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Microbial Fuel Cells for Wastewater Treatment

Liliana Alzate-Gaviria
Yucatan Centre for Scientific Research (CICY), Mexico

1. Introduction

A typical domestic wastewater treatment plant consists of a series of unit processes, each of which is designed with specific functions. Process trains will be more variable for industrial wastewater and for nutrient control.
Conventional sewage treatment may involve these stages:

1.1 Screening

The influent is strained to remove all large objects carried in the sewage stream. This is most commonly performed with an automated mechanically-raked bar screen in modern plants serving large populations, whilst in smaller or less modern plants a manually-cleaned screen may be used. The raking action of a mechanical bar screen is typically paced according to the accumulation on the bar screens and/or flow rate. The solids are collected and later disposed of in landfill or incinerated. Bar screens or mesh screens of varying sizes may be used to optimise solids removal, so as to trap and remove the floating matter, such as pieces of cloth, paper, wood, kitchen refuse, etc. These floating materials will choke pipes or adversely affect the working of the pumps if not removed. They should be placed before the grit chambers. However, if the quality of grit is not of much importance, as in the case of landfilling etc., screens may even be placed after the grit chambers. They may sometimes be accommodated in the body of the grit chambers themselves.

1.2 Primary treatment

In the primary sedimentation stage, tanks commonly called "primary clarifiers" or "primary sedimentation tanks" are used to settle sludge while grease and oils rise to the surface and are skimmed off. Primary settling tanks are usually equipped with mechanically driven scrapers which continually drive the collected sludge towards a hopper in the base of the tank where it is pumped to sludge treatment facilities. Grease and oil from the floating material can sometimes be recovered for saponification. The dimensions of the tank should be designed to effect removal of a high percentage of the floatables and sludge. A typical sedimentation tank may remove from 60% to 65% of suspended solids, and from 30% to 35% of biochemical oxygen demand (BOD) from the sewage.

1.3 Secondary treatment

This is designed to substantially degrade the biological content of the sewage which is derived from human waste, food waste, soaps and detergent. The majority of municipal

plants treat the settled sewage liquor using aerobic biological processes. To be effective, the biota require both oxygen and food to live. The bacteria and protozoa consume biodegradable soluble organic contaminants (e.g. sugars, fats, organic short-chain carbon molecules, etc.) and bind much of the less soluble fractions into floc. Secondary treatment systems are classified as fixed-film or suspended-growth.

It has been estimated that the activated sludge process in publically owned treatment works in the U.S. requires 0.349 kWh of electricity per cubic metre of wastewater, accounting for about 21 billion kWh of electricity consumption per year (Goldstein and Smith, 2002). Pumping and aeration are the predominant energy consuming processes (21% and 30–55% of the total treatment energy demand, respectively) (EPA, 2008). Similarly in the UK, 3–5% of national electricity consumption goes towards wastewater treatments. If activated sludge processes were adopted by engineers in the rapidly developing world to serve, say 19 million people, this would produce an energy bill equivalent to 6.8% of the entire U.S. electricity consumption (UNICEF, 2000; Water, 2006). We suggest that this is unsustainable, both on economical and environmental grounds (Oh et al., 2010). The cost of energy will undoubtedly rise as carbon-based resources become depleted and renewable sources struggle to make up the shortfall. Operating costs of treating wastewater are therefore likely to become prohibitively expensive.

Anaerobic digestion of wastewater, particularly industrial wastewater, is usually a cheaper, if more fickle, option than aerobic technologies. However, the effluent often requires further treatment to remove residual organics.

1.4 Tertiary treatment

Finally, the purpose of tertiary treatment is to provide a final treatment stage to raise effluent quality before it is discharged to the receiving environment (sea, river, lake, ground, etc.). More than one tertiary treatment process may be used at any treatment plant. If disinfection is performed, it is always the final process. It is also called "effluent polishing".

The organic matter concentration in wastewater is usually evaluated in terms of either its biochemical oxygen demand (BOD) in a five day test (BOD_5) or its chemical oxygen demand (COD) in a rapid chemical oxidation test. Total BOD or COD can be viewed as consisting of two fractions: soluble BOD (sBOD) and particulate BOD (pBOD). Most pBOD is removed in the primary clarifier sludge and sBOD is converted to bacterial biomass (Logan, 2008).

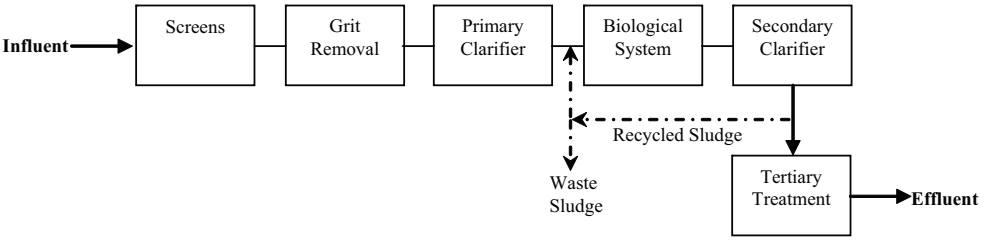

Fig. 1. Process flow for a typical wastewater treatment plant. (Metcalf and Eddy, 2003)

Based on this summary of a wastewater treatment process train, we can see that a microbial fuel cell (MFC) would replace the secondary treatment system and tertiary treatment (removal of nutrients, ammoniacal nitrogen, phosphorus and organics components) (Yokoyama et al., 2006). These organics are often volatile fatty acids, which are metabolic

products of anaerobic digestion, whose accumulation has been reported to hinder the process (Hawkes et al., 2007; Logan and Regan, 2006b; Oh and Martin, 2009). However, these acids, such as acetate and butyrate, are effectively consumed in MFCs, even at low concentrations (Kim et al., 2010, Lee et al., 2008; Liu et al., 2005). The sensitivity of MFCs to low levels of organic contaminants is well documented and has led to their application as biosensors (Chang et al., 2004; Kim et al., 1999). In addition, multi-stage treatment combining anaerobic digestion and/or hydrogen fermentation and MFC technologies may result in reduced accumulation of inhibitory by-products and allow effluent polishing to more stringent discharge standards (Kim et al., 2010, Logan and Regan, 2006b; Pham et al., 2006). Combining an MFC with AD and Bio-hydrogen would therefore maximise total energy recovery and consequently increase the sustainability of wastewater treatment. The additional heating system to maintain temperature may not be necessary for energy recovery or wastewater treatment using MFC technology.

2. Exoelectrogens

The idea of using microorganisms as catalysts in an MFC has been explored since the 70s and 80s (Suzuki, 1976; Roller et al., 1984). MFCs used to treat domestic wastewater were introduced by Habermann and Pommer (1991). However, these devices have recently become attractive again for electricity generation, providing opportunities for practical applications (Schröder et al., 2003; Liu and Logan, 2004; Liu et al., 2004a).

Most microorganisms use respiration to convert biochemical energy into ATP. This process involves a cascade of reactions through a system of electron-carrier proteins in which electrons are ultimately transferred to the terminal electron acceptor. Most forms of respiration involve a soluble compound (e.g. oxygen, nitrate, and sulphate) as an electron acceptor. However, some microorganisms are able to respire solid electron acceptors (metal oxides, carbon, and metal electrodes) in order to obtain energy. Several mechanisms explain how microorganisms respire using a solid electron acceptor (Hernandez and Newman, 2001; Weber et al., 2006; Rittmann, 2008). Some of these mechanisms involve the use of chelators or siderophores which effectively solubilise the solid electron acceptor and introduce them into the cell (Gralnick and Newman, 2007). Other mechanisms involve extracellular electron transfer (EET), in which microorganisms externalise their electron transport to the surface of the solid electron acceptor. Researchers have proposed three distinct EET mechanisms, which are depicted in Figure 2. The first mechanism proposes direct electron transfer between electron carriers in the bacteria and the solid electron acceptor. This mechanism is supported by the presence of outer-membrane cytochromes which can interact directly with the solid surface to carry out respiration (Beliaev et al., 2002; Magnuson et al., 2001). Bacteria using this mechanism require direct contact with the solid electron acceptor and therefore cannot form a biofilm. The second mechanism proposes the presence of a soluble electron shuttle: a compound which carries electrons from the bacteria by diffusive transport to the surface of the metal oxide (or electrode) and is able to react with it, discharging its electrons. This compound in its oxidised state then diffuses back to the cells, which should be able to use the same compound repeatedly (hence the name 'shuttle'). Bacteria are known to produce compounds which act as electron shuttles, including melanin, phenazines, flavins, and quinones (Newman and Kolter, 2000; von Canstein et al., 2008). The third mechanism proposes a solid component which is part of the extracellular biofilm matrix and is conductive for electron transfer from the bacteria to the solid surface. This mechanism is

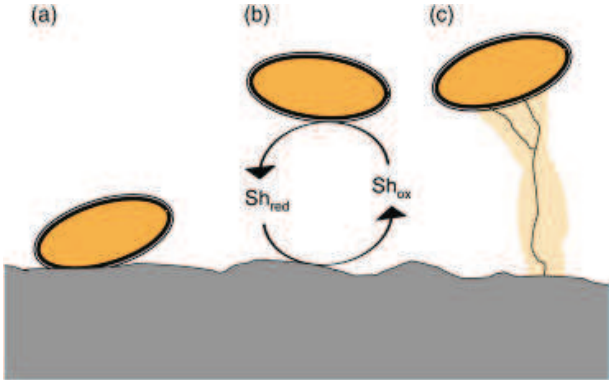

Fig. 2. Schematic of three EET mechanisms used by ARB: (a) direct electron transfer, (b) an electron shuttle, and (c) a solid conductive matrix. (Torres *et al*., 2010)

supported by the recent discovery of the possible role of cellular pili as nanowires (Reguera et al., 2005; Gorby et al., 2006), which are being characterised for their capability to conduct electrons. Other components may also be conductive and contribute in EET, such as extracellular cytochromes or bound electron mediators (Marsili et al., 2008; Rittmann, 2008).
Currently, researchers have not reached a consensus regarding the conditions under which these EET mechanisms are dominant in natural and engineered systems. Evidence can be found to support more than one EET mechanism in some cases. For example, recent discoveries have shown that Shewanella oneidensis is capable of producing shuttles (Marsili et al., 2008; von Canstein et al., 2008) and nanowires (Gorby et al., 2006). It is not obvious under which conditions an EET mechanism would be used and whether more than one mechanism is concurrently utilised by S. oneidensis and other bacteria.
The use of EET is of special importance in microbial fuel cells and electrolysis cells (collectively referred to as MXCs). In MXCs, anode-respiring bacteria (ARB) carry out a respiration process in which a solid electrode (the anode) is their electron acceptor. Because most MXC electrodes are solid conductors which can neither be solubilised nor reduced (they only act as a conductor), ARB can only externalise electrons through EET in order to respire using the anode. To date, ARB include members from diverse phyla, such as Alpha-, Beta-, Gamma-, and Deltaproteobacteria, Firmicutes, Acidobacteria, and a yeast (Logan, 2009, Alzate et al., 2010). Most of these members are known to utilise solid Fe (III) as an electron acceptor, and they are anaerobic, gram-negative oligotrophs. Substrate-utilisation capabilities of most of these bacteria are limited to simple fermentation products, such as acetate and H_2. However, some members can utilise a wider range of substrates, such as propionate, butyrate, lactate, and glucose (Debabov, 2008).
A few studies have shown that the maximum current densities produced by ARB are limited by proton transport inside the biofilm (Torres et al., 2008b; Franks et al., 2009). If protons produced as a result of substrate oxidation accumulate inside the biofilm, they decrease the pH and inhibit the ARB. The maximum current density obtained therefore appears to depend on proton transport rather than factors associated with EET. The highest current densities reported so far are consistent with relatively high buffer concentrations (4100mM buffer) (Fan et al., 2007; Logan et al., 2007; Torres et al., 2008; Xing et al., 2008). It is therefore possible that higher current densities are achievable in ARB biofilms if better proton transport is achieved (Torres et al., 2010).

3. MFC

MFCs convert a biodegradable substrate directly into electricity and are new types of bioreactors which use exoelectrogenic biofilms for electrochemical energy production (Logan, 2008; Logan and Regan, 2006b; Rabaey et al., 2005). (Figure 3).

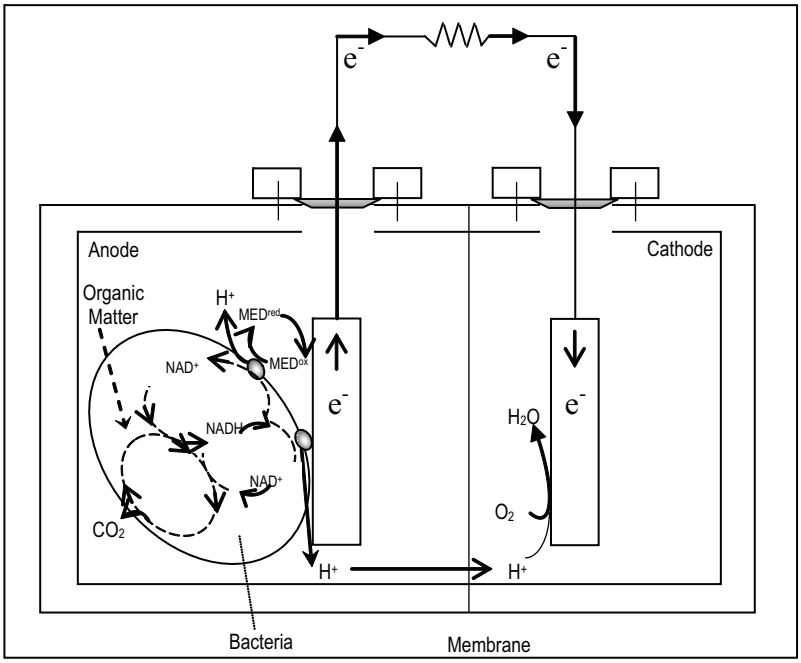

Fig. 3. Schematic of the basic components of a MFC. Bacteria grow on the anode, oxidising organic matter and releasing electrons. The cathode is sparged with air to provide dissolved oxygen for the reaction of electrons, protons and oxygen at the cathode, completing the circuit and producing power. (Logan, 2008)

MFCs have advantages over other technologies used for generating energy from organic matter. First, the direct conversion of substrate into electricity permits high conversion efficiencies. Second, they operate efficiently at ambient temperature, including low temperatures. Third, they do not require the treatment of biogas generated in the cell. Fourth, they do not require additional energy to aerate the cathode, given that it can be aerated passively. Fifth, they have the potential for application in remote areas without electrical infrastructure, making them an additional renewable energy option to meet global energy requirements. Finally, MFCs involve an anaerobic process, and bacterial biomass production will therefore be reduced compared to that of an aerobic system. Estimated cell yield from a MFC process is in the order of Yx/s=0.16 g-COD-cell/g-COD. This is about 40% of the value produced by an aerobic process of Yx/s=0.4 g-COD-cell/g-COD (Logan, 2008)

A variety of biofuels and by-products can be obtained from organic biomass present in solid and liquid waste, with glucose forming the main source of carbon (Logan, 2004; Alzate et al., 2007; He and Angenent, 2006). The main stoichiometric reactions in fermentative microbiological metabolism include:

Bio-ethanol:

$$C_6H_{12}O_6 \longrightarrow 2\ C_2H_5OH + 2\ CO_2$$

Biogas:

$$C_6H_{12}O_6 \longrightarrow 3\ CH_4 + 3\ CO_2$$

Hydrogen gas:

$$C_6H_{12}O_6 + 6\ H_2O \longrightarrow 12\ H_2 + 6\ CO_2$$

Microbial fuel cell:

$$C_6H_{12}O_6 + 6\ O_2 \longrightarrow 6\ H_2O + 6\ CO_2$$

There are three typical configurations amongst MFCs with a proton exchange membrane (PEM) (Figure 4): A. Bioreactor separate from the MFC: the microorganisms generate hydrogen, which is then used as fuel in a fuel cell. B. Bioreactor integrated into the MFC: the microorganisms generate hydrogen which is converted into electricity in a single cell. C. MFC with direct electron transfer: microbiological electricity generation and direct transfer to the anode (Rabaey et al., 2005).

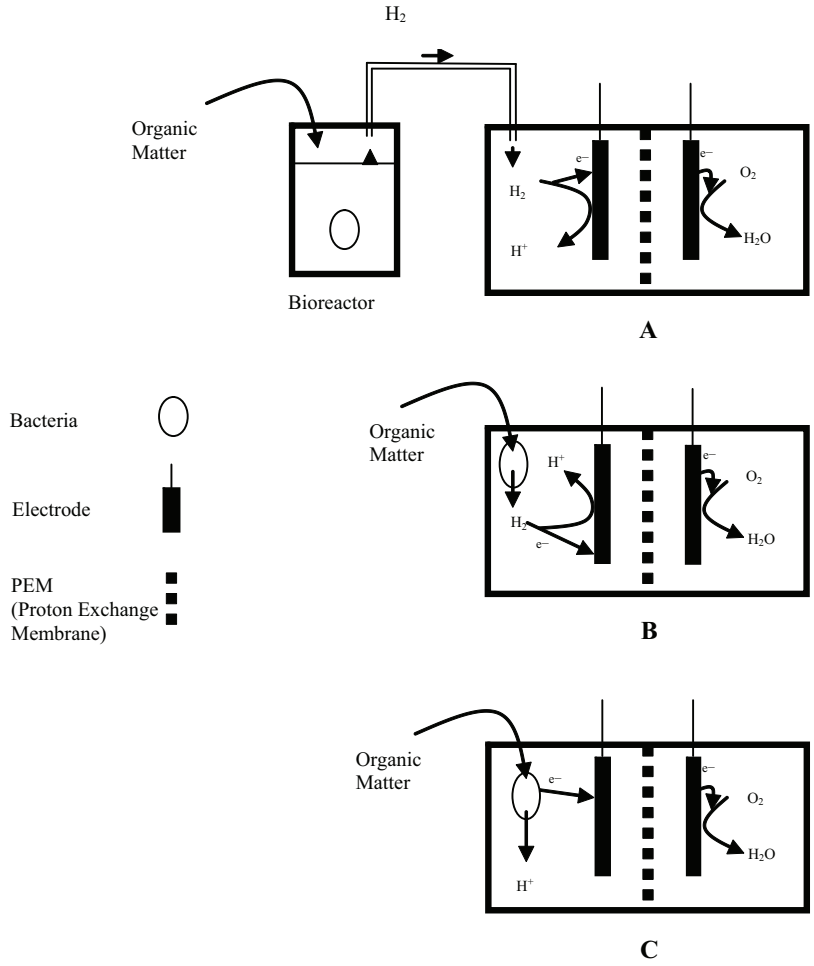

Fig. 4. Different MFC configurations with PEM. (Rabaey et al., 2005)

MFCs can be monitored via electrochemical parameters, such as power density, generated electrical current and voltage. Equally, a very important biological parameter is the organic load of the substrate to be used, expressed in Kg m^{-3} d^{-1} (Rabaey et al., 2003).
Recently, much attention has been focused on the tubular type of MFCs (Clauwaert et al., 2007; Kim et al., 2010; Rabaey et al., 2005a) which increase sludge retention time and reduce hydraulic retention time, which would reduce the long term operating cost. Power densities from industrial and domestic wastewater using MFCs range from 4 to 15 W/m^3 (Cheng et al., 2006; Feng et al., 2008; Liu and Logan, 2004). The anode has, for example, been made of graphite granules (diameters between 1.5 and 5 mm, surface areas between 1000 and 3000 m^2/m^3), which microorganisms can easily attach to. Rabaey et al. (2005) observed a maximum power density of 90 W/m^3 with acetate feeding at 1.1 kg COD/m^3/day. Clauwaert et al. (2007) used a similar configuration but with a biocathode exposed to air which produced a maximum power density of 65 W/m^3 at 1.5 kg COD/m^3/day (Oh et al., 2010).
Finally according to Oh et al. (2010), innovation in the design of new MFC reactors has been driven by the desire to increase power output and decrease capital costs. Therefore, materials which minimise internal electrical resistance, designs which maximise the surface area which electrogenic bacteria can attach to and the removal of expensive materials such as noble metal catalysts on the cathode have been the focus of much of the research activity. This iteration towards optimal design has paid dividends. Reported power outputs in laboratory-scale MFCs have increased from 0.001 to 6.9 W/m^2 (Fan et al., 2008) in less than a decade. Material costs have deceased, but need to decrease further to make MFCs attractive alternatives to other forms of wastewater treatment and pilot plants are emerging (Cha et al., 2009, Rabaey and Keller, 2008). Electricity produced by MFCs may never be a cost effective source of energy in its own right. Rather their contribution will be one of reducing the energy used in wastewater treatment. Switching wastewater treatment from an aerobic to anaerobic process would dramatically cut energy consumption by obviating the need to aerate the sludge. However, conventional anaerobic treatment technologies are often thought of as being slow, need concentrated waste and high temperatures to operate reliably, the effluent often requires further treatment before it can be discharged and sludge disposal is still required. Microbial fuel cells appear to operate at lower temperatures and yield less biomass. In addition, the fact that the bacteria donate electrons to an external circuit with a controllable resistance may ultimately make the whole treatment process amenable to real-time control. The electrical current is a continuous index of the efficiency of the process. This is a neglected area of research for microbial fuel cells which will assume greater importance when MFCs are scaled up for use in real wastewater treatment plants. Least is known about the ecology of microbial communities which metabolise the waste or catalyse the reactions on biocathodes. Microbial communities have been used in conventional wastewater treatment technologies without necessarily having a deep knowledge of the dynamics of the populations, so perhaps our lack of knowledge is not a barrier to the adoption of MFCs. However, when microbial communities behave in unexpected ways and treatment technologies go wrong it can be baffling. A good understanding of the acclimatisation of the communities in MFCs and their response to environmental perturbations would reduce the perceived risks and accelerate the adoption of MFCs. New sequencing technologies combined with proteomics and metabolomics could provide us with a much clearer picture of the changes in community composition and

metabolic pathways which occur in response to different operating conditions. However, even if this deep understanding of the biology at work in an MFC takes many years to achieve it seems clear that, even in the short term, MFCs will have a role to play in sustainable wastewater treatment.
We go on to present how a MFC can generate electricity with electron transfer from the anode to the cathode using a mixed microbial consortium previously adapted as biocatalysts. We examined three factors which could affect MFC operation: external resistance, pH and the effect of temperature.

4. Methodology

4.1 Microorganisms and substrate source

The biocatalysts used for electricity generation were obtained from a previously stabilised MFC (Alzate et al., 2010). The source of the substrate was Synthetic Wastewater (SW) (Poggi et al., 2005), with Sigma® brand reagent grade glucose as the carbon source. The SW had a pH of between 5 and 6 and the following composition per litre: 4g glucose; 310mg NH_4Cl; 130mg KCl; 4.97g NaH_2PO_4; and 2.75g $Na_2HPO_4.H_2O$ (Lovley and Philips, 1998).

4.2 Microbial fuel cell

A large range of materials and designs have been used in MFCs. In this study a MFC was built from glass with a working volume of 350 ml for both the anolyte and catholyte. The anode chamber was bubbled with N_2 to displace the O_2 present before the anode was closed. Untreated carbon paper distributed by Fuelcell (Toray carbon paper®) was used for the electrode.
The PEM cell consisted of 2 chambers, one for the anode and one for the cathode, joined by a proton exchange membrane called Nafion® 117, with a film thickness of 183μm reinforced with a PTFE copolymer (teflon/perfluorosulphonic acid). Its molecular structure permits the absorption of water and once moist, it selectively conducts positively charged ions, blocking those with a negative charge. This characteristic is combined with the established chemical inertness, mechanical resistance and stability of Teflon® resins (Fuelcell Internacional, USA). The membrane was activated before use with 1N H_2SO_4 at 45°C for 24h (Kim et al., 2005).
In the cathode chamber an aqueous catholyte with air bubbling for O_2 use was used with untreated carbon paper with Pt (0.5 mg Pt 10% per cm^2) for the electrode, whilst the previously selected and stabilised flocculent-type mixed inoculum was used at the anode. No catalyst was applied to the latter electrode, given that this function is performed by the microorganisms present in the inoculum.
The carbon paper electrodes used in each chamber were 1.7 cm x 1.6 cm, with a total area of 5.44 cm^2.
MFC start-up consisted of colonising the electrode with the microbial consortium contained in the inoculum in order to form a biofilm; or a complex community of microorganisms which adhere to the electrode and produce a cellular polymer coating which helps them to retain nutrients and protect themselves from toxic agents, and finally produce electricity.
During this process three sequential inoculum transfers were performed until a constant electrochemical response with a constant voltage was obtained. In addition, the voltage pattern was reproduced on the third addition of mixed inoculum to the anode. It is worth noting that strict anaerobic conditions were not maintained for the change of inoculum. The

experiments were performed at mesophilic temperatures by placing the cell in a thermostatic bath.
Two external resistances were used for the PEM cell circuit, one of 1000Ω over a period of 102 days and a second of 600Ω during the remaining days. Based on previous experiments (Liu et al., 2004a; Logan, 2004), the MFC was operated for a period of no greater than 155 days, not including start-up. The changes which occurred in the microbial community during this time were monitored via electrochemical monitoring.

4.3 Electrochemical monitoring

This was performed by measurements of power density produced by the MFC, using a Fluke® multimeter. A resistance was set for the circuit to obtain current data. The current (I) in amps was obtained as: I=VxR-1=Qxt-1, where V is the voltage (volts), Q is the charge (coulombs) and t is the time (seconds). Power (P; watts) was measured as P=IxV and energy production was measured in joules using the equation E=Pxt.
Efficiencies are expressed based on the experimental coulombic efficiency compared to the theoretical one, which varies in accordance with the type of substrate used in the MFC (Rabaey et al., 2004).

4.4 Analysis

The electrode was monitored by taking measurements of volatile fatty acids by titration, hydrogen potential (pH), temperature and soluble chemical oxygen demand (COD) in the liquid current. These parameters were determined in accordance with APHA procedures (2005). Finally, current and voltage measurements were performed with a multimeter and coulombic efficiency was calculated as $CE = \frac{Cp}{Cti} \times 100\%$, where CP is total coulombs calculated as the integral of current with respect to time and Cti is the theoretical amount of coulombs calculated from the following equation $C_{ti} = \left[\frac{F \times b \times S \times v}{M} \right]$, where F: Faraday's constant, b: is the number of moles of electrons produced per mole of substrate, S: substrate concentration, V: liquid volume and M: molecular weight of the substrate used in the MFC.

5. Results and discussion

5.1 MFC Start-up

When the MFC was inoculated with biocatalysts from a previously stabilised MFC there was a 30h lag phase followed by a rapid increase in voltage over the following 40h, reaching a maximum voltage of 0.4V (Figure 5). The voltage subsequently decreased gradually as the organic matter contained in the inoculum was consumed. On adding the third transfer of inoculum to the MFC the behaviour was similar, producing a stability range of 0.37 ± 0.03V, comprising the last stage in the pattern of bacterial growth. Growth ceased and cell death occurred once the substrate was consumed, and voltage generation was affected.
After 120h in operation, part of the inoculum was replaced with SW and just 10% of the inoculum was conserved. Electricity was immediately seen to be generated in the previously inoculated MFC (Figure 6), reaching a maximum voltage of 1.05V and maintaining a range of 0.90 ± 0.1V over the following 55h.

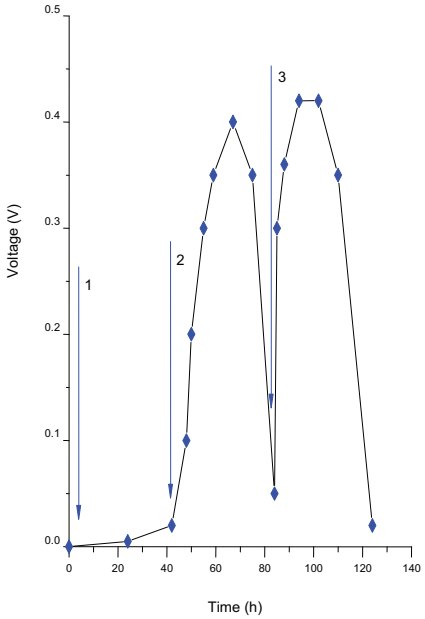

Fig. 5. Voltage generation by MFC during start-up. Arrows indicate replacement.

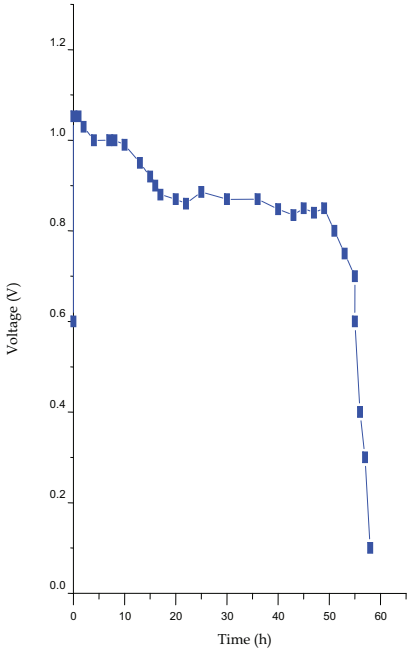

Fig. 6. Voltage generation from glucose as substrate.

5.2 Effect of substrate concentration

Voltage production in the MFC (Figure 7) followed a saturation kinetic, or in other words, the use of substrate in biological systems according to concentration and transport speed (Liu and Logan, 2004). As can be seen in the figure, voltage increased as glucose concentration increased, and remained constant at 1.15 ± 0.05V from a concentration of 1000 mg·L-1. The maximum rate of substrate use therefore occurs in high concentrations of the same (Metcalf and Eddy, 2003).

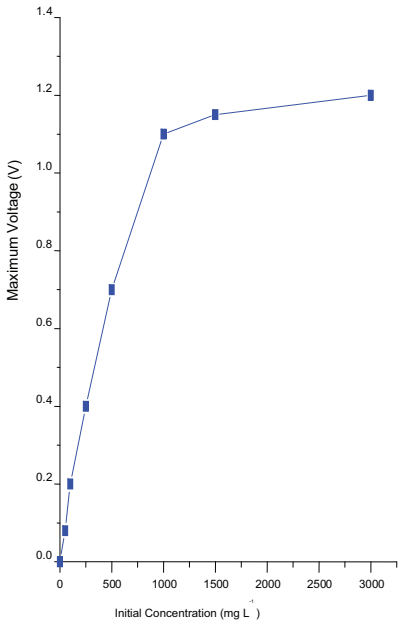

Fig. 7. Maximum voltage generation as a function of glucose concentration.

5.3 Continuous measurement of electricity generation

In this stage electricity generation was monitored over a period of 130 days. With a resistance of 1000Ω the voltage remained at 0.88 ± 0.17V during the first 102 days. After 102 days, a resistance of 600Ω was used, giving values of 0.91 ± 0.08V. With greater fuel oxidation by the microorganisms we expect greater oxidation rates of the electron transporters in the culture at low resistances. In addition, a MFC can be started at low resistances to remove pollutants with high organic indices (Jang et al., 2004).

5.4 Power generation in the MFC

The power density generated by the MFC was measured in W·m-3 based on liquid volume, and the power equation was used for calculations. Using a resistance of 1000Ω, the maximum power density generated was 4.41 $W \cdot m^{-3}$ with a voltage of 1.05V. When a resistance of 600Ω was used, a maximum power density of 6.53 $W \cdot m^{-3}$ was obtained with 0.99V and organic matter removal expressed in COD was 65% and 82%, with 1000 and 600Ω respectively. Table 1, shows the comparison of selected performance parameters of MFCs

with a proton exchange membrane, and we can see that there is a wide range of power values related to the electrode and MFC architecture, the substrate, the inoculum and the redox mediator. Our results are found in the mid-to-low range given that we used a basic architecture, without an external redox mediator.

Substrate	Mixed Culture	Electrode Type	Redox Mediator	CE (%)	P (W/m^3)	References
Glucose	Mixed consortium	Plain graphite	Ferricyanide solution cathode	89	216	Rabaey, 2003
Acetate	Sewage sludge	Plain graphite	Ferricyanide solution cathode and Mn(4+) graphite anode and Fe (3+) graphite cathode	-	32	Park, 2003
Wastewater	Bacteria present in wastewater	Plain graphite	None	12	1.6	Liu, 2004
Wastewater	Activated sludge	Plain graphite	None	-	1.7	Kim, 2004
Glucose	Bacteria present in wastewater	Woven graphite	None	40	13	Liu, 2005
Synthetic wastewater	Anaerobic and aerobic sludge	Granular graphite	Hexacyanoferrate cathode	-	258	Aelterman, 2006
Acetate	Microbial fuel cell	Granular graphite	None Biocathode exposed to air	90	65	Clauwaert, 2007
Wastewater	Bacteria present in wastewater	Graphite brush anodes	None	23	2.3	Logan, 2007
Sucrose	Anaerobic sludge collected from septic tank	Stainless steel	None	7.29	36.72	Behera, 2009
Sodium acetate	Anaerobic digested sludge	Carbon cloth	None	39.6	16.7	Cha, 2010
Synthetic wastewater	Non-anaerobic	Carbon paper	None	59	4.41-6.53	Alzate, 2008

Table 1. Comparison of selected performance parameters of MFC with proton exchange membrane

The results show that operating with lower external resistances increases power density production and leads to increased organic matter removal (Jang et al., 2004). This system

uses an aqueous catholyte to provide the electrode with dissolved O_2, without using external mediators. Microbial consortiums generate greater power density than pure cultures (Pham et al., 2006; Rittmann, 2006).
One of the highest power densities reported in the literature is 386 $W \cdot m^{-3}$ (Aelterman et al., 2008), where sodium acetate was used as a substrate and potassium hexacyanoferrate was used to optimise cathode performance. Ferricyanide is very popular as an electron acceptor in MFC experiments and reaches greater voltages than using O_2. The great advantage of ferricyanide is the low overpotential using flat carbon cathodes. However, power generation with ferricyanide is not sustainable as a result of insufficient reoxidation via O_2, which requires regular replacement of the catholyte. Furthermore, long periods of system operation can be affected by ferricyanide diffusion to the anode chamber (Logan and Reagen, 2006b).

5.5 Influence of pH

Another important parameter in MFC performance is the pH of the anode chamber. The experimental results clearly showed the dependence of MFC performance on the influent pH. During the experiment the pH of the anolyte was maintained at 6.7. The highest power densities occurred at pH values near neutral, with results ranging from 3.68 to 4.41 $W \cdot m^{-3}$ in the case of 1000Ω. Recorded power density decreased slightly when the pH was < 7.0, remaining at 3.55 $W \cdot m^{-3}$. In the measurements taken when using a resistance of 600Ω, a maximum power density of 6.53 $W \cdot m^{-3}$ was obtained at a pH of between 6.8 and 7.0. This result agrees with the results reported by Gil et al. (2003) and He et al. (2008). Both studies observed that low pH (pH 5 and 6) resulted in lower electricity generation. The lower pH in the MFC might have inhibited the activity of electrogenic bacteria. Other researchers have also reported that an acidic pH in the anode chamber reduces power production. Ren et al. (2007) reported a significant decrease in power production when the pH in the anode compartment dropped to 5.2 due to the acidic products of fermentation, and power production was rapidly resumed when the pH of the anolyte was increased to 7.

5.6 Effect of temperature on MFC performance

Anaerobic digestion requires 30–50°C for optimal operation but MFCs are known to operate well at ambient temperature (Ahn and Logan, 2010; Jadhav and Ghangrekar, 2009; Min et al., 2008). Organic removal increased but the electricity production decreased, which might be due to increased activity of methanogens. The additional heating system to maintain temperature may not be necessary for energy recovery or wastewater treatment using MFC technology. The MFC operated at a mesophilic temperature of 35 ± 5°C during the first 102 days. During this period the maximum power density reached was (4.41 $W \cdot m^{-3}$) using 1000Ω at 37°C. A constant temperature of 40°C was maintained for the following days, obtaining a maximum power density of (6.53 $W \cdot m^{-3}$) with 600Ω. Under this last scheme the temperature was increased by 5°C, obtaining 6.54 $W \cdot m^{-3}$. We should note that the temperature increase to 45°C did not lead to significant increases in power density, given that the result obtained is very similar to the one reached at an operational temperature of 40°C. These results reflect the strong influence of the external resistance used, together with an optimum operational temperature (Rozendal et al., 2006).
A significant advantage of MFCs is that they can produce electricity from organic matter whilst operating at moderate temperatures, for example 20-40°C (Min and Logan, 2004; Niessen et al., 2004; Oh et al., 2004; Kim et al., 2005; Liu et al., 2005; Aelterman et al., 2006; Cheng et al., 2006; Zhao et al., 2006; Logan et al., 2007; Oh and Logan, 2007).

5.7 Efficiency obtained in the MFC

Current efficiency is determined based on Coulombic Efficiency (CE), which is defined as the quantity of organic matter recovered as electricity.

$$CE = \frac{Cp}{Cti} \times 100\%$$

The graph of current against MFC operation time was used to determine Cp. The total charge (q) in coulombs is obtained by integrating the area under the curve (from t = 0 to 130 days), which was Cp=12367.23 (Figure 8). Glucose was used as the substrate. The previously described equation (Liu et al., 2005) for Cti is used to calculate the theoretical quantity of coulombs which can be produced by glucose:

$$C_{ti} = \left[\frac{F \times b \times S \times v}{M} \right]$$

where F: is Faraday's constant (98485 C·mol-1 of electrons), b: number of moles of electrons produced per mole of substrate (glucose substrate b=24), S: substrate concentration (g·L-1), v: liquid volume and M: molecular weight of the substrate (glucose, M=180). We therefore obtain Cti=20681.85 and in turn, the coulombic efficiency of the MFC is:

$$CE = \left[\frac{12367.23}{20681.85} \right] \times 100 = 59.79\%$$

The CEs calculated for microbial fuel cells present in the literature vary, but they generally increase with power density because there is less time for substrate to be lost during competing physical and biological processes (Logan and Regan, 2006a).

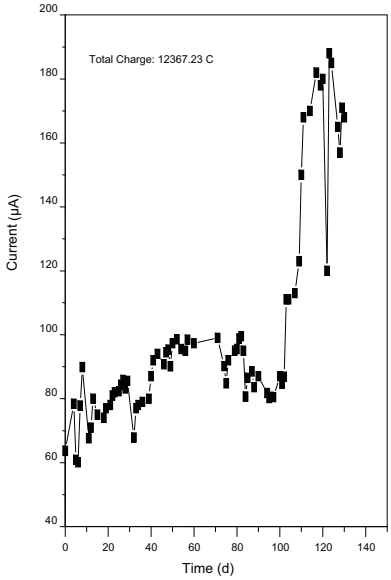

Fig. 8. Total charge calculated from the integration of current over time for substrate consumption.

In this study a CE of 59.79% was obtained. Table 1, presents efficiencies reported in other studies and we can see that the efficiencies produced vary in terms of the type of substrate or electrode used. For example, efficiencies of 23% (Logan et al., 2007) were obtained with bottle (B-MFC) air-cathode MFCs inoculated with wastewater which produced up to 2.3 $W \cdot m^{-3}$ and a CE = 23% with brush electrodes, versus 0.97 $W \cdot m^{-3}$ with a plain carbon paper electrode. These findings show that brush anodes which have high surface areas and a porous structure can produce high power densities, and therefore have qualities which make them ideal for scaling up MFC systems.
Efficiencies of 65% (Min and Logan, 2004) and 63-78% (Oh et al., 2004) were obtained with acetate. With glucose CEs were 89% using potassium hexacyanoferrate at the cathode (Rabaey et al., 2003), whilst Liu and Logan obtained 40-55% using a PEM and 9-12% without a membrane, but using an air cathode, and noting that the main disadvantage of this system was the loss of substrate due to aerobic oxidation at the anode. In other words, there is greater O_2 diffusion in the anode chamber in the absence of a PEM. With wastewater CEs were 3-12% (Liu et al., 2004), with protein efficiency was 6% (Heilman and Logan, 2006) and finally, using lactate and potassium ferricyanide efficiency was 2.4% (Ringeisen et al., 2006).

6. Conclusions

- A PEM microbial fuel cell can generate electricity and simultaneously purify wastewater, which makes it attractive for in situ treatments or for the modification of current conventional treatment plants.
- Switching from aerobic to anaerobic wastewater treatment would cut energy consumption by obviating the need to aerate the sludge. However, conventional anaerobic treatments are often thought of as being slow, need concentrated waste and high temperatures to operate reliably, the effluent often requires further treatment before it can be discharged and sludge disposal is still required. Microbial fuel cells appear to operate at lower temperatures and yield less biomass.
- An aspect to be improved in future studies is to increase the area of the anode to compensate for losses due to death and space occupied by other non-electricity generating bacteria in the biofilm.
- It was shown that as is the case with an external electron acceptor, the presence of conductivity is imminent in the anolyte of the MFC.

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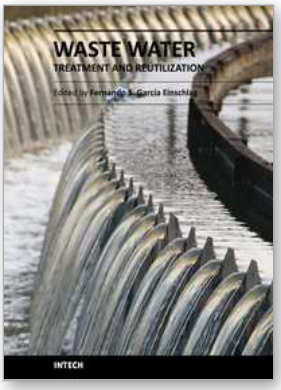

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The steady increase in industrialization, urbanization and enormous population growth are leading to production of huge quantities of wastewaters that may frequently cause environmental hazards. This makes waste water treatment and waste water reduction very important issues. The book offers a collection of studies and findings concerning waste water treatment, minimization and reuse.

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Slavka Krautzeka 83/A
51000 Rijeka, Croatia
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Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821