were taken with sterilised scissors at the end of open circuit (OC) and closed circuit (CC) operations for use in the isolation of genomic DNA. DNA was extracted by the phenol:chloroform method (Oude Elferink et al., 1997). PCR analyses and identification of 16 S rDNA were performed as previously described (Premier et al., 2011) using archeal and bacterial primers.

3. Results

3.1. Sensor development and operation with acetate, butyrate and propionate

The three H-type MFC reactors were enriched with the sludge using acetate, propionate and butyrate as electron donor and substrates (Fig. 1). Enrichment/initiation need only occur once, before the sensor is deployed. Start-up time of the acetate enriched cell (A-MFC) shows 100 h of lag phase followed by a rapid increase in cell voltage to 320 mV over the next 50 h. By comparison, the MFCs fed with butyrate (B-MFC) and propionate (P-MFC) did not result in appreciable voltage increase until 500 h and even after the whole media was replaced at 550 h (< 10 mV). At this point the pH changes of B- and P-MFCs were 6.5 and 6.7 respectively, as compared to A-MFC (pH 6.9).The B- and P-MFCs showed rapid increases in voltage when the media were replaced at 570 h. Once the reactors were fully enriched and produced stable voltage generation, the maximum voltage was reached within 2–4 h upon replacement of the media and VFA substrate. This result indicates that the electrogenic biofilm for each VFA was established on the anode electrode and was resilient in the face of media replacement. When all the reactors were fully enriched, maximum power generated from each reactor was calculated to be 0.13 mW, 0.1 mW and 0.06 mW.

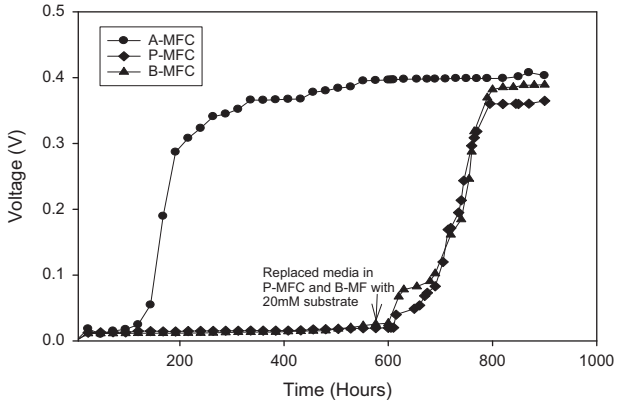

Fig. 1. Typical voltage generation from three MFCs during the enrichment process using 40 mM acetate, propionate and butyrate as the fuel. MFCs were inoculated with activated sludge and fed continuously with artificial wastewater with 1000 Ω load.

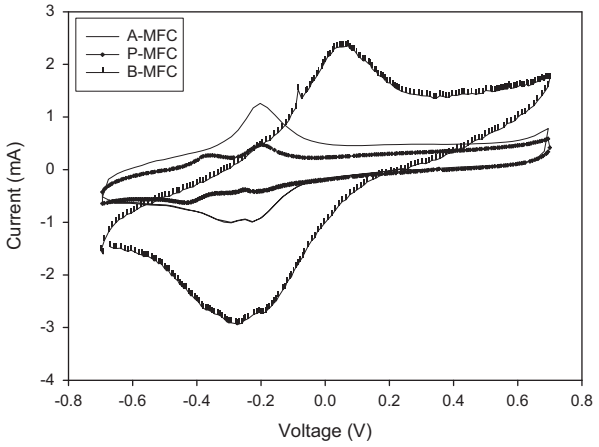

Fig. 2. Cyclic voltammogram showing the difference between A-MFC, P-MFC and B-MFC with 10 mg l^{-1} substrate concentration. Differences in shape and oxidation (A-MFC: 1.01 mA at −0.205 V, P-MFC: −0.378 V, 0.24 mA and −0.231 V, 0.37 mA and B-MFC: 0.0373 V, 2.20 mA) and reduction (A-MFC: 1.0 mA at −0.226 V, P-MFC: −0.219 V and −0.408 V and B-MFC: −0.1645 V with −2.63 mA and −0.2430 V with −2.91 mA), peak voltage and current are noteworthy.

3.2. Coulombic efficiency

In order to calculate the recovered electrons (charge) through the previously enriched electrogenic biofilm, and to determine the coulombic efficiencies, the substrate concentration was varied over the range of 2–20 mg l^{-1} and compared. The microbial community in each MFC responded in 1–2 h on addition of VFA whereas coulombic yield of the MFCs varied with the initial dose of VFA. When VFA concentrations were higher than 20 mg l^{-1}, the maximum current values were similar, indicating a typical saturation kinetics. The highest coulombic yield obtained from 20 mg l^{-1} of acetate and butyrate were 92% and 7.2%, respectively. Coulombic efficiencies calculated for butyrate (4–8%) were significantly lower than those of acetate (50–90%), indicating substantial electron loss to processes other than electricity generation. The correlation between VFA concentration and coulomb generation showed good linearity up to 10 mg l^{-1} concentration of acetate, and butyrate up to 20 mg l^{-1}. However, the propionate reactor did not respond to concentrations below 20 mg l^{-1} but achieved maximum voltage when supplied with 50 mg l^{-1} of substrate with 34% of maximum coulombic efficiency. In the case of acetate, the coulombic efficiencies were consistent and repeatable with an error range of ±4–5% but those with propionate and butyrate show significant variations of ±20% and ±30–35%, respectively. Coulombic efficiency, as reported, is unlikely to be useful for rapid or frequent on-line measurements of concentrations and species of VFA as the sampling time (> 24 h for 20 mg l^{-1} initial substrate concentration) would be excessive.

3.3. Cyclic voltammetry

Cyclic voltammetry (CV) tests were conducted to demonstrate that current generation was coupled to VFA oxidation and to examine if the concentration of the substrate can be detected from the current produced. The oxidation and reduction peaks obtained from each VFA were very distinct in shape (Fig. 2). Different VFA concentrations were tested in individual VFA enriched MFC reactor by considering the validity of the enriched community on electrode to different VFAs and to measure the current response. Table 1 shows the cross-sensitivity responses of individual VFA enriched MFCs to all the respective VFA species. When 5 mg l^{-1} acetate was added to A-MFC, oxidation (1.01 mA at −0.205 V vs. Ag/AgCl) and reduction peaks (1.0 mA at −0.226 V vs. Ag/AgCl) were obtained. Each current peak increased as acetate concentration increased, indicating that these peaks resulted from acetate metabolised through the enriched electrochemically active bacteria at the anode. Typical traces of the current variation due to the electrochemical activity of the biofilm on the electrode with different concentrations of VFAs are shown in Fig. 3.

Table 1
Cross-sensitivity of MFC reactors enriched on acetate, propionate and butyrate, to each species of VFAs; and electrode and liquid phase biomass total DNA concentrations in OC and CC.

MFC reactor	Sensitivity of reactors to VFA species at 5 ppm concentration			DNA concentration electrode		DNA concentration suspension	
	Acetate (5 mg l^{-1})	Propionate (5 mg l^{-1})	Butyrate (5 mg l^{-1})	Closed (ng/μl)	Open (ng/μl)	Closed (ng/μl)	Open (ngμl)
A-MFC	+	−	−	176.5	225.1	141.6	432.7
P-MFC	−	+	−	196.6	143.9	218.1	141.6
B-MFC	+	+	+	279.2	25.0	117.8	374.8

Further CV scans were performed to determine the cross response of the acetate enriched biofilm to propionate and butyrate. The A-MFC enriched biofilm did not show increase in peak current at various concentrations of propionate and butyrate, indicating that B-MFC and P-MFC might have additional metabolic capability for degrading butyrate and propionate over acetate. This result suggests that specificity of the enriched bacterial community towards acetate exists. Therefore, the acetate acclimated bacterial community uses only acetate as a carbon source, and can be used to measure acetate concentrations in the MFC and possibly, if incorporated into an AD system up to certain range of concentration.

The CV scan of an anode colonized in P-MFC exhibited two oxidation peaks (−0.378 V, 0.24 mA and −0.231 V, 0.37 mA) and two reduction peaks (−0.219 V and −0.408 V) (vs. SCE) (Fig. 2). One of the redox couples, i.e. −0.231 V, 0.37 mA, was active and showed an increase in peak current when different concentrations of propionate were added. A linear relationship was found within the range of 5–40 mg l^{-1}, after this point there was a decrease in the current response. The same range of concentrations of acetate and butyrate was also tested in P-MFC but no current response was observed, which again shows the specificity of P-MFC enriched anode bacterial community towards propionate.

In contrast to A-MFC and P-MFC, the B-MFC responded to all the VFA species but the degree of response was very different. The shape of CV from B-MFC showed one oxidation peak at (0.0373 V, 2.20 mA) and two small reduction peaks at (−0.1645 V

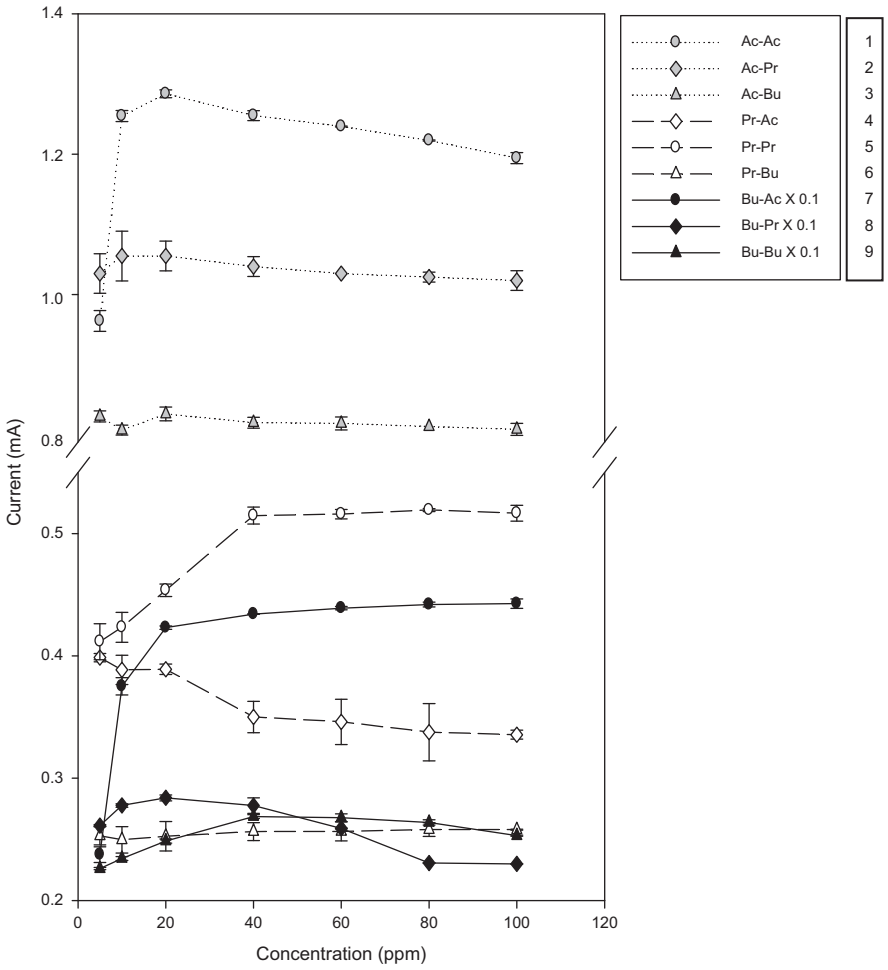

Fig. 3. Cyclic voltammetry based oxidation peak current response to the addition of different concentrations of VFA species in A-MFC (Ac–Ac, Ac–Pr, and Ac–Bu) P-MFC (Pr–Ac, Pr–Pr, and Pr–Bu) and B-MFC (Bu–Ac, Bu–Pr, and Bu–Bu). The flat lines (2, 3, 5 and 6) show selective responses of individual VFA enriched reactors to other VFA species. Error bars represent the range of duplicate experiments.

with −2.63 mA and −0.2430 V with −2.91 mA) which is very distinctively different from A-MFC and P-MFC. The acetate concentrations were first checked in B-MFC. A very sharp increase was observed when 5 mg l^{-1} concentration of acetate was added to B-MFC. There was an increase in current up to the range of 20 mg l^{-1} acetate, after that no further increase in current response was observed in B-MFC up to 100 mg l^{-1}. The same range of concentrations for propionate and butyrate were tested to check the current response. Butyrate showed a linear response up to 40 mg l^{-1} although the difference in current response was very limited, but after that no change in response was observed. On the other hand propionate showed positive linearity against propionate concentration up to 20 mg l^{-1}.

On the basis of the above CV results, the responses between all the VFAs were different and this response therefore discriminates between different concentrations and species of VFAs. Although the range within which discrimination of concentration was limited to circa 20 mg l^{-1}, samples at higher concentrations could be diluted to measure the VFA concentration.

3.4. Substrate utilisation in an open circuit and closed circuit MFCs

The effect of current flow on VFA degradation and consequent microbial products in the anode liquid phase and headspace was analysed for each MFC for different VFAs and OC/CC modes. VFA degradation was more rapid in the reactor in CC operation than in OC operation. The starting concentration of each VFA in both OC and CC was 20 mM. At the end of 5 days operation in OC the substrate consumed was significantly less than in CC i.e. 1350 mg l^{-1} and 1620 mg l^{-1} in P-MFC and B-MFC respectively, i.e. 392 mg l^{-1} and 253 mg l^{-1} respectively. Acetate eventually degraded in both systems in contrast to propionate and butyrate, and its consumption rate was much faster in the CC operation (Fig. 4).

Propionate and butyrate degradations resulted in the accumulation of 3.4% and 14% of CO_2 respectively in the headspace after 140 h for the CC operation. Carbon dioxide production also occurred in OC, but not until 24 h had lapsed and at a lower final concentration of $< 0.7\%$ in the headspace; very low concentrations of methane were also found in the headspace of the OC and CC in P-MFC, i.e. 0.4% and 1.1% respectively (Fig. 5). However methane was not detected in the butyrate acclimated reactor in either OC or CC operation.

The preceding results show that the electrode reaction (acting as terminal electron acceptor or a simple bacterial attachment media), plays a very important role in the degradation of propionate and butyrate. However, the metabolic pathway is not clearly understood in either OC or CC operation, but the dependence of VFA degradations on the electrode reaction is clear.

3.5. Molecular analysis

The total amount of biomass was analysed as an indicator of biological activity by quantifying the level of DNA present at the end of the OC and CC operations in both liquid and electrode

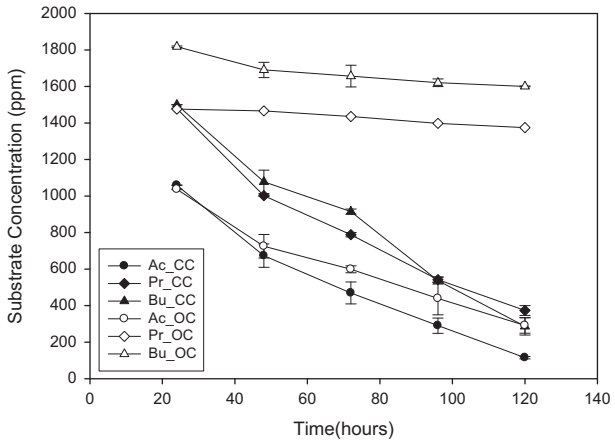

Fig. 4. Characteristics of MFCs operated in open and closed circuits showing degradation of acetate, propionate and butyrate (CC: closed circuit and OC: open circuit). Error bars represent the range of duplicate experiments.

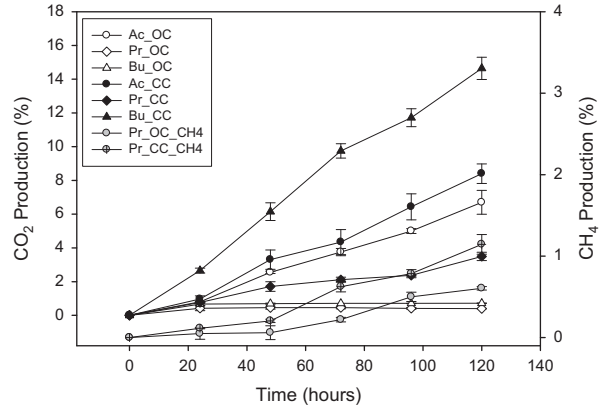

Fig. 5. Headspace gas analyses from individual VFA reactor during OC and CC operations. Error bars represent the range of duplicate experiments.

samples. The biomass present in the liquid samples was very different from the electrode samples and was affected by open and closed circuit operations; specifically in B-MFC (Table 1). In open circuit the B-MFC bacterial biomass was found to be higher in preponderance in the liquid phase and lower on the electrode. This suggested that when the MFC is shifted from the CC to OC mode, the biomass on the electrode moved in large part into the suspension in B-MFC. However, in A-MFC and P-MFC the OC and CC bacterial biomass was not much affected; but in A-MFC the OC bacterial biomass was at higher concentrations both on the electrode and in solution, as compared to CC. On the other hand, in P-MFC, CC bacterial biomass was found to be in higher concentration on both electrode and in liquid samples, as compared to OC.

4. Discussion

Rapid and accurate online monitoring of VFA levels could be of great importance in the wastewater industry, environmental treatment processes and within the environmental regulatory framework to monitor effluent quality and to prevent the system imbalance. MFCs have many applications in addition to their main notional function of electricity generation. MFCs have the potential to be direct, quantitative sensors for BOD, microbial respiration (Tront et al., 2008), and on the strength of this work, VFAs. While the detailed design and performance specification of the MFC based VFA sensor are yet to be established, this study considers whether MFCs can be used to speciate VFAs and measure their concentrations. Such information measured at low cost and continually on-line, may be of considerable significance to the control and monitoring of AD and other bioprocesses. Monitoring of VFAs may be achieved cost effectively by using the MFC technology and may be suitable for preventing susceptible systems from seeing adverse effects from high VFA concentrations. We have investigated coulombic efficiency and cyclic voltammetric methods to measure the concentration of VFAs in known samples. Also, the enhanced degradation of propionate and butyrate with electrodes as terminal electron acceptor was studied as a mechanism for removing the thermodynamically unfavourable fermentation end-products in MFCs.

Enrichment of MFCs is required to establish electrogenic functionality. Enrichment was conducted with acetate, propionate and butyrate and took different lengths of time as shown in Fig. 1, but enrichment time is not related to time required for measurement. Propionate and butyrate degradations has been known to be thermodynamically less favourable as compared to acetate degradation (Stams et al., 1992). This lag period of 3 weeks for propionate and butyrate could be due to the establishment of different metabolic pathways for degradation of propionate and butyrate which may involve syntropism between bacterial species and which may take some time to develop because they are thermodynamically less favourable than acetate degradation by electrogens.

In order to quantify the concentration of VFAs in solution using MFC methods, there are several options, two of which might be: peak voltage and/or electrochemical analysis of peak current in relation to VFA concentrations; and quantification of charge recovered from the specific VFA dose. The higher the concentration of the VFA in the sample, the longer the MFC takes to consume the substrate, at a static electrical loading. The full recovery of charge for low concentration samples for example, was relatively short (within 2 h) while the sample with VFA concentration $>20\ mg\ l^{-1}$ took significantly longer (about 20 h). Therefore the analysis of concentration based on charge recovered might delay measurements and would not be the most applicable approach to *in-situ* monitoring for VFAs. High strength samples may therefore have to be diluted, then introduced to a small chambered MFC based sensor, to analyse the sample within a reasonable time.

In contrast to coulombic efficiency, voltage response induced from bacterial degradation of specific VFAs for the measurement of VFA concentration was significantly faster in the range of several minutes for the analysis to be completed. Coulombic efficiency and cyclic voltammetry (Fig. 2) showed linearity over a range of concentrations of VFAs and the current produced (Fig. 3). Therefore, they may provide appropriate data to compensate for each other's deficiencies in order to derive quantitative speciated VFA measurements. Table 1 presents discrimination between VFAs; specificity and cross sensitivity of the bacterial community towards VFAs can be inferred from these results. The metabolic pathway used in the oxidation of recalcitrant fermentation end products such as propionate and butyrate, known to be difficult to degrade in bioprocesses, was investigated in these bioelectrochemical systems. In this study, OC and CC operations reveal that the MFC technology can be used to overcome thermodynamic hurdles which normally require syntrophic methanogenesis to proceed. It is suggested that propionate and butyrate can be more efficiently degraded in MFCs, compared to the syntrophic degradation in an anaerobic digester. The metabolic pathway for degradation of propionate and butyrate is very much affected by an electrode reaction, as shown in Figs. 4 and 5, which could overcome the effects of VFA accumulation in e.g., an anaerobic digester. DGGE analysis results suggest that the microbial community is not affected by the OC or CC operation, but the biocatalyst can change its metabolic pathways delivering faster degradation of propionate and butyrate in an MFC.

Although cyclic voltammetry has not yet provided comprehensive calibration information on VFA species and concentrations, the data presented in this paper does indicate qualitative features for analysis of VFAs, with plausible quantitative analysis in particular circumstances. Qualitative analysis may be possible on the basis of different current responses from different VFA enriched reactors; and quantitative analysis could be achieved within a defined range of VFA concentrations. Also, by increasing the degradation of VFAs in CC operation, an MFC could be used as a sensor to quantify and discriminate between different concentrations of VFAs. This provides a promising basis for the development of a VFA sensor, indicating that the current response to particular VFA concentrations may be interpreted, calibrated and maintained over time and from instrument to instrument.

The result obtained from DNA analysis shown in Table 1 indicates a predisposition of the microbial community to be in solution when there is no current flowing and no terminal electron acceptance from the electrode. However, this phenomenon varies for different species of VFAs. For example, propionate shows a reversed result from that of acetate and butyrate enriched cells. Further investigations of biofilm metabolic capability toward VFAs might increase understanding and applicability of the MFC type biosensor for the measurement of VFAs.

These results are encouraging and demonstrate the possibility of practical application of the MFC technology in VFA sensing. Further work is needed to enhance the current to VFA sensitivity of the MFC sensing discussed.

5. Conclusions

On the basis of the results obtained from this study it is suggested that an acclimated mixed community can be operated stably in an MFC and could be used as a basis of offline or on-line VFA monitor. MFCs can be enriched with different VFAs and the acclimatized fuel cells can be used to monitor the VFA concentrations over a limited range. Coulombic efficiency and cyclic voltammetric methods were found to represent good measures for detecting VFA concentrations between certain limit and qualitatively discriminating between the VFA species, although the former would require excessive sampling times. Also, the enhanced degradation rate of propionate and butyrate in closed circuit operation would be advantageous for VFA sensing and indeed as a mechanism for organic contaminant removal. However, further advances are needed in the MFC sensor design and configuration in order to achieve a practical technology for application in bioprocess and effluent metrology.

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