ENVIRONMENTAL BIOTECHNOLOGY

Production of hydrogen from domestic wastewater in a pilot-scale microbial electrolysis cell

E. S. Heidrich · J. Dolfing · K. Scott · S. R. Edwards · C. Jones · T. P. Curtis

Abstract Addressing the need to recover energy from the treatment of domestic wastewater, a 120-L microbial electrolysis cell was operated on site in Northern England, using raw domestic wastewater to produce virtually pure hydrogen gas (100 ± 6.4 %) for a period of over 3 months. The volumetric loading rate was 0.14 kg of chemical oxygen demand (COD) per cubic metre per day, just below the typical loading rates for activated sludge of 0.2–2 $kgCOD\,m^{-3}day^{-1}$, at an energetic cost of 2.3 kJ/gCOD, which is below the values for activated sludge 2.5–7.2 kJ/gCOD. The reactor produced an equivalent of 0.015 $LH_2\,L^{-1}day^{-1}$, and recovered around 70 % of the electrical energy input with a coulombic efficiency of 55 %. Although the reactor did not reach the breakeven point of 100 % electrical energy recovery and COD removal was limited, improved hydrogen capture and reactor design could increase the performance levels substantially. Importantly, for the first time, a 'proof of concept' has been made, showing that this technology is capable of energy capture as hydrogen gas from low strength domestic wastewaters at ambient temperatures.

Keywords Microbial electrolysis cell · Hydrogen · Wastewater · Energy

E. S. Heidrich (✉) · J. Dolfing · S. R. Edwards · T. P. Curtis
School of Civil Engineering and Geosciences, Newcastle University,
Newcastle upon Tyne NE1 7RU, UK
e-mail: elizabeth.heidrich@ncl.ac.uk

K. Scott
School of Chemical Engineering and Advanced Materials,
Newcastle University,
Newcastle upon Tyne NE1 7RU, UK

C. Jones
Northumbrian Water Ltd.,
Durham DH1 5FJ, UK

Introduction

In an era of increasing energy costs and environmental awareness, wastewater treatment industries need to look at alternative treatment options to reduce their net energy expenditure. It has been estimated that domestic wastewater alone may contain 17.8 kJ/g of chemical oxygen demand (COD) of energy (Heidrich et al. 2011). There is an increasingly urgent need to recover some of this energy, or at the very least not expend additional energy on treatment; the activated sludge process uses 2.5–7.2 kJ/gCOD (Pant et al. 2011). Energy recovery could be achieved through anaerobic digestion to methane gas or microbial fuel cell technology directly to electricity; however, life cycle assessment has shown that the production of a higher value product through the suite of bioelectrochemical systems may be the most viable solution (Foley et al. 2010). One such technology is the production of hydrogen in a microbial electrolysis cell (MEC) (Rozendal et al. 2006).

Since the MEC process was first reported (Liu et al. 2005; Rozendal et al. 2006), MECs have emerged as a potential option for a new generation of wastewater treatment systems (Rozendal et al. 2008a; Foley et al. 2010; Oh et al. 2010). In an MEC, bacteria use the energy stored in the organic compounds to metabolise and grow, donating electrons to an electrode which then travel in a circuit to the cathode producing current (Rozendal et al. 2006; Logan 2009). Oxygen is excluded from the cathode, and additional power is supplied to the circuit allowing endergonic reactions to take place, generating products such as hydrogen gas (Liu et al. 2005) and hydrogen peroxide (Rozendal et al. 2009). The added potential at the cathode must overcome the overpotentials in the system and supply the additional energy needed for the reaction to proceed. For example, to convert acetate into hydrogen in a microbial electrolysis, the theoretical voltage required is 0.14 V, in practice between 0.4 and 0.9 V are needed (Logan 2008).

There are many hurdles to overcome if microbial fuel cell technologies are to offer a sustainable future for wastewater treatment (Pant et al. 2012). Progress is being made with new reactor design (Call and Logan 2008; Rozendal et al. 2008b; Cheng and Logan 2011; Wang et al. 2011), improved materials (Cheng et al. 2006; Cheng and Logan 2008; Zhang et al. 2010; Fan et al. 2011; Sleutels et al. 2011; Zhang et al. 2011), greater understanding of the electrochemical mechanisms involved (Aelterman et al. 2008; Clauwaert et al. 2008; Wang et al. 2010; Aboutalebi et al. 2011; Kiely et al. 2011a; Villano et al. 2011) and even improved understanding of the microbes that are at work in these systems (Holmes et al. 2004; Kim et al. 2004; Rabaey et al. 2004; Lovley 2008; Bretschger et al. 2010; Kiely et al. 2011b; Lu et al. 2011; Villano et al. 2011). Many problems have been overcome, such as using multi electrode systems (Rader and Logan 2010) and finding a low-cost alternative to the platinum cathode (Zhang et al. 2010). However, most of this research is performed at laboratory scale, using simple substrates, often at a controlled warm temperature. Although of great value in improving our understanding of MECs, these studies do not tell us about the challenges or even benefits of running such systems at a larger scale with real wastewaters in temperate climates. There is a need to demonstrate that these systems can work at a larger scale and under realistic conditions, elevating the technology from a laboratory curiosity into a practical solution to a global environmental problem.

The only previous published pilot-scale MEC study to date is by Cusick et al. (2011) using a 1,000-L pilot-scale reactor run on winery wastewater in California. The reactor proved slow to start up, with pH and temperature control being problematic. When these issues were corrected by heating to 31 °C, controlling the pH and adding acetic acid, the reactor did improve in performance in terms of current generation; however, CH_4 rather than H_2 was produced. Calculations indicated the CH_4 production was likely to be independent of the current generation. The energy content of the CH_4 formed during the operation exceeded the input of electrical energy (heating not included), but only trace amounts of hydrogen were measured. Methane production was attributed to the reactor being membraneless, allowing hydrogen produced at the cathode to be directly consumed by hydrogenotrophic methanogens within the reactor (Cusick et al. 2011). The study has provided valuable insights into the operation of MECs; however, it has not provided a proof of concept that real, un-supplemented wastewaters can be used to produce H_2 gas at ambient temperature.

To test whether MEC systems have a chance of achieving these goals under realistic conditions, a pilot-scale 120-L reactor was placed on a wastewater treatment site in North East England. This site takes in primarily domestic wastewater

with an average influent total COD of 450 mg/L. The reactor was built using low-cost alternatives to the standard lab materials used for the cathode and membrane. It was run on influent domestic wastewater which after the initial acclimatisation period was not supplemented with acetate, or pH controlled. The reactor was not heated, held inside a large unheated building, and run throughout a UK spring and summer (5–20 °C minimum and maximum temperatures) and is still in operation at the time of writing this paper. These operating conditions are likely therefore to represent close to a worst case scenario, i.e. low-concentration feed, non-optimal components, no heating and no additional supplement of acetate or buffering capacity. The aim of this study was to establish reactor operation, forming a proof of concept for this technology.

Materials and methods

Field site

The pilot-scale reactor was set up and run at Howdon wastewater treatment site, Northumbrian Water Ltd, situated in the city of Newcastle Upon-Tyne in the North East of England (54°58′N, 01°36′W). An average of 246,500 m³ of domestic wastewater is treated daily at this site using 96 MWh; the activated sludge process uses around 60 % of this. The wastewater used in the MEC was taken from the grit channels after primary screening but before settling.

MEC reactor

The reactor was based on a cassette style design, with six identical cassettes being placed into a rectangular polypropylene tank with a total working volume of 120 L as shown in Fig. 1. The tank has a Perspex plate fitted over the liquid layer giving a small head room to the anode compartment of 2.2 L. Each of the cathode gas tubes from the cassettes projected above this Perspex sheet. The cassettes were set along alternate sides of the reactor to allow S-shaped flow and, once in place, gave a final anode volume of 88 L.

Each cassette was constructed using 10-mm-thick plastic sheeting and consisted of an internal cathode section of 0.280×0.200×0.048 m deep, with a volume of 2.6 L. The cathode section was filled with 50 mM pH 7 phosphate buffer which was not replenished during the course of the trial. The cathode material was stainless steel wire wool grade 1 (Merlin, UK), 20 g was used in each cathode, giving a projected cathode surface area for each electrode of 0.056 m². A 0.8-m length of stainless steel wire was wound several times into the wire wool to make a firm electrical connection and then to the outside of the cell. Each cathode electrical assembly had an internal resistance from the

Fig. 1 Schematic diagram of the reactor module components: *a* PVC outer frame, *b* wire wool cathode, *c* Rhinohide membrane fixed around a PVC frame, *d* stainless steel wire mesh and *e* anode with wire mesh current collector. These components fit together to form a single module (*f*), and six of these go into the reactor vessel where wastewater flows around them. Gas is collected through tubing into a gas bag


(d)　(e)　(d)　(c)　(a)　(b)　(c)　(d)　(e)　(d)

(f)
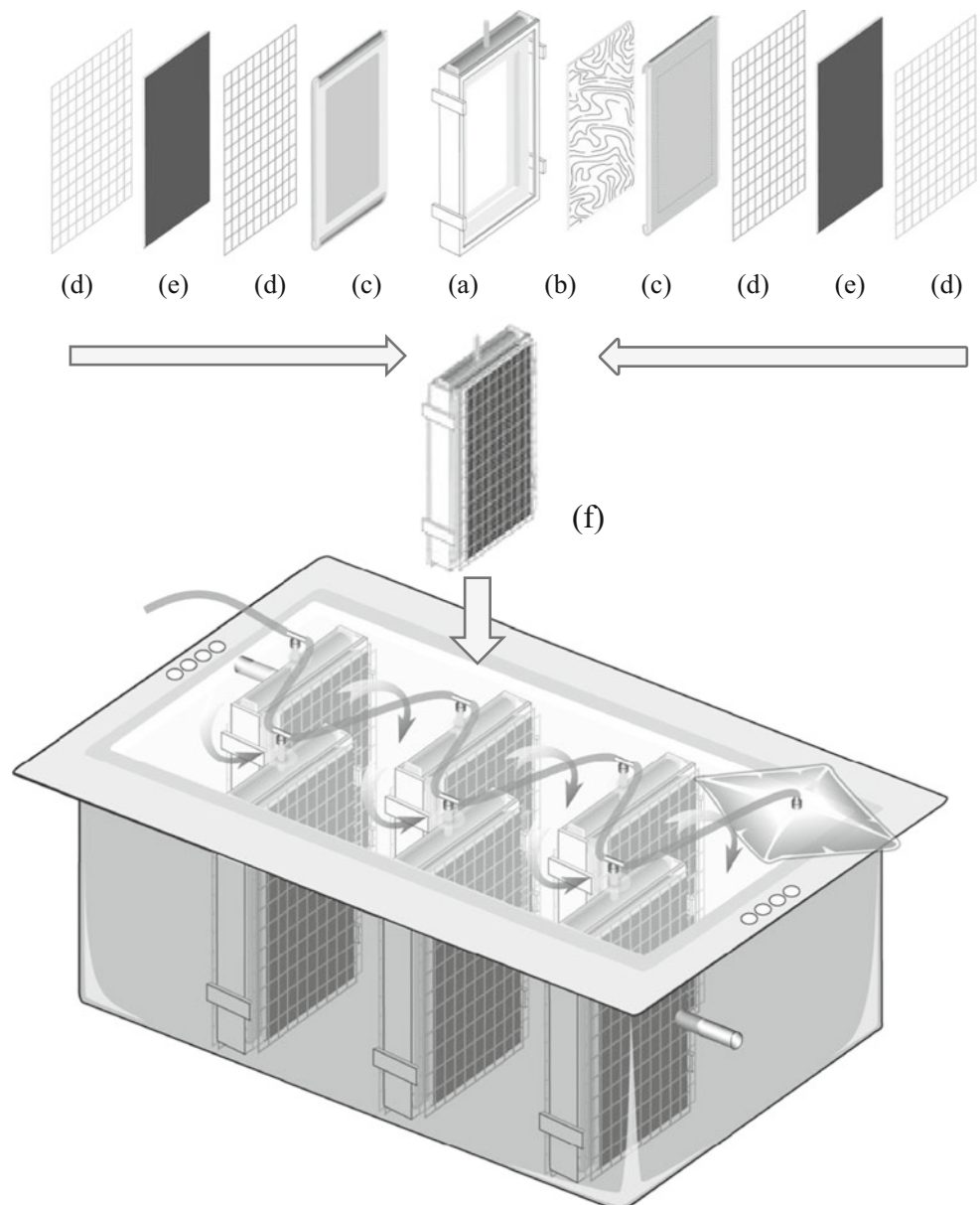
extremities of the wire wool to the end of the exposed wire of less than 2.75 Ω. The cathode was separated using a membrane wrapped around a plastic frame inserted into the electrode assembly on both sides. The membrane used was RhinoHide (Entek Ltd., UK), a durable low-cost microporous membrane typically used as a battery separator. The anode material was a sheet of carbon felt (Olmec Advanced Materials Ltd., UK), 0.2 m wide by 0.3 m high and 10 mm thick. This was sandwiched between two sheets of stainless steel mesh acting as a current collector. The anode assemblies were also connected by a 0.8-m length of stainless steel wire fed through the centre of the felt material, each electrode having an internal resistance less than 3.4 Ω. This electrode assembly is shown in Fig. 2. This gave an anode electrode surface area to reactor volume ratio of 16.4 m^2/m^3.

The total material cost of the reactor, not including pumps, power supply and data logging instruments, was equivalent to £2,344/m^3, of which the cathode and membrane combined represented less than 2 %.

The reactor was situated on site in a large unheated building housing the grit channels seen in Fig. 3. During operation, a peristaltic pump (Watson Marlow 520S, Watson and Marlow, UK) was used to pump water into a preliminary storage tank providing some primary settling. The wastewater then flowed from the top of the settling tank into bottom of the reactor, through the reactor in an S-like flow and back out to the grit channels. The wastewater was pumped at a rate to give a hydraulic retention time (HRT) of 1 day. Two small polypropylene sampling vessels, 0.5 L in size and fitted with dissolved oxygen (DO), pH and temperature probes, were placed one between the settling tank and main reactor,

Fig. 2 Photographs of the electrode assembly: **a** PVC outer frame, **b** wire wool cathode, **c** Rhinohide membrane and **d** anode with wire mesh current collector
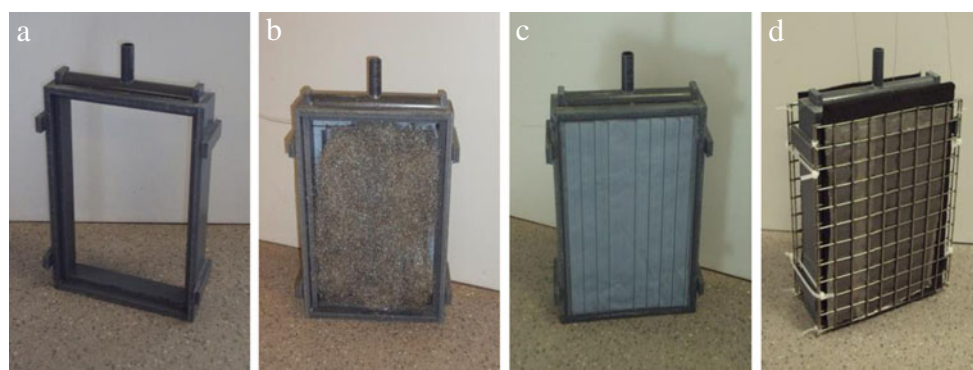
the other at the effluent of the reactor. All wastewater samples were taken from these sampling vessels.

The gas production from the anode compartment was captured from the ports in the Perspex lid, using 3 mm ID PVC tubing (VWR Jencons, UK). The cathode gas was initially captured using 4-mm annealed copper gas chromatograph (GC) tubing connected to each cathode compartment using copper compression fittings, (Hamilton Gas Products Ltd, Northern Ireland), but due to rapid corrosion, this was later replaced by 3 mm ID PVC tubing (VWR, UK). Both pipelines contained a gas sampling port.

Analytical procedures

Power was provided to the electrodes using a PSM 2/2A power supply (Caltek Industrial Ltd., Hong Kong); the voltage of each cassette was monitored across a 0.1 Ω Multi-comp Resistor (Farnell Ltd., UK) using a Pico AC-16 Data Logger (Pico Technology, UK) and recorded on a computer every 30 min.

In both the influent settling tank and the effluent tank, the DO and pH were measured using pH and DO submersion probes (Broadley James Corporation, USA) connected to a pH DO transmitter (Model 30, Broadley James Corporation, USA), feeding an electrical output to a Pico EL 037 Converter and Pico EL 005 Enviromon Data Logger (Pico

Technology, UK). The pH and DO data were recorded onto the computer every 30 min, and the probes were recalibrated weekly. Temperature was logged using 3 EL-USB-TC Thermocouple data loggers (Lascar Electronics, UK) placed in the settling tank, effluent sampling vessel and the reactor itself.

The gas pipelines were connected to optical gas bubble counters (made 'in-house' at Newcastle University), giving a measurement of gas volume. The operation of these counters failed after several weeks of operation. They were replaced with 1 L and then 5 L Tedlar gas bags (Sigma Aldrich, U.K.); the volume of gas was then measured by removal from the bags initially using a 100-ml borosilicate glass syringe and then using a larger 1-L gas tight syringe (both SGE Analytical Science, Australia). The sampling ports on each pipeline were initially used to take a duplicate samples of cathode gas three times a week, into a 3-ml Labco Evacuated Exetainer (Labco Ltd, UK). Once gas production had risen to a higher volume, 2 L of the cathode gas was dispensed from the collecting gas bag into another 5-L gas bag which was taken away for analysis. Anode gas was not measured volumetrically due to leakage but was sampled directly from the anode compartment into a 3-ml exetainers for compositional analysis.

Hydrogen gas was measured using a Membrane Inlet Mass Spectrometer (MIMS, Hiden Analytical, Warrington, UK) using duplicate injections, set against a three point calibration made with a range of calibration standards (Scientific Technical Gases, UK). These gas measurements were verified using a Trace Ultra GC with a thermal conduction detector and a Restek Micropacked 2 m Shincarbon column using argon as the carrier gas (Thermo Scientific, USA) also with a three-point calibration, both measurements were concordant with each other. The oxygen concentration of the anode headspace was also measured using both of these instruments. Methane produced was quantified using a SRI 8610C GC FID with methaniser, with hydrogen as the carrier gas (SRI Instruments, USA) using the same calibration approach described above. All measurements for anode and cathode gas were completed using a 100-µl gas tight syringe (SGE Analytical Science, Australia).

Fig. 3 Photograph of the reactor in situ at Howden wastewater treatment site

To ensure accuracy, calibration standards used for the gas measurements were injected into a Labco evacuated exetainers in the laboratory at the same time (±10 min) as the samples taken in the field. Tests carried out previously had indicated that these containers were not completely gas tight especially for hydrogen. This procedure did not have to be carried out for the cathode gas once operation had been switched to gas bags.

Liquid samples of the influent and effluent were taken three times a week. The total chemical oxygen demand (COD) and soluble chemical oxygen demand (SCOD) were measured in duplicate using Spectroquant COD test kits (25–1,500 mg/L range, Merck & Co. Inc., USA). Volatile fatty acids (VFAs) were determined using an Ion Chromatograph (IC) Dionex ICS-1000, with an Ionpack ICE ASI column, and heptafluorobutyric acid as the eluent and tetrabutylammonium hydroxide as the regenerant. Anions were measured using an IC Dionex ICS-1000, with an Ionpack AS 14A column, with carbonate as the eluent. The conductivity of the solution was measured using a conductivity metre, EC 300 (VWR Ltd., UK).

Reactor control

To eliminate the possibility that hydrogen could be produced abiotically at the voltages applied, a control was run a using small laboratory tubular double chamber PVC reactor with a volume of 78 mL in each chamber. The same electrode materials and resistor, similar electrode spacing and the same wastewater at the anode were used as in the larger reactor, although it is likely that the internal resistance of this reactor was lower than the large reactor as the wires were shorter. Once assembled, and before any biofilm could have developed on the anode, a voltage of 0.7 volts was applied using a regulated DC power supply PSM 2/2A, (CALTEK, Hong Kong), the Pico AC-16 Data Logger (Pico Technology, UK), and recorded on a computer every minute. This voltage was maintained for 30 min and then the voltage increased by 0.2 V for a further 30 min; this was continued until gas bubbles began to be generated at the cathode. The cathode gas was sampled and its hydrogen content measured on the GC as described above.

Start-up and operation

The reactor was initially started up in batch mode, allowing all the oxygen, nitrates and sulphates within the wastewater to be consumed. Based on the lessons learnt from the previous pilot study (Cusick et al. 2011), the wastewater was supplemented with acetate at a concentration of 0.5 g/L. The applied voltage initially of 0.6 V was provided by a regulated DC power supply PSM 2/2A (CALTEK, Hong Kong). The dosing was repeated and the reactor refilled after a 2-week period and left in batch mode for 30 days, during which time, no gas production was observed. The reactor was then operated as

continuous flow with an HRT of 1 day, also at 0.6 V for a further 10 days, and the voltage was then increased to 0.9 V. It was run at this voltage for 24 days and then finally the voltage increased to 1.1 V and run for 85 days.

Efficiency calculations

Four efficiency calculations are made in this study on the basis of the electrical and substrate energy used (Logan 2008).

1. Electrical energy recovery (η_E)—energy recovery is the amount of electrical energy put into the reactor that is recovered as hydrogen.

   The electrical energy input W_E is calculated as:

$$W_E = \sum_1^n \left(IE_{ps}\Delta - I^2 R_{ex}\Delta t \right) \qquad (1)$$

where I is the current calculated for the circuit based on the measured voltage E and external resistor R_{ex} ($I=E/R_{ex}$), and E_{ps} is the applied voltage of the power supply, this value is adjusted for the losses caused by the external resistor ($I^2 R_{ex}$), which in reality are negligible. The time increment denoted by Δt represents the conversion of samples taken every 30 min into seconds. The data are summed for all six cells over the each batch cycle. The output of energy (W_{out}) is calculated from the measured moles of hydrogen produced N_{H2} and the standard higher heating value of hydrogen of 285.83 kJ/mol ΔH_{H2}.

$$W_{out} = \Delta H_{H2} N_{H2} \qquad (2)$$

The higher heating value is chosen over the lower heating value which takes into account the heat lost through the production of water vapour during burning. It is expected that this H_2 product would be used either as a commercial product for industry or in a clean H_2 consuming fuel cell to create electricity, not for combustion. Methane could also be added to this value to further increase the quantity of output energy but was not included for these same reasons. Electrical energy recovery (η_E) (excluding pump requirements) can then be calculated as follows:

$$\eta_E = \frac{W_{out}}{W_E} \qquad (3)$$

2. Total energy efficiency (η_{E+S})—the amount of input energy both electrical and substrate that is recovered as hydrogen.

   The substrate energy (W_S) is calculated as

$$W_S = \Delta COD \Delta H_{ww/COD} \qquad (4)$$

where ΔCOD is the change in COD in grammes, estimated as the difference in COD of the influent and effluent at the

end of each batch, and $\Delta H_{ww/COD}$ is the energy content per gramme of COD as measured on similar domestic wastewater of 17.8 kJ/gCOD (Heidrich et al. 2011). Total energy efficiency is then calculated as:

$$\eta_{E+S} = \frac{W_{out}}{W_E + W_S} \quad (5)$$

3. Coulombic efficiency (CE)—the amount of hydrogen produced compared to the amount theoretically possible based on the current or total charge passing through the cell.

Theoretical hydrogen production based on current (N_{CE}) is calculated as:

$$N_{CE} = \frac{\sum_1^n I\Delta t}{2F} \quad (6)$$

where I is the current calculated from the measure voltage and Δt is the conversion of the time interval 30 min to 1 s to give coulombs per data sample; this is then summed over the six cells for the whole batch and divided by Faradays constant (F) (96,485 coulombs/mol e^-) multiplied by 2 to give moles of H_2. Coulombic efficiency CE is then calculated as:

$$CE = \frac{N_{CE}}{N_{H2}} \quad (7)$$

4. Substrate efficiency—the amount of hydrogen produced compared to the amount theoretically possible based on substrate removed in the reactor.

Theoretical hydrogen production based on substrate removal (N_S) is calculated as:

$$N_S = 0.0625 \, \Delta COD\Delta t \quad (8)$$

As 64 gCOD can be converted to 4 mol H_2, each gramme of COD is equivalent to 0.0625 mol H_2. The change in COD is measured at the end of each batch and used to calculate the total COD removed from the 88-L reactor over the duration of the sampling period based on an HRT of 1 day. Substrate efficiency is then calculated as:

$$S_E = \frac{N_S}{N_{H2}} \quad (9)$$

The (η_E) correlates directly to the CE by re-arrangement of their respective equations. It is assumed that the phrase $I^2 R_{ex}\Delta t$ in calculating W_E is negligible by comparison to the first term (this is observed to be the case in practice):

$$\eta_E = \frac{\Delta H_{H2} \times 1,000}{2F \times E_{ps}} CE \quad (10)$$

This means halving the E_{ps} doubles the η_E if the CE can be maintained. An increase in CE at the same E_{ps} causes a linear increase in η_E.

Statistical analysis

All statistical tests were run using Minitab 15 (Minitab Inc., State College, USA).

Results

Start-up and acclimatisation

During the first 30 days of operation, the reactor was run in batch mode with a supplement of 0.5 g/L of sodium acetate and an input voltage of 0.6 V. During this time, there was no observed gas production and current density was very low reaching 0.04 A/m^2 after the first 2 weeks. After this period, wastewater was pumped through the reactor with an HRT of 1 day with no further addition of acetate. For the subsequent 10 days, very little gas was produced and the current density remained at this very low level. At day 40, the input voltage was raised from 0.6 to 0.9 V. The reactor was run with this input of voltage for the next 24 days; the average current density during this time reached 0.14 A/m^2. Gas production was low, with an average of 9 mL/day, with H_2 concentrations reaching nearly 100 % after air in gas lines had been displaced. The electrical energy efficiency η_E was only 1 %. The voltage was then further increased to 1.1 V, and current densities rose to 0.27 A/m^2. This led to an improvement in gas production, and the reactor entered its hydrogen-producing phase, the results of which are shown below. The start-up period took 64 days.

The electrode resistance with this reactor design is relatively high, creating a high overpotential reducing the efficiency of the reactor performance and increasing the electrical load needed for hydrogen evolution to occur. The current densities measured when plotted against input voltage indicate that within the reactor the inherent overpotential is around 0.6 V (as seen as the x-intersect in Fig. 4). The current density only increases by around 0.6 A/m^2/V, far lower than two early MEC laboratory studies of 1.3 A/m^2/volt in (Liu et al. 2005) and 1.78 A/m^2/volt in (Rozendal et al. 2006). The added voltage of 1.1 V used in the study actually equates to a potential difference of around 0.5 V between the electrodes, well below that required for abiotic hydrogen evolution from water of 1.23 V at 25 °C.

The control further verified that the current production was biological, enabling the electrochemical hydrogen production. During this test, hydrogen was not produced at the cathode until an applied voltage of 2.5 V was added.

Performance during the hydrogen-producing phase of MEC reactor operation

After the long start-up and subsequent increase in the voltage to 1.1 V, the MEC worked for the following 85 days and continues to do so. The results presented here are for this period.
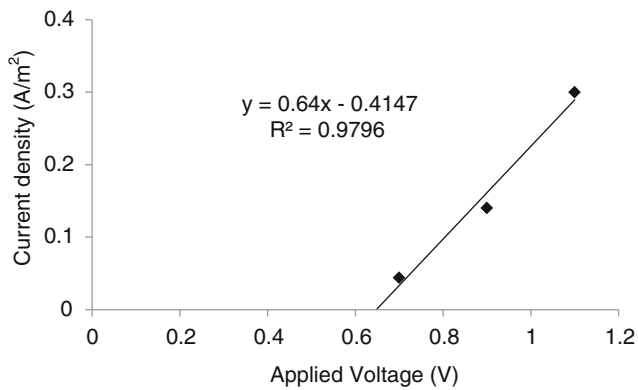
Fig. 4 Current density as a function of applied voltage as measured in the pilot-scale reactor after the initial 2-week acclimatisation period, showing the linear regression equation and R^2 value. The *intersect of the x-axis* indicates the overpotential of the system

The volume of gas produced per day was highly variable. However, the gas composition was consistent, H_2 100±6.4 % and methane 1.8±0.9 %. No trace of CO_2, N_2 or O_2 could be detected using the GCs or MIMS. H_2S could not be quantified; however, the MIMS did not detect any gas at this atomic weight and there was no detectable odour present. The daily H_2 production is shown in Fig. 5. H_2 production gradually increased during the first 30 days; after this, the average production was around 1.2 L per day (±0.4 L/day) for the reactor, equivalent to 0.015 L $H_2 L^{-1} day^{-1}$ (±0.005 L $H_2 L^{-1} day^{-1}$).

The electrical energy recovery of the cell was quite variable (as seen in Fig. 6a) but did show an increasing trend and, on occasion, approached 100 % (complete electrical energy recovery), averaging around 68.9 % after day 40, though with a high standard deviation of 21.3 %. The total energy efficiency (Fig. 6b) which gives the true performance of the cell was also variable (standard deviation 18.4 %) and considerably lower as both the electrical and substrate energy are considered as inputs. The total energy efficiency does show an increasing trend, reaching the 30 %
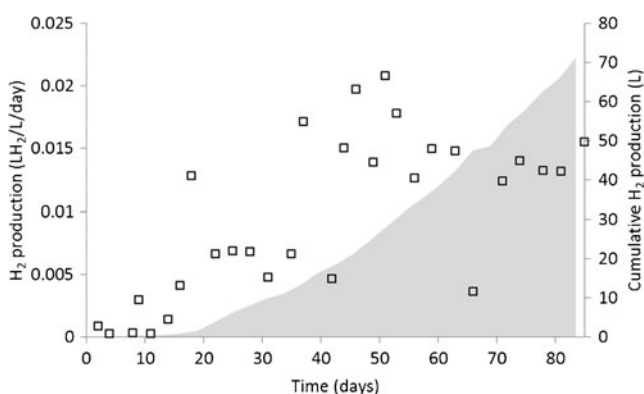

Fig. 5 Hydrogen production during the working phase of reactor after the 64-day acclimatisation period, points showing the production rate at each time of sampling and the area showing the cumulative production of the course of this period

level at the end of the study. The peak values are associated with very low COD removal measurements (making substrate energy input very low) and are not therefore likely to be representative of the true performance of the reactor.

Coulombic efficiency (Fig. 6c) shows a similar trend to electrical energy recovery (Fig. 6a), stabilising after 40 days to 55.0 % (±17.5 %). The coulombic efficiency (CE) correlates with electrical energy recovery (η_E) (R^2=0.998, Pearsons correlation). This correlation factor is calculated as N_E=1.29 CE using the average input power voltage; this value is also seen in the data and is consistent over the course of the study. If the CE could remain at the 60 % and the power input dropped to 0.9 V, 100 % η_E would be achieved. Alternatively, with 1.1 V power input, CE needs to reach 75 % to achieve 100 % η_E. The substrate efficiency (Fig. 6d) was very low, on average 16 % for whole the operational period with a standard deviation of 49.8 %. This was due to the variable influent and effluent TCOD values (as shown in Fig. 7).

The levels of influent TCOD were highly variable which is likely to be one of the factors underlying the variation in performance, as shown in Fig. 7. This was particularly the case at day 30 when the settling tank became full with sludge and influent COD was extremely high. This variability led to occasional negative values for percent COD removal. The average removal of 33.7 % (±54.0 %) equates to 0.14 kg $COD m^{-3} day^{-1}$, below the range for activated sludge of 0.2–2 kg $COD m^{-3} day^{-1}$ (Grady et al. 1999). However, due to the low TCOD of the wastewater used, the effluent levels did occasionally approach and drop below the UK standard of 125 mg/l (EEC 1991).

Despite the variable influent COD and therefore variable performance, many of the other measured factors remained relatively constant throughout the operational period. The headspace of the anode compartment (2.2 L volume) contained elevated levels of CO_2 (1.9±0.2 %) and low levels of CH_4 (0.4±0.1 %), equivalent to 8.8 ml of CH_4 or 0.006 mgCOD and 0.3 kJ. The gas production at the anode could not be measured quantitatively due to leakage; however, the low levels of methane, which did not vary or build up through the course of the study, indicate that this was not likely to be a major loss of COD. The daily production of methane at the cathode was 22 mL/day, equivalent to 0.014 mgCOD and 0.8 kJ of energy, approximately 5–6 % of the amount of energy recovered as hydrogen.

The pH values of the influent and effluent were continuously monitored; the influent was on average pH7.0 (±0.4) and the effluent pH6.7 (±0.2), never dropping below pH6. The DO of the influent was on average 4.2 mg/L (±1.4) and the effluent was 0 mg/L (±0.0), equating to 4.2 mgCOD/L of potential aerobic COD removal. The O_2 levels of the anode headspace were below the detection limit of 1.5 %. The amount of VFAs dropped between the influent and the effluent, but there was frequently some acetic acid left in

Fig. 6 MEC reactor efficiencies over the 85-day working period: **a** electrical energy recovery, **b** total energy efficiency, **c** coulombic efficiency and **d** substrate efficiency
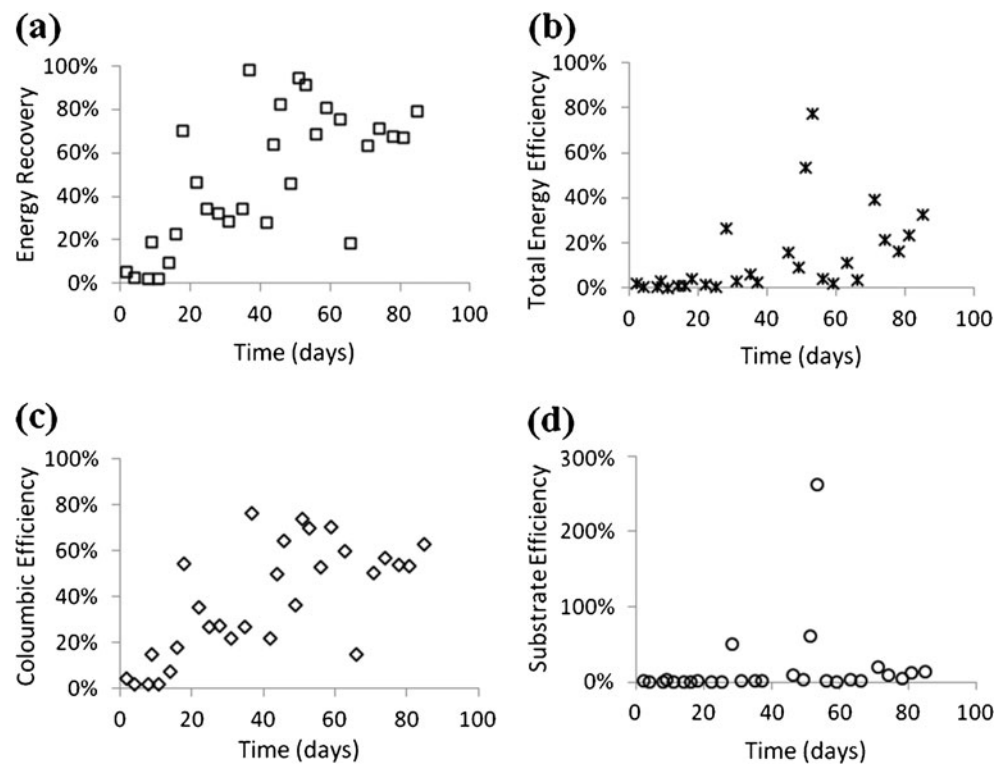
the effluent up to 45 mg/L (i.e. the available food source was not used up). This was confirmed by the average SCOD of the effluent of 115 mg/L (±56 mg/L). There was an average removal of 1.8 g/day of sulphate in the reactor but never full depletion with the effluent containing 89.6 mg/L on average (±35.3). The reactor removed an average of 0.2 g/day (±4.0) of chloride, although this value was highly variable. Fluoride and phosphate remained relatively constant between the influent and effluent, and nitrates and nitrites were not present in either. There was no measured drop in conductivity between the influent and effluent.

The temperature of the influent wastewater varied considerably throughout the hydrogen-producing period between June and September. The range of temperature was more stable within the reactor and was on average 0.9 °C higher than the temperature of the influent as shown in Table 1. With an 88-L capacity and HRT of 1 day, this means 0.37 kJ/day of energy was lost to heat, equivalent to 20 mg COD or 31 mlH$_2$. Temperature did not significantly influence electrical energy recovery ($p=0.678$ influent, $p=0.664$ reactor, $p=0.778$ effluent, Pearson correlation). Most of the fluctuation observed was diurnal,

Fig. 7 TCOD influent and effluent shown by the *lines* along with the UK discharge standard of 125 mg/l, percentage COD removal is also shown using the squares calculated from the different in effluent and influent COD at the point of sampling, hence occasional negative values
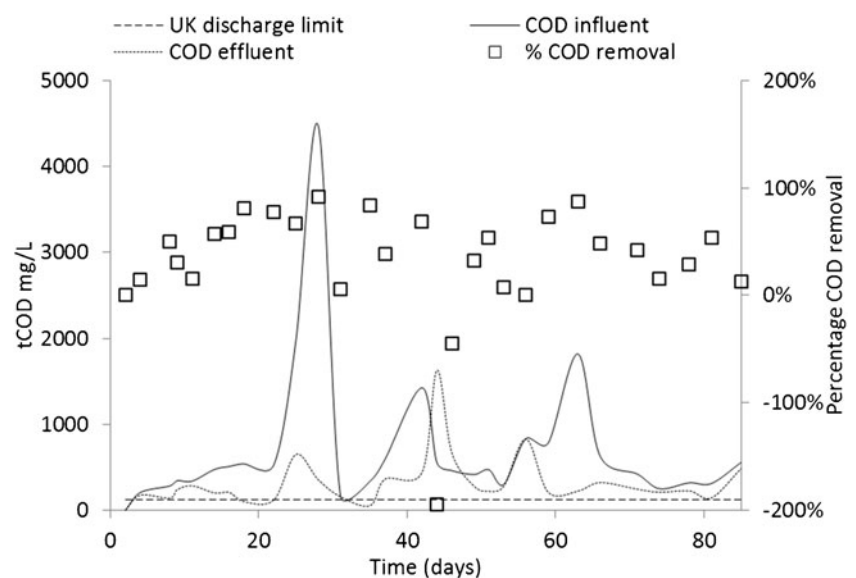
Table 1 Maximum, minimum and average temperature (degrees Celsius) of the influent, effluent and reactor±1 standard deviation which were continually logged over the experimental period

	Influent	Reactor	Effluent
Maximum	27.0±2.3	21.0±1.2	22.5±1.6
Minimum	8.5±2.3	13.5±1.2	12.0±1.6
Average	15.8±2.3	16.6±1.2	16.6±1.6

and periods of the more extreme temperatures were short lived.

Discussion

This pilot-scale reactor produced almost pure hydrogen gas from raw influent domestic wastewater at UK ambient temperatures for a 3-month period and continues to do so. It is believed to be the first successful 'proof of concept' for MECs, bringing the prospect of sustainable domestic wastewater treatment and hydrogen production through the use of bioelectrochemical systems into a new and exciting phase.

The reactor treated raw influent wastewater, removing on average 34 % of TCOD, and occasionally reaching the UK discharge standard of 125 mgCOD/L, equating to a treatment rate of $0.14 \, \mathrm{kgCOD \, m^{-3} \, day^{-1}}$, just below the range for activated sludge. The reactor has performed this task using less energy than would be needed for aeration in a traditional activated sludge process. However, it is clear that COD removal would need to be improved for the technology to be industrially viable. The electrical energy recovery on occasion nearly reached values of 100 % and was consistently around 70 % during the later stages of the study. At this level of performance (i.e. 70 %), the energetic treatment costs were 2.3 kJ/gCOD, below the values for activated sludge of 2.5–7.2 kJ/gCOD (Pant et al. 2011). Clearly, higher COD removal rates would be required for industrial application. The costs of additional reactor volume, increased HRT or closer electrode spacing would need to be weighed against potential benefits; this kind of economic assessment of the technology is beyond the scope of this study.

To achieve 100 % electrical energy recovery, the CE would need to increase to 75 %, i.e. 20 % more of the hydrogen theoretically produced based on the current would need to be captured; alternatively, if the overpotentials could be reduced by 0.2 V, this would bring the input voltage needed down to 0.9 V and again 100 % electrical energy recovery would be achieved (Eq. 10). By implementing improvements to the reactor, such as increasing electrode surface areas, reducing the distance between electrodes, reducing electrode resistance (e.g. by using different materials or thicker wiring), having a more efficient flow paths, consistent pumping and improved materials, it is believed that the η_E could exceed 100 %, making it a net energy producer. Alternatively, only a 6 % increase in substrate efficiency would result in a positive electrical energy recovery. To engineer this improvement would require a greater understanding of the biological community involved as well as a greater understanding the engineering aspects of constructing a reactor such as the HRT and loading rate, this should be a future goal.

The total energy efficiency showed an increasing trend during the course of the study, levelling out at around 30 %, with around a third of all energy both from the wastewater and from the power supply being recovered as hydrogen gas. Coulombic efficiencies of the reactor were higher, levelling out at around 55 %. It is likely that a large portion of the missing 4 % of CE can be attributed to a loss of hydrogen gas from the system. Hydrogen is an extremely small molecule and is able to permeate most plastics, and is therefore likely to be leaking out of the reactor. In a tightly engineered system, theoretically the coulombic efficiency could approach its maximum of 100 %, resulting in an electrical energy recovery of 129 %. If the hydrogen were being lost to hydrogenotrophic methanogens at the anode or cathode, methane would be produced. This is not likely to have been a significant problem with both the anode and cathode gas containing only low levels of methane equating in total to 3.5 % loss of the COD removed.

The substrate efficiency of the cell was considerably lower than the other efficiencies measured. This efficiency represents how much of the substrate is actually recovered as hydrogen and gives an indication of how much substrate is used in the MEC process. Even if the 45 % loss of hydrogen through leakage (as suggested by the CE of 55 %) is accounted for in this calculation, then the substrate efficiency would only increase from 10 % to around 23 %. Losses may be taken to suggest that substrate is being used in competitive oxidation processes, but only low levels of oxygen and sulphates entered the cell potentially accounting for 1.1 and 3.6 % of total COD removal, respectively. Some leakage of oxygen into the reactor headspace cannot be excluded, but the most likely cause of the incomplete COD balance is the build-up of sludge in the reactor. This is evidenced by the constant COD removal value throughout the study despite the increasing efficiency of the reactor; additionally, on three occasions, a very high COD peak entered the reactor, on two of these occasions the peak of COD is not seen to leave the reactor. This sludge build-up could have been reduced using a recirculation pump, increasing the flow rate through the reactor.

All of the efficiency losses identified above could be minimised by improving the detailed engineering of the system. The two 'new' materials used in this study for the

membrane and cathode have not been truly evaluated. More expensive alternatives such as Nafion membrane and a Pt-coated cathode may prove to be worthwhile investments if performance increases greatly with their use. The high resistance of the reactor means the overall efficiencies of the reactor will be low. The resistance observed is more problematic in this larger-scale system than at the laboratory scale and would also become increasingly challenging with further scale up. Reduction in these overpotentials is a clear area for improvement with future design. The biological MEC process works, and works relatively consistently for a period of at least three months. Although tested in realistic conditions, this was over a spring/summer period; survival over periods of sustained low temperature has yet to be confirmed.

The relationship between electrical energy recovery, electrical power input and coulombic efficiency has been defined; however, the prediction of energy requirements for a larger-scale MEC system may be difficult to make. Theoretical input voltages lie far from those needed in reality even for acetate fed cells, typically between 0.4 and 1.0 V compared to the 0.114 V theoretically needed (pH 7, 298 K) (Logan 2008). A relatively small change in the electrical power input can have a large effect of the overall electrical energy recovery; yet, if this value is not high enough to overcome the losses in the cell, no hydrogen will be produced.

Undoubtedly, there are many factors that require further investigation. Many of the inefficiencies could be overcome by improved engineering and hydrodynamics. A greater understanding of the biological processes, community structure and ecology (both working with and against the cell performance) would allow for more confident design and manipulation.

For the first time, this research publishes details of a MEC producing hydrogen gas from real domestic wastewater, at a pilot scale, for a sustained period of time, under ambient temperature conditions and using low-cost materials. 'Breakeven' energy recovery was not achieved during this research, but given the losses of hydrogen gas and the potential for improved future design, energy neutral or even energy positive wastewater treatment is likely to be possible with the use of this technology. This has massive implications for a significant reduction of energy use in this sector and could lead to the worldwide water industry becoming a leader in the field of sustainability and climate change mitigation. The success of this research at this scale and with real wastes sets a new and exciting agenda into the application of microbial fuel cell technologies into industry.

References

Aboutalebi H, Sathasivan A, Krishna KCB, Kohpaei AJ (2011) Expediting COD removal in microbial electrolysis cells by increasing biomass concentration. Bioresour Technol 102:3981–3984

Aelterman P, Freguia S, Keller J, Verstraete W, Rabaey K (2008) The anode potential regulates bacterial activity in microbial fuel cells. Appl Microbiol Biotechnol 78:409–418

Bretschger O, Gorby YA, Nealson KH (2010) A survey of direct electron transfer from microbes to electronically active surfaces. In: Rabaey K, Angenent L, Schröder U, Keller J (eds) Bioelectrochemical systems: From extracellular electron transfer to biotechnological application. IWA Publishing, London, p 488

Call D, Logan BE (2008) Hydrogen production in a single chamber microbial electrolysis cell lacking a membrane. Environ Sci Technol 42:3401–3406

Cheng S, Logan BE (2008) Evaluation of catalysts and membranes for high yield biohydrogen production via electrohydrogenesis in microbial electrolysis cells (MECs). Water Sci Technol 58:853–857

Cheng SA, Logan BE (2011) High hydrogen production rate of microbial electrolysis cell (MEC) with reduced electrode spacing. Bioresour Technol 102:3571–3574

Cheng S, Liu H, Logan BE (2006) Increased performance of single-chamber microbial fuel cells using an improved cathode structure. Electrochem Commun 8:489–494

Clauwaert P, Aelterman P, Pham TH, De Schamphelaire L, Carballa M, Rabaey K, Verstraete W (2008) Minimizing losses in bioelectrochemical systems: the road to applications. Appl Microbiol Biotechnol 79:901–913

Cusick RD, Bryan B, Parker DS, Merrill MD, Mehanna M, Kiely PD, Liu GL, Logan BE (2011) Performance of a pilot-scale continuous flow microbial electrolysis cell fed winery wastewater. Appl Microbiol Biotechnol 89:2053–2063

EEC (1991) Council directive of 21 May 1991 concerning urban waste water treatment (91/271/EEC). Page 40. Official Journal of the European Communities.

Fan YZ, Xu ST, Schaller R, Jiao J, Chaplen F, Liu H (2011) Nanoparticle decorated anodes for enhanced current generation in microbial electrochemical cells. Biosens Bioelectron 26:1908–1912

Foley JM, Rozendal RA, Hertle CK, Lant PA, Rabaey K (2010) Life cycle assessment of high-rate anaerobic treatment, microbial fuel cells, and microbial electrolysis cells. Environ Sci Technol 44:3629–3637

Grady CPL, Daigger GT, Lim HG (1999) Biological wastewater treatment, 2nd edn. Marcel Dekker, New York

Heidrich ES, Curtis TP, Dolfing J (2011) Determination of the internal chemical energy of wastewater. Environ Sci Technol 45:827–832

Holmes DE, Bond DR, O'Neil RA, Reimers CE, Tender LR, Lovley DR (2004) Microbial communities associated with electrodes harvesting electricity from a variety of aquatic sediments. Microb Ecol 48:178–190

Kiely PD, Rader G, Regan JM, Logan BE (2011a) Long-term cathode performance and the microbial communities that develop in microbial fuel cells fed different fermentation endproducts. Bioresour Technol 102:361–366

Kiely PD, Regan JM, Logan BE (2011b) The electric picnic: synergistic requirements for exoelectrogenic microbial communities. Curr Opin Biotechnol 22:378–385

Kim IS, Hwang MH, Jang NJ, Hyun SH, Lee ST (2004) Effect of low pH on the activity of hydrogen utilizing methanogen in biohydrogen process. Int J Hydrog Energy 29:1133–1140

Liu H, Grot S, Logan BE (2005) Electrochemically assisted microbial production of hydrogen from acetate. Environ Sci Technol 39:4317–4320

Logan B (2008) Microbial fuel cells. John Wiley & Sons, Inc., New Jersey

Logan BE (2009) Exoelectrogenic bacteria that power microbial fuel cells. Nat Rev Microbiol 7:375–381

Lovley DR (2008) The microbe electric: conversion of organic matter to electricity. Curr Opin Biotechnol 19:564–571

Lu L, Ren NQ, Zhao X, Wang HA, Wu D, Xing DF (2011) Hydrogen production, methanogen inhibition and microbial community structures in psychrophilic single-chamber microbial electrolysis cells. Energ Environ Sci 4:1329–1336

Oh ST, Kim JR, Premier GC, Lee TH, Kim C, Sloan WT (2010) Sustainable wastewater treatment: how might microbial fuel cells contribute. Biotechnol Adv 28:871–881

Pant D, Singh A, Van Bogaert G, Gallego YA, Diels L, Vanbroekhoven K (2011) An introduction to the life cycle assessment (LCA) of bioelectrochemical systems (BES) for sustainable energy and product generation: relevance and key aspects. Renew Sust Energ Rev 15:1305–1313

Pant D, Singh A, Van Bogaert G, Olsen SI, Nigam PS, Diels L, Vanbroekhoven K (2012) Bioelectrochemical systems (BES) for sustainable energy production and product recovery from organic wastes and industrial wastewaters. Rsc Adv 2:1248–1263

Rabaey K, Boon N, Siciliano SD, Verhaege M, Verstraete W (2004) Biofuel cells select for microbial consortia that self-mediate electron transfer. Appl Environ Microbiol 70:5373–5382

Rader GK, Logan BE (2010) Multi-electrode continuous flow microbial electrolysis cell for biogas production from acetate. Int J Hydrog Energ 35:8848–8854

Rozendal RA, Hamelers HVM, Euverink GJW, Metz SJ, Buisman CJN (2006) Principle and perspectives of hydrogen production through biocatalyzed electrolysis. Int J Hydrog Energ 31:1632–1640

Rozendal RA, Hamelers HVM, Rabaey K, Keller J, Buisman CJN (2008a) Towards practical implementation of bioelectrochemical wastewater treatment. Trends Biotechnol 26:450–459

Rozendal RA, Jeremiasse AW, Hamelers HVM, Buisman CJN (2008b) Hydrogen production with a microbial biocathode. Environ Sci Technol 42:629–634

Rozendal RA, Leone E, Keller J, Rabaey K (2009) Efficient hydrogen peroxide generation from organic matter in a bioelectrochemical system. Electrochem Commun 11:1752–1755

Sleutels T, Hamelers HVM, Buisman CJN (2011) Effect of mass and charge transport speed and direction in porous anodes on microbial electrolysis cell performance. Bioresour Technol 102:399–403

Villano M, De Bonis L, Rossetti S, Aulenta F, Majone M (2011) Bioelectrochemical hydrogen production with hydrogenophilic dechlorinating bacteria as electrocatalytic agents. Bioresour Technol 102:3193–3199

Wang A, Liu W, Ren N, Zhou J, Cheng S (2010) Key factors affecting microbial anode potential in a microbial electrolysis cell for H(2) production. Int J Hydrog Energ 35:13481–13487

Wang AJ, Sun D, Cao GL, Wang HY, Ren NQ, Wu WM, Logan BE (2011) Integrated hydrogen production process from cellulose by combining dark fermentation, microbial fuel cells, and a microbial electrolysis cell. Bioresour Technol 102:4137–4143

Zhang YM, Merrill MD, Logan BE (2010) The use and optimization of stainless steel mesh cathodes in microbial electrolysis cells. Int J Hydrog Energ 35:12020–12028

Zhang F, Pant D, Logan BE (2011) Long-term performance of activated carbon air cathodes with different diffusion layer porosities in microbial fuel cells. Biosens Bioelectron 30:49–55