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Operation of a bioelectrochemical system as a polishing stage for the effluent from a two-stage biohydrogen and biomethane production process

Katrin R. Fradler^a, Jung Rae Kim^b, G. Shipley^a, J. Massanet-Nicolau^a, Richard M. Dinsdale^a, Alan J. Guwy^a, Giuliano C. Premier^a,*

^a Sustainable Environment Research Centre (SERC), Faculty of Computing, Engineering and Science, University of South Wales, Pontypridd, Mid-Glamorgan, CF37 1DL, UK
^b School of Chemical and Biomolecular Engineering, Pusan National University (PNU), Busan, 609-735, South Korea

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A B S T R A C T

Anaerobic bioenergy production processes including fermentative biohydrogen (BioH2), anaerobic digestion (AD) and bioelectrochemical system have been investigated for converting municipal waste or various biomass feedstock to useful energy carriers. However, the performance of a microbial fuel cell (MFC) fed on the effluent from a two-stage biogas production process has not yet been investigated extensively in continuous reactor operation on complex substrates. In this study we have investigated the extent to which a microbial fuel cell (MFC) can reduce COD and recover further energy from the effluent of a two-stage biohydrogen and biomethane system. The performance of a four-module tubular MFC was determined at six different organic loadings (0.036–6.149 g\text{COD} L\text{−1} d\text{−1}) in terms of power generation, COD removal efficiency, coulombic efficiency (CE) and energy conversion efficiency (ECE). A power density of 3.1 W m\text{−3} was observed at the OLR = 0.572 g\text{COD} L\text{−1} d\text{−1}, which resulted in the highest CE (60%) and ECE (0.8%), but the COD removal efficiency decreased at higher organic loading rates (35.1–4.4%). The energy recovery was 92.95 L\text{−1} and the energy conversion efficiency, based on total influent COD was found to be 0.48–0.81% at 0.572 g\text{COD} L\text{−1} d\text{−1}. However, the energy recovery by the MFC is only reported for a four-module reactor and improved performance can be expected with an extended module count, as chemical energy remained available for further electrogenesis.

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1. Introduction

The environmental benefits of sustainable waste management with simultaneous energy recovery have been discussed widely in the literature and have motivated efforts to develop effective processes to recover bioenergy from waste. The polishing of effluents derived from wastewater treatment processes such as anaerobic bioprocesses, with the collateral intention of converting COD to useful power and maximizing the recovery of the chemical energy are essential environmental and economic considerations. The reduction of environmental impacts by removing pollution potential, reusing water and sustainably producing bioenergy from waste/wastewater treatment processes, has been rising in importance worldwide, with the adoption of more stringent regulations. For example, the EU has published a roadmap [1] on carbon abatement to 2015 and several directives including Renewable Energy (2009/28/EC), Landfill (1999/31/EC), Water Framework (2000/60/EC) and Urban Wastewater (91/271/EEC) have impinged on such process development.

Anaerobic systems such as anaerobic digestion (AD) or biomethane (BioCH₄) and biohydrogen (BioH₂) will generally discharge effluents which are still burdened with relatively high concentrations of organic contaminants. The soluble components of these contaminants include several volatile fatty acids (VFAs), which are odorous and increase biological oxygen demand (BOD) in the receiving environment. Post-processing to remove contaminants and/or realise this energy potential would be desirable; and would benefit from appropriate technologies [2]. The performance of two-stage anaerobic processes have been widely studied by several research groups and are known to provide potential to increase conversion efficiency over single stage processes [3–6].
Biohydrogen (a mixture of BioH₂ and BioCH₄) production from two-stage fermentation is of rising interest for the valorisation of waste biomass by generating gaseous biofuel. Furthermore, the combined use of biohydrogen and biomethane is a promising approach to displacing fossil energy sources [7]. The context [2], and degree to which VFAs and other components in synthetic wastewater can be removed in multi-modular MFC system have been considered [8]. However, the performance of, and energy recovery from MFC systems using real effluent from two-stage AD and BioH₂ have not yet been investigated. Several studies have shown increased bioelectricity generation by using pre-fermented wastewaters in MFCs [9]. Microbial fuel cells were linked to a hydrogen fermenter fed on food processing wastewaters [10] or vegetable waste [11]. Recently Sharma and Li combined an anaerobic BioH₂ fermenter, continuously fed with synthetic glucose wastewater with a MFC [12]. In this context it is noteworthy that the removal of nutrients is a significant issue in dealing with AD effluent. However, this is less significant when considering wheatfeed as the substrate to the preceding BioCH₄/BioH₂ processes. Nutrient retention for recycling to land as fertiliser may be of greater interest with biomass energy crops. Studies have shown, that nitrification and denitrification [13–16] as well as sulfate [17] and sulfite [18] removal can be carried out in bioelectrochemical systems.

To the author’s knowledge the combination of a realistically scalable MFC reactor with a two-stage biogas producing system has been recently proposed [19], but has not yet been investigated. In this work the effluent from a sequentially connected hydrogen fermenter (BioH₂) and methanogenic reactor (BioCH₄) system was introduced to a MFC to determine its ability to polish the effluent at low organic loading. Massanet-Nicolau et al. [20] have shown that the two-stage process increased the methane yield by 37% compared to the single stage fermentation. To further reduce effluent COD and increase the energy recovery from wheatfeed pellets fed to the system, a tubular four-module MFC reactor was fed with the two-stage effluent at different OLRs in the study reported here. The effects of changing OLRs on the performance of the tubular four-module MFC were investigated and power production was determined. Coulombic efficiency, COD removal efficiency and energy conversion efficiency were determined on the basis of the MFC’s influent COD concentration and COD removal

2. Materials and methods

A tubular axial flow MFC was operated on the effluent of a two-stage biogas process in order to investigate the suitability of the two-stage effluent as a substrate for BES and to investigate the effectiveness of the oxidation reactions in the anode chamber, albeit in the context of an MFC.

2.1. Microbial fuel cell (MFC) construction and operation

The two-stage BioH₂ and BioCH₄ reactors were operated in series hydraulically, as described in the previous report [20]. The BioH₂/BioCH₄ effluent was fed to a longitudinal tubular reactor with four MFC modules (each module of 0.25 L) as previously reported [8,21]. The complete three stage system is illustrated in Fig. 1. The carbon veil anodes (230 × 450 mm per module; PRF Carbon, UK) were spirally rolled around a perspex cylinder of diameter 1 cm. The membrane electrode assembly was made from a cation exchange membrane (CMI-7000, Membrane International Inc.; 122 × 192 mm) assembled with a carbon cloth (163 × 82 mm) cathode containing 0.5 mg cm⁻² Pt. The modules were separated by ballast and orifice plates, to maintain a degree of compartmentalisation in the tubular MFC. The reactor was inoculated with anaerobic digester sludge (1:10); 40 mM acetate in 50 mM phosphate buffer, vitamins and minerals. After batch start-up, the MFC reactor was inclined (30°) and operated continuously at five different organic loading rates (OLRs). The effluent from the anaerobic digester was filtered through a stainless steel sieve to exclude particles larger than 0.21 mm. The composition of the filtered effluent determined on a daily basis varied and contained on average 3.300 g COD L⁻¹, 2.500 g sCOD L⁻¹, 0.080 g L⁻¹ acetic acid, 0.030 g L⁻¹ butyric acid; a pH of 7.7 and a conductivity of 12.9 mS cm⁻¹. Different OLRs (0.036; 0.053; 0.086; 0.337; 0.572 g sCOD L⁻¹ d⁻¹) designated OLR1 to OLR5, respectively) were maintained by dilution of the filtered BioH₂/BioCH₄ reactor effluent. The undiluted filtered effluent from the BioCH₄ reactor at the end of the experiment was higher in sCOD (6.149 g sCOD L⁻¹) and resulted in an organic loading rate of 4.427 g sCOD L⁻¹ d⁻¹, which was also supplied to the MFC reactor (see Fig. 3b and Fig. 4). The MFC influent was kept refrigerated and was introduced to the tubular reactor at a rate of 0.5 mL min⁻¹ through an external peristaltic pump (Watson and Marlow, Falmouth, UK). The constant flow rate lead to a hydraulic retention time (HRT) of 33.3 h for the whole reactor or 8.3 h for each module, respectively.

![Fig. 1. 10L hydrogen fermenter, anaerobic digester (V>25L) and tubular MFCs.](Image)

![Fig. 2. Voltage generation from each module at different OLRs (0.036–0.572 g sCOD L⁻¹ d⁻¹).](Image)
independently connected in series to resistors ($R = 1000\, \Omega$) and operated at room temperature ($20 \pm 4\, ^\circ\mathrm{C}$).

2.2. Analyses

The voltage output across the load of each MFC module was monitored at 10 min intervals using a virtual instrument module coded in LabVIEW™ software (National Instruments). After three HRTs samples were taken from the influent and from the end of every module, using a syringe. The pH value (pH meter, Mettler Toledo Inc.: Urdorf, Switzerland) and the conductivity (737 Conductivity meter; Mettler Toledo Inc.: Urdorf, Switzerland) were determined before the liquid samples were acidified (HCl, 12 M) and preserved frozen. Before analysing the sCOD content with a standard method (Methode 5220, HACH COD system, Loveland, CO, USA) the defrosted samples were centrifuged at 12,000 rpm for 3 min. Volatile fatty acids (VFAs) where assayed using a gas chromatograph (Perkin Elmer Clarus 500 GC). Power curves were determined using a potentiostatic method using a Solartron 1287 Electrochemical Interface (Amatek–Solartron Analytical; Farnborough, UK). The power measurements were carried out after three HRTs and the potential was changed after a stable value was observed (approx. 10 min).

The coulombic efficiency (CE) and COD removal efficiency were calculated according to methods previously reported [22]. The energy production per COD consumed ($E_{\text{COD}}\, \text{Wh g sCOD}^{-1}$ consumed) was calculated at each OLR and was based on the measured MFC potential and the COD consumption measured after three hydraulic retention times (99.9 h).

$$E_{\text{COD}} = \frac{\sum_{i=1}^{4} \int_{0}^{t_i} E_{MFC} \times i_{\text{dt}}}{\Delta \text{COD} \times V_{\text{rec}}}$$

(1)

where $E_{\text{MFC}}$ is the observed MFC potential (V) after three retention times, $t_i$ is the current (A) integrated over one retention time, $t_i$ (8.3 h) and the four modules, $i = 1$ to 4; $V_{\text{rec}}$ represents the whole reactor volume (1 L) and $\Delta \text{COD}$ is the difference between the influent and the effluent (4th module). The recovered energy from MFC modules ($E_R$) is

$$E_R = \frac{\sum_{i=1}^{4} \int_{0}^{t_i} E_{MFC} \times i_{\text{dt}}}{\Delta \text{COD} \times V_{\text{rec}}}$$

(2)

$E_R$ ($\text{J L}^{-1}$) over the entire reactor lengths was calculated by using the voltage $E_{\text{MFC max}}$ and current $i_{max}$ at the maximum power production, determined from the polarisation test. The energy conversion efficiency (ECE) was calculated on the basis of the total influent energy content (ECE$_{\text{total COD}}$) and on the basis of the energy content of the consumed COD (ECE$_{\text{ACOD}}$). The published heat of combustion values for wastewater varies over a broad range of 13.89 to 28.7 MJ kg COD$^{-1}$, due to different compositions and measurement methods [23–25]. Therefore the energy conversion efficiencies (ECE$_{\text{total COD}}$, ECE$_{\text{ACOD}}$) were estimated using two values which represented plausible upper and lower estimation limits; $a = 13.89\, \text{MJ kg COD}^{-1}$ [23] and $a = 23.25\, \text{MJ kg COD}^{-1}$, which represents the average of two heat of combustion values for different waste wasters after having been freeze dried, calculated using the COD, as reported by Heidrich et al. [24].

$$\text{ECE}_{\text{total COD}} = \frac{E_R}{E_{\text{inf}}} = \frac{\sum_{i=1}^{4} \int_{0}^{t_i} E_{MFC} \times i_{\text{dt}}}{a \times \text{COD}_{\text{inf}}} \times 100 \quad (3)$$

$$\text{ECE}_{\text{ACOD}} = \frac{E_R}{E_{\text{COD}}} = \frac{\sum_{i=1}^{4} \int_{0}^{t_i} E_{MFC} \times i_{\text{dt}}}{a \times \Delta \text{COD}} \times 100 \quad (4)$$

A pseudo-half saturation constant $K_s$ was calculated by fitting Monod-like kinetics (using SigmaPlot™ 10.0) to the plot of scOD concentration $S$ (g scOD L$^{-1}$) vs. average current $i$ (mA) in the four modules, according to $I = I_{max} \left(S/K_s + S \right)$. The fit from which $K_s$ was determined was shown to have 95% confidence and $R^2 = 0.92$.

3. Results and discussion

3.1. Voltage development at different organic loading rates

Fig. 2 shows the response of voltage generation for each of the four modules to changes in the OLRs (0.036–0.572 g scOD L$^{-1}$ d$^{-1}$) while under constant load resistances ($R = 1000 \, \Omega$). The voltage progressively increased, responding within one retention time from module 1 to 4 as OLR was increased. The average MFC voltage decreased as location along the reactor lengths increased. This was attributed to the depleting organic concentrations reaching successive modules. The two lowest OLRs (0.036 and 0.053 g scOD L$^{-1}$ d$^{-1}$) resulted in no significant changes in MFC output voltage, apart from in module four. The fact that the voltage output in this module was virtually zero during operation at OLR1 indicates there were low concentration of degradable substrate
(e.g. VFAs) and/or limited mass transport from the bulk liquid to the biofilm/electrode. It is likely that available substrates such as acetate and butyrate were largely depleted in preceding modules. The effluent from the 4th module still contained 32 mg L\(^{-1}\) sCOD at OLR1 (0.036 g sCOD L\(^{-1}\) d\(^{-1}\)) and might be expected to convert this COD to electrical energy, but this organic content may not represent available organic compounds suitable for bioelectricity generation under the operation conditions of the experiment. The effluent from the preceding two-stage BioH\(_2\)/BioCH\(_4\) process contained recalcitrant or non-biodegradable organic compounds e.g. non-utilizable or structurally bound carbohydrates including holocellulose, hemicelluloses, α-cellulose, lignin and protein and conceivably even starch. These residual organic components may in part become available through hydrolytic, chemical or physical degradation processes, should additional MFC modules and capacity be attached in the third stage.

3.2. Power production in the 4-module tubular MFC reactor

Table A.1 presents the volumetric power densities determined after three retention times for each module at the five different OLRs. It can be seen that the maximum volumetric power density (MVPD) correlates to increasing OLR and decreases with increasing module numbers, i.e. distance along the reactor length. The highest MVPD for each module was observed at OLR5 (2.3–3.4 W m\(^{-3}\)). Furthermore the power curves measured while feeding the undiluted AD-effluent showed that the MVPD of each module could be increased further to 5.5 W m\(^{-3}\) (data not presented). A similar reactor with only two modules was shown to achieve an output power of 1.35 mW in the 1st module when fed with a synthetic sucrose wastewater at 0.41 g sCOD L\(^{-1}\) d\(^{-1}\) [8]. These results indicate, that operation on BioH\(_2\)/BioCH\(_4\) effluent resulted in a moderate reduction in power with respect to OLR and compared to the synthetic sucrose wastewater, as an OLR of 0.57 g sCOD L\(^{-1}\) d\(^{-1}\) generated 0.82 mW.

Table A.1 also shows that the power produced in the final module increases disproportionally when the OLR is increased from 0.34 to 0.57 g sCOD L\(^{-1}\) d\(^{-1}\). This is probably attributable to an increased availability of utilizable substrate. In addition, the conductivity increased with increasing influent OLRs (0.44 to 3.98 mS cm\(^{-1}\)) by virtue of reduced dilution, so contributing to the higher power output through reduced internal ohmic losses. This is also reflected in the internal resistance, which is implicated in these ohmic losses. However, internal resistance may include a dilution derived component from reduced mass transfer resulting from diminished concentration gradients, which would drive the utilizable substrate mass transfer to the biofilm.

It should be noted that the process of diluting the influent to the MFC reactor in order to vary the OLR, significantly affected the conductivity (see Table A.1). If the effluent from the preceding BioH\(_2\)/BioCH\(_4\) process were to be treated directly in a scaled-up multi-module tubular MFC reactor without dilution, the conductivity would not undergo such significant reduction. Therefore, a stacked multi-modular system has the potential to achieve higher power densities than those reported here, because it should present lower internal ohmic resistance, as indicated in Table A.1.

3.3. COD removal efficiency of the bioelectrochemical MFC system

Fig. 3a presents the CE and the COD removal efficiency achieved by the longitudinal tubular MFC and the MFC’s dependence on the influent organic loading. It can be seen that the COD removal efficiency tends to decrease with increasing reactor OLR, whereas the CE shows the opposite trend when using the BioH\(_2\)/BioCH\(_4\) process effluent. At the lowest OLR (0.036 g sCOD L\(^{-1}\) d\(^{-1}\)) the COD was reduced by 35.1% through the four-module MFC reactor system. Even though the volume specific COD removal increased in absolute terms, only 4.4% (37 mg sCOD) were removed at the highest OLR. The same reactor configuration fed with synthetic sucrose wastewater at 0.08–0.8 g COD L\(^{-1}\) d\(^{-1}\) reached COD removal efficiencies of 93–43% [21]. These results indicate that a tubular reactor fed with BioH\(_2\)/BioCH\(_4\) effluent requires more modules (i.e. a longer tubular system) to achieve efficient polishing, compared to the same reactor fed with sucrose, particularly at high COD influent concentrations. The trend towards lower removal efficiencies at higher organic loading has been observed in several studies where MFCs were fed with domestic wastewater [26], swine wastewater [27], or the effluent of an hydrogen biofermenter [12].

3.4. Coulombic efficiency and pseudo-half saturation constant \(K_s\)

CEs of less than 10% were observed at the three lower OLRs, but CE increased to 42% and 60% for OLR4 (0.337 g COD L\(^{-1}\) d\(^{-1}\)) and 5 (0.572 g sCOD L\(^{-1}\) d\(^{-1}\)), respectively. The higher CEs achieved when processing the effluent from the wheatfeed fed BioH\(_2\)/BioCH\(_4\) were in fact higher than a comparable sucrose fed longitudinal tubular reactor with the same MFC configuration; as the highest CE obtained from 0.24 g sCOD L\(^{-1}\) d\(^{-1}\) sucrose feed, was 38–49% [8]. Other studies have demonstrated the dependance of CE on the substrate availability for electrogenesis. Min et al. reported that the CE with non-fermentable substrates such as acetate (CE = 65%) are much higher as they can be more directly consumed by electrogenic bacteria, whereas fermentable substrates such as starch or glucose resulted in significantly lower CEs of 21% and 14%, respectively [28].

As opposed to Fig. 3a, which focuses on the five lower OLRs (0.036–0.572 g sCOD L\(^{-1}\) d\(^{-1}\)), Fig. 3b includes the CE of the undiluted BioH\(_2\)/BioCH\(_4\) effluent at OLR = 4.427 g sCOD L\(^{-1}\) d\(^{-1}\), which resulted in a clearly lower CE of 3.6%. Furthermore, Fig. 3b summarizes previous studies conducted on MFCs operated in continuous mode, fed on more complex substrates such as sucrose wastewater [8,29], the effluent from fermentative hydrogen production [12,30], domestic wastewater [31] or wastewater from a primary clarifier [32], in various reactor configurations and organic loading rates, to give an overview and indicate trends. This summary of several continuous studies indicates, that high CEs are achieved at lower OLRs (<0.6 g COD L\(^{-1}\) d\(^{-1}\)). In particular, the results obtained from the tubular reactor operated in 4-module mode in this study, as well
as in 2-module mode fed on sucrose in a previous study [8], show that the CE increases to a maximum at low organic loading and after peaking, the tubular reactor results are comparable to the findings of other studies in continuous operation, i.e. CE decreases significantly at higher organic loading; from 59.8% (0.572 g scOD L−1 d−1) to the 3.6% previously mentioned, if operated with the undiluted effluent. In a study using effluent from hydrogen fermentation of coffee processing wastewater, the CE decreased from 0.98% (1.92 g COD L−1 d−1) to 0.3% (4.8 g COD L−1 d−1) [30] or from 5% (0.7 g COD L−1 d−1) to 1.5% (6.5 g COD L−1 d−1) [12]. However, Fig. 3b suggests that the maximum CE from system arrangements other than those reported here appear to occur over a narrower range of organic loading. The peak observed in the studies with the tubular MFC might be attributed to mass transfer limitations at very low substrate concentration; hence the substrate does not reach electrogenic bacteria, but may be degraded by anaerobic bacteria, such as methanogens in the solution.

Higher organic loading rates probably adversely affected the CE because more substrate is available for methanogenesis and other ‘side’ reactions such as extracellular enzymatic processes, polysaccharide deposition, direct oxidation and aerobic processes driven by oxygen ingress to the anodic chamber and alternative electron accepting process such as occur with nitrate- or sulphate reducing bacteria [29,33,34]. The concentration of available substrate for electrogens and microbial affinity towards the available substrate is of great importance so far as electrogens compete for the substrate with methanogens or any other bacterial processes. The pseudo-half saturation concentration Ks gives an indication of the substrate affinity of the electrogens, but one should consider that the substrate availability must be rate limiting in order to determine the Monod-like Ks values [35]. Therefore, the published Ks values are influenced by factors such as the load resistor used, electrolyte conductivity and the reactor configuration [31,36], along with other system specific parameters which makes direct comparison difficult. The pseudo-half saturation concentration for the 4-module tubular reactor fed on the BioH2/BioCH4 effluent, in a least squares fit with Monod-like kinetics, resulted in Ks = 446.6 mg COD L−1 (R = 1000 Ω), which is significantly higher than the Ks value obtained with sucrose in a very similar tubular system (Ks = 50 mg COD L−1; R = 150 Ω) [8]. The higher half saturation concentration for the complex BioH2/BioCH4 effluent indicates a lower affinity towards the less complex sucrose waste water. However, the higher external load may have contributed to the higher Ks value. As can be seen in Fig. 4, the saturation concentration for electrogens on the provided substrate is above 6000 mg scOD L−1. Mass transfer limitations at low organic loadings, which might have affected the determined pseudo-Ks value, cannot be excluded. Furthermore it has to be kept in mind that the Ks value based on COD provides only limited information on the composition and the ratio of easily degradable to complex carbohydrates, which is of higher importance for electrogens, known to preferentially consume VFAs.

The results from Fig. 3b suggest that a multi-modular tubular reactor fed on complex waste streams for COD removal which seeks to achieve predefined discharge limits; may not deliver consistently high CEs. Although power generation is not reduced in these modules, the high organic loading rate introduced in the first few modules makes a significant amount of substrate available for methanogenesis, even though the Ks value was found to be relatively high, because the BioH2/BioCH4 effluent itself contains methanogens and continually seeds the MFC with these microorganisms. Also, the diminishing substrate concentration with reactor length tends to disadvantage methanogenesis or other competitive reactions, as complex organic compounds are degraded to lower carbohydrates and VFAs which then progressively increase the CE, following the increasing dominance of the electrogenic activity. Controlling the competition between electrogenically active bacteria and hence the CE, has been reported; using other methods such as exposure to oxygen [37], low pH and temperature [38] or the addition of 2-bromoethanesulfonate [39]. However, these mechanisms become less relevant as the flow proceeds along the tubular reactor. In a multi-modular reactor, the CE will vary in each module according to the substrate availability to electrogenic bacteria and their corresponding affinity in contrast to methanogens etc. The degradation of complex organic compounds along the reactor and the decreasing dominance of methanogens should result in an increasing CE with reactor length.

3.5. The effect of the OLR on the energy efficiency of a tubular MFC

Table A.2 presents estimates of the energy recovered by the tubular MFC reactor; as well as energy recovered per COD consumed (E COD) and presents the energy conversion efficiencies (ECE). As expected, E COD increases with the OLR, as it is directly correlated to the CE. E COD reaches its highest value of 0.276 Wh g scOD−1 consumed at the highest organic loading rate of 0.572 g scOD L−1 d−1.

The energy produced or recovered (E R) from the MFC influent COD through the four-module reactor ranged from 0.33 to 92.95 J L−1, assuming that each module operated at its maximum power output for an entire HRT (8.3 h). Sharma and Li [12] achieved a higher energy recovery of 259 to 337 J L−1 with higher OLRs of 0.61 to 2.35 g COD L−1 d−1. However, in contrast to this study, a synthetic glucose feed was used and the two-stage process operated at a significantly smaller scale with 2 L biofermenter and 0.1 L MFC. They noted that a further increase in the organic loading also resulted in a lower energy recovery.

The energy conversion efficiencies were described in terms of total substrate energy available and energy consumed. ECE total COD calculated with respect to the total energy content of the influent; and ECEsCOD calculated in terms of energy content of the COD removed. ECEsCOD was between 0.08–0.14% at OLR1 and 10.9–18.24% at OLR5. The lower energy recovery at OLR1 is attributed to the substrate availability and non-electrogenic side reactions as indicated by the CE and discussed above. Furthermore, the ECEsCOD is suppressed by the energy necessary to maintain bacterial metabolism, which lowers the available portion of total theoretical Gibbs Free Energy from substrate oxidation. Schroeder [40] reported that direct electron transfer reactions result in a high CE but low energy conversion efficiency and suggested that theoretically only 54% of the total Gibbs Free Energy could be recovered from the oxidation of glucose; representing a high degree of energy dissipation. McCarthy et al. [41] reported that the losses to microbial growth, maintenance and carbohydrate conversion to CH4 in biomethanation are approximately 15%. Even if growth, maintenance and conversion losses from VFAs to electricity were lower in MFC, carbohydrate conversion would likely follow the estimates of McCarthy et al.

In this study, ECE has been based on the heat of combustion, which includes the non-biodegradable or recalcitrant fraction of the wheatfeed. This along with the losses previously mentioned, significantly affects the ECE. More accurate measures of the energy content of wastewater and feed stocks may be determined using calorimetry. ECEtotal COD lies between 0.03–0.05% (OLR 1) and 0.48–0.81% (OLR 5). As the energy conversion efficiency depends on the bio-degradability of the substrate, the values reported in Table A.2 are significantly lower than for less complex synthetic wastewater. Previous investigations resulted in much higher ECEs; for example, acetate (43%) compared to glucose (3%) in
batch mode [42] and 17% and 3% in continuous mode, respectively [28].

Higher ECEs may be expected if the tubular reactor system employed were extended by the addition of further modules, as the values reported here refer only to a four-module unit. In such a multi-modular reactor more complex organic matter may be further degraded to a substrate for which electrochemically active bacteria have greater affinity. This would however, be governed by the recalcitrance of the residual COD which has already passed through two biological process stages before the MFC. Furthermore, the liquid phase conductivity in the tubular system would not change significantly were dilution with water not used. Therefore, the ohmic losses would be expected to be lower, tending to positively impact on the ECE.

4. Conclusion

In this study a MFC was fed with five different low organic loading rates (0.036 to 0.574 gCOD L\(^{-1}\) d\(^{-1}\)) from a two stage anaerobic biohydrogen and biomethane process on wheatfeed to determine effluent polishing capacity and the energy conversion efficiency. The voltage development and power production in the MFC increased with the OLR and decreased within the four-module reactor according to their position along the reactor length. The COD removal efficiency was found to decrease with organic loading (35–4.4%) whereby the CE presents the opposite trend up to an organic loading of 0.574 gCOD L\(^{-1}\) d\(^{-1}\), but then decreases at higher organic loading, which is in accordance with other studies.

The energy conversion efficiency of the MFC, calculated with respect to the COD consumption (ΔCOD) over the four modules showed that the highest efficiency (\(E_{\text{ΔCOD}}\)) was in the range of 10.9–18.24% (OLR5) and as expected was higher than the energy recovery based on the total influent energy content (11.5–19.3 kJ L\(^{-1}\)), which resulted in 0.48–0.81% energy recovery. This study shows that MFCs can be used as an effluent polishing stage when fed with the effluent from a two stage anaerobic process fed on wheatfeed. However, the complexity of the waste to be treated requires more than the four modules used here, and non-biodegradable compounds might remain in the effluent.

The MFC performance in terms of the power production and energy recovery would be increased if the OLRs were not altered by dilution with tap water. Furthermore, the four modules of the MFC reactor did not deplete the available chemical energy and therefore higher recovery rates may be achieved in the event that the number of modules in the MFC reactor were to be extended.

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Appendix A. Appendices

Tables A.1 and A.2

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### Table A.1

MFC parameters during the continuous operation.

<table>
<thead>
<tr>
<th>OLR (g sCOD L(^{-1}) d(^{-1}))</th>
<th>pH (-)</th>
<th>conductivity (mS cm(^{-1}))</th>
<th>MVPD (W m(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Inf.</td>
<td>Eff.</td>
<td>1st module</td>
</tr>
<tr>
<td>OLR1</td>
<td>0.036</td>
<td>7.48</td>
<td>0.018 (4256)</td>
</tr>
<tr>
<td>OLR2</td>
<td>0.053</td>
<td>7.55</td>
<td>0.020 (3141)</td>
</tr>
<tr>
<td>OLR3</td>
<td>0.081</td>
<td>7.84</td>
<td>0.175 (913)</td>
</tr>
<tr>
<td>OLR4</td>
<td>0.337</td>
<td>8.45</td>
<td>2.370 (207)</td>
</tr>
<tr>
<td>OLR5</td>
<td>0.572</td>
<td>7.87</td>
<td>3.316 (109)</td>
</tr>
</tbody>
</table>

|                               | Eff.   |                        | 2nd module          |
| OLR1                          | 7.46   | 0.44                     | 0.010 (5904)        |
| OLR2                          | 7.46   | 0.74                     | 0.014 (6616)        |
| OLR3                          | 7.58   | 1.45                     | 0.136 (1834)        |
| OLR4                          | 7.65   | 2.68                     | 0.365 (439)         |
| OLR5                          | 7.45   | 3.98                     | 3.383 (106)         |

|                               |        |                          | 3rd module          |
|                               |        |                          | 3.388 (189)         |
|                               |        |                          | 2.307 (351)         |

|                               |        |                          | 4th module          |

\(\text{Inf. and Eff. stands for the influent and effluent pH and conductivity.}\)

\(\text{The internal resistance in ohm (Ω) obtained at the maximum volumetric power density (MVPD) is present in brackets next to the associated MVPD value.}\)

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### Table A.2

Energy production and efficiency in MFC.

<table>
<thead>
<tr>
<th>OLR (g sCOD L(^{-1}) d(^{-1}))</th>
<th>(E_{\text{COD}}) (Wh g sCOD(^{-1}\ \text{consumed})</th>
<th>(E_{\text{f}}) (JL(^{-1}))</th>
<th>(E_{\text{f}}) (JL(^{-1}))</th>
<th>(E_{\text{f}}) (JL(^{-1}))</th>
<th>(E_{\text{ΔCOD}}) (JL(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>OLR1</td>
<td>0.036</td>
<td>0.001</td>
<td>0.33</td>
<td>668–1147</td>
<td>0.03–0.05</td>
</tr>
<tr>
<td>OLR2</td>
<td>0.053</td>
<td>0.003</td>
<td>0.41</td>
<td>1028–1721</td>
<td>0.02–0.04</td>
</tr>
<tr>
<td>OLR3</td>
<td>0.081</td>
<td>0.004</td>
<td>2.96</td>
<td>1570–2627</td>
<td>0.11–0.19</td>
</tr>
<tr>
<td>OLR4</td>
<td>0.337</td>
<td>0.166</td>
<td>42.62</td>
<td>6994–11703</td>
<td>0.36–0.61</td>
</tr>
<tr>
<td>OLR5</td>
<td>0.572</td>
<td>0.276</td>
<td>92.95</td>
<td>11543–19313</td>
<td>0.48–0.81</td>
</tr>
</tbody>
</table>

|                               | ECE\(_{\text{total COD}}\) (%) | ECE\(_{\Delta\text{COD}}\) (%) |
| OLR1                          | 10.90–18.24                     | 0.08–0.14        |
| OLR2                          | 9.95–17.84                      | 0.12–0.20        |
| OLR3                          | 8.63–15.53                      | 0.43–0.73        |
| OLR4                          | 7.31–14.21                      | 5.29–8.85        |
| OLR5                          | 6.00–12.91                      | 5.29–8.85        |
References


[41] P.L. McCarty, J. Bae, J. Kim, Domestic wastewater treatment as a net energy producer—can this be achieved? Environmental Science & Technology 45 (2011) 7100–7106.