UNIVERSIDAD DE LEÓN

INSTITUTO DE MEDIO AMBIENTE, RECUROS NATURALES Y BIODIVERSIDAD

DEPARTAMENTO DE QUÍMICA Y FÍSICA APLICADAS

TESIS DOCTORAL

BIOCATALYZED ELECTROLYSIS FOR WASTEWATER TREATMENT AND HYDROGEN PRODUCTION

Presentada por Adrián Escapa González para optar al grado de doctor por la Universidad de León

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León, Noviembre de 2012

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CERTIFICA QUE:

ADRIÁN ESCAPA GONZÁLEZ ha realizado bajo su dirección el trabajo " Biocatalyzed Electrolysis for Wastewater Treatment and Hydrogen Production" , en el Instituto de Medio Ambiente, Recursos Naturales y Biodiversidad de la Universidad de León. Considerando que dicho trabajo reúne los requisitos para ser presentado como Tesis Doctoral expresa su conformidad con dicha presentación.

Y para que conste firma la presente a de de

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ABSTRACT: conventional systems for wastewater treatment require the use of large blowers that are energy intensive and increase the treatment costs. In fact, it has been estimated that ~1% of the national energy consumption goes for wastewater treatment. Biocatalyzed electrolysis (BE) is a relatively novel technology aimed at reducing the global energy consumption during the wastewater treatment process by recovering part of the energy investment as hydrogen. The main objective of this thesis has been to study the ability of BE for organic matter removal and energy production during industrial and urban wastewaters treatment, and also to study the feasibility of combined BE and activated sludge systems for wastewater treatment.

When a 250 mL microbial electrolysis cell (MEC) was continuously fed with an industrial synthetic effluent (from the biodiesel production industries), a fast conversion of glycerol to fermentation products was observed. Hydrogen was produced at a maximum rate of 0.6 L L_a^{-1} d^{-1} with energy consumption below the threshold traditionally associated to water electrolysis and achieving a hydrogen yield of up to 77% of the theoretical maximum value.

It is known that bioelectrochemical systems fed with fermentation products usually outperform those fed with fermentable substrates. Therefore, the performance of a MEC fed with a synthetic effluent of a dark fermentation process was also studied focusing on the effect of the hydraulic retention time (HRT) and the applied voltage. The study showed that it requires applied voltages of 1V and a HRTs of 12 h to remove more that 90% of the influent COD and to achieve a hydrogen production rate of 1.42 L L_a^{-1} d^{-1}. Moreover, the influence of Vapp and HRT on hydrogen production and COD removal rate was found to be interdependent.

When the MEC reactor was fed with actual domestic wastewater, it was found that hydrogen production rates of ~0.3 L L_a^{-1} d^{-1} can be achieved at organic loading rates above 2,000 mg-COD L_a^{-1} d^{-1} with associated energy consumption below the threshold traditionally associated to aerobic treatments. COD removal rate was in the range between 44-76% which means that within the present state of the art, BE technology would require of a polishing step in order to be implemented in actual wastewater treatment plants.

Finally, a preliminary estimation of investment costs of a full-size MEC-based plant for wastewater treatment revealed that in order to make this technology feasible, the manufacturing costs of a MEC should be in the range between 1,100 and 1,350 € m^{-3} of anodic chamber to break even at the turn of 7 years. In addition, it was found that domestic wastewater treatment by BE may become feasible (from an economical point of view) if the current density, energy consumption and hydrogen production rate could achieve 5 A m^{-2}, 0.9 kWh kg-COD^{-1} and 0.8 m^3 m^{-3}_a d^{-1} respectively.

RESUMEN: los tratamientos convencionales de las aguas residuales hacen uso de soplantes y compresores de elevada potencia y elevado consumo de energía, cuyo empleo incrementa los costes del tratamiento. De hecho, se ha estimado que ~1% del consumo nacional de energía eléctrica se destina actualmente al tratamiento de aguas residuales. La electrolisis biocatalítica (EB) es una tecnología relativamente novedosa que surge con la intención de reducir el consumo global de energía durante el tratamiento de las aguas residuales mediante la recuperación, en forma de hidrógeno, de parte de la energía invertida. El objetivo principal de esta tesis es el estudio de la capacidad de la EB para eliminar materia orgánica y generar energía durante el tratamiento de aguas residuales urbanas e industriales. Asimismo, se plantea la realización de una estimación de la viabilidad de una planta de tratamiento de aguas residuales urbanas en la cual se combina la EB con un tratamiento convencional de lodos activos.

En los ensayos de laboratorio, cuando un reactor de EB de 250 mL fue alimentado de forma continua con un agua residual industrial sintética (con la cual se pretendía modelar el efluente residual generado durante la producción de biodiesel), se observó una rápida conversión de glicerol (principal subproducto generado durante la producción de biodiesel) a metabolitos propios de un proceso de fermentación. Además se produjo hidrógeno con una tasa de 0,6 L L_a^{-1} d^{-1}, y con un consumo de energía inferior al que tradicionalmente se asocia a la producción de hidrógeno mediante la electrolisis convencional del agua, alcanzando una tasa de conversión de glicerol a hidrógeno de un 77% del máximo teórico.

Es un hecho conocido que los sistemas bioelectroquímicos alimentados con productos de fermentación normalmente presentan un rendimiento superior a aquellos alimentados con sustratos fermentables (como el glicerol). Por ello, se estudió el comportamiento de un reactor de EB cuando es sometido a un efluente sintético de un proceso de fermentación oscura, haciendo especial hincapié en el efecto del tiempo de retención hidráulica (TRH) y de la tensión aplicada. En este estudio se observó que se necesita una tensión de 1V y un TRH de 12 h para eliminar más de un 90% de la demanda química de oxígeno (DQO) del efluente, alcanzando tasas de producción de hidrógeno de hasta 1,42 L L_a^{-1} d^{-1}. Además, la influencia de la tensión aplicada y del TRH sobre la producción de hidrógeno y la tasa de eliminación de DQO resultó ser interdependiente.

Cuando el reactor de EB fue alimentado con agua residual urbana real, se observó que es posible obtener tasas de producción de hidrógeno de ~0,3 L L_a^{-1} d^{-1} a cargas orgánicas superiores a los 2.000 mg-DQO L_a^{-1} d^{-1} con un consumo de energía muy por debajo del que tradicionalmente se asocia a los sistemas aerobios. Sin embargo, las tasas de eliminación de DQO fueron relativamente bajas (44-76%).

Finalmente, cuando se llevó a cabo una estimación preliminar de los costes futuros de una planta de tratamiento de aguas residuales urbanas basada en EB, se obtuvo que los costes de producción de los reactores de EB se deberían mantener en el rango de 1.100-1.350 € m^{-3} para poder recuperar la inversión al cabo de 7 años. Además, se estableció que la densidad de corriente, el consumo de energía y la tasa de producción de hidrógeno deberían alcanzar 5 A m^{-2}, 0,9 kWh kg-COD^{-1} y 0,8 m^3 m^{-3}_a d^{-1} respectivamente para que la EB pueda ser implantada a nivel comercial.

TABLE OF CONTENTS

ÍNDICE

INDEX OF TABLES

INDEX OF FIGURES

LIST OF SYMBOLS AND ABREVIATIONS

ARB	Anode Respiring Bacteria
ARU	Agua Residual Urbana
BE	Biocatalyzed Electrolysis
BES	Bioelectrochemical System
BOD	Biochemical Oxygen Demand [g L^{-1}]
CCE	Cathodic Conversion Efficiency [%]
$CC_{MEC,N}$	Capital Costs Attributable to MEC in Scenario N [€]
$CC_{PUR,N}$	Purchase Costs of the MEC in Scenario N [€]
$CC_{S,N}$	Capital Costs of the Entire WWTP in Scenario N [€]
CE	Coulombic Efficiency [%]
CF_N	Cash Flow in scenario N [€]
COD	Chemical Oxygen Demand [g L^{-1}]
DC	Direct Current
DQO	Demanda Química de Oxígeno [g L^{-1}]
dWW	Domestic Wastewater
e^-	Electron
E_a	Anodic Potential [V]
EB	Electrolisis biocatalítica
E_c	Cathodic Potential [V]
E_{cons}	Energy Consumption [wh kg^{-1} COD] – [wh L^{-1}_{H2}]
EE	Energy Efficiency [%]
EI	Equivalent Inhabitant
emf	Electromotive Force [V]
EU	European Union
EU ETS	European Union Emissions Trading Scheme
F	Faraday constant (96500 C mol^{-1})
GDE	Gas Diffusion Electrode
H^+	Proton
HER	Hydrogen Evolution Reaction
H_{max}	Maximum Hydrogen Production Constant [L L_a^{-1} d^{-1}]
HRT	Hydraulic Retention Time [h]
I	Current (A)

i	Current density (A m^{-2})
IEM	Ion Exchange Membrane
$I_{H,N}$	Yearly Incomes in the Scenario N [€]
k	Half Saturation Coefficient [L L_a^{-1} d^{-1}]
L_a	Liter of Anodic Chamber
L_{H2}	Liter of Hydrogen
MEC	Microbial Electrolysis Cell
MFC	Microbial Fuel Cell
NHE	Normal Hydrogen Electrode
N	Scenario Identification (sub-index)
N_U	Number of MEC units in one stack
$OC_{S,N}$	Yearly Operational Costs of the Entire WWTP [€]
OLR	Organic Loading Rate [g L^{-1}_a d^{-1}]
ox	Oxidation
PEM	Polymeric Electrolyte Membrane
Q	Flow Rate
R	Universal gas constant (8.314 J mol^{-1} K^{-1})
red	Reduction
SCE	Saturated Calomel Electrode
T	Temperature [ºC]
TKN	Total Kjeldahl Nitrogen [g m^{-3}]
TRH	Tiempo de Retención Hidráulica [h]
V_{app}	Applied Voltage [V]
VFA	Volatile Fatty Acid
WAS	Waste Activated Sludge
WW	Wastewater
WWTP	Wastewater Treatment Plant
Y	Yield [%]

Greek symbols

ε_c	Coulombic Efficiency [%]
ε_{COD}	COD removal efficiency [%]
ε_{cth}	Cathodic Efficiency [%]
ε_E	Energy efficiency [%]

Chapter 1

General Introduction

1.1 BACKGROUND

Industrial, agricultural and domestic wastewaters often consist of a complex mixture of organics that must be removed before discharge into the environment. Activated sludge systems, which have become a conventional wastewater treatment in developed nations, usually makes use of large blowers (to favor oxygen transfer from air into the mixed liquor) that are energy intensive and increase the treatment costs. In 2009, 12,800,974m^3 of wastewater were daily treated in Spain (INE, 2010), resulting in a power consumption of 2,476 GWh $year^{-1}$ (assuming that in Spain 0.53 kWh of electrical energy per cubic meter of wastewater is required for activated sludge process (IDAE, 2010)), which means that around 1% of the national electricity consumption goes for wastewater treatment (IEA, 2011).

In addition, energy prices in Europe have been continuously rising during the second half of the past decade (and will likely raise in the near future as carbon-based fuels become depleted) from an average of 0.0756 € kWh^{-1} in the EU-27 in 2005 to 0.1023 € kWh^{-1} in 2009 (Eurostat, 2010). Thus, the operating cost of treating wastewater are likely to become more and more expensive despite a significant amount of the energy investment can be recovered as natural gas from anaerobic digesters. To make matters worse, aerobic wastewater treatments produce large amounts of sludge that needs to be disposed-off at a cost which can rise up to 500 € per ton dry matter (Weemaes and Verstraete, 2001). Nevertheless, the costs of operating treatment plants could be greatly reduced if we manage to use the energy in the waste water. For example, at a conventional wastewater treatment plant in Toronto, Canada, the potential energy available in the raw wastewater exceeded the electricity requirements of the treatment process by a factor of 9.3 (Shizas, 2004), and thus, such wastewaters can be seen as potential commodities from which bioenergy and biochemicals may be produced (Angenent et al., 2004). However, due to its complex composition, wastewater exploitation requires flexible and robust technologies. In this perspective, biological treatment is the ideal candidate as biological conversions in natural ecosystems commonly occur in dilute aqueous environments (Rozendal, 2007). Among the several chemicals that may be extracted from wastewaters, hydrogen occupies a preeminent

position because of its interesting characteristics as a fuel: it is a clean and CO_2-neutral energy carrier and can be converted directly into electrical energy very efficiently using fuel cell technology. The biological methods for generating H_2 include light-dependent methods (direct and indirect bio-photolysis and photo-fermentation) and non-light-dependent methods which traditionally include the dark fermentation process, and water–gas shift reaction mediated by photoheterotrophic bacteria (Gómez et al., 2011). However all these methods are characterized by its low efficiency in terms of hydrogen yield (Angenent et al., 2004) which is commonly attributed to thermodynamic limitations and the methanogenic consumption of hydrogen (Hawkes et al., 2002; Kim et al., 2004). In fact, under standard conditions complete oxidation of glucose and xylose to CO_2 and H_2 is thermodynamically not possible because a significant amount of volatile fatty acids and some other organics (e.g. lactate, ethanol, butanediol, succinate) are always produced.

$$C_6H_{12}O_6 + 12H_2O \rightarrow 6HCO_3^- + 6H^+ + 12H_2 \qquad \Delta G'^0 = +3.2 \text{ Kj/mol} \qquad (1.1)$$

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2C_2H_3O_2^- + 2HCO_3^- + 4H^+ + 4H_2 \qquad \Delta G'^0 = -206 \text{ Kj/mol} \qquad (1.2)$$

Alternatively, it was discovered a few years ago that this thermodynamic barrier may be overcome by means of a small input of electrical energy (Liu et al., 2005b; Rozendal and Buisman, 2005; Rozendal et al., 2006b) in what has been called a microbial electrolysis cell (MEC). More recent developments in bioelectrochemical systems (BESs) suggest that MECs may represent a promising technology for combining wastewater treatment and energy recovery (Ditzig et al., 2007; Rozendal et al., 2008b; Rozendal et al., 2008a; Logan et al., 2008; Tartakovsky et al., 2009; Pinto et al., 2011) by using the wastewater stream as free electron supply. However, before bench scale MEC reactors can be upgraded to economically feasible applications, there exists the need to investigate the effect of basic operational parameters on hydrogen production and organic matter removal rates, and a number of hurdles (i.e. ohmic voltage losses, activation and concentration overpotentials, coulombic losees, hydrogen recirculation) that limit the overall performance need to be overcome (Clauwaert, 2009; Lee et al., 2009).

1.2 BIOELECTROCHEMICAL SYSTEMS (BES).

A bioelectrochamical system (BESs) can be defined as an electrochemical system in which at least one of the anodic or cathodic reactions is microbially catalyzed (Rabaey et al., 2007). In BESs microoganisms function as catalysts to convert chemical energy into other various types of energy. If a BESs is producing electrical energy, them the system is referred to as microbial fuel cell (MFC), whereas if it consumes electrical energy to drive the electrochemical reactions the it is termed as microbial electrolysis cell (MEC) (Rozendal et al., 2006b). In addition, by controlling reduction reactions at the cathode a plethora of valuable products can be produced at the cathodic chamber of BESs (apart from electricity and hydrogen production and without being exhaustive): (i) CO_2 reduction to form hydrocarbons (Gattrell et al., 2007), (ii) caustic production (Rabaey et al., 2010) (iii) H_2O_2 production (Fu et al., 2010), (iv) nitrogen removal form waste waters (Clauwaert et al., 2007), and (vi) transformation of strongly oxidized functional groups in persistent chemicals (Mu et al., 2009).

A standard MFC (Figure 1.1 left) consists of two electrodes separated from each other by means of a membrane forming two separate chambers: the anodic and the cathodic chambers. The former is where microorganism degrades organic matter producing electrons that are released to the anode through a series of respiratory enzymes in the cell. The later houses the cathode, where the electrons react with a terminal electron acceptor which typically is oxygen. The two electrodes are connected by a wire containing a load which allows electron transfer from the anode to the cathode. In principle, the membrane that separates anode from cathode is permeable to protons produced in the anode, so they can migrate to the cathode where they can combine with the electrons transferred via the wire and with oxygen, forming water (Logan, 2008). The maximum electromotive force attainable (emf) in a MFC is theoretically in the order of 1.1 V (Rozendal, 2007), however due to potential losses and irreversibilities, the emf usually falls below 0.6V under operating conditions (Logan et al., 2006).

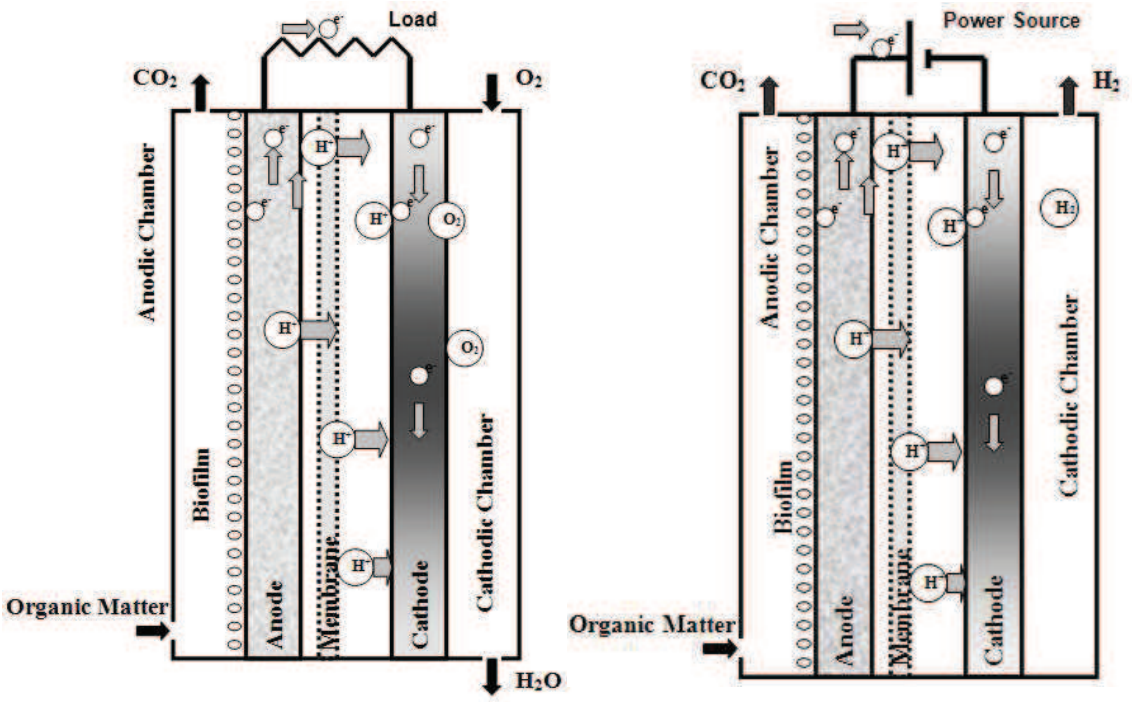

Figure 1.1. Schematic representation of electricity production (left) and hydrogen production (right) through MFC and MEC respectively. Electrons (e-) protons (H+) and carbon dioxide (CO2) are the main sub-products of the metabolism of the anode respiring bacteria (ARB) present in the biofilm. The electrons flow through an external circuit (either an electric load or a power source depending on whether the BES operates in electricity or hydrogen production mode). In both cases, protons migrate through the membrane into the cathodic chamber where they re-combine with electrons, producing either water when oxygen is allowed to enter into the cathodic chamber (MFC), or hydrogen when no oxygen is allowed to get into the cathodic chamber and electrons are forced to circulate by means of a power source (MEC).

The evolution of hydrogen in a MFC-like reactor is made possible when the biological oxidation of organic material at the anode is coupled to the reduction of protons at the cathode, and this process is referred to as microbial electrolysis. Therefore, the MEC-reactor architecture (Figure 1.1 right) will be very much like that of a MFC. However, there are two main distinctions between MEC-type and MFC-type reactors. First, oxygen needs to be prevented from entering the cathodic chamber of a MEC in order to avoid the oxygen reduction reaction. Second, as the hydrogen evolution reaction (HER) does not proceed spontaneously in a MEC, it is necessary to supply a certain amount of electrical power by means of a power supply. In theory, 0.114 V is the minimum applied voltage (V_{app}) necessary for the HER to start; in practice, experiments have shown that V_{app}s above 0.25 V must be applied to obtain reasonable current densities.

1.2.1 Underlying Principles. The Process of Electrogenesis

The electron transfer mechanism is undoubtedly a decisive step in microbial metabolisms, where electrons flow from an electron donor (lower potential) to an electron acceptor (higher potential). Depending on whether the electron acceptor is found inside or outside the microorganism, the metabolism is termed as fermentation or respiration respectively. In the latter case, when soluble electron acceptors are depleted in the microbial environment, exocellular electron transfer represents an important mechanism to sustain microbial metabolism (Stams et al., 2006). This is a common situation in nature, where mainly minerals containing iron and manganese oxides (i.e., Fe(III) and Mn(IV)) are being reduced. Thus, in theory electricity could be generated by exploiting this ability of microorganism to transport electrons outside of the cell. It was Potter in 1911 (Potter, 1911) the firs who observed electricity production in microbial cultures, creating a biological anode where microorganism could release the produced electrons.

Electrogenic microorganism (also known as anode respiring bacteria (ARB)) are known to release the electrons to the anode by means of one of the following mechanism: (i) direct contact with the electrode surface (Kim et al., 1999; Holmes et al., 2004), (ii) aided by redox mediators (Rabaey et al., 2003) and (iii) through conductive cellular pili known as nanowires (Reguera et al., 2005; Gorby et al.,). The first of these categories (i.e., direct electron transfer) requires electrical contacts between the outer surface of the cell and the electrode surface (Figure 1.2), and has primarily been studied in dissimilatory metal reducing bacteria (Arnold et al., 1988; Nealson and Saffarini, 1994). Although direct electron transfer occurs within complex communities and across diverse phyla, the investigation of its mechanism has mainly revolved around two model microorganism: *Shewanella oneidensis* MR-1 and *Geobacter sulfurreducens* (Rabaey, 2010).

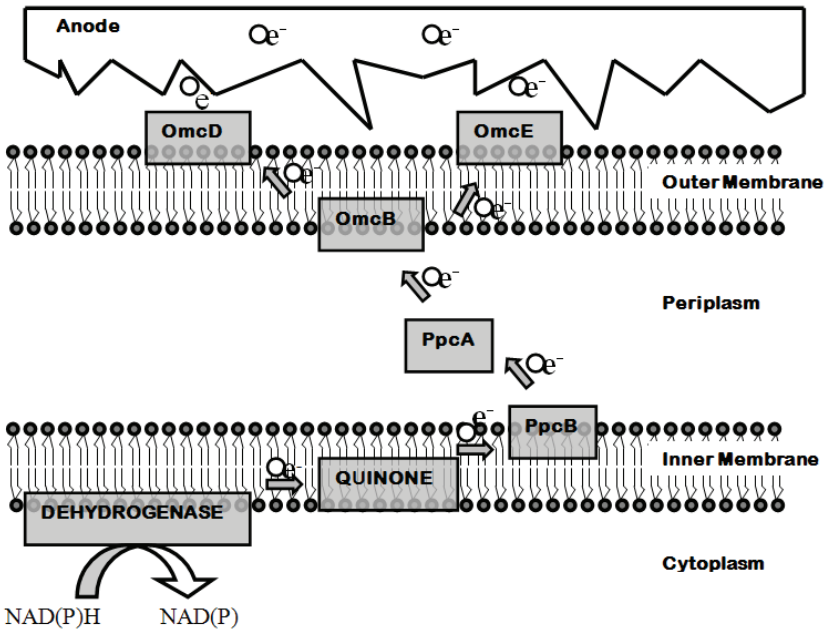

Figure 1.2. Summary of the electron transfer chain proposed to be involved in the ARB metabolism in BESs using metal reducing microorganisms (Geobacter species). (Figure drawn with modifications after (Lovley et al., 2004)).

The second mechanism (Figure 1.3) of electron transfer (i.e., aided by redox mediators) proposes the presence of a soluble electron shuttle: a compound that carries electrons form the bacteria by diffusive transport to the surface of the electrode (or metal oxide), and is able to react with it, discharging its electrons (Torres et al., 2010). Then the oxidized redox mediator diffuses back to the microorganism where it is re-reduced again being subjected to a new oxidation-reduction cycle. The electron shuttles involved in this process can be endogenous chemical mediators (i.e., self-produced) such as quinones and phenazine (Rabaey et al., 2004; Rabaey et al., 2005) and also they can be found naturally in the environment as in the case of humic acids (Straub et al., 2001; Hernandez and Newman, 2001). Furthermore, artificially added chemicals such as ferric chelate and thionin can be used to facilitate the shuttling of electrons (Tanaka et al., 1983a; Tanaka et al., 1983b), nevertheless its applicability to industrial scale BES is limited because of its economic costs and the environmental burdens derived from the toxic nature of most artificial electron shuttles (Du et al., 2007).

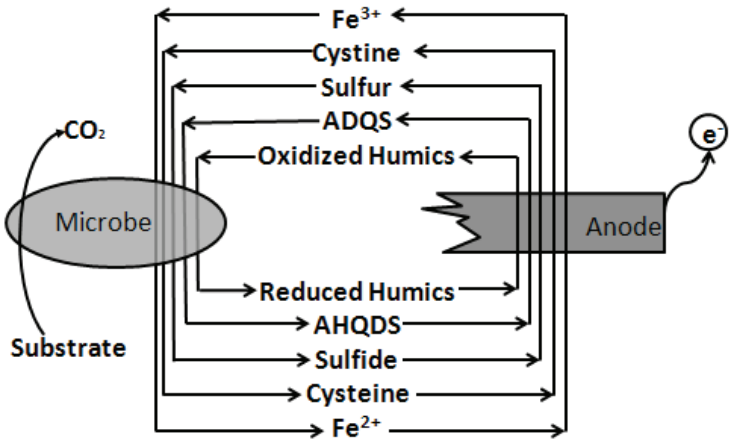

Figure 1.3. Schematic representation of electron transfer through soluble electron shuttles. (Figure drawn with modifications after (Lovley et al., 2004)).

The third mechanism of electron transfer takes place through electrically conductive appendages called "bacterial nanowires". Members of the *Geobacteraceae* family, which are known to transfer electrons through mediator-less mechanisms, can form relatively thick (>50μm) anode biofilms (Derek R, 2008). Nevertheless, cells at this considerable distance from the anode contribute to current production (Nevin et al., 2008), and bacterial nanowires are known to play an important role in this long-range electron transfer (Reguera et al., 2006).

1.2.2 Thermodynamics of Bioelectrochemical Reactions

In an electrochemical reactor the oxidation and reduction reactions proceed at separate electrodes, and the electrical work W_{el} that can be done by the system is:

$$W_{el} = -Q\Delta E = -nF\Delta E \qquad (1.3)$$

where ΔE *(V)* is the potential difference between the electrodes, Q (C) is the transported charge, which is n times the Faraday constant (96,484.6 C mol^{-1}), and n is the number of electrons transferred within the reaction.

For an overall electrochemical reaction $q_A A + q_B B \rightarrow q_c C + q_D D$, the electrical work can also be computed in terms of the change in its Gibbs free energy:

$$W_{el} = -\Delta G_r = \Delta G_r^0 + RTln\left(\frac{a_C^{\vartheta c}\, a_D^{\vartheta D}}{a_A^{\vartheta A}\, a_B^{\vartheta B}}\right) \qquad (1.4)$$

with ΔG_r *(J)* the Gibbs free energy of a reaction at specific conditions, ΔG^0_r (J) the Gibbs free energy of a reaction at standar conditions (298.15 *K*, 1bar, 1*M* concentration for all species), R the universal gas constant (8.3145 J mol^{-1} K^{-1}), T (K) the absolute temperature, a_i the activity of a specific product or reactant i and u_i the reaction coefficient of a specific product or reactant.

Combining Equations 1.4 and 1.3 yields the following expression for the potential difference between the electrodes of the electrochemical system:

$$\Delta E = \Delta E^0 - \frac{RT}{nF} ln\left(\frac{a_C^{\vartheta c}\, a_D^{\vartheta D}}{a_A^{\vartheta A}\, a_B^{\vartheta B}}\right) \quad (1.5)$$

where ΔE^0 (V) *is* the potential difference between the electrodes at standard conditions. When $\Delta E>0$ the process is called a galvanic cell and the overall reaction proceeds from left to right. On the contrary, when $\Delta E<0$ an electrolytic process takes places and the overall reaction proceeds in the reverse direction. In a MFC, where anodic oxidation of organic matter (e.g., acetate) is coupled to a cathode that reduces oxygen to water and therefore $\Delta E>0$; whereas in a MEC the cathode reduces protons to hydrogen and thus $\Delta E<0$.

ΔE is often expressed as the difference in the anode (E_A) and cathode (E_C) potentials, (i.e., the potentials of the half-cell reactions), which in literature are reported relative to the normal hydrogen electrode (NHE), which is defined to be zero at standard conditions (i.e., 298K, pH_2=1bar, $[H^+]$=1M):

$$\Delta E = E_C - E_A \quad (1.6)$$

If we assume that acetate is oxidized by electrochemically active microorganism at the cathode, the anodic half reaction can be written as:

$$2HCO_3^- + 9H^+ + 8e^- \rightarrow C_2H_3O_2^- + 4H_2O \quad (1.7)$$

Consequently, and according to Equation 1.5, anodic potential at specific conditions (E_A) can be computed as:

$$E_A = E_A^0 - \frac{RT}{8F} ln\left(\frac{[C_2H_3\, O_2^-]}{[HCO_3^-]^2[H^+]^9}\right) \quad (1.8)$$

where E_A^0 (V) is the anodic potential at standard conditions relative to the NHE. Similarly, for a cathode that reduces oxygen, the electrode potential at specific conditions (E_{C_O2}) can be calculated as:

$$O_2+4H^++4e^-\rightarrow 2H_2O \quad (1.9)$$

$$E_{C\_O2} = E^0_{C\_O2} - \frac{RT}{4F} ln\left(\frac{1}{pO_2[H^+]^4}\right) \quad (1.10)$$

where $E_{C\_02}^0$ (V) is the cathodic potential at standard conditions relative to the NHE and pO_2 (bar)is the partial pressure of oxygen. Likewise, when a cathode reduces protons instead of oxygen, the electrode potential at specific conditions (E_{C_H2}) can be calculated as:

$$2H^++2e^-\rightarrow H_2 \quad (1.11)$$

$$E_{C\_H2} = E^0_{C\_H2} - \frac{RT}{2F} ln\left(\frac{pH_2}{[H^+]^2}\right) \quad (1.12)$$

where $E_{C\_H2}^0$ (V) is the cathodic potential at standard conditions relative to the NHE and pH_2 (bar)is the partial pressure of hydrogen.

1.2.3 Overpotentials

Due to various potential losses, actual cell and electrodes potentials differ from voltages computed as in Equations 1.5, 1.6, 1.8, 1.10 and 1.12, which are indeed theoretical potentials. These potential losses (commonly known as overpotentials) usually include, ohmic losses, activation losses, concentration losses and the loos that results from the microbial metabolic activity. All these overpotentials are graphically depicted in Figure 1.4 and explained below:

Ohmic overpotentials are derived from electron transfer through electrodes and ion transfer through the electrolyte, and they obey Ohm's law. Thus, the ohmic overpotential (h_Ω) is proportional to the current (I):

$$\eta_\Omega = IR \quad (1.13)$$

where *I (A)* represents the current flow, and *R (Ω)* the total cell resistance. Ohmic overpotentials can be decreased by using electrolyte solutions with high ionic strength

(thus higher conductivity), through the decrease of anode-to-cathode spacing, and the use of current collectors (to minimize the effect of large electrode surface area).

Concentration overpotentials are often associated with inefficient mass transfer through migration, diffusion and convention of substrates or removal of products. In bioelectrochemical devices also includes the rate of biocatalytic substrate conversion (i.e. the conversion rate of substrate into species that may be oxidized on the electrode surface area). In the absence of other type of overpotentials, concentration overpotentials (η_C, [V]) can be expressed as (Bagotsky, 2005):

$$\eta_{c=}\frac{RT}{nF}\cdot ln\left(\frac{1+(i/i_{l,red})}{1-(i/i_{l,ox})}\right) \quad (1.14)$$

where i (A m^{-2}) stands for the current density, and $i_{l,red}$ and $i_{l,ox}$ (A m^{-2}) represent the limiting currents of reduction and oxidation respectively of the electrochemically active species. Concentration polarization in BES can be decreased by better reactor mixing and/or by increasing buffer concentration; however, the necessity of additional energy input and the addition of chemicals have to be taken into consideration (Rabaey, 2010).

Activation overpotentials are derived from slow electrode kinetics (i.e., the rate at which electrons are transferred to the electrode). The relation between activation overpotential (η_A, [V]) and current density for a given electrode can often be written in the form of (Bagotsky, 2005):

$$\eta_A = a + b \cdot \ln(i) \quad (1.15)$$

where *a* is a parameter that depends on the type of electrode and the electrochemical reaction studied, and ranges from 0.03 to 3V. Parameter *b* changes within much narrower limits; in many cases at room temperature b ≈0.05V. Activation over potentials can be minimized by using more effective catalysts, increase the real surface electrode area (by increasing the electrode roughness) or even using higher reaction temperatures.

As a result, the cell voltage (E_{cell}) produced at any specific current can be computed as:

$$E_{cell} = \Delta E - (\eta_{\Omega} + \eta_C^A + |\eta_C^C| + \eta_A^A + |\eta_A^C|) \quad (1.16)$$

where $\eta_C{}^A$ and $\eta_C{}^C$ represent the concentration overpotential at the anode and cathode respectively and and $\eta_A{}^A$ and $\eta_A{}^C$ stand for the activation overpotential at the anode and cathode respectively. Note that when the reactor is operated in MEC mode E_{cell} becomes negative.

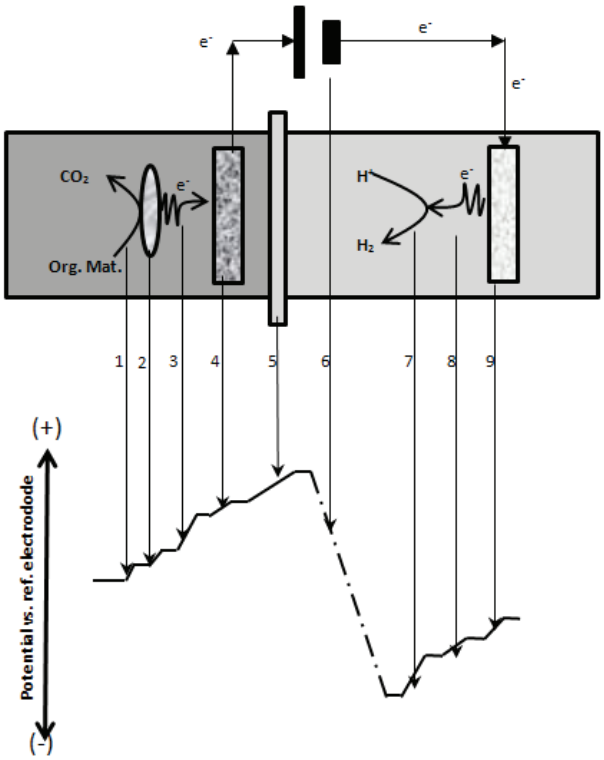

Figura 1.4. The several bioelectrochemical loses associated to a MEC reactor: mass transfer and substrate diffusion in the anodic chamber (1), bacterial metabolism (2), electron transfer to the anode (3), anodic ohmic loses (4), ohmic and mass transfer loses associated to ions circulation (5), mass transfer and hydrogen diffusion in the cathodic chamber (7), electron transfer from the cathode (8), and cathodic ohmic looses (9). The applied potential needed for the global bioelectrochemical reaction to proceed has also been included (6).

1.2.4 Performance Parameters

The main goal of a bioelectrochemical reactor is to produce either electricity or hydrogen (or any other of the products discussed in paragraph 1.4) while at the same time remove the organic contamination from an aqueous effluent. However, these two parameters (energy/hydrogen production and organics removal) are insufficient to describe the performance of a BES. We also need to take into account many other

factors such the recovery of electrons in the anode, the energy efficiency or the energy conversion efficiency. Following, how the most important of this performance parameters are computed is detailed:

Treatment efficiency (CODr, %). BESs have been proposed as technology for wastewater treatment, and as so it is important to compute its ability to remove organic matter from a waste effluent. Even though its performance can be evaluated in terms of biochemical oxygen demand (BOD) removal, total oganic carbon (TOC) removal and several other parameters (Metcalf & Eddy Inc., 2003), in this work chemical oxygen demand removal (*CODr*) has been selected as the preferred parameter to compute the BES treatment efficiency:

$$CODr = \frac{(COD_{in} - COD_{out})}{COD_{in}} \quad (1.17)$$

where COD_{in} and COD_{out} are the COD concentration of MEC influent and effluent respectively.

Coulombic efficiency (CE, %): has been defined as the ratio of total electronic charges transferred to the anode from the substrate, to maximum possible charges if all substrate removal produced current (Logan et al., 2006). It is calculated as:

$$CE = \frac{\int_0^{86400} Idt}{(COD_{in} - COD_{out})/M \cdot Q_{in} \cdot e \cdot F} \cdot 100 \quad (1.18)$$

where I is the circulating electrical current (A), M is the weight of 1 mol of COD (32 g mol^{-1}), Q_{in} is the influent flow rate (L d^{-1}), e is the number of mol of electrons exchanged per mol of COD equivalent consumed (8 mol mol^{-1}), and F is the Faraday constant (96,485 C mol^{-1}).

Cathode conversion efficiency (CCE, %), also known as cathodic efficiency. It represents the ratio of hydrogen recovery to the maximum theoretical production if all the electronic charges that arrive to the cathode were converted to hydrogen:

$$CCE = \frac{(p \cdot Q_{H2} \cdot V_a)/(R \cdot T) \cdot e_{H2} \cdot F}{\int_0^{86400} Idt} \cdot 100 \quad (1.19)$$

where p is the pressure in the cathodic chamber (p=1 atm); Q_{H2} is the hydrogen flow rate ($L_{H2}\ L_a^{-1}\ d^{-1}$); V_a is the anode volume (L); R is the ideal gas constant (R=0.08205 L atm K^{-1} mol^{-1}); T is the temperature (K); e_{H2} is the number of mol of electrons exchanged per mol of hydrogen (2 mol mol^{-1}).

Hydrogen yield (Y_{H2}, mol mol^{-1}), is the number of mol of hydrogen harvested from 1 mol of COD consumed:

$$Y_{H2} = \frac{(p \cdot Q_{H2} \cdot V_a)/(R \cdot T)}{(COD_{in} - COD_{out})/M \cdot Q_{in}} \quad (1.20)$$

Specific energy consumption (E_{cons}, Wh g^{-1}-COD) is the electrical energy supplied to the MEC relative to the amount of organic matter consumed, and is calculated as:

$$E_{cons} = \frac{\int_0^{86400} V_{app} \cdot I \cdot dt}{(COD_{in} - COD_{out})/M \cdot Q_{in}} \quad (1.21)$$

where V_{app} is the voltage applied to MEC (V)

1.2.5 Operational Parameters Affecting Bio-Electrochemical Systems

There are several factors that have a significant influence on the performance of bioelectrochemical systems. Without being exhaustive, here is a list of the most relevant ones in the author's opinion:

pH. Changes in internal and external pH usually affects bacterial activity, adaptation to acidic or basic conditions and the dissociation of compounds such ammonia, sulphide and organic acids among others. Substrate degradation in BESs has been observed to be higher under neutral operating conditions (pH in the range of 6.25 to 6.50) (Raghavulu et al., 2009; Martin et al., 2010; He et al., 2008). Besides, in regular urban wastewater, the concentration of cations other than protons (e.g., Na^+, K^+, NH_4^+) are typically 10^5 times higher than the concentration of protons (Rozendal et al., 2007). In this situation these species rather protons are responsible for the transport of positive charges (Zhao et al., 2006). In bicameral systems, where cation exchange membrane is interposed between both the anodic and the cathodic chamber, this transport creates a pH gradient

between the anodic and cathodic chambers that can affect negatively the cell performance (Rozendal et al., 2007).

Temperature. The effect of temperature on BESs performance is still not clear. While it has been shown that current generation in a MFC at 8–22 °C was much higher than that at 20–35 °C (Jadhav and Ghangrekar, 2009), other studies have shown that power output increases when temperature increases from ~20 to ~30 °C and that little activity was detected at 15 °C (Liu et al., 2005a; Min et al., 2008). More recently, when studying electrochemically active biofilm activity, it was found that when temperature is in the range between 30 and 45 °C, the catalytic currents increase following the Arrhenius law and that at 53 °C and above negligible catalytic current was observed (Liu et al., 2011). Optimum working temperature was 45 °C.

Electrolyte ionic strength. Solution resistance between electrodes has been identified as an important responsible in BES performance limitations (Rozendal et al., 2008a; Logan et al., 2008), particularly when BESs are fed with domestic and many industrial wastewaters, which typically exhibit low conductivities (in the order of only 1 mS cm^{-1}) (Rozendal et al., 2008a), leading to high ohmic loses. Undoubtedly, electrolyte conductivity could be increased by adding salts, although this solution might not be economically nor environmentally feasible at industrial scale. A more reasonable solution has to do with the reactor architecture and consists of reducing electrode spacing, since conductivity is inversely proportional to the distance between electrodes (Logan et al., 2006; Ghangrekar and Shinde, 2007).

Applied potential. As low as 0.11-0.23 V is the applied potential needed to produce hydrogen in MEC (Liu et al., 2005b; Rozendal et al., 2006b; Ditzig et al., 2007; Rozendal et al., 2007); still applied potentials of 0.4 V and below usually fail to produce significant amounts of hydrogen and to remove organic matter (Tartakovsky et al., 2009). In addition, tests performed in an acetate-fed single-chamber MEC revealed that applied voltages between 0.4-1.2 V, acetate removal and hydrogen production rates were proportional to V_{app} (Tartakovsky et al., 2009). Tests performed with other substrates showed a similar dependence between applied voltage and hydrogen production and substrate removal rates (Lu et al., 2009; Escapa et al., 2009). Applied voltages above 1.2 V did not improve significantly hydrogen production nor the

substrate removal rate. It has been suggested that applied voltages above 1.2V, electron transfer becomes limited by the metabolic activity of electrogenic microbes (Tartakovsky et al., 2008).

External resistance. A microbial fuel cell can be regarded as a particular type of battery, and as such can be modeled simply as an ideal power source in series with a resistance known as internal resistance. The internal resistance has a decisive influence in the power produced by the MFC, which can be maximized by selecting an external load with a resistance equal or similar to the internal resistance (Logan, 2008).

1.3 BIOELECTROCHEMICAL SYSTEMS FOR WASTEWATER TREATMENT AND ENERGY PRODUCTION

From a wastewater treatment perspective, BESs can also be seen as a method to produce a high-valuable commodity (i.e., hydrogen, electricity, etc.) from a diluted COD stream (e.g., domestic wastewater) at the cost of a small (or even null) input of energy (Rozendal, 2007). In addition, BES have advantages over other technologies used for generating energy from organic matter. First, MFCs produce energy in a much more efficient way than combustion engines, which are limited by the Carnot limit. Second, the hydrogen produced in a bicameral-MEC usually has high purity levels resulting from interposing a separation between the anodic and the cathodic cambers. Third, BESs do not require additional energy for aeration since MFC can be aerated passively and MEC do not require air at all. Finally, since BESs involve an anaerobic process, the yield of biomass is usually relatively low compared to that of aerobic treatments. Even though biomass yields have not yet been thoroughly investigated for bio-electrochemical reactors, a range of yields of 0.07g to 0.31g COD-biomass g^{-1} COD-substrate have been reported (Rabaey et al., 2003; Freguia et al., 2007), which is well below to what is consider "typical" for an aerobic treatment (0.4 g COD-biomass g^{-1} COD-substrate) (Logan, 2008).

Before we consider how a BES might be implemented in a WWTP, it is important to know how a conventional wastewater treatment plant (WWTP) is designed. Traditionally, wastewater treatment has been a combination of physical, biological and

chemical treatment methods, the final arrangement depending on the type of WW to be treated. Here, we will focus on the arrangement of a "typical" large WWTP used for domestic WW treatment. Although water may be polluted by many materials and substances, the most common contaminants found in domestic WW are: *(i) Organic materials*, as measured by the biological demand for oxygen (BOD) or the chemical demand for oxygen (COD); *(ii) nitrogen*, which includes biological nitrogen, nitrates, nitrites and ammonium; *(iii) phosphorus*; *(iv) suspended solids; (v) pathogenic organisms* (as estimated by coliforms); and *(vi) traces of persistent organics* (such as chlorinated pesticides).

Despite large urban WWTP can vary greatly in terms of their design, often they take a general form as shown in Figure 1.5, which includes the most characteristic elements that conform the water-treatment line: *(i)The preliminary treatment*, where the WW is first screened to remove large debris and grit in order to protect pumps and the remainder of the unit operations. *(ii)The primary treatment*: its purpose is to remove all particles that are settable. *(iii)The secondary treatment,* which typically consists of two components: a bioreactor where soluble organic materials gets converted mainly to bacterial biomass and carbon dioxide, and a settling tank (called secondary clarifier) where the bacterial biomass is removed. *(iv) Advanced treatment*, which includes several polishing or cleanup processes, such as nutrients removal (mainly phosphorous and nitrogen) and chlorination to kill bacteria. *(v) Residuals management,* where solids removed by other process are collected, stabilized and subsequently disposed.

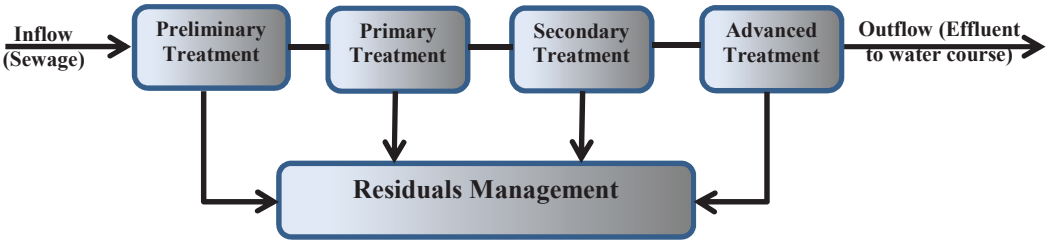

Figure 1.5. Arrangement of a typical large wastewater treatment facility (picture reproduced from (Aarne Vesilind, 2003)).

Up to now, several treatment process trains where BES can be integrated in a WWTP have been envisioned (Rosenbaum et al., 2010). Since the anodic chamber of a BES usually contains undefined mixed cultures (including electrogenic microorganisms) that can oxidize a wide variety of organics with the anode as an electron acceptor (Rabaey et

al., 2003; Liu et al., 2005a; He et al., 2005; Heilmann and Logan, 2006; Huang and Logan, 2008; Liu et al., 2004), the first and simplest process train seems to be a "stand-alone" arrangement, where the BES could be incorporated replacing the bioreactor in the secondary treatment. Nevertheless, experiments conducted with real domestic wastewater-fed reactors have revealed that COD removal at bench-scale tests is limited (tipically 40-80%) (Liu et al., 2004; Rodrigo et al., 2007; Min and Logan, 2004), and may not accomplish what local regulations allow in terms of BOD removal and BOD concentration of the effluent. In addition nitrogen removal in a MFC-MEC is usually low, and it is mostly attributable to nitrogen assimilation into bacterial biomass, which accounts for only a small percent of the total removal usually needed (Logan, 2008; Freguia et al., 2007). For these reasons, it seems unlikely that a BES may operate alone in a WWTP, and so a polishing step may be required. This leads us to the second configuration or niche for BESs application which consists of a bio-electrochemical treatment followed by an aerobic/anoxic step.

Usually, BESs fed with non-fermentable substrates appear to outperform (in terms of CE) those fed with readily fermentable substrates (Lee et al., 2008), for the anodic food web in the former dos not need to support hydrolysis and digestion of high molecular-weight constituents. Therefore, wastewater acidification prior to the BESs treatment would likely increase its performance, since it accelerates soluble organic constituents and hydrolysis, and almost all organic materials in wastewaters, regardless of its origin can be uniformly degraded to relatively simple volatile fatty acids (VFAs), which are readily converted to electricity in a BES (Li and Yu, 2011) even at low concentrations (Lee et al., 2008; Kim et al., 2010). In addition, this "two-stage" process favors the enrichment of specific species in the individual reactors (De La Rubia et al., 2009; Fezzani and Ben Cheikh, 2010), and increases the process stability (Held et al., 2002). However, a two-stage arrangement may complicate the reactor configuration and operation, and so resulting in increased investment and operation costs. Another drawback of this arrangement is, as it happens with the "stand-alone" one, little nitrogen is removed from the effluent, and so an aerobic/anoxic polishing step might be required after the BES reactor.

BESs can also be integrated in a WWTP as a postreatment of the effluent of waste activated sludge (WAS) and primary sludge (PS) co-digestion. Anaerobic digestion of

WAS at thermophilic temperatures (55°) presents several advantages over mesophilic temperatures (35-37°), namely: they increase the rate of solubilization, double the methane production, achieve volatile solids removal efficiencies up to 40 % (Lafitte-Trouqué and Forster, 2002) , and also allow for sufficient pathogen removal (Welper et al., 1997). However, high temperatures increase the concentrations of propionate and ammonia, which can inhibit methanogenesis and lead to increased accumulation of VFAs (Bocher et al., 2008), and therefore the effluent thermophilic anaerobic codigestion of WAS+PS becomes an ideal substrate for BESs, as VFAs can be easily converted into current by electrogenic microorganisms.

Another potential niche for BESs is as a postreatment of anaerobic digestion of industrial wastewaters (Pham et al., 2006; De Schamphelaire and Verstraete, 2009). Usually, high-strength wastewaters (more than 1 g-COD L^{-1}) go through anaerobic digestion because of its remarkable bioconversion efficiency (often depassing 90 %) and its ability to recover the energy content of the substrate in the form of methane (Pham et al., 2006). As BES can operate at low strength effluents (Rozendal et al., 2008a), BES processes such as MECs may replace conventional activated sludge polishing systems after anaerobic digestion (Kim et al., 2010).

1.4 CURRENT STATUS OF MEC TECHNOLOGY

MECs for hydrogen production

Since the principle of hydrogen production through MEC was first demonstrated in 2005/6 (Liu et al., 2005b; Rozendal et al., 2006b), continuous improvements and breakthroughs have been made in the performance and architecture of the reactors. The first remarkable change made in the architecture of the MECs was the development of single-chamber MECs that lacks membrane, which allowed to boost the hydrogen production in acetate-fed MECs (Logan et al., 2008; Tartakovsky et al., 2009; Rozendal et al., 2007; Call and Logan, 2008) while reducing significantly the production cost of hydrogen (Rozendal et al., 2008a). Through the use of a membrane-less system, a graphite fiber brush anode, and close electrode spacing, hydrogen production rates reached a maximum of 3.12 m^3H_2 m^{-3} (Call and Logan, 2008), which was more than

double than that obtained in previous MEC studies (Cheng and Logan, 2007). However, the absence of a polymeric membrane between the anode and the cathode of the MEC, makes possible the conversion of the cathodic hydrogen to methane by Methanobacteriales in anode and cathode biofilms (Lee et al., 2009), which limits significantly the overall performance of hydrogen production. Therefore methanogenic activity is an issue that must be carefully addressed to increase MEC performance, yet none of the several various approaches that have been proposed (Call and Logan, 2008; Lee and Rittmann, 2010; Chae et al., 2010; Wang et al., 2009) can satisfactorily suppress hydrogenotrophic activity. Interestingly, rather than avoid methane production, it has been suggested that the conversion of hydrogen to methane in a MEC may represent a viable method for bioenergy production from hydrogen gas (Clauwaert and Verstraete, 2009; Clauwaert et al., 2008). This new approach would also bring extra environmental benefits, since the CO_2 produced during biomass oxidation in the cathode, can be further converted to additional fuel (Van Eerten-Jansen et al., 2012).

The highest hydrogen production reported up to now in a MEC (50 L L_a^{-1} d^{-1}), was observed using a Ni-foam electrode (Jeremiasse et al., 2010b), although it was also reported a reduction in the rate over time. More usually hydrogen production rates in MECs are reported to be in the range of 0.01-6 L L_a^{-1} d^{-1} (Rozendal et al., 2006b; Tartakovsky et al., 2009; Escapa et al., 2009; Call and Logan, 2008). Notably, low cost materials such as stainless steel cathodes are performing also satisfactorily as cathodes in MEC allowing to hydrogen production rates of 1.7 L L_a^{-1} d^{-1}. Although when compare with other hydrogen production technologies such as dark fermentation, MEC is lagging behind in terms of hydrogen production rates (a maximum rate of 189 L L_a^{-1} d^{-1} has been reported for dark fermentation (Lo et al., 2009)), hydrogen yields in MECs are much more favorable (Lee et al., 2010; Borole, 2011).

MECs for chemicals and reagents production

In addition to hydrogen and methane, a plethora of valuable industrial products can be produced in the cathode of MECs. One of the firs process investigated was the production of sodium hydroxide in the cathode of a MEC (Rozendal et al., 2006a), which is based in part on the poor selectivity of the cation exchange membranes and in part on the much higher concentration of metallic cations than protons in conventional

wastewater streams. More recently, a novel device which combines a microbial electrolysis cell with a microbial desalination cell had the feature of simultaneous HCl and NaOH production, while reducing the organic load of a synthetic wastewater (Chen et al., 2012). Hydrogen peroxide is another valuable product that can be generated by stabilizing oxygen reduction in the cathode of a MEC (Rozendal et al., 2009). More recently, Cusick and Logan (2012) have succeeded in precipitating phosphorus as struvite, while producing in parallel a significant amount of hydrogen (2.3 L L_a^{-1} d^{-1}) in the cathode of a MEC.

It has also been shown that biofilms of *Sporomusa ovata* growing on graphite cathode surfaces consumed electrons with the reduction of carbon dioxide to acetate (Nevin et al., 2010), which can be further reduced to ethanol with methyl viologen in the cathode compartment of MEC (Steinbusch et al, 2010).

Biotic vs. abiotic cathodes

A significant modification of the MEC architecture came with the use of biotic cathodes, in which the hydrogen evolution reaction is catalyzed by electrochemically active microorganisms (Rozendal et al., 2008b). In the referred work, a microbial biocathode outperformed by more than three times the performance of a control Pt-based abiotic cathode in terms of hydrogen production and current density. Even though this achievement has attracted the attention of several research groups (Croese et al., 2011; Huang et al., 2011; Xie et al., 2011; Jeremiasse et al., 2010a), the use of biotic cathodes have not yet proved to be a feasible alternative for abiotic ones. On the contrary, abiotic cathodes have experienced continuous improvements, mainly regarding to the catalyst used. First row transition metals such as iron, cobalt, titanium and nickel , has been widely employed in bioelectrochemical systems (Kim et al., 2011; HaoYu et al., 2007; Selembo et al., 2009; Manuel et al., 2010) because of their stability, abundance in nature, stability and low toxicity for living organisms (Selembo et al., 2009). Particullarly, Ni-based cathodes have provided very promising results in terms of hydrogen production and energy efficiency, in many cases outperforming Pt-based cathodes (Selembo et al., 2009; Manuel et al., 2010; Selembo et al., 2010; Hrapovic et al., 2010; Escapa et al., 2012).

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Chapter 2

Scope of the Thesis

2.1 OBJECTIVES

The main objective of this Thesis has been to study the ability of Biocatalyzed Electrolysis (BE) as a wastewater treatment for organic matter removal and energy production. To achieve this main objective several research works have been conducted:

i) evaluating the performance of a microbial electrolysis cell (MEC) when treating synthetic industrial wastewaters such as those derived from biodiesel production which contain large amounts of glycerol.

ii) investigating the influence of operational conditions on the performance of MECs by examination of the combined effects of hydraulic retention time and applied voltage on hydrogen and methane production and the chemical oxygen demand (COD) removal rate in a continuous membrane-less MEC reactor fed with a synthetic dark-fermentation effluent.

iii) evaluating MEC performance under optimized conditions when treating full-strength, un-amended domestic wastewater.

iv) studying the feasibility of combined MEC and activated sludge for wastewater treatment.

2.2 THESIS OUTLINE

Wastewater treatment represents roughly 1% of the yearly electrical energy consumption in Spain, which poses a problem for our country in the future. Even though this energy consumption in domestic wastewater treatment plants can be reduced through online and dynamic control of aeration systems, and recovering natural gas from anaerobic digesters, the energy content of the organic matter dissolved in the wastewater still remains largely unexploited. BE represents a relatively new alternative to conventional aerobic wastewater treatments, since it can convert directly the energy content of the organic matter into valuable energy products such as hydrogen. However, as BE is a new process, many of its potential advantages are still unexplored.

The scope of this PhD thesis is to investigate the potential of the BE for its application in industrial and domestic wastewater treatment for organic matter removal and hydrogen production.

In **Chapter 1,** a general overview is presented regarding bioelectrochemical systems and their role in the field of wastewater treatment. In **Chapter 2**, the objectives of the thesis and the thesis outline are presented.

In **Chapter 3**, it is studied the ability of the BE to treat a fermentable industrial sub-product such as glycerol. A MEC reactor was continuously fed with a synthetic effluent at organic loads of glycerol of 0.3-5.3 g L_a^{-1} d^{-1}. Evaluation of the glycerol degradation and hydrogen production processes was performed in terms of cathodic efficiency, Coulombic efficiency and energy efficiency. Overall, it was observed a fast conversion of glycerol to fermentation products, revealing that fermentation products rather than glycerol are the most likely source of electrons used by electrogenic microorganisms. It is known that in bioelectrochemical systems, fermentation substrates usually outperform fermentable substrates in terms of substrates conversion to either electricity or hydrogen. Therefore, in **Chapter 4** it was studied the performance of a MEC when it was fed with a synthetic effluent of a dark-fermentation process, focusing on the effect of the hydraulic retention time (HRT) and the applied voltage. The study showed that it requires applied voltages of 1V and HRTs of 12 h to remove more that 90% of the influent COD and to achieve a hydrogen production rate of 1.42 L L_a^{-1} d^{-1}.

Domestic wastewater treatment plants represent a good candidate for the practical implementation of MECs. **Chapter 5** evaluates the potential of BE for domestic wastewater treatment in parallel to hydrogen production. The reactor was subjected to ORLs in the range between 243 and 3,128 mg-COD L_a^{-1} d^{-1} and applied voltages that ranged from 0.5 to 1.2 V trying to find a set of operational parameters that improve the performance the MEC during domestic wastewater treatment. Overall, it was found that hydrogen production can be maximized at OLR's above 2,000 mg-COD L_a^{-1} d^{-1}, although COD removal rates are relatively low (~50%).

Before practical implementation of BE, it would be useful to have a preliminary estimation of the maximum acceptable investment cost associated to this technology. This issue was addressed in a case study in **Chapter 6,** in which the aerobic reactor of

an already existing wastewater treatment plant was replaced by a MEC reactor followed by an aerobic polishing step. Overall the study revealed that the manufacturing costs of a MEC should be in the range between 1,100 and 1,350 € m^{-3} of anode surface area to break even at the turn of 7 years.

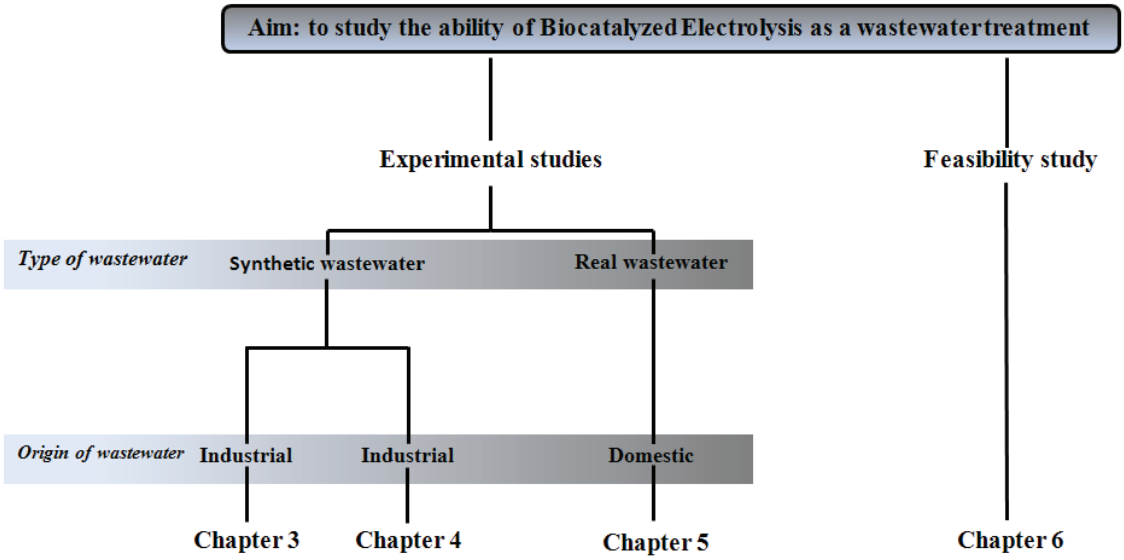

Figure 2.1. Organization of this PhD thesis.

Chapter 3

Hydrogen Production from Glycerol in a Membrane-less Microbial Electrolysis Cell

Abstract. Hydrogen production from glycerol was studied in a microbial electrolysis cell (MEC) with a 250 mL anodic chamber and a gas-phase cathode. A membrane-less MEC design was employed, where a graphite felt anode and gas diffusion cathode were only separated by a 0.7 mm thick highly porous synthetic fabric (J-cloth). Glycerol (fuel) was continuously fed to the anodic chamber at loads of 0.3-5.3 g L_a^{-1} d^{-1}. Fast conversion of glycerol to fermentation products, mainly 1,3-propanediol, propionate, and acetate was observed, i.e. the fermentation products rather than glycerol were the most likely source of electrons for the anodophilic microorganisms. Hydrogen formation at the cathode required additional input of energy, which was provided by a controllable power supply. Hydrogen formation was observed starting from an applied voltage of 0.5 V. The highest volumetric rate of hydrogen production was 0.6 L L_a^{-1} d^{-1}, which was obtained at a glycerol load of 2.7 g L_a^{-1} d^{-1} and an applied voltage of 1.0 V. Hydrogen yield reached 5.4 mol per mol glycerol consumed, which corresponded to 77% of the theoretical value.

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Energy & Fuels 23 (9), (2009) 4612–4618

3.1 INTRODUCTION

Glycerol is the principal co-product of biodiesel production. Crude glycerol derived from the biodiesel production process has many impurities, which decrease its commercial value. At the same time, glycerol purification to food or cosmetic usage grade is costly. The recent worldwide increase in biodiesel production has generated a glycerol surplus resulting in a drop in glycerol prices. This means that glycerol produced during biodiesel production has become a "waste-stream" with a disposal cost associated to it (Yazdani and Gonzalez, 2007).

Several technologies based on chemical transformation of glycerol into more valuable products, mainly 1,3-propanediol (Yazdani and Gonzalez, 2007; Barbirato et al., 1995; Zeng et al., 1996) and hydrogen (Valliyappan et al., 2008; Zhang et al., 2007; Adhikari et al., 2008), have been proposed. While hydrogen yield in the pyrolitic decomposition of glycerol can almost reach its theoretical maximum of 7 mol_{H2} mol^{-1} glycerol (Zhang et al., 2007; Adhikari et al., 2008), this technology requires high process temperatures thus leading to significant energy losses. Recently, hydrogen production from glycerol-water solution in a PEM electrolysis cell has been proposed (Marshall and Haverkamp, 2008). In this process, electrochemical reforming of glycerol was achieved using Pt/Ru-Ir oxide. Electrical energy consumption of 1.1 kWh $m^{-3}{}_{H2}$ was reported and a volumetric hydrogen production rate of up to 10 $m^3{}_{H2}$ m^{-3} d^{-1} was projected based on current measurements. However, this process required the use of noble catalysts at the anode and poisoning of anode catalytic activity by glycerol or its oxidation products has been observed.

In general, hydrogen production from glycerol via biological fermentation process is less energy intensive. Biohydrogen production can be achieved via fermentative processes involving bacteria of the genera *Klebsiella*, *Citrobacters*, *Enterobacter* and *Clostridia* (Yazdani and Gonzalez, 2007). Liu and Fang (2007) demonstrated fermentative hydrogen production from glycerol with a maximum hydrogen evolution rate of 0.4 L_{H2} L^{-1} h^{-1} using *Klebsiella pneumoniae* DSM 2026. Ito et al. (2005) used *Enterobacter aerogenes* on porous ceramics as a support material obtaining a hydrogen

production rate of 1.4 L_{H2} L^{-1} h^{-1}. However, thermodynamic limitations of the fermentation process result in only partial conversion of glycerol and therefore low hydrogen yields below 1 mol_{H2} mol^{-1} glycerol (Liu and Fang, 2007; Ito et al., 2005; Fabiano and Perego, 2002), due to the production of several metabolites such as 1,3-propanediol, ethanol and volatile fatty acids (Murarka et al., 2008)

Microbially catalyzed electrolysis is a novel technology capable of converting organic matter into hydrogen in a modified microbial fuel cell (MFC) (Logan et al., 2008). In a MFC, the anodophilic microorganisms convert chemical energy of organic matter (fuel) to electricity by transferring electrons to the anode and releasing protons, while oxygen reduction occurs at the cathode electrode (Bond and Lovley, 2005; Liu et al., 2004; Rabaey and Verstraete, 2005). In the microbial electrolysis cell (MEC) no oxygen is provided to the cathode and protons are reduced to molecular hydrogen provided that additional energy is supplied by an external power supply (Call and Logan, 2008; Rozendal et al., 2006; Liu et al., 2005; Tartakovsky et al., 2008). A detailed description of hydrogen production in a MEC can be found elsewhere (Logan et al., 2008; Rozendal et al., 2006; Liu et al., 2005).

So far, hydrogen production in a MEC has been demonstrated on several volatile fatty acids, glucose, and cellulose (Tartakovsky et al., 2008; Rozendal et al., 2007; Cheng and Logan, 2007; Chae et al., 2008; Hu et al., 2008). However, thus far only results on hydrogen production from glycerol in a batch-fed MEC have been reported (Selembo et al., 2009). This study is aimed at demonstrating hydrogen production from glycerol in a membrane-less MEC with a gas-phase cathode, which was shown to improve the volumetric rate of hydrogen production in comparison with a PEM or liquid-phase cathode MECs (Tartakovsky et al., 2008; Rozendal et al., 2007; Cheng and Logan, 2007; Chae et al., 2008; Hu et al., 2008; Selembo et al., 2009; Tartakovsky et al., 2009).

3.2 MATERIAL AND METHODS

3.2.1 Media Composition

The stock solution of carbon source contained 265.0 g L^{-1} of glycerol. The nutrients stock solution was composed of (in g L^{-1}): yeast extract (0.83), NH_4Cl (18.7), KCl (148.1), K_2HPO_4 (64.0), and KH_2PO_4 (40.7). The stock solution of the trace metals was prepared according to Rozendal et al. (2007), and contained (in mg L^{-1}) $FeCl_24H_2O$ (2000), H_3BO_3 (50), $ZnCl_2$ (50), $CuCl_2$ (30), $MnCl_24H_2O$ (500), $(NH_4)_6Mo_7O_{24}4H_2O$ (50),$AlCl_3$ (50), $CoCl_26H_2O$ (50), $NiCl_2$ (50), EDTA (500), and HCl (1mL). All solutions were filter sterilized and stored at 4°C to prevent microbial growth. Distilled water was used for solution preparation, and the chemicals and reagents used were of analytical grade.

3.2.2 Analytical Measurements

Volatile fatty acids (VFAs) were analyzed on an Agilent 6890 gas chromatograph (Wilmington, DE, USA) equipped with a flame ionization detector and a 1 m x 2 mm 60/80 mesh Carbopack C column (Supelco, Bellafonte, PA, USA) coated with 0.3% Carbowax 20M and 0.1 % H_3PO_4. The carrier gas was helium, which had a flow rate of 20 mL min^{-1}. The injector and the detector were maintained at 200 °C. 0.5 µL samples were fortified at a ratio of 1:1 (V/V) using an internal standard of iso-butyric acid dissolved in 6% formic acid.

1,3-propanediol was analyzed on a gas chromatograph (6890 Series, Hewlett Packard, Wilmington, DE) coupled to an FID detector. 1 µL of water sample was injected on a DB-ACL2 capillary column of 30 m x 530 µm x 2 µm from Agilent Technologies (Wilmington, DE, USA) The column was heated at 60°C for two minutes then raised to 190°C at a rate of 10°C/min. Helium was used as carrier gas. The injector and detector were maintained at 240^{O}C and 250^{O}C, respectively.

Glycerol was measured by HPLC (Waters Corp, Milford, MA, USA) using model 717 Plus equipped with an autosampler, a refractive index detector (Waters model 2414) and a PDA detector (model 2996). Transgenomic ICSep IC-ION-300 (300 mm x 7.8 mm

OD) HPLC column was used. The mobile phase was 0.01N H_2SO_4 at 0.4 ml min^{-1}. Analysis was carried out at 35°C. Standard deviations of all analytical methods did not exceed 5%.

Gas production in the MEC was measured on-line using bubble counters connected to glass U-tubes and interfaced with a data acquisition system (Tartakovsky et al., 2008). The U-tubes contained a dye, which facilitated bubble counting. Gas composition was measured using a gas chromatograph (6890 Series, Hewlett Packard, Wilmington, DE) equipped with a 3.5 m x 2 mm I.D. Chromosorb 102 column (Supelco, Bellefonte, PA, USA) and a thermal conductivity detector. The column was heated at 50°C for 4 min. The carrier gas was argon.

3.2.3 Electrochemical Measurements and Calculations

In hydrogen-production mode (MEC), an adjustable DC power supply (IF40GU Kenwood, Japan) was used to maintain voltage at the preset setpoint. In electricity-production mode (MFC), voltage was measured on-line at 10 min intervals using a data acquisition system (Labjack U12, Labjack Corp, Lakewood, CO, USA). In MEC mode, voltage scans were carried out by changing the applied voltage from 1.2 to 0.4 V in 0.2 V steps. Once voltage setting was changed, current was measured after 10 min using a multimeter (Fluke 189, Fluke Corp, Everett, WA, USA). MEC internal resistance (i.e. the sum of the charge transfer resistances and the solution resistance) was estimated using the linear part of the voltage scan. Anode potential at each voltage was measured using a standard calomel electrode (SCE, 0.2412 V vs NHE).

Following previous reports (Call and Logan, 2008; Liu et al., 2005; Tartakovsky et al., 2008; Rozendal et al., 2007; Rozendal et al., 2007; Ditzig et al., 2007), MEC performance was evaluated in terms of hydrogen yield from glycerol, specific energy consumption, energy efficiency (the amount of energy contained in hydrogen as compared to the power input necessary to produce this amount of hydrogen), as well as in terms of Coulombic efficiency, cathodic efficiency, and chemical oxygen demand (COD) removal efficiency. Detailed explanations of the calculation methods for these parameters are provided below.

Hydrogen yield on glycerol ($Y_{H2,}$ mol_{H2} mol^{-1}_{g}) was calculated as

$$Y_{H2} = \frac{(p \cdot Q_{H2} \cdot V_a)/(R \cdot T)}{(G_{in} - COD_{out}/r_g)/M_g \cdot Q_{in}}, \quad (3.1)$$

where p is the pressure (p=1 atm); Q_{H2} is the hydrogen flow rate (L_{H2} L_a^{-1} d^{-1}); V_a is the anode volume (V_a=0.25 L); R is the ideal gas constant (R=0.08205 L atm K^{-1} mol^{-1}); T is the temperature (T=298 K); G_{in} is the concentration of glycerol in the influent (g L^{-1}); COD_{out} is the COD of the effluent (g L^{-1}); r_g is the COD equivalent of 1 g of glycerol (r_g=1.2 g g^{-1}); M_g is the molecular weight of glycerol (M_g =92.09 g mol^{-1}); Q_{in} is the influent flow rate (L d^{-1}).

Specific energy consumption ($E_{cons,}$ Wh L^{-1}_{H2}) was calculated as:

$$E_{cons} = \frac{\int_0^{86400} E_{app} \cdot I \cdot dt}{(Q_{H2} \cdot V_a) \cdot 3600}, \quad (3.2)$$

where E_{app} is the voltage applied to MEC (V) and I is the current (A).

Coulombic efficiency (ε_C) was calculated as the ratio between the total Coulombs actually transferred to the anode from the substrate to the anode, and the theoretical maximum (Liu et al., 2005):

$$\varepsilon_C = \frac{\int_0^{86400} Idt}{(G_{in} - COD_{out}/r_g)/M_g \cdot Q_{in} \cdot e_g \cdot F} 100\%, \quad (3.3)$$

where e_g is the number of mol of electrons exchanged per mol of glycerol equivalent consumed (14 mol mol^{-1}), and F is the Faraday constant (96485 C mol^{-1}).

Cathodic efficiency (ε_{Cth}), was calculated as the ratio of hydrogen recovery in the cathode to maximum possible if all the current is converted to hydrogen:

$$\varepsilon_C = \frac{(p \cdot Q_{H2} \cdot V_a)/(R \cdot T) \cdot e_{H2} \cdot F}{\int_0^{86400} Idt} 100\%, \quad (3.4)$$

e_{H2} is the number of mol of electrons exchanged per mol of hydrogen (2 mol mol^{-1}).

Energy efficiency (ε_E), was calculated as the amount of energy recovered as hydrogen compared to the power input necessary to produce this amount of hydrogen :

$$\varepsilon_E = \frac{(p \cdot Q_{H2} \cdot V_a)/(R \cdot T) \cdot \Delta G^0 r_{H2O}}{\int_0^{86400} E_{app} \cdot I \cdot dt} 100\%, \quad (3.5)$$

where $\Delta G^0 r_{H2O}$ is the Gibbs free energy of hydrogen combustion (equal to water formation, $\Delta G^0 r_{H2O}$ =-237 kJ mol^{-1}). Notably, Gibbs free energy of glycerol is not considered in Eq. (3.5), hence ε_E could reach values higher than 100%.

COD removal efficiency (ε_{COD}) is defined as the ratio between the effluent and influent concentrations of glycerol and degradation products expressed in COD equivalents:

$$\varepsilon_{COD} = \frac{(G_{in} \cdot r_g - COD_{out})}{G_{in} \cdot r_g} 100\%, \quad (3.6)$$

where G_{in} is the influent glycerol concentration (mg L^{-1}) and COD_{out} is the sum of effluent concentrations of glycerol and all measurable degradation intermediates expressed in COD equivalents (mg L^{-1}).

3.2.4 MEC Design, Instrumentation, and Operation

All experimentation was carried out in a continuous-flow MEC constructed with a series of polycarbonate plates arranged to form an anodic chamber and a gas collection chamber as described elsewhere (Tartakovsky et al., 2008; Tartakovsky et al., 2009). The anodic chamber retained 210 mL of liquid and had a headspace of 40 mL. The gas collection (cathodic) chamber also had a volume of 250 mL.

Graphite felt, 5 mm thick, measuring 25 x 10 cm (Speer Canada, Kitchener, ON, Canada) was placed in the anodic chamber filled with liquid. E-TEK gas diffusion electrode (GDE) with a Pt load of 0.5 mg cm^{-2} (GDE LT 120EW, E-TEK Division, PEMEAS Fuel Cell Technologies, Somerset, NJ, USA) was used as a cathode. The cathode was separated from the anode by a piece of porous cellulosic non-woven fabric

(J-cloth®) with a thickness of 0.5 mm. The MEC was inoculated with 25 mL of heat treated (20 minutes at 100°C) homogenized anaerobic sludge (Lassonde Inc, Rougemont, QC, Canada).

A stock solution of carbon source was fed using an infusion pump (model PHD 2000, Harvard Apparatus, Canada) at a rate of 0-5 mL d^{-1}. 1 mL of trace metals stock solution and 42 mL of nutrients solution were added to 1 L of the dilution water. The dilution water was fed at a rate of 750 mL d^{-1} using a peristaltic pump (Cole-Parmer, Chicago, IL, USA) providing a retention time of 8 h. Mixing in the anodic chamber was provided by an external recirculation loop. A recirculation rate of 1.44 L h^{-1} was used.

MEC temperature was maintained at 25°C by means of a thermocouple placed in the anodic chamber, a temperature controller (Model JCR-33A, Shinko Technos Co. Ltd. Osaka, Japan) and a 5 cm x 10 cm heating plate located on the anodic chamber side of the MEC. The pH was maintained at a set-point of 7.0 using a pH probe installed in the recirculation line, a pH controller (Model PHCN-410, Omega Engineering, Stamford CT, USA) and a solution of 0.05N NaOH, which was fed into the recirculation line.

MEC performance during hydrogen production from glycerol was evaluated using several techniques. First, the amount of glycerol fed to the MEC was optimized in glycerol load tests, where a preset value of applied voltage was maintained while periodically changing the glycerol load (Table 3.1).

Table 3.1. Influent end effluent composition in glycerol load tests. Unless specified, tests were carried out at an applied voltage of 1.0 V. COD recovery is calculated by comparing COD equivalents of glycerol fed to MEC (in g day^{-1}) with the sum of COD equivalents of all measurable products in the liquid (glycerol, acetate, propionate, butyrate, propanediol) and gas (hydrogen, methane) phases.

OLR	**Influent**	**Effluent and off-gas**						
g L_a^{-1} d^{-1}	Glycerol (mg/L)	acetate (mg/L)	propionate (mg/L)	butyrate (mg/L)	glycerol (mg/L)	propanediol (mg/L)	hydrogen (mg/day)	COD recovery (%)
5.3	1433.2	281.2	17.5	83.6	7.1	304.0	5.9	59.3
2.7	743.6	103.0	178.1	52.8	1.8	56.0	12.7	69.8
1.3	397.7	32.8	33.8	38.4	0.0	25.0	9.6	50.8
0.7	209.1	14.7	45.7	17.4	1.7	13.5	8.6	72.9
0.3	106.6	5.0	3.8	0.0	1.9	0.0	5.5	32.6
2.7*	743.6	116.1	176.3	58.4	0.0	59.0	0.0	64.8

** - no applied voltage*

Next, the dependence of hydrogen production on applied voltage was studied in applied voltage tests, where the load of glycerol was maintained at a constant level while the voltage was varied (Table 3.2). Each set of operating conditions was maintained for at least 2 days (6 retention times), except a glycerol load of 5.3 g L^{-1}_{a} d^{-1}, which was maintained for 7 days. At the end of each test, the hydrogen production rate was estimated by averaging the measurements obtained during last 8 hours of the test.

Table 3.2. Influent and effluent composition in applied voltage tests. All tests were carried out at a glycerol load of 0.7 g L^{-1}_{a} d^{-1}.

	Influent	**Effluent an off-gas**						
Vapp (V)	Glycerol (mg/L)	acetate (mg/L)	propionate (mg/L)	butyrate (mg/L)	glycerol (mg/L)	propanediol (mg/L)	hydrogen (mg/day)	COD recovery (%)
1.0	209.1	14.7	45.7	17.4	1.7	13.5	8.6	72.9
0.7	209.1	17.1	8.7	0.0	0	14.2	8.4	38.9
0.5	209.1	13.8	16.3	0.0	0	0.0	6.1	27.9
0.0	209.1	36.0	16.3	0.0	0	11.2	0.0	31.0

3.3 RESULTS

3.3.1 Start-up Procedure

After anodic chamber inoculation with heat-treated anaerobic sludge, the cell was fed with acetate and operated in electricity production (MFC) mode by exposing the gas-collection chamber to air. Anode and cathode electrodes were externally connected through a 400 Ω resistor and the potential was continuously measured thus permitting on-line monitoring of the anode colonization process. Initially, an acetate load of 0.9 g L_a^{-1} d^{-1} was used, then the acetate load was gradually increased to 4.8 g L_a^{-1} d^{-1} as shown in Fig. 3.1A.

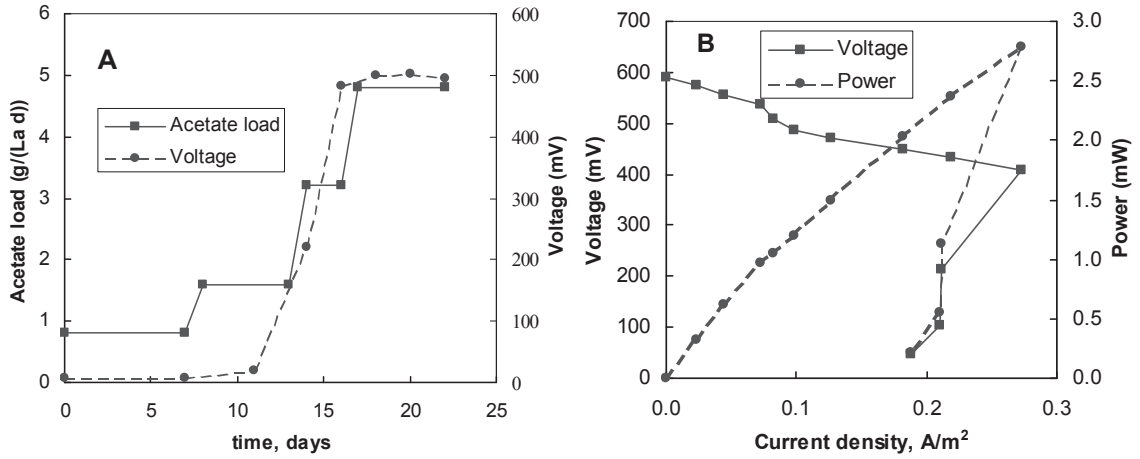

Figure 3.1. (A) Acetate load and resulting voltage during the start-up process in MFC mode. MFC was operated at R_{ext}=400 Ω and a temperature of 25°C. (B) Polarization and power curves obtained at the end of the start-up period (day 18).

This startup strategy was aimed at providing a sufficient amount of substrate while avoiding excessive levels of acetate in the anodic chamber, which could inhibit microbial activity (i.e. organic overload conditions). The choice of acetate as the initial carbon source enabled a comparison of MEC performance on acetate and glycerol. After ten days of operation the potential started to increase steadily and ten days later it stabilized at 490 mV. An open circuit voltage of 589 mV was measured. At the end of the start-up process (day 18) a polarization test was conducted by gradually decreasing the external resistance. Based on the linear section of the polarization plot, an internal resistance of 17.2 Ω was calculated. However, a maximum power of 2.78 mW (11.2 mW L_a^{-1}) was obtained at a higher resistance of 40 Ω. A sharp drop in MFC performance was observed below an external resistance of 40 Ω as shown in Fig. 3.1B, likely due to mass transfer limitations of the carbon source and its degradation products (Aelterman et al., 2006).

Hydrogen production mode was initiated by flushing the gas-collection (cathode) chamber with pure nitrogen and applying an external voltage of 1V, while continuing to feed MEC with acetate. Hydrogen production began almost immediately. After 2 days of operation, a current density of 77 mA (3.08 A m^{-2}) was observed corresponding to a hydrogen production rate of 4.34±0.76 L_{H2} L_a^{-1} d^{-1}. After subtracting background current as described below, a power consumption of 1.71±0.23 Wh L^{-1}_{H2}. Gas-collection

(cathodic) chamber off-gas consisted of H_2 (96.6%), N_2 (0.3 %), and water vapor (3.1%). Methane was not detected and no gas production was observed in the anodic chamber. Two days after hydrogen production mode was initiated the carbon source was changed from acetate to glycerol, which was fed at a rate of 5.3 g L_a^{-1} d^{-1}. Changing the carbon source from acetate to glycerol led to a decrease in hydrogen production from 4.34±0.76 L_{H2} L_a^{-1} d^{-1} to 0.29±0.03 L_{H2} L_a^{-1} d^{-1}. This drop in hydrogen production was accompanied by an increase in power consumption (from 1.7±0.23 to 4.29±0.50 Wh L^{-1}_{H2}) and an accumulation of 1,3 propanediol and other fermentation products.

3.3.2 Glycerol Load Tests

The glycerol load tests were aimed at optimizing the amount of glycerol fed to the MEC. An initial verification of hydrogen production in the absence of glycerol was carried out at an applied voltage of 1.0 V. In this test MEC was fed with the solution containing no glycerol, while all other medium components were retained. No hydrogen production was detected in this case, even though a background current density of 0.36 A m^{-2} was measured. This background current was attributed to redox processes associated with salts in the medium. To confirm that the background current is not related to microbial activity, a second MEC was assembled and operated for 48 h abiotically, i.e. in the absence of an anodophilic microbial inoculum at the anode. This MEC was filled with the standard solution of salts and nutrients, except no glycerol was added. Once again, at an applied voltage of 1.0 V no hydrogen production was detected but a current density of 0.32-0.36 A m^{-2} was measured. A voltage scan showed that at 0.75 V the background current density decreased to 0.04 A m^{-2}, and at 0.5 V no measurable current was detected. Thus, measurements of background current obtained in the absence of glycerol represent non-biological reactions, such as electrochemical reactions due to high concentration of salts in the medium. In all subsequent calculations the measurements at each applied voltage were corrected with respect to these background measurements.

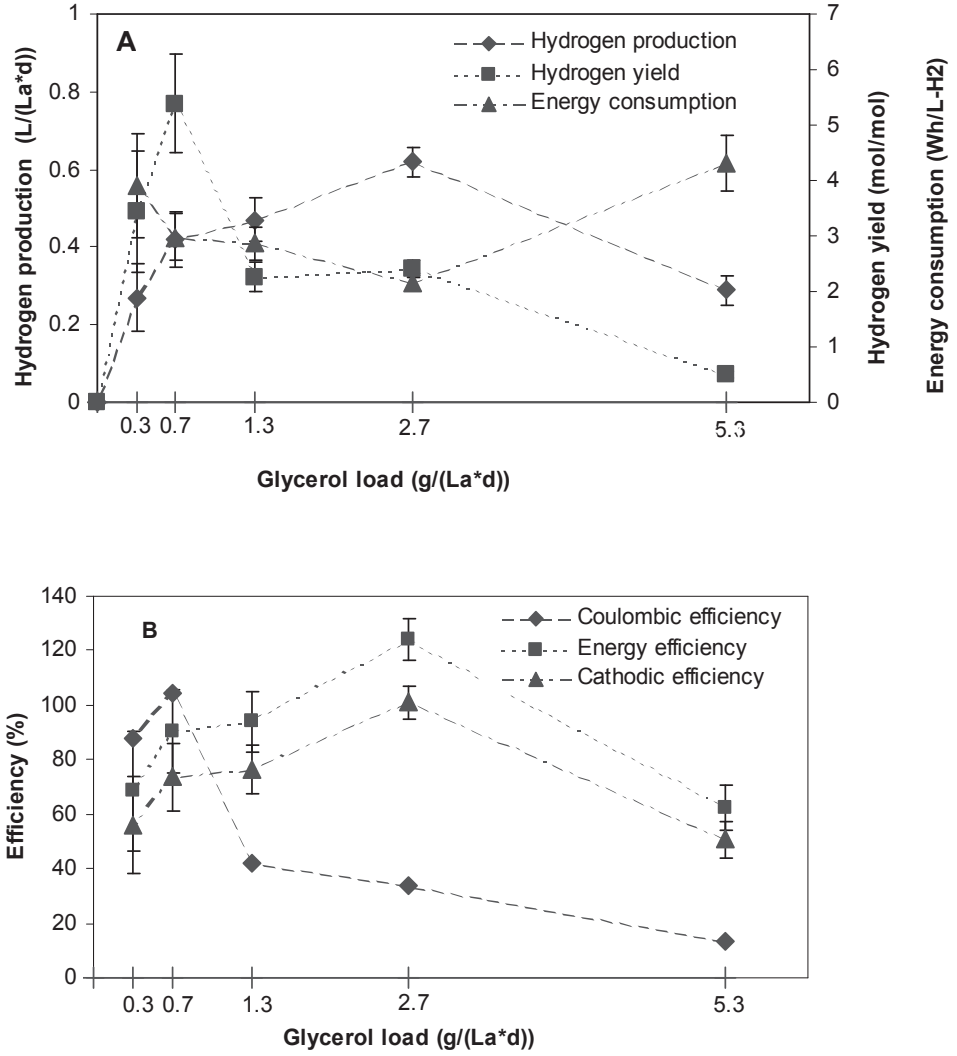

Figure 3.2. Dependence of (A) hydrogen production rate, hydrogen yield, specific energy consumption and (B) hydrogen production efficiency (Coulombic, cathodic, and energy efficiency) on glycerol load. All tests were carried out at an applied voltage of 1.0 V. Energy efficiency calculation (Eq. 3.5) does not consider Gibbs free energy of glycerol thus leading to values above 100%.

MEC was operated at several glycerol loads ranging from 0.3 to 5.3 g L_a^{-1} d^{-1}. Glycerol fed to MEC was readily transformed to fermentation products, mainly 1,3-propanediol and acetate (Table 3.1). At a glycerol load of 5.3 g L_a^{-1} d^{-1} high concentrations of all fermentation products found in the anodic chamber effluent suggested organic overload. Analysis of hydrogen production rates and hydrogen yields given in Figure 3.2A show that glycerol overload led to a decrease in the rate of hydrogen production (0.29±0.03

L_{H2} L^{-1}_{a} d^{-1}) with a corresponding hydrogen yield of only 0.49±0.06 mol_{H2} mol^{-1}glycerol.

When glycerol load was decreased to 2.7 g L^{-1}_{a} d^{-1} the concentration of metabolites in the effluent decreased with the exception of propionic acid, which had increased 10 times (Table 3.1). Hydrogen production doubled to 0.62±0.04 L_{H2} L^{-1}_{a} d^{-1}, while current remained almost unchanged thus leading to a 50% decrease in specific energy consumption (Fig. 3.2A). Also, hydrogen yield increased five-fold and Coulombic efficiency improved from 13% to 34%. At glycerol loads of 1.3 and 0.7 g L^{-1}_{a} d^{-1} hydrogen production rates were 0.47±0.05 and 0.42±0.07 L_{H2} L^{-1}_{a} d^{-1}, respectively. Specific energy consumption values (2.86±0.30 and 2.97±0.42 Wh L^{-1}_{H2}, respectively) were similar to those observed at a glycerol load of 2.7 g L^{-1}_{a} d^{-1} (Fig. 3.2A). A further decrease in the glycerol load to 0.7 g L^{-1}_{a} d^{-1} improved the Coulombic efficiency as shown in Fig. 3.2B. Also, hydrogen yield increased from 2.26±0.27 to 5.39±0.90 mol_{H2} mol^{-1} glycerol (Fig. 3.2A).

However, at a much reduced glycerol load of 0.3 g L^{-1}_{a} d^{-1}, hydrogen production was found to decrease and energy consumption went up. Hydrogen yield and Coulombic efficiency also decreased considerably. At all glycerol loads current density was between 0.89-0.92 A m^{-2}. Notably, Coulombic efficiency was low at high glycerol loads suggesting the existence of unidentified intermediates of glycerol degradation at high loads. Glycerol degradation (i.e. mineralization) efficiency was up to 90% at the lowest glycerol load but remained below 40% at glycerol loads above 1.3 g L^{-1}_{a} d^{-1} (Fig. 3.3A) due to high concentrations of degradation intermediates in the effluent as shown in Table 3.1. Highest glycerol degradation was achieved at medium applied voltages (Fig. 3.3B).

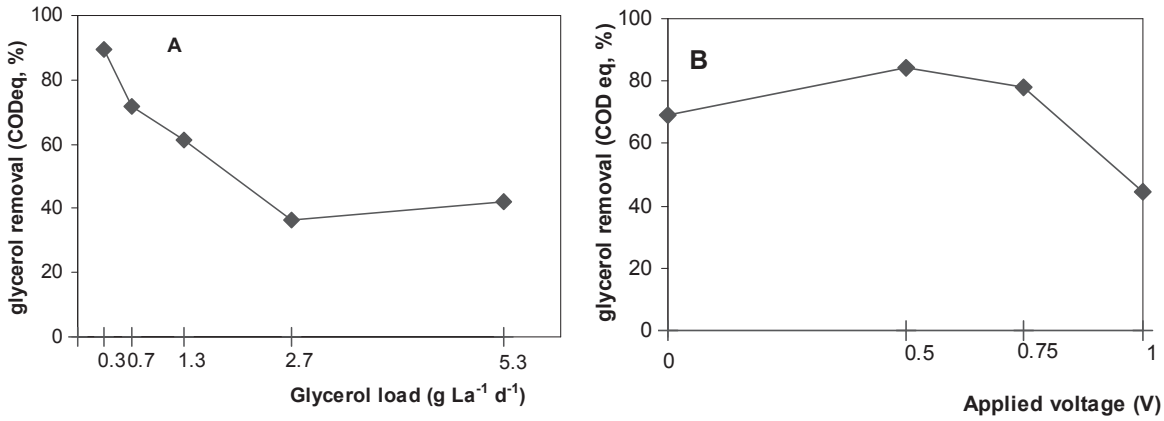

Figure 3.3. Glycerol removal efficiencies (expressed in COD equivalents) at different glycerol loads (A) and different applied voltages (B). In glycerol load tests voltage was maintained at 1.0 V. In applied voltage tests glycerol load was maintained at $0.7 gL^{-1}_{a}\ d^{-1}$.

3.3.3 Applied Voltage Tests

In order to investigate the effect of the applied voltage on MEC performance, the cell was operated at three different voltages of 1.0, 0.75, and 0.5 V, and in the fermentation mode, i.e. when no voltage was applied to MEC. During these tests glycerol load was always maintained at 0.7 g L_a^{-1} d^{-1} to avoid accumulation of glycerol degradation products. As can be seen from a comparison of hydrogen production rates shown in Fig. 3.4A, between 0.5 and 0.75 V the hydrogen production rate increased with increasing voltage, however energy consumption per L of produced hydrogen also increased. Current density changed from 0.64 to 0.72 A m^{-2} when the applied voltage was increased from 0.5 to 0.75 V. Above 0.75 V the hydrogen production reached a plateau and the current density only slightly increased to 0.88 A m^{-2}. Also, the Coulombic efficiency improved with increasing voltage (Fig. 3.4B).

Glycerol removal efficiency remained between 69% and 84% at applied voltages of 0.5 and 0.75 V, then it dropped to 44% at 1.0 V (Fig. 3.3B). The main metabolites found in the effluent were acetate, propionate and 1,3-propanediol. Butyrate only appeared when the applied voltage was set at 1.0 V. A detailed composition of the anodic chamber effluent is provided in Table 3.2. When no voltage was applied to MEC thus limiting activity of anodophilic microorganisms, acetate and butyrate concentration in the

effluent increased 11% and 9% respectively while concentrations of other metabolites only varied within ±4%.

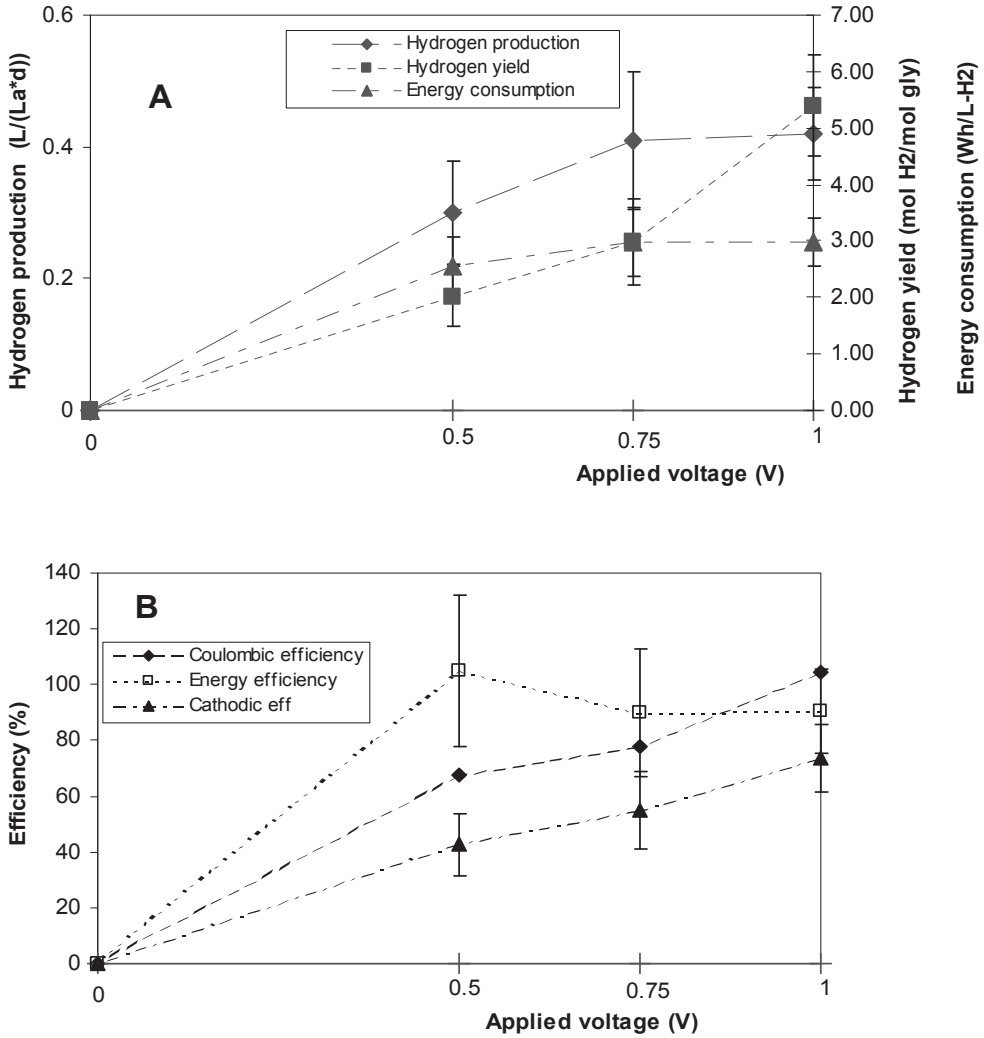

Figure 3.4. Dependence of (A) hydrogen production rate, hydrogen yield, specific energy consumption and (B) Coulombic, energy and cathodic efficiencies on applied voltage.Results were obtained at a glycerol load of 0.7 g L^{-1}_{a} d^{-1}. Energy efficiency calculation (Eq. 3.5) did not include Gibbs free energy of glycerol.

Both in glycerol load and an applied voltage test, no net gas production was measured in the anodic chamber. However, headspace analysis showed the appearance of methane after the first 20 days of MEC operation. During the last week of MEC operation, which lasted 57 days, methane concentration in the anodic chamber headspace approached 30% and up to 2% of methane was found in the hydrogen stream. Apparently, this

methane diffused from the anodic chamber where it was produced by methanogenic microorganisms, which survived the heat treatment procedure.

3.3.4 Electrochemical Performance

The electrochemical performance of the MEC was evaluated by measuring the anode potential and internal resistance at the end of each test. Results of anode potential measurements are shown in Fig. 3.5A. The highest anode potentials were observed at the lowest glycerol load (0.3 g L_a^{-1} d^{-1}), while the lowest values were obtained at glycerol loads of 2.7 and 1.3 g L_a^{-1} d^{-1}. Cathode potential, computed as the difference between the anode potential and applied voltage remained almost constant at all voltages. It was estimated at -621± 77 mV vs. NHE.

Calculation of MEC internal resistances based on the results of the voltage scan tests shown in Fig. 3.5B yielded values between 18-100 Ω. Interestingly, the highest internal resistance was obtained when the glycerol load was low or high, while the lowest values once again corresponded to glycerol loads of 2.7 and 1.3 g L_a^{-1} d^{-1}, i.e. when hydrogen production was the highest. Measurements of anodic liquid conductivity showed no difference between the tests conducted at different glycerol loads and different applied voltages. The conductivity always remained at 15-16 mS cm^{-1} due to the high ionic strength of the phosphate buffer.

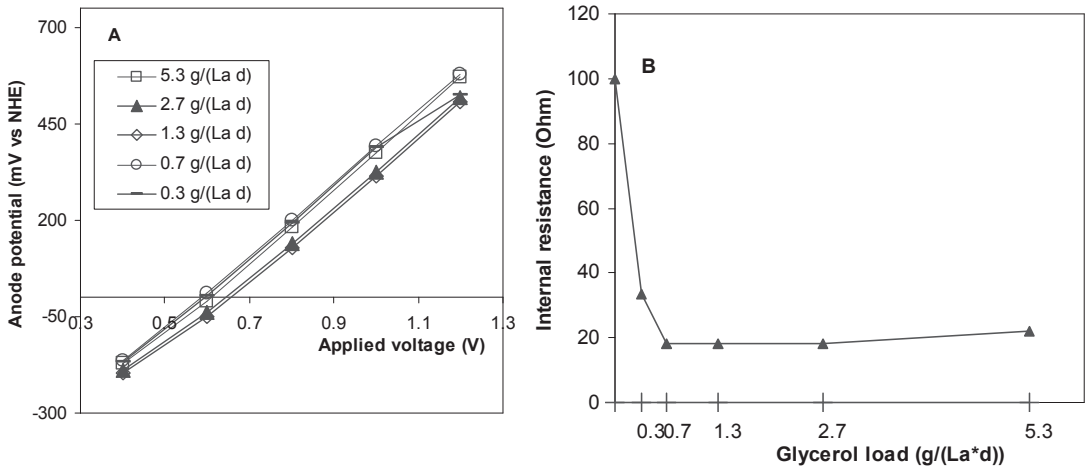

Figure 3.5. Electrochemical characterization of MEC showing (A) anode potentials and (B) dependence of internal resistance on glycerol load.

3.4 DISCUSSION

3.4.1 Hydrogen Formation From Glycerol

Microbially catalyzed production of hydrogen from glycerol is described by the following reaction :

$$C_3H_8O_3 + 6H_2O \rightarrow 3HCO_3^- + 3H^+ + 7\ H_2, \quad (3.7)$$

which indicates a yield of 7 mol hydrogen per mol of glycerol. Accordingly, the anodic half-reaction of glycerol oxidation is given by:

$$C_3H_8O_3 + 6H_2O \rightarrow 3HCO_3^- + 17H^+ + 14e^- \quad (3.8)$$

while the cathodic half-reaction of hydrogen formation is:

$$2H^+ + 2e^- \rightarrow H_2 \quad (3.9)$$

Calculation of the anode and cathode potentials at pH 7 according to the Nernst equation (assuming 20 mM of glycerol, 2mM of bicarbonate and a hydrogen partial pressure of 1 atm) results in values of –425 mV and –414 mV vs NHE (normal hydrogen electrode), respectively. Since the potential at the anode is lower than the potential at the cathode, it theoretically suggests that hydrogen production from glycerol at pH 7 does not require an additional input of energy. In contrast, hydrogen production from acetate requires an energy input of 104.6 kJ/mol, which corresponds to an applied voltage of 0.14 V (Rozendal et al., 2006; Liu et al., 2005). However, the experimental results presented above provide no evidence of direct glycerol oxidation at the anode by anodophilic microorganisms since hydrogen production was not observed below an applied voltage of 0.5 V. An energy input of at least 2.17 W h L_{H2}^{-1} was required to achieve hydrogen formation from glycerol, which could be explained by energy losses due to electrode overpotentials, glycerol consumption by fermentative rather than anodophilic microorganisms, and production of several metabolites. Indeed, analysis of the anodic chamber effluent given in Table 3.1 shows the presence of several fermentation products namely acetate, propionate, butyrate, and 1,3-propanediol. These

fermentation products, rather than glycerol, were likely used by the anodophilic microorganisms.

Moreover, it appeared that not all fermentation products were consumed by the anodophilic microorganisms. Table 3.1 describes fermentation products found in the anodic chamber effluent at an applied voltage of 1.0 V and when no voltage was applied to the MEC (fermentation mode). A comparison shows similar concentrations of 1,3-propanediol, propionate, and butyrate, while acetate concentration is lower when voltage was applied. It can be hypothesized that acetate was the preferred carbon source for anodophilic microorganisms. Nevertheless, consumption of other fermentation products cannot be excluded without further investigation. Also, material balance calculations showed COD recovery in a range of 50% - 70% (Table 3.1), which suggests that not all metabolites of glycerol fermentation (i.e. succinic acid, 1,2-propanediol, isopropanol-amine (Murarka et al., 2008)) were accounted for by the analytical procedures used in this study.

Electrode overpotentials also contributed to the relatively high energy consumption observed throughout the experiments. Anode potentials measured during the voltage scans (Fig. 3.5A) were between -193.8 mV vs. NHE (glycerol load = 2.7 g L_a^{-1} d^{-1}; applied voltage = 0.4 V) and 697 mV vs. NHE (glycerol load = 0.0 g L_a^{-1} d^{-1}; applied voltage=1.2 V), which corresponded to anode overpotentials between 222 and 996 mV, respectively. High anode overpotential at 1.2 V might explain the high power requirement at this voltage. As a result energy efficiency declined at applied voltages above 0.5 V (Fig. 3.4B).

3.4.2 Glycerol Load and Applied Voltage Optimization

MEC operation at different glycerol loads clearly demonstrated the importance of this operational parameter in optimizing process performance. When glycerol loads were low, the concentration of degradation intermediates detected in the anodic chamber effluent was insignificant indicating a high glycerol removal efficiency. However, a comparison of Figs. 3.2A and 3.3A shows that the volumetric rate of hydrogen production was low. By increasing the glycerol load to 2.7 g L_a^{-1} d^{-1} the hydrogen

production increased, but the concentrations of fermentative products, in particular 1,3-propanediol, also increased and glycerol removal efficiency declined. Further increase in the glycerol load to 5.3 g L_a^{-1} d^{-1} led to a sharp decrease in hydrogen production, coinciding with an increase in specific energy consumption (Fig. 3.2A). Also, a glycerol load of 2.7 g L_a^{-1} d^{-1} corresponded to the lowest specific energy consumption, which was estimated at 2.17 Wh L^{-1}_{H2}. Hydrogen yield and Coulombic efficiency exhibited a similar trend, but the best values were obtained at a lower glycerol load of 0.7 g L_a^{-1} d^{-1}.

Interestingly, MEC internal resistance was found to be dependent on the glycerol load such that the lowest internal resistance was measured at 2.7 g L_a^{-1} d^{-1} (Fig. 3.5B). This glycerol load also corresponded to the lowest anode overpotential (Fig. 3.5A) suggesting a link between the activity of anodophilic microorganisms and the electrochemical properties of the MEC. Overall, the MEC performance was considered most efficient at a glycerol load of 2.7 g L_a^{-1} d^{-1}, but this value might be dependent on MEC design, microbial populations, influent composition, and other factors. A feedback control system that adjusts glycerol load in response to varying operational conditions can be used to maximize MEC performance and should be considered for future research.

In addition to the formation of 1,3-propanediol at the anode, the possibility of 1,3-propanediol production by electrochemical reduction of glycerol at the cathode was hypothesized. However, 1,3-propanediol concentrations in MEC effluent were similar when no voltage was applied and at 1.0 V (Table 1, a glycerol load of 2.7 g L_a^{-1} d^{-1}). Also, no 1,3-propanediol formation was observed in the abiotic control MEC fed with glycerol and operated at 1.0 V. Thus, 1,3-propanediol was produced from glycerol by fermentative microorganisms rather than electrochemically, which is in agreement with the reductive pathway of glycerol biotransformation by anaerobic microorganisms, which has been reported to result in 1,3-propanediol formation at high glycerol loads (Barbirato et al., 1996). This might explain the 6-fold increase of 1,3-propanediol observed in the experiment when the glycerol load was increased (Table 3.1).

The results of MEC operation at several voltages with a constant glycerol load of 0.7 g L_a^{-1} d^{-1} demonstrated the highest energy efficiency at 0.5 V (Fig. 3.4). Glycerol removal efficiency significantly declined when applying voltages above 0.75 V (Fig. 3.3B). Nevertheless, since the hydrogen production rate and yield were highest at an applied voltage of 1 V, MEC operation at 0.75 V can be suggested as a compromise between energy efficiency and volumetric performance objectives.

3.5 CONCLUSION

Results of this study demonstrated the feasibility of hydrogen production by microbially catalyzed electrolysis of glycerol. Microbial electrolysis of glycerol resolves the thermodynamic limitations associated with dark fermentation thus resulting in almost complete conversion of organic matter to hydrogen (Rozendal et al., 2006; Liu et al., 2005). The rate of hydrogen production from glycerol observed in a MEC was comparable to that observed in the glycerol fermentation process (Liu and Fang, 2007). However, the hydrogen yield was significantly higher and reached 5.39 mol H_2 mol^{-1}glycerol as opposed to yields below 1 mol H_2 mol^{-1} glycerol reported in the literature (Liu and Fang, 2007; Fabiano and Perego, 2002). Although relatively high power inputs (2-3 Wh LH_2^{-1}) were required when using glycerol, these values were always below a minimum of 5 Wh LH_2^{-1} required for hydrogen production by water electrolysis (Liu et al., 2005). Power inputs below 1 Wh LH_2^{-1} might be expected if anode overpotential could be decreased, i.e. through improved electrode materials (Tartakovsky et al., 2008). Also, a decreased power consumption and an improved volumetric hydrogen production rate can be expected if operating conditions are further optimized or an acidification step is added to ensure glycerol conversion to volatile fatty acids. Notably, a volumetric rate of up to 6 L L_a^{-1} d^{-1} was observed in the acetate-fed MEC (Tartakovsky et al., 2009) while a power consumption as low as 0.6 Wh L_{H2}^{-1} was observed at low applied voltages (Liu et al., 2005). Furthermore, selection of anodophilic microorganisms capable of direct glycerol utilization might also improve MEC volumetric performance and further decrease the required power input.

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Chapter 4

Hydrogen Production and COD Elimination rates in a Continuous Microbial Electrolysis Cell (MEC): the Influence of Hydraulic Retention Time and Applied Voltage

Abstract. The influence of applied voltage (V_{app}) and hydraulic retention time (HRT) on hydrogen and methane production, and on the removal rate for chemical oxygen demand (COD) was studied in a membrane-less microbial electrolysis cell (MEC) with a Ni-based cathode. When synthetic effluent from a dark fermentation process was fed continuously to the anodic chamber, an increase in both applied voltage (V_{app}) (from 0.6V to 1.0V) and hydraulic retention time (HRT) (from 8 to 12 hours) increased the hydrogen production rate from 0.18 to 1.42L L_A^{-1} d^{-1} (litres per litre of anode per day) and the COD elimination rate from 46% to 94%. The influence of Vapp and HRT on hydrogen production and COD removal rate was found to be interdependent. Whilst acetic and butyric acids were easily degraded, propionic acid showed a pseudo-recalcitrant behaviour.

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Environmental Progress & Sustainable Energy, (2012). In press.
DOI: 10.1002/ep.11619

4.1 INTRODUCTION

The activated sludge process, which is the most widely used biological wastewater treatment for both domestic and industrial plants in the world, is a process demanding large amounts of energy: the removal of 1 kg of organic matter requires about 1 kWh of electrical energy for wastewater aeration (Rabaey et al., 2005). Another serious challenge of conventional activated sludge processes is the excess of sludge production, which treatment and disposal may account for even up to 60 % of the total cost of a wastewater treatment plant (Davis and Hall, 1997). These large energy and capital requirements highlight the importance of investigating new methods and technologies, in order to reduce operational and investment costs. One possible way of achieving this cost and energy reduction might be to harvest electricity from organic wastes through a microbial fuel cell (MFC).

A MFC for wastewater treatment is an engineered system that produces electricity from the anaerobic oxidation of biodegradable organic matter, which turns it into an attractive source of energy as the oxidation of organic matter merely releases fixed carbon back into the atmosphere. By adding power to the MFC, hydrogen is produced at the cathode, and in this case the system is referred to as a microbial electrolysis cell (MEC) (Logan, 2008). MEC is often also presented as a second stage technological process to convert into hydrogen the by-products of dark fermentation, which is characterized by its low efficiency and low hydrogen yield (Gómez et al., 2011). Both, MFCs and MECs have been grouped together as Bioelectrochemical Systems (BES) (Rabaey et al., 2007).

BES technology dates back to the time when Potter (Potter, 1911) demonstrated bio-electricity generation from biomass using bacteria. Few practical advances were achieved in this field until 1999, when Kim and co-workers (Kim et al., 1999) demonstrated that exocellular electron transfer was possible without soluble mediators. Since then, MFC performance has been investigated as a function of several operational parameters, (including temperature, pH, electrode potential, organic loading rate (OLR), electrolyte, oxygen exposure, and many others (Kim et al., 1999; Martin et al., 2010; Liu et al., 2005a; Srikanth et al., 2010; Gil et al., 2003; Manohar and Mansfeld, 2009)).

Much less attention has been paid to the influence of operational conditions on the performance of bio-electrochemical reactors when they are operated in hydrogen production mode, (i.e. as a MEC). The present work is aimed at filling this gap in the investigation of the influence of operational conditions on the performance of MEC by examining the combined effect of hydraulic retention time (HRT) and applied voltage (V_{app}) on hydrogen and methane production, and COD removal rate in a continuous membrane-less MEC reactor fed with a synthetic dark fermentation effluent. Surprisingly, few pieces of work have reported the effect of these parameters on the performance of an MEC when it is operated in continuous mode (Lee and Rittmann, 2010; Tartakovsky et al., 2009), although it is clear that HRT and V_{app} must have a great influence over operational and investment costs and also energy requirements. In general, higher HRTs and V_{app}s will lead to greater investment and operating costs respectively. The research being reported here thus examined whether it is efficient to modify HTR and Vapp at a given stage in operation, and would, if so, determine the gain in hydrogen production and COD removal and the reduction in methane generation.

4.2 MATERIALS AND METHODS

4.2.1 Composition of Media

The synthetic dark fermentation effluent was prepared according to (Rozendal et al., 2006). It incorporated the following salts, in grams per litre (g L^{-1}): KCl (2.22), KH_2PO_4 (0.61), K_2HPO_4 (0.96), NH_4Cl (0.28), $MgSO_4 \cdot 7H_2O$ (0.01), $CaCl_2 \cdot 2H_2O$ (0.01), yeast extract (0.1) and 1mL of trace element mixture which contained (in mg L^{-1}) $FeCl_2 4H_2O$ (2000), H_3BO_3 (50), $ZnCl_2$ (50), $CuCl_2$ (30), $MnCl_2 4H_2O$ (500), $(NH_4)_6Mo_7O_{24} 4H_2O$ (50),$AlCl_3$ (50), $CoCl_2 6H_2O$ (50), $NiCl_2$ (50), EDTA (500), and HCl (1mL).

Acetate, propionate and butyrate were included as the main carbon source in the influent to the reactor**.** They were continuously fed into the anodic chamber in a concentration of: acetate (0.8 to 1.2 g L^{-1}), propionate (0.6 to 0.8 g L^{-1}), and butyrate (0.2 to 0.4 g L^{-1}), which was varied to provide a constant organic loading rate (OLR) of 6.4 g COD L_A^{-1} d^-

[1] (grams of chemical oxygen demand per litre of anode per day) for all the HRTs tested. The carbon source composition and concentration was inspired by the VFA distribution found in the effluent of a dark fermentation process (Cuetos et al., 2007). However, since it is widely known that biological degradability of propionic acid is not straightforward, the concentration of this VFA was increased to assess its biodegradability when fed to a MEC.

The chemicals and reagents used were of analytical grade and distilled water was used for preparing the solution.

4.2.2 MEC Design, Instrumentation and Operation

All tests were conducted in duplicate, and carried out in a continuous-flow MEC constructed with a series of polycarbonate plates arranged to form an anodic chamber and a gas collection chamber, as described elsewhere (Tartakovsky et al., 2008). The anodic chamber held 210 mL of liquid and had a headspace of 40mL. The gas collection (cathodic) chamber also had a volume of 250 mL.

A 5mm-thick graphite felt measuring 25 cm by 10 cm (SIGRATHERM soft felt GDF 2) was placed in the anodic chamber filled with liquid. A Ni-based gas diffusion electrode (GDE) with a Ni load of 0.4 milligrams per square centimetre (mg cm^{-2}) was used as a cathode, and was prepared as described by Hrapovic et al. (2010). The cathode was separated from the anode by a piece of porous cellulosic non-woven fabric (J-cloth®) with a thickness of 0.7 mm. The MEC was inoculated with 25mL of homogenized anaerobic sludge obtained from the wastewater treatment plant of the city of Leon in Spain).

The MEC temperature was maintained at 25 ºC by means of a thermocouple placed in the anodic chamber, a temperature controller (National Instruments PCI-6221) and a 10 cm by 10 cm heating plate located on the anodic chamber side of the MEC. The value for pH was maintained at a set-point of 7.0 using a pH probe installed in the recirculation line, a pH controller (EUTEC-PH-200) and a solution of 0.05 N NaOH, which was fed to the recirculation line. A 16 Ω resistor was added to the circuit for current measurements on-line at sixty-second intervals using a data acquisition system

(National Instruments PCI-6221). An adjustable DC power supply (BK PRECISION 9120) was used to maintain voltage at the preset point.

4.2.3 Analytical Measurements and Calculations

Gas production was measured on line by means of bubble counters connected to glass U-tubes and interfaced with a data acquisition system (National Instruments PCI-6221). Anodic and cathodic off-gas composition was analysed using a gas chromatograph (Varian CP 3800 GC) equipped with a thermal conductivity detector. A four-metre-long column packed with HayeSep Q 80/100 followed by a one-metre-long molecular sieve column were used to separate methane (CH4), carbon dioxide (CO2), nitrogen (N2), hydrogen (H2) and oxygen (O2). The carrier gas was argon and the columns were operated at 331 kPa and a temperature of 50 ºC. Volatile fatty acids (VFAs) were analysed using a gas chromatograph (Varian CP 3800 GC) equipped with a capillary column (from Supelco) and a flame ionization detector. The carrier gas was helium and the temperature of the injector was 250 ºC. The temperature of the oven was set at 150ºC for three minutes and thereafter increased to 180 ºC.

MEC performance was evaluated in terms of hydrogen production rate, COD removal efficiency, specific energy consumption (the amount of electrical energy required to remove 1g of COD), energy efficiency (the amount of energy contained in hydrogen compared to the amount of electrical energy fed to the MEC reactor), as well as in terms of cathodic conversion efficiency (the fraction of electrical current actually converted to hydrogen) and Coulombic efficiency (the amount of electrons present in the substrate that are actually converted into electrical current). A detailed explanation of the calculation methods for these parameters can be found in elsewhere (Escapa et al., 2009).

4.2.4 Start-up Procedure

After anodic chamber inoculation with non-acclimated anaerobic sludge (obtained from a three-litre laboratory-scale reactor digesting the organic fraction of municipal solid wastes), the cell was fed with a mixture of VFAs comprising 50 %, 35 % and 15 % (m/m) of acetic, propionic and butyric acids respectively and operated in hydrogen

production mode (MEC) by flushing the gas-collection (cathode) chamber with pure nitrogen and applying an external voltage of 1.0 V. The VFA load was gradually increased from 0.8 to 6.4 g L_A^{-1} d^{-1}, in order to avoid organic overload while providing a sufficient amount of substrate. After 24 days of continuous operation the current density started to increase and four days later it stabilized at 206 mA L^{-1}, corresponding to a hydrogen production of 0.95 L L_A^{-1} d^{-1}. Gas-collection (cathodic) chamber off-gas consisted of H_2 (84 %), and CH_4 (16 %).

Before the experimental section (in the strict sense) started a period of 46 days was included to allow the microbial communities to stabilize and adapt to the substrate. Both HRT and V_{app} were randomly selected to minimize the effect of microbial adaptation on MEC performance (Tartakovsky et al., 2008).

4.3 RESULTS AND DISCUSSION

4.3.1 Gas Production Results

Cathodic Off-Gas Production

Hydrogen production (Figure 4.1) followed an almost linear growth trend with increasing HRT at all V_{app}s tested, showing that an increment in the HRT at high applied voltages is more effective (in terms of hydrogen production rates) than the same increment when V_{app} was set at 0.8 or 0.6 V (i.e.: hydrogen production seems to be more sensitive to HTR at higher V_{app}s). Trend lines in Figure 4.1 show that a one-hour increase in the HRT when V_{app} = 1.0 V, boosts hydrogen production by 0.11 L L_A^{-1} d^{-1}, while the same increase in HRT improves hydrogen production only by 0.04 L and 0.03 L L_A^{-1} d^{-1} at V_{app}s of 0.8 V and 0.6 V respectively.

Similarly, an analysis of the influence of V_{app} on the hydrogen production rate while HRT was kept constant revealed that increasing the V_{app} with a higher HRT is more effective than doing so with a lower HRT (Figure 4.1). In fact, an increase of 0.1V with HRT = 12 h led to a boost of 0.30 L L_A^{-1} d^{-1} in hydrogen production, while the same

increase in V_{app} at HRTs of 10 h and 8 h increased hydrogen production by 0.26 and 0.20 L L_A^{-1} d^{-1} respectively.

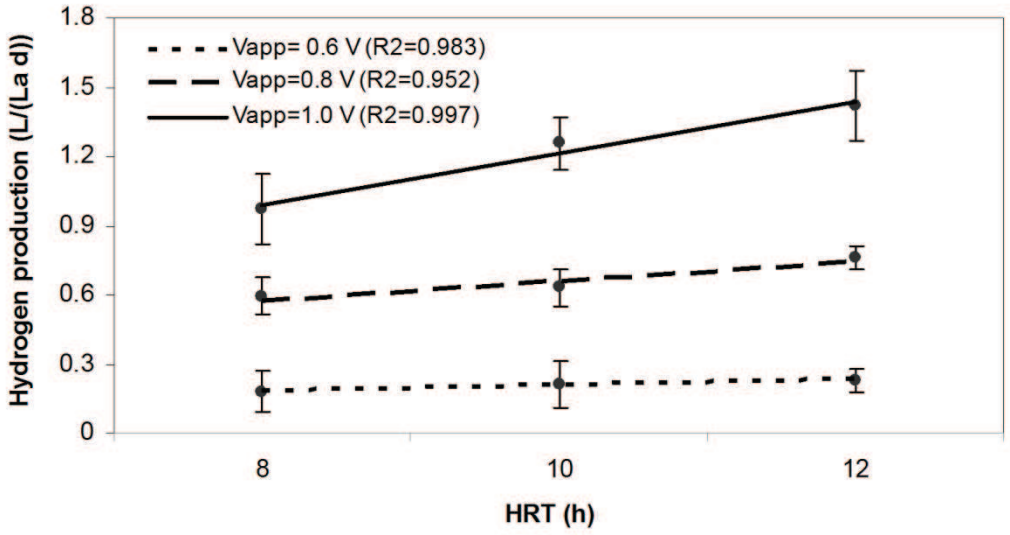

Figure 4.1. Cathodic off-gas production as a function of HRT

No or negligible amounts of hydrogen were measured when applied potential was set below 0.5 V regardless of the HRT imposed.

The impact of V_{app} and HRT on hydrogen production was further investigated by computing the cathodic conversion efficiency (CCE) and the energy efficiency (EE) (Table 4.1). CCE did not seem to be affected by HRT and only V_{app} showed any clear influence upon it. Similar results were obtained in a previous work, in which an increase in V_{app} also resulted in a steady growth in CCEs (Escapa et al., 2009).

Likewise, EE did not seem to be affected by HRT in any clear way (Table 4.1), and it was only when voltages below 1.0 V were applied that EE rose above 100 %. Cheng and Logan (2007) also found a rapid drop in EE as V_{app} was increased (from ~700 % at 0.2 V to ~200 % at 0.8 V) using acetate as the only carbon source. Thus, the positive effects of voltage increases on the hydrogen production rate and on CCE were counteracted by a drop in EE.

Table 4.1. Coulombic efficiency (CE), cathodic conversion cfficiency (CCE) and energy efficiency (EE) with the various different lLevels of HRT and Vapp used.

HRT (h)	Voltage (V)	CE (%)	CCE (%)	EE (%)
8	0.6	7.8	55.7	131.3
	0.8	18.7	60.8	107.6
	1.0	23.3	66.7	94.3
10	0.6	10.9	55.1	129.9
	0.8	14.5	60.4	106.8
	1.0	23.2	68.0	96.2
12	0.6	6.9	53.8	127.0
	0.8	16.1	60.2	106.4
	1.0	24.5	68.6	97.0

Methane concentration in the cathodic off-gas ranged from 4 % to 27 %, and its origin is still not clear. Evidence has been provided that this methane is not produced on the cathode, being likely to be an outcome of the growth of micro-organisms on the anode (Wang et al., 2009). However, Lee et al. (2009) have reported the presence of H_2-oxidizing *Methanobacteriales* in the anode and cathode biofilms, which suggests that hydrogen might be converted to methane as soon as it is produced on the cathodic surface. Contrary to what occurred with hydrogen production, no clear dependency of cathodic methane production either on HRT or on V_{app} was observed (results not shown). Similar results were obtained in one study (Tartakovsky et al., 2009) carried out in a MEC operated in continuous mode, where a methane concentration below 2.1 % was detected in the gas collection chamber, with no clear connection between cathodic methane production and V_{app}.

Anodic Off-Gas Production

Only methane and carbon dioxide were detected in the anodic off-gas produced (methane concentration always being in the range 80 % to 96 %). If compared with the total gas produced in the reactor (anodic and cathodic), methane could account for 87 % (v/v) in the most unfavourable conditions and 45 % when V_{app} and HRT were set at 1 V and 8 h respectively, resulting in an average methane proportion of 66 %.

A brief analysis of the slope of trend-lines represented in Figure 4.2, revealed that methane production rate seemed to be slightly more sensitive to HRT variations at low V_{app}s, suggesting that in order to reduce methane production, a one hour decrease in the HRT is more efficient at high Vapp.

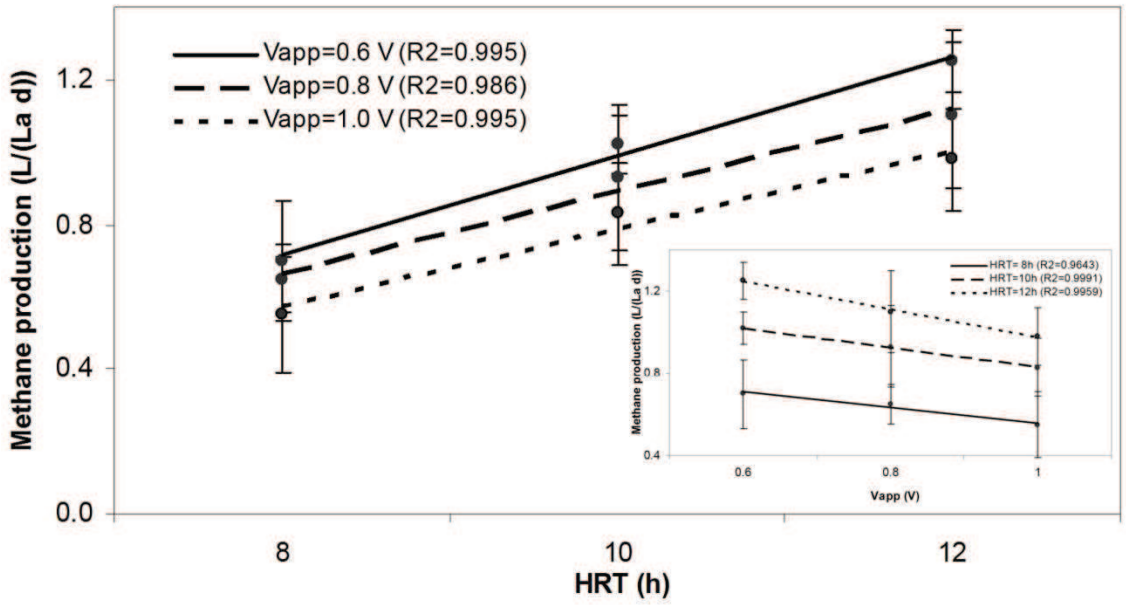

Figure 4.2. Anodic methane production as a function of HRT and Vapp (insert).

Similarly, variations in V_{app} while HRT was kept constant (Figure 4.2 insert), revealed that in order to reduce the methane production rate, an increase in the V_{app} with higher HRTs is slightly more effective than the same increase with lower HRTs. These results are in accord with other studies (Tartakovsky et al., 2008), where an increase in V_{app} from 0.70 V to 0.96 V resulted in a decrease of 25 % in the methane production. Moreover, the increase in methane production when low V_{app}s were employed might be explained by the fact that smaller V_{app}s decreased the anode potential, which can influence the competition between anode respiring bacteria (ARB) and methanogens by lowering the energy gain for ARB (Finkelstein et al., 2006) (i.e.: lower applied potentials may favour substrate intake by other microorganims to the detriment of ARB).

4.3.2 Rate of VFA Degradation and Removal of COD

Figure 4.3 shows the influent and effluent compositions with the various levels for V_{app} and HRT tested. It must be kept in mind that OLR was kept constant, so the influent concentration was dependent on the HRT.

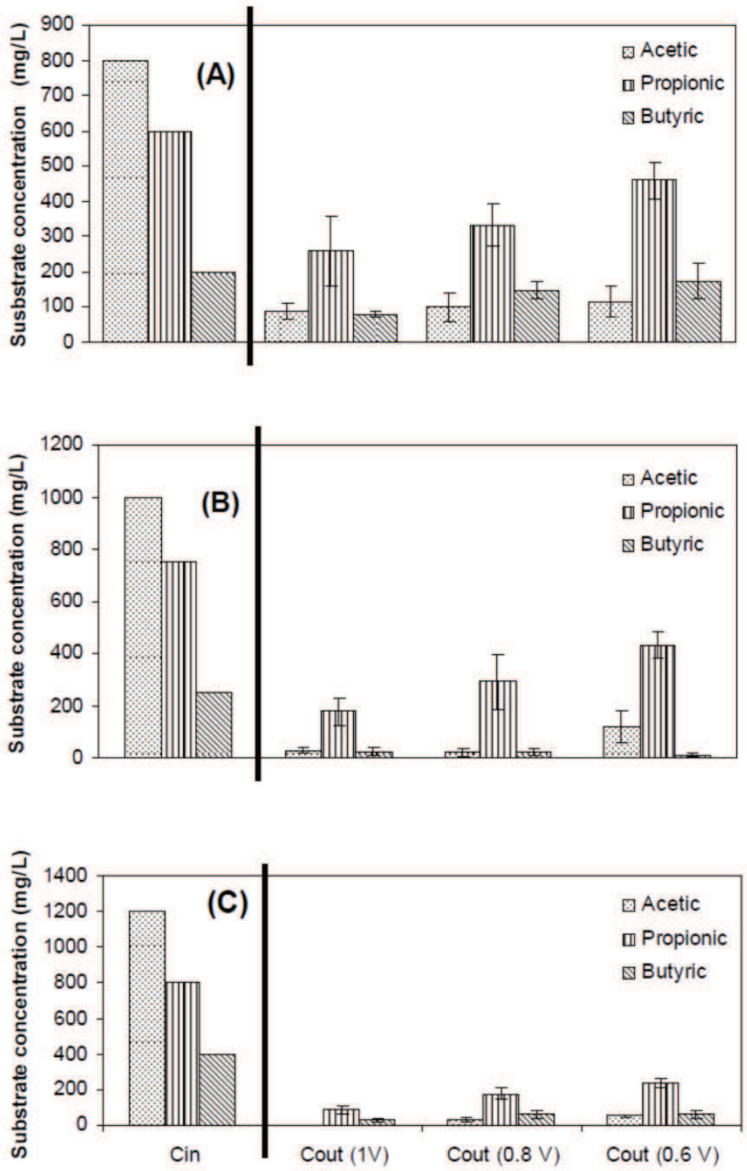

Figure 4.3 Influent (Cin) and effluent (Cout) composition with the various different V_{app}s (in brackets) and HTRs Tested. A) HRT = 8h, B) HRT = 10 h and C) HRT = 12 h.

When HRT was set at 8 h (Figure 4.3A) a relatively low level of VFA degradation was achieved. Although the proportion of acetate in the effluent was reduced to roughly 10 % of that in the influent at all values of V_{app}, propionate and butyrate underwent no such significant conversion, particularly at low V_{app} values. Liu et al. (2005b) proved that the electron transfer rate for an acetate-fed anode is much higher than that of a butyrate-fed one, which may explain this limited consumption rate of butyrate compared to acetate at HRT=8 h.

However, when HRT was set at 10 h (Figure 4.3B), acetate and butyrate were rapidly removed at all applied voltages (their presence in the effluent was always below 10 % of that in the influent). The conversion rate for propionic acid increased in comparison with that at 8 h, but it was still relatively low (compared with acetate and butyrate). This low conversion rate for propionate might be related to the fact that formate is not directly used by ARB (instead it is readily used by acetogens to produce acetate (Ha et al., 2008)).

With a retention time of 12 h (Figure 4.3C), acetate and butyrate disappeared almost completely, although at low and medium V_{app}s (0.8V and 0.6V), a small fraction of these VFAs still remained in the effluent. Again, propionate proved to be more difficult to degrade.

Throughout the tests, COD removal rate (Figure 4.4) was proportional to V_{app}. An analysis of the trend lines revealed that a 0.1V increment in the V_{app} when HRT was set at 8 h, was followed by a 6 % boost in the COD removal rate. The same increase in V_{app} led to improvements in COD removal rates of 4.2 % and 2.5 % at HRTs of 10 h and 12 h respectively. This COD removal dependence on applied voltage confirms that the VFAs were consumed by anodophilic micro-organisms (Tartakovsky et al., 2009), although the relatively high production of methane discussed in section 4.3.1 leads to the conclusion that some part of the COD fed to the reactor was removed by other microorganisms, and not only by the ARB.

Coulombic efficiency (CE) was found to lie in a range between 6.9 % and 24.5 % (Table 4.1), showing a clear dependence on V_{app} (a 0.1 V increment in the applied voltage boosted CE by 3.8% at all HRTs). Nonetheless, when compared with other studies where acetate was used as the only carbon source (Tartakovsky et al., 2009; Liu et al., 2005c), these are indeed relatively low CE values. One possible explanation for this discrepancy can be attributed to the low conversion of propionate into current, and the competition between ARB and other microorganisms for substrate.

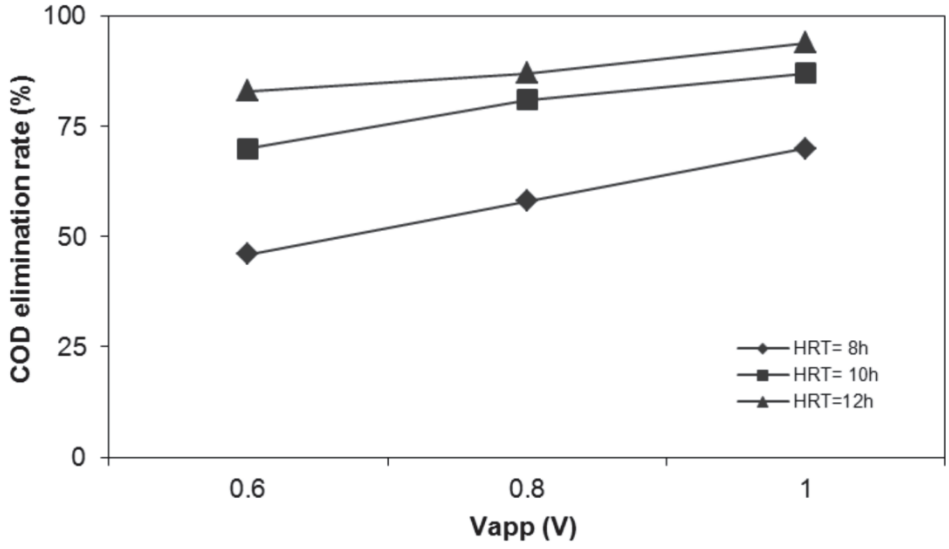

Figure 4.4. COD removal rate as a function of Vapp with the various different HRTs used. (Variation across duplicates is not shown.)

Material Balance

Although the existence of a mixed microbial community should be accounted for in the MEC material balance, a simplified COD recovery calculation (COD_{rec} [%]) was written as follows:

$$COD_{rec} = \frac{COD_{out} + COD_{H_2} + COD_{CH_4}}{COD_{in}} \quad (4.1)$$

where COD_{out} and COD_{in} are the influent and effluent COD flows in g COD per litre of affluent per day (L_a^{-1} d^{-1}) respectively; COD_{H2} and COD_{CH4} are the hydrogen and methane COD equivalent flows (in g COD L_a^{-1} d^{-1}). Effluent COD was calculated from its VFA composition, assuming COD equivalences of 1.06 g, 1.51 g and 1.81 g of COD per g of VFAs for acetate, propionate and butyrate, respectively. The presence of biomass and other metabolites (soluble microbial products) in the effluent were not accounted for in the balance. Methane and hydrogen COD equivalence were calculated using yields of $Y_{CH4} = 0.35L\ g^{-1}$ and $Y_{H2} = 1.49L\ g^{-1}$:

$$COD_{H_2/CH_4} = \frac{Q_{H_2/CH_4}}{Y_{H_2/CH_4}} \quad (4.2)$$

COD recovery correlated strongly with V_{app}, as it decreased from 84 % at 0.6 V to 71 % at 1.0 V, revealing the existence of a relatively large gap in COD recovery (29%) at high V_{app}s. This result might be partially explained by the gain in the availability of free energy for ARB to grow, that arises from the increase of the anodic overpotential when high V_{app} are imposed (it is well known that the more positive the redox potential of a terminal electron acceptor (or electrode) for a given substrate or electron donor is, the higher is the energy gain for an organism).

Even though biomass yields have not yet been thoroughly investigated for bio-electrochemical reactors, a range of yields of 0.070g to 0.304g COD-biomass g^{-1} COD-substrate have been reported (Rabaey et al., 2003) (a more recent study (Freguia et al., 2007) indicated values of biomass yield of 0.24 and 0.31g COD-biomass g^{-1} COD-substrate). In addition typical values of biomass yield in the wastewater field for anaerobic growth are around 0.040 g COD-biomass g^{-1} COD-substrate (Rabaey and Verstraete, 2005). Given that not only electrogenic micro-organisms are present in the anodic chamber of the reactor, a yield of biomass between 0.040 g and 0.304 g COD-biomass g^{-1} COD-substrate might be expected, which is in good agreement with the biomass production attributed in this work (0.16 to 0.29 g COD-biomass g^{-1} COD-substrate) (i.e., the gap in COD recovery). However this analysis does not take into account the presence of soluble microbial products in the effluent which may reach 11 % of COD_{in} (Lee and Rittmann, 2010), so biomass yield may be even lower than the values hypothesized above.

4.3.3 Reactor Performance. General Remarks

Although the hydrogen production rates reported in section 4.3.1 are analogous to, or even higher than, the values reported in the literature (Table 4.2), still a large proportion of the VFAs fed to the reactor were converted into methane rather than hydrogen.

A body of literature has reported that most of methane produced in a MEC reactor may be attributed to hydrogenothrophic micro-organisms (Lee and Rittmann, 2010; Wang et al., 2009; Lee et al., 2009) (direct CO_2 reduction to methane has being ruled out because of the limited kinetics of methane evolution on a Ni-based electrode (Hori, 2010)). Thus, if hydrogenotrophic activity could be suppressed and all the measured current

were captured as hydrogen, production rates could reach 2.07 L L_a^{-1} d^{-1}, representing 77 % v./v. of the total gas produced in the reactor, which would also bring a significant improvement in energy efficiency (from 151 % to 235 %). Hence, there is no doubt that methanogenic activity is an issue that must be carefully addressed in order to increase MEC performance; yet, none of the several various approaches that have already been proposed up to now (Lee and Rittmann, 2010; Lee et al., 2009; Chae et al., 2010; Call and Logan, 2008; Rozendal et al., 2008)) can satisfactorily suppress hydrogenotrophic activity.

Table 4.2. Hydrogen recoveries obtained in MEC studies.

Operation mode	Substrate	Vapp (V)	H2 production rate (L L_A^{-1} d^{-1})	EE (%)	Reference
Batch	Urban WW	0.58	0.01	122	Ditzig et al., 2007
Batch	Acetate	0.50	0.02	157	Rozendal et al., 2006
Batch	Acetate	0.45	0.37	300	Liu et al., 2005c
Continuous	Glycerol	1.00	0.62	120	Escapa et al., 2009
Batch	Acetate	0.60	1.10	230	Cheng and Logan, 2007
Continuous	Mixture of VFAs	1.00	1.42	97	This study
Batch	Acetate	0.80	3.12	176	Call and Logan, 2008
Continuous	Acetate	1.00	5.22	142	Hrapovic et al., 2010
Continuous	Acetate	1.00	6.32	166	Tartakovsky et al., 2009
Batch	Acetate	1.00	17.8	115	Parkin and Owen, 1986

In addition to this, apparent energy consumption per kilogram of COD removed (Figure 4.5) was found to be as low as 0.11 kWh kg^{-1} COD (kilowatt-hours per kilogram of COD), whilst the highest energy consumption reached 0.84 kWh kg^{-1} COD, exhibiting a strong linear dependence with applied voltage (a rise of 0.1V in the applied voltage led to an increase of 0.14 kWh kg^{-1} COD to 0.18 kWh kg^{-1} COD in the amount of electrical energy consumed). However, the lower value of energy consumption (0.11 kWh kg^{-1} COD) is well below the threshold of energy consumption required for the hydrogen evolution reaction to occur in a MEC (0.47 kWh kg^{-1} COD assuming V_{app}=0.11 V). This discrepancy is mainly attributed to substrate removal by microorganisms other than

ARB which makes difficult to compute the real value of energy consumption. Nevertheless it can be estimated an energy consumption in the range between 2.01 to 3.35 kWh kg^{-1} COD by assuming CE=100 % (i.e. assuming that the measured current corresponds to the actual DQO removed by ARB).

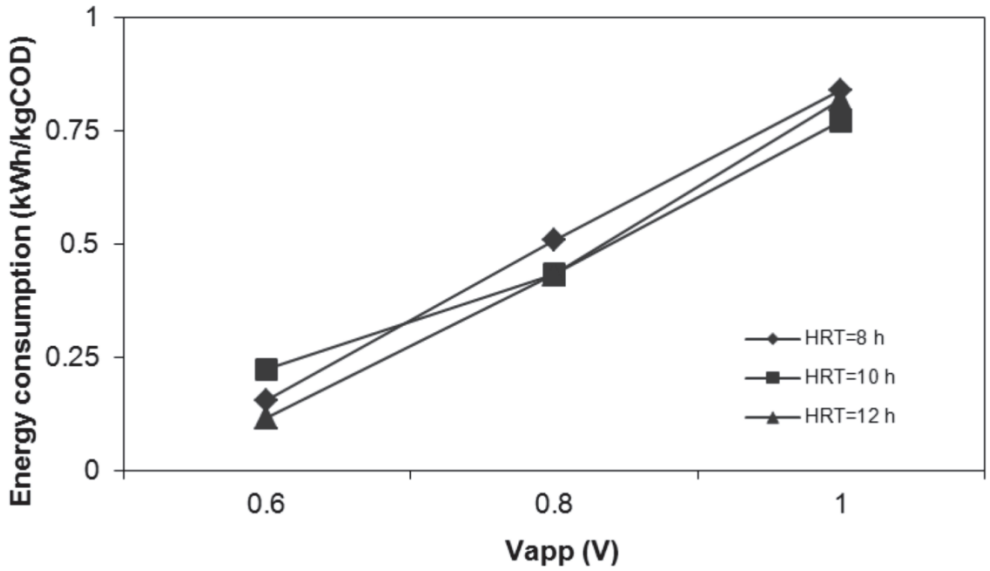

Figure 4.5. Energy consumption per unit of COD removed as a function of Vapp with the various different HRTs used. (Variation across duplicates is not shown.)

There is still another major point that deserves consideration. The influent was fed into the reactor under very favourable conditions: well-balanced nutrients, easily degradable substrate (although propionate developed a pseudo-recalcitrant behaviour), mesophilic conditions (T = 25 ºC) and high conductivity (13.6 mS cm^{-1}). Even though real effluents from dark fermentation processes usually contain substantial amounts of VFAs in their composition (Cuetos et al., 2007), it is not realistic to expect such conditions as those above described. Hence, although COD elimination rates higher than 80 % were achieved at HRTs of 10 h and 12 h and V_{app}s of 0.8 V and 1.0 V, with reasonable energy consumption rates, real substrates may require different operational conditions.

4.4 CONCLUSSIONS

Hydrogen production is more sensitive to HRT changes when the V_{app} is high. Similarly, in order to increase hydrogen and reduce methane production rates, an increase in V_{app} proved to be more effective with longer HRTs. Increases in HRT and V_{app} led to greater COD removal rates, but it was only at V_{app}s higher than 0.8 V and with HRTs longer than 10 h that COD removal rates above 80 % were attained. Although acetate and butyrate proved to be easily degradable, propionate showed a pseudo-recalcitrant behaviour throughout the tests performed. Even though HRT apparently did not seem to have any clear influence on the performance parameters (CE, CCE and EE), an increase in V_{app} had a positive effect on CE and CCE, while affecting EE negatively.

Acknowledgements

Funding for this study was provided by Isolux-Corsan, S.A. and the Spanish Ministry of Science and Innovation (Project Number: ENE2009-10395).

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Chapter 5

Performance of a Continuous Flow Microbial Electrolysis Cell (MEC) Fed with Domestic Wastewater

Abstract. In this study, MEC performance was investigated in terms of chemical oxygen demand (COD) removal, hydrogen production rate and energy consumption during continuous domestic wastewater (dWW) treatment at different organic loading rates (OLR) and applied voltages (V_{app}). While the COD removal efficiency was improved at low OLRs, the electrical energy required to remove 1g of COD was significantly increased with decreasing the OLR. Hydrogen production exhibited a Monod-type trend as function of the OLR reaching a maximum production rate of 0.30 L/(Lr d). Optimal V_{app} was found to be highly dependent on the strength of the dWW. The results also confirmed the fact that MEC performance can be optimized by setting V_{app} at the onset potential of the diffusion control region.

Although low columbic efficiencies and the occurrence of hydrogen recycling limited significantly the reactor performance, these results demonstrate that MEC can be successfully used for dWW treatment.

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Bioresource Technology 117, (2012) 55-62

5.1 INTRODUCTION

Global energy needs and increasing concern about fossil fuel emissions have prompted scientists to research alternative fuels and energy production technologies. Hydrogen (H_2) has been suggested as the energy carrier of the future because it is a clean fuel, producing only water when combusted, and has a high-energy yield (142.35 kJ g^{-1}). Among the technologies currently available for hydrogen production, biological methods are generally preferred over chemical and thermal methods because organic wastes can be used as substrates (Gómez et al., 2011). As a result, wastes such as wastewater (WW) are now being regarded as potential commodities for bioenergy and biochemical production rather than as useless materials (Angenent et al., 2004). In contrast, activated sludge systems, a conventional WW treatment in developed nations, use large blowers to favor oxygen transfer from air into the mixed liquor that are energy intensive and increase treatment costs (Rosenbaum et al., 2010). Therefore, there is great interest in seeking new methods and technologies to reduce treatment costs or produce other products from WW.

A microbial electrolysis cell (MEC) is a device capable of converting the chemical energy contained in wastewater into hydrogen while reducing its organic load with an input of electricity. Since the production of hydrogen through MECs was first demonstrated (Liu et al., 2005), MEC performance has been evaluated using individual organic compounds such as acetate (Rozendal et al., 2006), glucose (Tartakovsky et al., 2008) and glycerol (Escapa et al., 2009). Few tests have been conducted with actual wastewaters, such as those from potato chip (Kiely et al., 2011) or swine facilities (Wagner et al., 2009) and wineries (Cusick et al., 2010; Cusick et al., 2011). Despite the great potential of microbial electrolysis in domestic wastewater (dWW) treatment, only two studies (Ditzig et al., 2007; Cusick et al., 2010) have explored the performance of MECs fed dWW to our knowledge. Ditzig et al. (2007) evaluated MEC performance in terms of hydrogen recovery, coulombic efficiency (CE) and treatment effectiveness. They achieved good results (91% removal of dissolved organic carbon and a final biochemical oxygen demand concentration below 7 mg L^{-1}) demonstrating that dWW treatment based on a MEC reactor is feasible. However they had to use relatively high

batch cycle times (30-108 h), a platinum-based cathode, and an ionic exchange membrane (IEM), the cost of which may prohibit MEC application. For instance Rozendal et al. (2008) have predicted that the IEM cost may represent up to 40% of the investment costs in a MEC reactor. Moreover, the presence of an IEM between the anode and the cathode usually results in a higher internal resistance (Huang, et al., 2010) and the appearance of a pH gradient between the electrodes (Rozendal et al., 2007), thus limiting the reactor performance.

Following the efforts made by other researchers (Tartakovsky et al., 2008; Zhuang et al., 2009) to improve the reactor design, to decrease the internal resistance, and to use low cost materials, the IEM has been replaced by a J-cloth in our set-up. However, with no IEM between the electrodes, if the hydrogen produced in the cathode is not harvested rapid enough, it can be used as a substrate by hydrogenotrophic methanogens or be re-oxidized by the anode-respiring bacteria (Lee and Rittmann, 2010). The anodic re-oxidation of the hydrogen produced in the cathode is usually termed as "hydrogen recycling" (Kiely et al., 2011; Call et al., 2009) and represents a great challenge since it increases the electrical current artificially. Even though a considerable number of papers has been devoted to this hurdle (Lee and Rittmann, 2010; Kiely et al., 2011; Call, Wagner and Logan, 2009; Parameswaran et al., 2011; Parameswaran et al., 2010; Lee et al., 2009) no clear solution has yet emerged.

Investment costs can be further reduced by replacing the Pt-based cathode by a low-cost-metal-based cathode. Several studies have shown that MECs with Ni-based cathodes can achieve performances similar to or even better that those with Pt-based cathodes (Selembo et al., 2010; Call et al., 2009; Manuel et al., 2010).

Besides process design also applied voltage and current density have to be taken into account in a full-scale MEC system. Undoubtedly, applied voltage (V_{app}) has a preeminent influence on MEC performance, not only because depending on its value the electrochemical reaction will take place or not (Liu et al., 2005), but also because it determines to a great extent the energy input (Tartakovsky et al., 2011) and as a result influences the operational costs. On the other hand, the current density relates to the size of the reactor (Lee and Rittmann, 2010) (i.e., the reactor volume and the electrodes surface area), and since current density is intimately related to the OLR (Juang et al.,

2011), the size of the reactor (and thus the operational costs involved) will depend indirectly on the OLR. Therefore, the investigation of the influence of V_{app} and OLR on MEC performance will pave the way to the scale-up and in parallel, help to identify the actual limits of hydrogen production, energy consumption and COD removal rate in a MEC during dWW treatment.

In this work we tested a continuous membrane-less single-chambered reactor with a Ni-based cathode at hydraulic retention times (HRTs) between 3-48 h, focusing on the effect of the organic loading rate (OLR) and applied voltage (V_{app}) on hydrogen production rates, energy consumption and the effectiveness of the treatment (COD removal) when treating full-strength, un-amended dWW.

5.2 MATERIALS AND METHODS

5.2.1 MEC Design and Operation

All tests were conducted in duplicate and performed in a continuous-flow single-chamber MEC constructed with a series of polycarbonate plates arranged to form an anodic chamber and a gas collection chamber, as described elsewhere (Tartakovsky et al., 2008). The anodic chamber retained 90 mL of liquid and had a headspace of 10 mL. The gas collection (cathodic) chamber also had a volume of 100 mL.

A 5 mm-thick graphite felt measuring 9 cm by 10 cm (SIGRATHERM soft felt GDF 2) was placed in the anodic chamber filled with liquid. A Ni-based gas diffusion electrode (GDE) with a Ni load of 0.4 mg cm^{-2} was used as a cathode and was prepared as described by Hrapovic et al., (2010). The cathode was separated from the anode by a piece of porous, cellulosic, non-woven fabric (J-cloth®) with a thickness of 0.7 mm.

The MEC temperature was maintained at 30ºC using a thermocouple probe placed in the anodic chamber, a temperature controller (National Instruments PCI-6221) and a 10 cm by 10 cm heating plate located on the same side of the MEC as the anodic chamber. A 16 Ω resistor was added to the circuit for on-line current measurements at 60 s intervals using a data acquisition system (National Instruments PCI-6221). An

adjustable DC power supply (BK PRECISION 9120) was used to maintain voltage at the preset level.

5.2.2 Inoculation and Substrate

The MEC was inoculated with 100 mL of domestic wastewater (i.e., effluent from pretreatment systems) from the Navalmorales wastewater treatment plant in Toledo (Spain) and operated in hydrogen production mode (MEC) by flushing the gas-collection (cathode) chamber with pure nitrogen and applying an external voltage of 1.0 V. The HRT was set at 12 h, which provided an OLR between 642 and 836 mg L_a^{-1} d^{-1} (milligrams per liter of anode and per day). Influent COD varied between 321 and 418 mg L^{-1}. After 6 days of continuous operation, the current density started to increase, stabilizing at 3.1 ± 0.2 mA (31 ± 2 mA L_a^{-1}), which corresponds to a hydrogen production rate of 0.11 L L_a^{-1} d^{-1}. The gas-collection (cathodic) chamber off-gas consisted of H_2 (97%) and CH_4 (3%). After the start-up, the microbial communities were allowed to stabilize for 29 days.

The wastewater, which served as both the inoculum and substrate, had a pH of approximately 6.7 and conductivity of 0.9 mS cm^{-1}.

5.2.3 Experimental Design

The first set of experiments evaluated the effect of organic loading rate (OLR) on wastewater treatment efficiency, hydrogen production rate and performance parameters (i.e., Coulombic efficiency, cathodic conversion efficiency, and energy consumption). Although we initially planned to study the effect of hydraulic retention time (HRT), the variability in the strength of the wastewater fed into the reactor prompted us to select OLR rather than HRT as the independent variable. Therefore, several HRTs between 3-48 h were selected to yield OLRs between 243-3,128 mg COD L_a^{-1} d^{-1} (Table 5.1); HRTs below 3 h were avoided to prevent possible damages of the biofilm due to high flow rates. The V_{app} was set at 1 V, and a series of voltage scans were performed at the end of the tests.

Table 5.1. Summary of tests and, performance parameters of the first set of experiments.

HRT	CODin	CODout	OLR	CE	CCE	COD rem.	Int. resist.
(h)	(mg L^{-1})	(mg L^{-1})	(mg L_a^{-1} d^{-1})	(%)	(%)	(%)	(Ω)
48	486±14	160±16	243	65	--[a]	67	94
24	448±10	170±13	448	59	45	62	104
12	310±6	130±18	620	57	44	58	105
6	310±7	121±14	1,240	55	42	61	--[b]
6	486±11	238±15	1,944	54	43	51	60
3	391±4	234±31	3,128	38	45	44	48

[a] No hydrogen production detected
[b] No voltage scan performed

The second set of experiments was intended to evaluate the effect of V_{app} on the same parameters as in the first set of experiments. Due to the variability of the influent COD, two HRTs were used (Table 5.2) to maintain a nearly constant OLR (493 ± 61 mg COD L_a^{-1} d^{-1}): 24 h for influent with a high COD (457± 19 g L^{-1}) and 10.5 h for influent with a lower COD (232±31 g L_a^{-1}).

Table 5.2. Summary of the test performed during the second set of experiments.

V_{app}	HRT	CODin	CODout	OLR
(V)	(h)	(mg L^{-1})	(mg L^{-1})	(mg L_a^{-1} d^{-1})
1.20	10.5	220±13	170±16	503
1.00	24.0	452±14	162±07	452
0.85	10.5	197±16	134±05	450
0.75	24.0	441±13	106±10	441
0.50	24.0	479±21	187±05	479
0.50	10.5	240±16	197±00	549
0.00	24.0	447±24	380±33	447

Both HRT and V_{app} were randomly selected to minimize the effect of microbial adaptation on MEC performance (Tartakovsky et al., 2008). The results were averaged, and the standard errors were determined to assess statistical variability.

Coulombic efficiency (CE) was computed as the ratio of electrons to the total electrons available from COD consumption. Cathodic conversion efficiency (CCE) was computed as the ratio of electrons recovered as hydrogen gas to the total number of electrons that reach the cathode. Energy consumption was computed as the ratio between the electrical energy consumed to the amount of COD removed. A detailed

explanation of the calculation methods for theses performance parameters can be found elsewhere (Lee et al., 2009; Escapa et al., 2009).

5.2.4 Analytical Measurements

Gas production was measured in-line by bubble counters connected to glass U-tubes that were interfaced with a data acquisition system (National Instruments PCI-6221), as previously described by Tartakovsky and co-workers (Tartakovsky et al., 2008). Anodic and cathodic off-gas composition was analyzed using a gas chromatograph (Varian CP 3800 GC) equipped with a thermal conductivity detector. A four-meter-long column packed with HayeSep Q 80/100 was connected to a one-meter-long molecular sieve column were used to separate methane (CH_4), carbon dioxide (CO_2), nitrogen (N_2), hydrogen (H_2) and oxygen (O_2). Argon was used as the carrier gas, and the columns were operated at 331 kPa and 50ºC.

COD concentration of the influent and effluent samples were measured using an automatic potentiometric titrator (Metrohm 862 Compact Titrosampler) after centrifugation at 3,500×g and digestion in the presence of dichromate at 150ºC for 2 h using a Hanna C9800 reactor.

Voltage scans were conducted with a potentiostat (μAutolab Type III) at a scan rate of 0.0001 V s^{-1}.

5.3 RESULTS AND DISCUSSION

5.3.1 Effect of the OLR Over MEC Performance at High Applied Voltages

Once the reactor achieved steady state, several HRTs (Table 5.1) were tested to investigate the effect of the OLR on COD removal, hydrogen production and power consumption.

The membrane-less flat reactor was able to reduce up to 67% of the total COD fed into the reactor (Table 5.1) at a V_{app} of 1 V and low OLR (243 mg $L_a^{-1}d^{-1}$). Further increases in the OLR at a constant V_{app} indicated a moderate influence of OLR over COD removal: an increase in OLR of 1,000 mg La^{-1} d^{-1} decreased the COD removal by 8.4%.

Similar results were obtained in a single-chamber batch-fed MEC (Cusick et al., 2011), which delivered a 58% COD removal at 24-h batch cycle and a V_{app} of 0.9 V when fed with dWW. The same laboratory (Kiely et al., 2011) also achieved a 79% COD removal when a MEC was fed with diluted potato chip WW (48-h batch cycle and 0.9-V applied voltage). In contrast, COD removal higher than 90% have been achieved in a two-chambered MEC reactor fed with dWW amended with a phosphate buffer solution (Ditzig et al., 2007). Although the retention times were relatively high (~30-110 h), the referred work demonstrated that high COD removal can be achieved during wastewater treatment, which highlights the need for further improvements in continuous dWW treatment in a MEC reactor.

Hydrogen was evolved only at OLRs above 448 mg L_a^{-1} d^{-1} (HRTs below 24 h), with a maximum at an OLR of 1,994 mg L_a^{-1} d^{-1} (Fig 5.1). Further increases in the OLR did not vary hydrogen production significantly, indicating that hydrogen production (and current) is saturated when the OLR is set above 2,000 mg L_a^{-1} d^{-1}. A Monod-like function fit the data well (Fig 5.1) with a maximum hydrogen production constant (H_{max}) of 0.462 L L_a^{-1} d^{-1} and a half saturation coefficient (K_H) of 1,342 mg L_a^{-1} d^{-1}. When the OLR was set at 243 mg L_a^{-1} d^{-1} (HRT=48 h), pressure in the cathodic chamber became negative (i.e., no hydrogen production was measured), and there was a substantial increase in the percentage of methane inside this chamber (from less than 2% in the cathodic off-gas at higher OLRs to 16%) likely due to the conversion of hydrogen into methane by methanogenic microorganisms (Lee et al., 2009).

The cathodic conversion efficiency (CCE) (Table 5.1) was relatively low (40-45%) compared to other studies where dWW was used as substrate (Ditzig et al., 2007; Cusick et al., 2011), indicating that a significant amount of the hydrogen produced was likely lost through gas tubing or microbial metabolism. In addition, because no membrane was placed between the electrodes of our cell, hydrogen could easily migrate from the cathode to the anode, causing significant hydrogen crossover and anodic re-oxidation. This hydrogen crossover would not only have a direct impact on CCE but would also lower the MEC performance and distort the values of columbic efficiency (CE) reported in Table 5.1. In fact, 62-76% of the observed current in a membrane-less MEC can be attributed to hydrogen oxidation in the anode (Lee and Rittmann, 2010)). Therefore, approximately 70% of the circulating current could be attributed to parasitic

currents, and thus, actual values of CE might lie between 9-24%, rather than the observed 35-68% (Table 5.1). Interestingly, quite similar CE values (5.3-26.2%) were observed in a dWW-fed MEC in which hydrogen crossover was limited by a cation exchange membrane (Ditzig et al., 2007), supporting the idea that significant hydrogen crossover occurred in our cell.

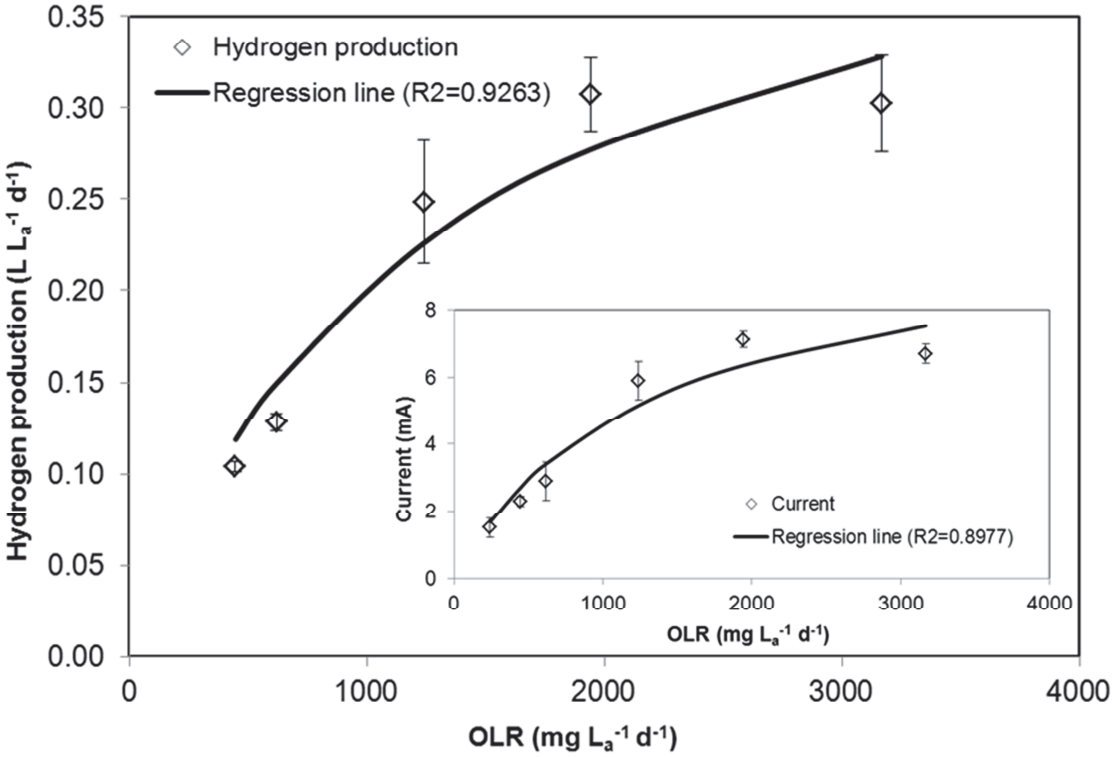

Figure 5.1. Hydrogen production, current (insert) and regression lines (Monod-type) as a function of the OLR.

In addition, such low CE values reveal the existence of a significant potential COD loss (i.e., COD that is not converted into current), which may be attributed to biomass production, methanogenic activity, or the presence of other electron acceptors (i.e., nitrates and sulfates), (Wang et al., 2009). Nitrates can be ruled out as a significant electron sink since nitrates levels in dWW are typically low (< 1mg/L). In contrast, biomass accumulation seems a more likely electron sink. According to Rabaey et al., (2003) and Freguia et al., (2007) the biomass production ranges from 0.07 to 0.31 g-COD-biomass g^{-1}-COD-substrate in an acetate-fed bio-electrochemical reactor, and can be as high as 0.51 g-COD-cell g-COD-substrate in a glucose-fed reactor. In addition, typical bacterial grow rates in anaerobic environments are approximately 0.040 g COD-

biomass COD^{-1}-substrate (Rabaey and Verstraete, 2005). Therefore, since in our own set-up the anodic chamber was feed with a fermentable substrate in anaerobic conditions, it seems reasonable to think that biomass production may lay in the range between 0.04 to 0.51 g COD-biomass g^{-1}-COD-substrate. A breakdown of a simplified COD balance is given in Table 5.3, where COD recoveries are calculated considering these two hypothesis: low biomass production (0.04 g COD-biomass g^{-1}COD-substrate) and high biomass production (0.51g COD-biomass g^{-1}COD-substrate).The relatively low COD recovery in both situations (Table 5.3) revealed the presence of a significant COD loss that has not been clearly identified.

Table 5.3. Breakdown of a simplified MEC COD balance as percentages of the total COD fed to the reactor. CODi: percentage corresponding to the influent; COD_e: percentage corresponding to the effluent; COD_{H2}:percentage corresponding to the hydrogen produced; COD_B^-:percentage corresponding to the biomass produced assuming a low biomass yield (0.04 g COD-biomass COD^{-1}-substrate). COD_B^+: percentage corresponding to the biomass produced assuming a low biomass yield (0.51 g COD-biomass COD^{-1}-substrate). COD_r^-: percentage of COD recovery computed as CODr= COD_e+ COD_{H2}+ COD_B^-. $CODr^+$: percentage of COD recovery computed as CODr= COD_e+ COD_{H2}+ COD_B^+. Hydrogen COD equivalence was calculated using a yield of Y_{H2} : 1.49 L g-COD^{-1}

OLR (mg L_a^{-1} d^{-1})	243	448	620	1,240	1,944	3,168
COD_i (%)	100	100	100	100	100	100
COD_e (%)	33	38	42	39	49	56
COD_{H2} (%)	0	16	14	13	11	6
COD_B^- (%)	3	2	2	2	2	2
COD_B^+ (%)	34	32	30	31	26	22
COD_r^- (%)	36	56	58	55	62	64
COD_r^+ (%)	67	86	86	83	86	84

Sulfates have proved to be an alternative electron sink in dWW fed-MEC (Ditzig et al., 2007). Although sulfates concentration was not analyzed in the present study, the occurrence of sulfate reduction was suggested by the sulfide-like odor noticed in the effluent of the reactor, and thus part of the COD loss may be attributed to sulfates reduction. However, it seems unlikely that only the presence of sulfates in the dWW can explain the large discrepancy in the COD balance presented in Table 5.3. Methane represents another plausible sink of electrons, since the utilization of a fermentable substrate (e.g. dWW) and the presence of hydrogen in a bioelectrochemical reactor has been usually associated with methanogenic activity (Parameswaran et al., 2009; Wang et al., 2009). Nevertheless, the almost negligible amounts of methane (~2% v./v.) detected in the cathodic chamber off-gas does not explain the above referred

discrepancy. Moreover, and despite methane concentration in the anode head space was relatively high (~85%), no significant gas production was observed in the anodic chamber. However, in the absence of a more likely candidate to fill-in the gap of the COD balance, we must admit the existence of relatively large gas leak on the anodic chamber side as the only explanation for the observed lack of methane production and thus, as the explanation for the discrepancy in the closure of the COD balance.

Energy consumption was found to be highly dependent on the OLR (Figure 5.2). When the OLR was set at 3,120 mg L_a^{-1} d^{-1}, the energy consumption per unit of COD removed was as low as 0.77 Wh g^{-1}COD, and then, it increased almost linearly until 2.20 Wh g^{-1}COD when the lowest OLR was imposed. This compares to what Cusick et al., (2009) achieved in a dWW batch-fed platinum-based MEC (2.0 Wh g^{-1}COD), suggesting that the use of a low-cost metal-based cathode in MECs can be successfully employed for dWW treatment. Moreover, other studies have shown that MECs with Ni-based cathodes can achieve performances similar to or even better that those with Pt-based cathodes (Selembo et al., 2010; Call et al., 2009; Manuel et al., 2010).

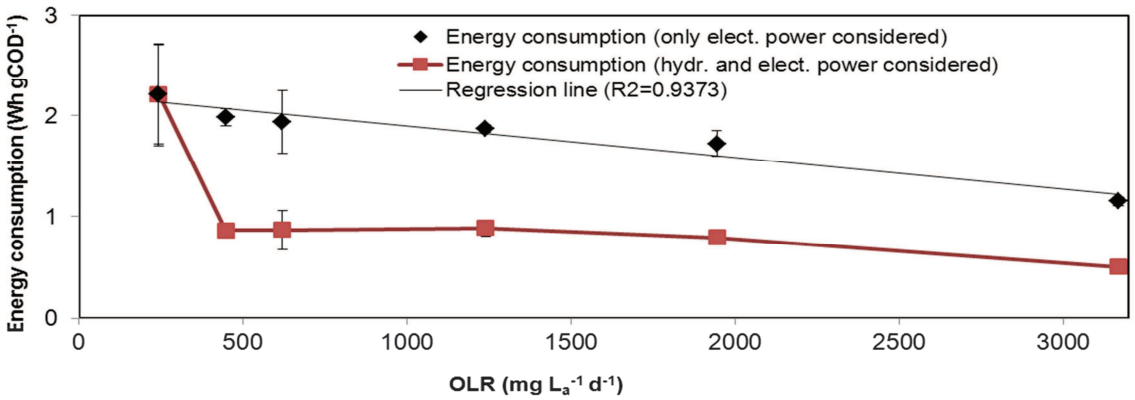

Figure 5.2. Energy consumption (with and without taking into consideration the energy content of the hydrogen produced) and regression line as a function of the OLR.

Interestingly, by including hydrogen's energy content into the computation of the energy consumption per unit of COD eliminated (Figure 5.2), the global energy consumption is significantly reduced, ranging narrowly from 0.79 to 0.89 Wh g^{-1}COD at medium OLRs and declining sharply to 0.5 Wh g^{-1}COD at high OLRs.

A series of voltage scans at different OLRs further evaluated the effect of the OLR on reactor performance (Figure 5.3). Although large differences were observed between medium-low and high OLRs, the electrical current started to flow at a significant rate at

applied potentials of approximately 0.3 V in all cases, which is associated to the onset of hydrogen production (Liu et al., 2005; Ditzig et al., 2007; Tartakovsky et al., 2011). Below this potential (SECTION A), it is assumed that activation overpotentials prevailed over ohmic (SECTION B) and concentration (SECTION C) overpotentials (Bagotsky, 2005).

The internal resistance was calculated based on the linear section of the plots (SECTION B). This parameter decreased with increasing OLR from approximately 100 Ω when low OLRs were imposed (Table 5.1) to 48 Ω at an OLR of 3,128 mg L_a^{-1} d^{-1}. This finding may partially explain the reduction in energy consumption as OLR increased. Similar results have been reported in a previous work (Escapa et al., 2009), where a MEC fed with glycerol as the carbon source increased its internal resistance when the OLR was decreased. This behavior was associated with the activity of anodophilic microorganisms and the electrochemical properties of the MEC.

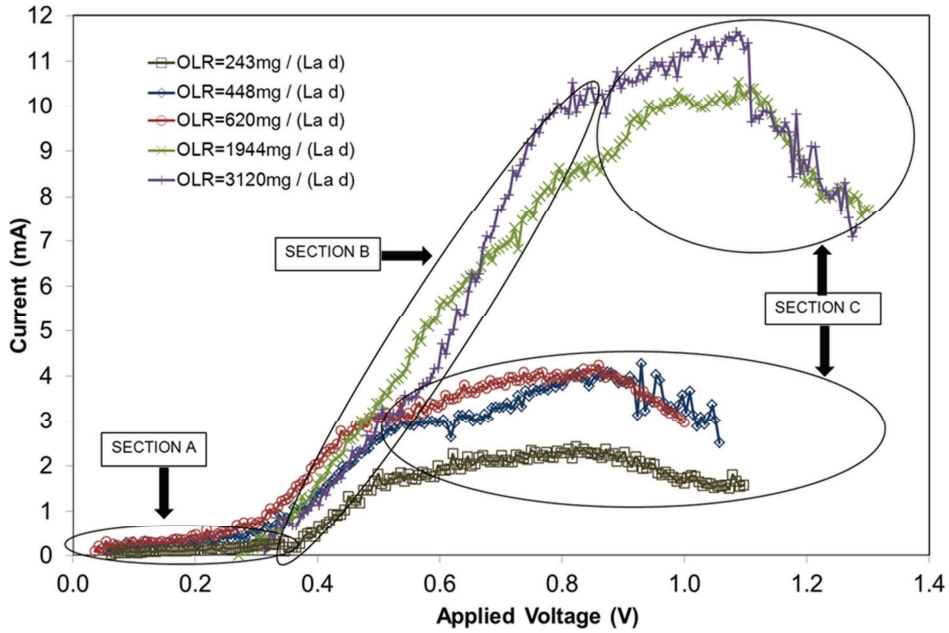

Figure 5.3. Electrochemical characterization of MEC. Voltage scans at 5 different OLRs.

In SECTION C, the reactor starts to operate under diffusion control (Bagotsky, 2005), indicating that concentration losses prevail over ohmic and activation losses. The onset of SECTION C depended on the OLR, and it was located at approximately V_{app}=0.5 V at medium-low OLRs and V_{app}=0.7 V at high OLRs (Figure 5.3). Despite a slightly increasing current with increasing voltage in SECTION C, the associated increases in

COD removal and hydrogen production rates would likely not justify the boost in energy consumption, at least at medium-low OLRs. To further investigate this hypothesis, the effect of V_{app} in hydrogen production, COD removal and energy consumption was evaluated at fixed, medium-low OLRs (493 ± 61 mg L_a^{-1} d^{-1}).

5.3.2 Effect of Applied Voltage on MEC Performance at Medium-low Organic Loads

Due to the variability of the influent COD, two HRTs (24 and 10.5 h) were used (Table 5.2) to maintain a nearly constant OLR.

Despite the OLR being held nearly constant during this second set of tests, it was only when high-strength dWW was fed into the MEC that relatively high COD removal rates (61-76%) were obtained (Figure 5.4). In contrast, removal rates below 32% were attained with low-strength dWW. Min and Logan (2004) reported similar behavior in a continuous dWW-fed MFC, where COD removal was found to be dependent on the COD concentration inside of the anodic chamber.

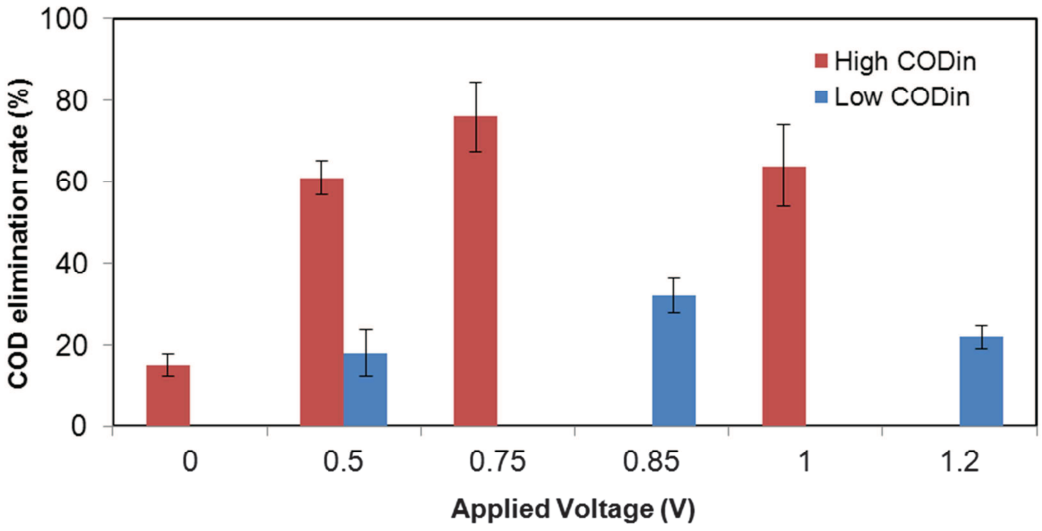

Figure 5.4. COD elimination rate dependence on the applied voltage and the influent COD concentration.

In light of these data (Figure 5.4), 0.75 V and 0.85 V are the optimum applied potentials for high- and low-strength dWW, respectively, because they maximized COD removal under their respective conditions. Still, this analysis must take into account the energy consumption (Figure 5.5), which was significantly boosted as V_{app} was increased. In fact, a 15% improvement in the COD removal rate (derived from increasing V_{app} from

0.5 to 0.75 V (Figure 5.4)) was accompanied by a 43% increase in energy consumption (Figure 5.5) at higher dWW strength. In other words, improving COD removal from 61 to 76% increased energy consumption from 1.43 to 2.05 Wh $gCOD^{-1}$ at 0.5 and 0.75 V respectively.

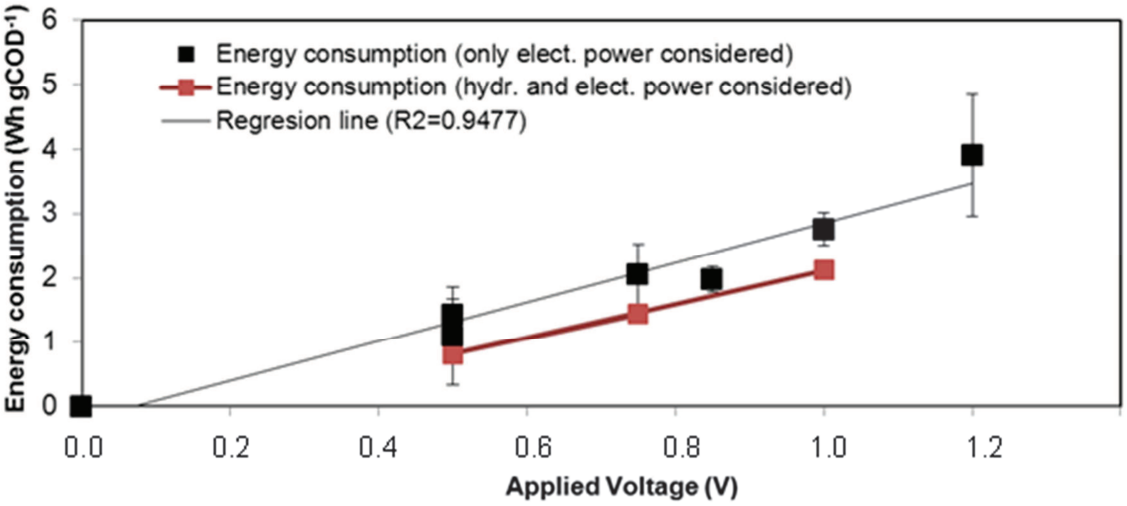

Figure 5.5. Energy consumption (with and without taking into consideration the energy content of the hydrogen produced) and regression line as a function of the applied voltage. Note that the energy content of the hydrogen has been included in the calculation of the energy consumption only in those cases when hydrogen production was measured (i.e. when high-strength dWW was fed to the MEC)

In both cases (i.e., 0.5 and 0.75 V), the final effluent COD concentration was higher than what many local regulations typically allow, and at full-scale an aerobic/anoxic polishing step would be required after MEC. Moreover, other authors maintain that it is highly unlikely that the oxidation of organic matter in the anodic chamber of a bio-electrochemical system will ever be a stand-alone technology (Rosenbaum et al., 2010). Therefore, assuming that the remaining COD (i.e., after MEC treatment) will be removed via aerated lagoons with a typical energy consumption of 1.5 Wh g^{-1}-COD (Metcalf & Eddy Inc., 2003), the total energy consumption of the treatment (i.e., MEC + aerated lagoon) can be estimated as the weighted mean of the energy consumption of the MEC and the aerated lagoon, which weights the COD removal rates in the MEC and in the aerated lagoon respectively:

$$EC_T = \frac{E_{MEC} \cdot W_{MEC} + E_{AL} \cdot W_{AL}}{W_{MEC} + W_{AL}} \quad (5.1)$$

where EC_T is the global energy consumption (Wh g^{-1}COD), E_{MEC} is the energy consumption in the MEC (Wh g^{-1}-COD), W_{MEC} is the COD removal efficiency in the MEC (%), E_{AL} is the energy consumption in the aerated lagoon (1.5 Wh g^{-1}-COD) and

W_{AL} is the COD removal efficiency in the polishing step (%). For example, if local regulations allow to discharge treated wastewaters only after 95% of COD removal (i.e. $W_{MEC+}W_{AL}=95$), then EC_T =1.45 Wh g^{-1}-COD at a V_{app} of 0.5 V and EC_T=1.91 Wh g^{-1}-COD at a V_{app} of 0.75 V. From this point of view, 0.5 rather than 0.75 V would be the optimum applied voltage.

Even though V_{app} was modified over a broad range (i.e., 0.5-1.2 V), hydrogen production (and current) either did not undergo large modifications (Fig 5.6), or it was not enough to offset the increment in energy consumption derived from raising the V_{app} from 0.5 to 0.75 V with high-strength dWW. Indeed, by including hydrogen's energy content into the calculation of the energy balance (Fig 5.6), the energy consumption decreases by 43% at low applied voltages and only by approximately 25% at medium high applied voltages (always with high-strength wastewaters) which supports 0.5 V as the optimum applied voltage when treating dWW at medium-low OLR . No hydrogen flow was measured with low-strength wastewater (Fig 5.6).

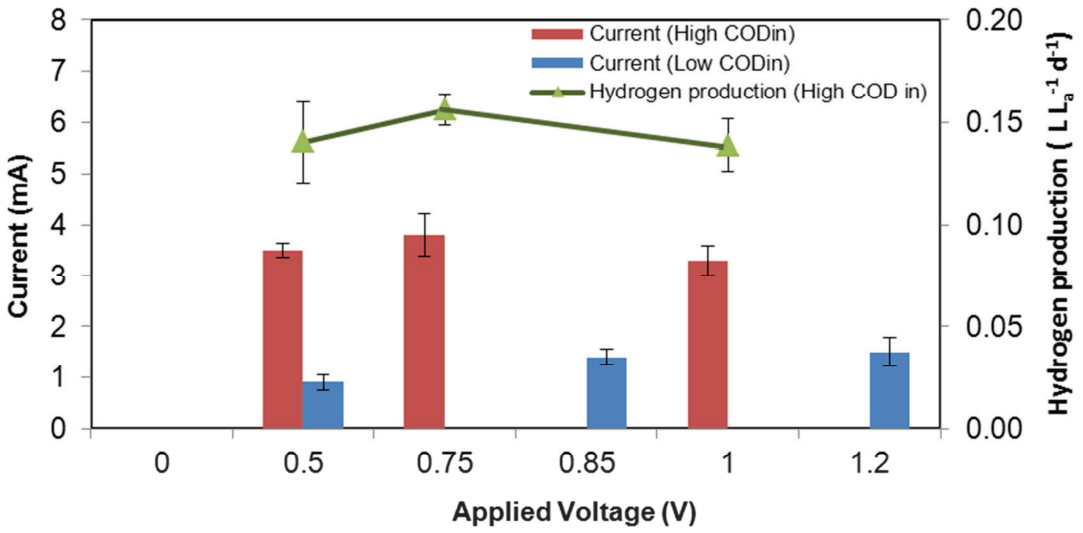

Figure 5.6. Hydrogen production and current as a function of the applied voltage and the COD concentration of the influent.

All of these results suggest that setting V_{app} above the onset potential of SECTION C in Fig 5.3 had a negligible effect on hydrogen flow and COD removal rates, and it only increased energy consumption. Thus, to optimize MEC performance during dWW treatment at medium-low OLRs, the applied voltage must be maintained as close to the onset of the diffusion control region as possible. Interestingly, by using a method of

real-time V_{app} optimization (based on tracking the minimal apparent resistance of the MEC), Tartakovsky and co-workers (Tartakovsky et al., 2011) arrived at similar conclusion: MEC performance can be optimized by operating the cell at the onset potential of the of the diffusion control region.

5.4 CONCLUSIONS

Wastewater treatment efficiency in a continuously-fed MEC reached a maximum of 76% COD reduction (OLR=441 mg L_a^{-1} d^{-1} and V_{app}=0.75 V). Hydrogen production exhibited a Monod-type trend as a function of the OLR and proved to be highly dependent on the influent COD. Energy consumption was comparable or even lower than that traditionally associated with activated sludge treatments, in spite of the relatively high internal resistance of the MEC. Importantly, the results confirmed that V_{app}s above the onset potential of the diffusion control region did not significantly increase hydrogen production or COD removal and only served to increase energy consumption.

Acknowledgements

Funding for this study was provided by Isolux-Corsan, S.A. (through a CDTI project) and the Spanish Ministry of Science and Innovation (Project Number: ENE2009-10395). Assistance of Diego M. García in the laboratory is greatly appreciated.

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Chapter 6

Estimating Microbial Electrolysis Cell (MEC) Investment Costs in Wastewater Treatment Plants

Abstract. Microbial electrolysis represents a new approach for harnessing the energy contained in the organic matter of wastewater. However, before this approach can be implemented on a practical basis, a cost-effective manufacturing process for microbial electrolysis cells (MECs) must be developed. The objective of this study is to estimate an acceptable purchase cost of an MEC reactor for a domestic wastewater treatment plant. We estimate that for a full-scale MEC operating at a current density of 5 A m_a^{-2} (amperes per square meter of anode) and an energy consumption of 0.9 kWh kg-COD^{-1} (kilowatt-hour per kg of removed chemical oxygen demand (COD)), a cost of €1,220 m_a^{-3} (euro per m^3 of anodic chamber) can be established as a target purchase cost at which a break-even point is reached after 7 years.

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International Journal of Hydrogen Energy, (2012). In press.

DOI: 10.1016/j.ijhydene.2012.09.157

6.1 INTRODUCTION

The inclusion of organic wastes in the energy system is becoming increasingly attractive because it increases the share of the renewable energy in the system, decreases CO2 emissions and reduces dependency on fossil fuels (Münster and Meibom, 2011; Angenent et al., 2004). Wastewater in general and domestic wastewater in particular contains significant amounts of organic waste, the energy content of which may be exploited. For example, at a conventional wastewater treatment plant (WWTP) in Toronto, Canada, the potential energy available in the raw wastewater exceeded the electricity requirements of the treatment process by a factor of 9.3 (Shizas, 2004). Wastewater can be observed as a potential commodity from which valuable products can be obtained (Angenent et al., 2004), thus offsetting the operational costs of wastewater treatment plants.

Bioelectrochemical systems in general and microbial electrolysis cells (MECs) in particular represent a novel approach to harnessing the energy content of the organic matter in wastewater. The roots of the concept can be traced back to Potter (Potter, 1911), who observed for the first time that the oxidation of organic matter can be accompanied by the appearance of an electrical potential difference between the electrodes of a bioelectrochemical reactor. This reactor was later termed a microbial fuel cell (MFC). However, it was not until 2005 and 2006 that two research groups demonstrated hydrogen production by means of an MEC (Rozendal et al., 2006; Liu et al., 2005). To date, the use of MECs for wastewater treatment and hydrogen production has been analyzed with a focus on technical and scientific issues such as substrate behavior (Logan et al., 2009; Escapa et al., 2009), hydrogen production and substrate removal rates (Tartakovsky et al., 2009; Ditzig et al., 2007), and the effect of operational parameters and reactor configurations on the reactor performance (Escapa et al., 2012b; Rozendal et al., 2007). During the second half of the past decade, a phase of intense research and development of MFCs and MECs led to the first attempts to bring bioelectrochemical reactors out of the laboratory and engineer systems on a pilot scale (Dekker et al., 2009; Logan, 2010; Cusick et al., 2011; Keller and Rabaey, 2008).

Nonetheless, if MEC technology is to achieve practical implementation, the following two key techno-economic challenges will have to be addressed: (i) the absence of clear cost estimate for MEC reactors, and (ii) the need to develop a cost-effective MEC manufacturing process and low-cost materials. Preliminary studies on the feasibility of bioelectrochemical reactors have revealed that, at least from economic and environmental points of view, MEC technology can be cost effective and provide significant environmental benefits (Foley et al., 2010; Cusick et al., 2010; Pant et al., 2011). Nevertheless, an accurate estimation of future MEC costs is still needed. Initial attempts to identify future capital costs of bioelectrochemical reactors based on readily available laboratory materials have suggested costs in a broad range between € 1,137 and 3,000 per m^3 of electrode compartment (Rabaey and Verstraete, 2005; Fornero et al., 2010; Rozendal et al., 2008; Pant et al., 2010). These cost estimates have prompted scientists in recent years to develop alternative materials and design new reactor configurations to produce low-cost MECs (e.g., operating MECs without membranes (Call and Logan, 2008; Fan et al., 2007), using low-cost materials such as stainless steel (Call et al., 2009; Zhang et al., 2010), using low-cost catalysts for the hydrogen evolution reaction (Selembo et al., 2009; Selembo et al., 2010; Harnisch et al., 2009), or using carbon nanocomposite proton-exchange membranes (Ghasemi et al., 2012)).

In this study, we try to obtain an answer to the first question above (the need for a cost estimate for MEC reactors) that in turn would also be relevant to the second question (the need to develop a cost-effective manufacturing process and low-cost materials). In particular, we attempt to estimate maximum acceptable manufacturing costs for an MEC in an existing domestic wastewater (dWW) treatment plant in three different scenarios, with the goal for each scenario being to break even at seven years. This cost estimate is accompanied by a sensitivity analysis of the purchase price of an MEC to variations in the prices of hydrogen and electricity, and also to the size and the arrangement of the MEC reactor. In addition, we offer a preliminary identification of the operational parameters that most influence the maximum acceptable manufacturing costs of MECs.

6.2 CASE STUDY DESCRIPTION. COMBINING AN MEC WITH AEROBIC WASTEWATER TREATMENT

This study is based on an existing domestic wastewater treatment plant (dWWTP) located in Andalucía, in southern Spain. The facility was designed for a population of 55,200 equivalent inhabitants (EI) and for a flow per capita of 230 L IE^{-1} d^{-1} (liters per equivalent inhabitant and per day), which renders a daily flow rate of 12,696 m^3 d^{-1}. Figure 6.1(top) represents a layout of the wastewater plant, which corresponds to scenario 0 in the scenarios definition presented in section 6.3. The plant lacks a primary clarifier, and the effluent from the grit chamber is fed directly into the biological reactor, in which the entering BOD is removed by prolonged oxidation. The biological reactor has a total volume of 16,000 m^3 with a hydraulic retention time (HRT) of 31 h (sludge residence time of 16 days). Chemical oxygen demand (COD), total Kjeldahl nitrogen (TKN) and total phosphorus concentration at the exit of the grit chamber are 695 g-COD m^{-3}, 48.15 g-TKN m^{-3} and 13.04 g m^{-3}, respectively. Removal efficiencies are 89%, 73% and 88% for COD, TKN and phosphorus, respectively. According to Spanish effluent standards, treated wastewater must contain less than 125 g-COD m^{-3} (or more than 75% of COD removal), less than 15 g-TKN m^{-3} and less than 2 g-P m^{-3} (Spain, 1996).

The first objective of this study was to estimate what the maximum acceptable cost of an MEC reactor would be in the case of it being used as a substitute for conventional aerobic treatment in a dWWTP. However, at the present time it does not seem practical to operate full-scale MECs as stand-alone reactors in future domestic wastewater treatment plants (Rosenbaum et al., 2010). Experiments conducted with real dWW-fed bioelectrochemical reactors have revealed that COD removal in bench-scale tests is limited to 40–80% (Rodrigo et al., 2007; Liu et al., 2004; Min and Logan, 2004; Escapa et al., 2012a), and the effluent may not comply with local regulations in terms of COD concentration of the effluent (Spain, 2011). In addition, nitrogen removal in an MFC–MEC (which is mostly attributable to nitrogen assimilation into bacterial biomass) is usually low, and accounts for only a small percentage of the total removal usually needed (Logan, 2008; Freguia et al., 2007). Thus, it is likely that a future full-scale MEC-based dWWTP would require a polishing step after the MEC treatment. For the

sake of simplicity, we assume that the polishing step will consist of a prolonged oxidation reactor, in which the remaining BOD and the nitrogen will be removed after the MEC treatment.

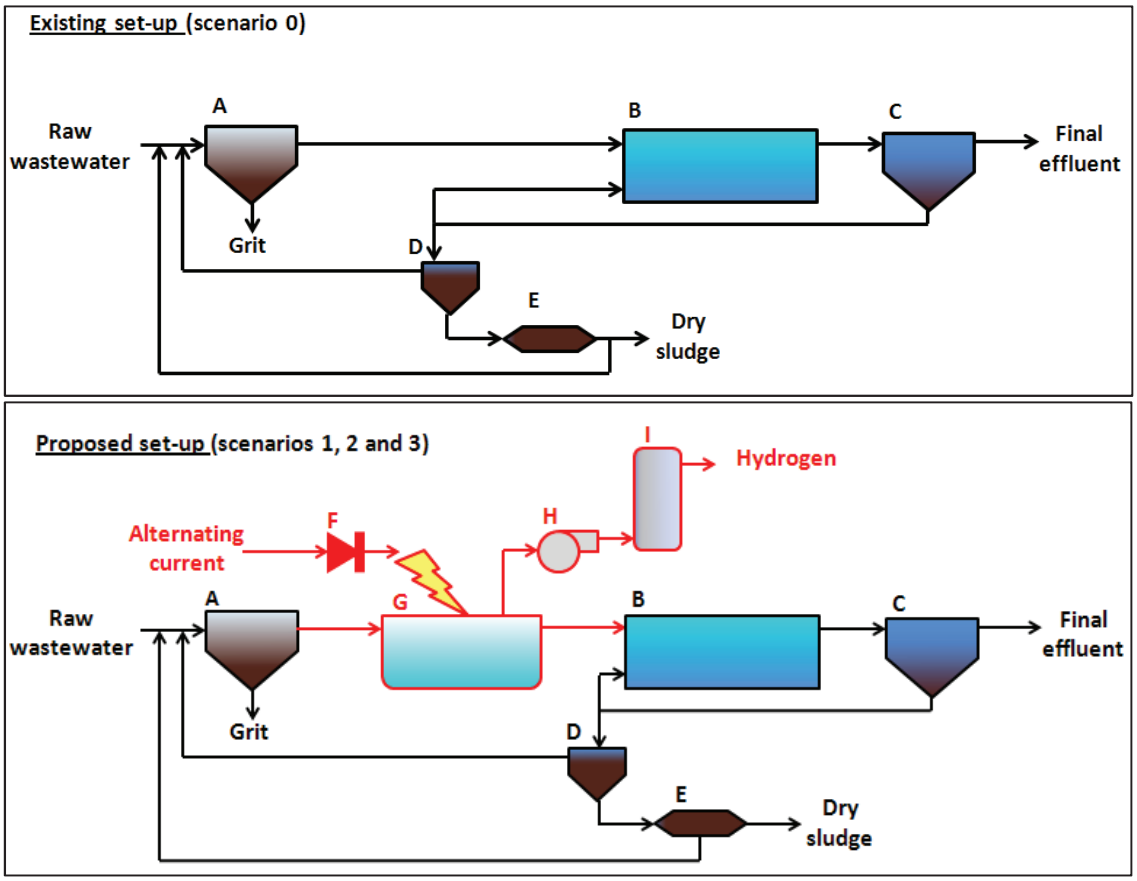

Figure 6.1. Flowchart of the existing wastewater treatment plant (top: scenario 0) and the proposed plant (bottom: scenarios 1, 2 and 3): A, screen and grit chamber; B, aerobic biological treatment (prolonged oxidation); C, secondary settling tank; D, gravity thickener; E, centrifuges; F, rectifier; G, MEC reactor; H, gas compressor; and I, gas storage tank.

To summarize, in scenarios 1, 2 and 3 (see the scenarios definition in section 6.3), where an MEC is included as part of the biological treatment (Figure 1 bottom), the effluent from the grit chamber is fed directly into the MEC reactor. This is followed by the polishing step, which removes the remaining COD, obtaining an effluent with TKN and COD concentrations below 15 and 125 g m^{-3}, respectively.

6.2.1 The MEC Architecture and Process Design Assumptions

Despite the MEC architecture being a key issue affecting the reactor performance (Logan, 2009), no clear consensus has yet emerged on what design is best suited to

implementation in a domestic wastewater treatment plant. Practical application of bioelectrochemical reactors will require not only the development of an economical design suitable for mass production (Logan, 2008) but also a design that can compete with conventional biological technologies. In this sense, the design of MECs needs to address at least three main constraints, related to the footprint, wastewater composition, and other technological constraints (Hamelers et al., 2010).

The footprint can be minimized by optimizing the thickness of MEC units. By assuming current densities in the range of 10 A m_a^{-2}, (amperes per m^2 of electrode area) and volumetric wastewater treatment capacities of ~7,000 g-COD m_a^{-3} d^{-1} (grams of COD per cubic meter of anodic chamber volume and per day), Rozendal et al. (2008) argued that the thickness of MEC units should be approximately 1 cm. In this study, the absence of a primary clarifier in the existing dWWTP and the reduced current densities achieved in the laboratory-scale MEC (less than 0.7 A m_a^{-2}) (Escapa et al., 2012a) prompt us to select a much more conservative thickness of 2.25 cm (see Figure 6.2C and section 6.2.2 for the determination of the reactor size).

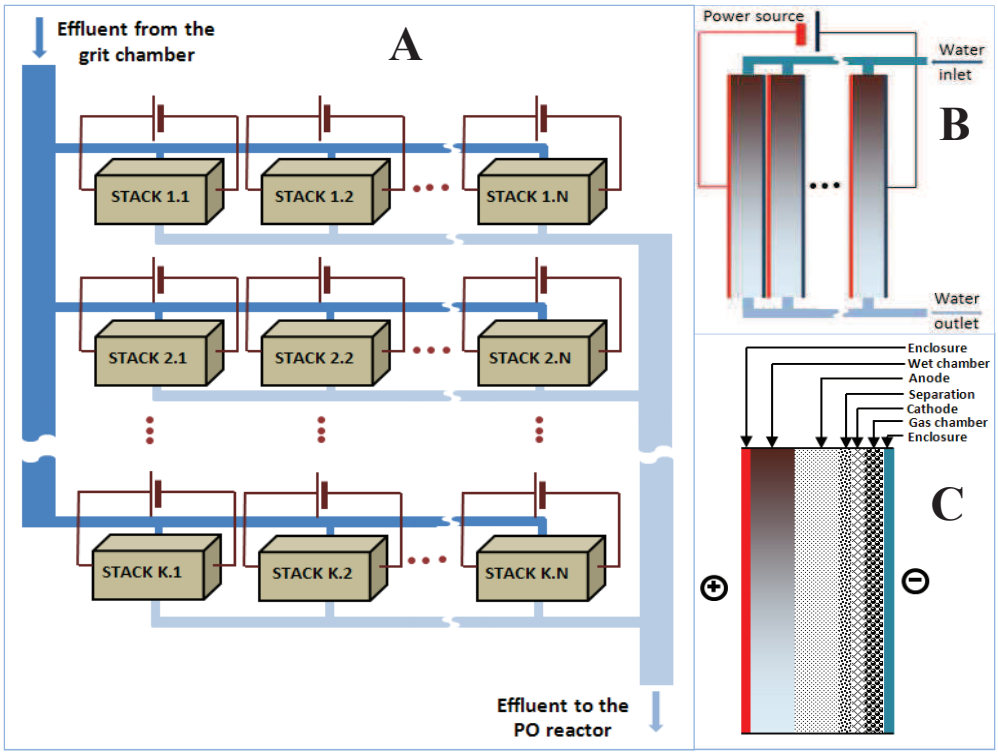

Figure 6.2. A: hydraulic disposition of the stacks of MEC units; B: cross section of a stack of MEC units; and C: cross section of an MEC unit. The thickness of each element in C is as follows (in mm): enclosure (2.5 each), wet chamber (10), anode (5), separation (0.3), cathode (0.3), gas chamber (2), total MEC thickness (22.6)

Wastewater composition also influences the MEC architecture. To minimize the internal resistance associated with low-conductivity wastewater, it is imperative that the anode and cathode be kept in close proximity (Rozendal et al., 2008). Thus, in our set-up, we assume a separation of less than 1 mm between the anode and cathode. A similar design was successfully used in several studies (Escapa et al., 2009; Tartakovsky et al., 2009; Escapa et al., 2012a; Tartakovsky et al., 2008).

Another technical issue that must be addressed is how the MEC units should be electrically connected. By connecting all the units in parallel, it is possible to optimize the performance of every single unit by real-time optimization of the applied voltage (Tartakovsky et al., 2011). However, this arrangement would require the existence of a rectifier able to manage relatively large currents at low potentials, whose relatively large purchase cost (about €4 A^{-1} [ABB, Siemens]) would be prohibitive for a practical application. In addition, energy losses would be increased by the use of low-voltage rectification. Therefore, a certain number of MEC units must be stacked in series to reduce the circulating current and increase the applied voltage. Figure 6.2A represents a possible design with several MEC stacks, where every stack is subjected to the same applied voltage and the same OLR. Nonetheless, the connection of several MEC units in series may bring additional technical difficulties: if one of the MEC units malfunctions, the whole stack will become affected. To overcome this obstacle, it would be necessary to monitor the current in real time so that any malfunction in one of the stacks could be immediately addressed and the stack disconnected for repair and/or cell re-arrangement.

Ohmic losses represent another technological constraint for MECs. Rozendal et al. (2008) suggested that the use of bipolar plates, such as those used in hydrogen microbial fuel cells, would reduce the ohmic loss in the stack. If each side of the enclosure were electrically connected to its respective electrode, the frames would serve as pseudo-bipolar plates, which in turn would simplify the manufacturing and maintenance of the stacks. Figure 6.2B shows how several MEC units can be electrically connected in series to form a stack. Because the optimal thickness and the optimal number of MEC units in a stack are not yet known, we also provide a sensitivity analysis to variations in these two parameters.

6.2.2 Determination of the Operational Conditions and Size of the MEC Reactor

Organic Loading Rate and MEC Reactor Size

The operational conditions of the MEC reactor have been determined based on laboratory-scale trials (Escapa et al., 2012a), where a 0.1-L single-chamber membraneless Ni-based MEC reactor was subjected to variations in the OLR. It was found that hydrogen production was maximized at OLRs above 2,000 g-COD m_a^{-3} d^{-1}, so that at least from the hydrogen production point of view, the performance of the MEC can be optimized by setting the OLR above the mentioned value. Moreover, the calculations show that by increasing the OLR to 3,100 g-COD m_a^{-3} d^{-1}, the energy consumption for COD removal would decrease by 49%, but that the COD removal efficiency would decline by 16%. This deterioration in the ability of the MEC to remove COD, accompanied by a significant improvement in the energy consumption, makes it difficult to choose an optimal OLR. Nevertheless, there is still one further constraint, related to the COD removal in the MEC that needs further consideration before selecting an optimal OLR: the removal of nitrogen in the polishing step, which requires the presence of a minimum amount of COD in the wastewater entering the aerobic reactor to favor the de-nitrification process. Therefore, the selection of the OLR in the MEC should lead to a set of operational conditions that will not jeopardize the ability of the aerobic reactor to remove nitrogen. All of these considerations lead us to select 3,100 g-COD m_a^{-3} d^{-1} as the optimal OLR of the MEC reactor, which corresponds to an HRT of 5.2 h.

Further information about the calculation methods for the MEC reactor are given in Appendix 6.1. Although the gap between lab scale and industrial full scale is indeed rather large, in the absence of full-scale results, we will use these results as a basis for the case study.

The size of the aerobic reactor was calculated so that nitrification, denitrification and COD removal can be accomplished effectively following the calculation methods described by (Metcalf & Eddy Inc., 2003; Aarne Vesilind, 2003). COD and TNK concentrations at the exit of the MEC treatment corresponded to COD and TNK

concentrations at the inlet of the aerobic treatment. The HRT and the sludge retention time were selected to be 17 h and 16.5 days, respectively, when the aerobic reactor was preceded by an MEC reactor.

An Excel-based spreadsheet model was used to recalculate and re-size all of the components of the new plant. Subsequently, the operation of the plant was simulated using the BioWin software (EnviroSim Associates Ltd.), which is widely used for the analysis and design of water treatment plants.

Biomass Production and Nitrogen Removal in the MEC Reactor

Biomass production and nitrogen removal in bioelectrochemical reactors are issues that have not been well investigated. According to Rabaey et al. (2003) and Freguia et al. (2007), the biomass production ranges from 0.07 to 0.31 g-COD-biomass g-COD^{-1}-substrate in an acetate-fed bioelectrochemical reactor, and can be as high as 0.51 g-COD-cell g-COD^{-1}-substrate in a glucose-fed reactor. In this study, we assume a mean value of biomass production of 0.30 g-COD-biomass g-COD^{-1}- substrate in the MEC reactor, which renders a daily sludge production rate of 1,425 kg of biomass per day.

With respect to nitrogen removal, it has been assumed that nitrogen may account for approximately 7% of the biomass produced in a bioelectrochemical reactor (Freguia et al., 2007), which means that approximately 100 kg of nitrogen per day can be removed in the MEC reactor. Therefore, the effluent leaving the MEC reactor and entering in the aerobic reactor is assumed to have a TKN concentration of approximately 40 g m^{-3}.

6.3 DESCRIPTION OF SCENARIOS

The following discussion is based on a comparison of four scenarios of dWWTP design. Each scenario definition is based on techno-economic issues that directly affect the viability of the MEC (e.g., MEC life, current density, cathodic conversion efficiency, hydrogen prices, etc.). Table 6.1 summarizes the main parameters that define the four scenarios considered in this study:

Table 6.1. Scenarios definition. All the items are referred to the MEC

Item	Scenario 1	Scenario 2	Scenario 3
COD removal (%)	44	44	44
Current density (A m^{-2})	0.68	2.50	5.00
Anode surface (m^2)	302,500	108,300	54,200
MEC total volume (m^3)	6,100	2,200	1,100
OLR (g m_a^{-3} d^{-1})	3,100	8,800	17,500
Coulombic efficiency (%)	38	50	50
Cathodic efficiency (%)	45	70	90
Energy consumpt. (kWh kg-COD^{-1})	1.15	1.00	0.90
Hydrogen production (m^{-3} m_a^{-3} d^{-1})	0.3	0.6	0.8
MEC durability (years)	5	>7	>7

Scenario 0, (S0, existing scenario) is the scenario that corresponds to the existing dWWTP (Figure 6.1, top). It is described in section 6.2.1.

Scenario 1 (S1, base scenario) incorporates an MEC reactor as a part of the biological treatment preceding the aerobic treatment (Figure 6.1, bottom).

The MEC is subjected to an OLR of 3,100 g-COD m_a^{-3} d^{-1}, which results in a current density of 0.68 A m_a^{-2}, requiring an anode surface area of 302,500 m^2 to remove 44% of the total COD fed to the MEC at a Coulombic efficiency (CE) of 38%. The total volume of the MEC reactor is estimated to be approximately 7,000 m^3, while the total volume of the aerobic reactor is reduced from 16,000 to ~9,000 m^3. The hydrogen production and the cathodic conversion efficiency (CCE) are established at 0.3 m^3 m_a^{-3} d^{-1} and 45%, respectively. The operational parameters presented here were obtained from (Escapa et al., 2012a) (see also section 6.2.2).

The durability of the MEC reactor is a parameter that has a large influence on the operating costs but has not yet been properly established. Bioelectrochemical reactors have been successively operated for more than 3 years (Kim et al., 2004) and for over 5 years in a stable manner without any servicing (Kim et al., 2003). Rozendal et al. (Rozendal et al., 2008) estimated the durability of an MEC reactor, including electrodes, membrane and current collectors, to be 5 years. So, for the purposes of this study, the life of an MEC has been assumed to be 5 years for scenario 1. The civil engineering work and other materials are assumed to have a life of 25 years (Rozendal et al., 2008)).

In scenario 2 (S2, moderate scenario), the COD removal in the MEC reactor remains at 44%, but it is assumed that future technological developments would make it possible to

achieve current densities on the order of 2.5 A m^{-2} and CEs and CCEs of 50% and 75%, respectively, as described in Table 6.1. In addition, improvements in the conductivity of the materials would make it possible to reduce the energy consumption to 1 kWh kg-COD^{-1}.

The hydrogen production would increase up to 0.60 m^3 m_a^{-3} d^{-1} in accordance with the improvements in the CE and CCE. The durability of the MEC is assumed to be more than 7 years.

In scenario 3 (S3, optimistic scenario), further improvements in the material and the MEC construction would make it possible to increase the current density to 5 A m^{-2} and reduce the energy consumption to 0.9 kWh kg-COD^{-1}. The CE would remain at 50% while the CCE would reach 90% (Rozendal, 2007), corresponding to a hydrogen production rate of 0.8 m^3 m_a^{-3} d^{-1} (Table 6.1). As in scenario 2, the durability of the MEC is assumed to be more than 7 years.

6.4 ECONOMIC ANALYSIS AND COST ESTIMATION

A detailed estimation of the capital and operational costs associated with all of the scenarios is beyond the scope of this paper, because only the differences between scenario 0 and the three other scenarios are relevant to the purpose of this study. Therefore, this section deals only with those items, elements and processes whose costs are modified by the inclusion of the MEC reactor in the dWWTP.

6.4.1 Capital Costs

A breakdown of the capital costs of the dWWTP for all four of the scenarios considered is given in Table 6.2. For simplicity, it is assumed that the funds used to acquire any capital item will come from equity sources, and thus no interest costs will be charged.

The purchase costs of the compressor, rectifier and hydrogen tank were calculated using data from several manufacturers (Weinert et al., 2007; Weinert, 2005) and have been scaled according to the six-tenths power rule: $Ci=Cj(Qi/Qj)^{0.6}$, where Cj and Ci are the purchase costs of an item at capacities Qi and Qj. These costs have also been actualized

to the present time by means of the Process Engineering Cost Index (Process Engineering, 2012). Aside from the purchase cost, other cost factors have been considered in the estimation of the total investment costs of the elements associated with the MEC installation. Table 6.3 summarizes the percentages of the capital costs associated with the direct and indirect cost segments of the reactor, compressor, rectifier and gas storage tank.

The hydrogen produced in the MEC reactor requires further compression to reduce the volume of the storage tank. It is assumed that the hydrogen will be compressed by a reciprocating compressor to a storage pressure of 430 bar. The purchase price depends on the flow rate of the compressed hydrogen and can be calculated as $P_C = 27{,}000*(HF)^{0.52}$ (Weinert et al., 2007), where Pc is the purchase cost (US$; 2007) and HF is the hydrogen flow rate (kg h^{-1}).

Table 6.2. Partial capital costs (€). Only those elements whose investment cost varies throughout the different scenarios are included.

Component	SCENARIOS			
	S0	S1	S2	S3
Civil engineering				
Earth moving	95,371	94,392	68,229	60,938
Biological reactors	1,430,354	1,415,670	1,023,282	913,928
Secondary settler	356,872	292,635	292,635	292,635
Sludge dewatering	117,668	96,488	96,488	96,488
Piping	36,235	20,382	20,382	20,382
Electromechanical equipment				
Air blowers	114,827	64,590	64,590	64,590
Thickening	48,514	39,781	39,781	39,781
Sludge carrying	73,603	60,354	60,354	60,354
Power transformer	43,383	35,574	35,574	35,574
Power installations	48,826	27,465	27,465	27,465
Rectifier	0	31,751	31,751	31,751
Compressor	0	58,967	88,705	97,527
Hydrogen tank	0	196,746	456,574	559,421
Partial investment cost	2,365,653	2,434,795	2,308,670	2,300,834
General costs +benefit margin (19%)	449,474	462,611	438,647	437,158
TOTAL	2,815,127	2,898,527	2,745,600	2,739,845
Difference to the S0	**0**	**82,279**	**-67,810**	**-77,135**

Similarly, the purchase price of the storage tank depends on its storage capacity and can be computed as $P_T = 1{,}000*(C)^{1.08}$ (Weinert et al., 2007), where PT is the purchase price of the storage tank (US$, 2007) and C is the capacity (kg). It is assumed that the hydrogen produced will be delivered on a daily basis, and thus the storage capacity

required will be that strictly necessary to store the hydrogen produced in one day. Although hydrogen delivery on a daily basis may not seem realistic, the economic value of the hydrogen produced (at least in scenarios 2 and 3) would justify this option. Nevertheless, to avoid any adverse eventuality, the capacity of the tank will be factored by 1.5. It is also assumed that 3% of the time the hydrogen collecting truck will fail to collect the hydrogen produced, and therefore it would have to be released to the atmosphere.

Table 6.3.Summary of the percentages of investment cost assumed for the different elements that configure the MEC installation (see figure 6.1)

Component	Rectifier	Compressor	H_2 tank	MEC reactor
Direct costs				
Purchase equipment	46	70	70	50
Purchased equipment installation	37	7	5	5
Instrumentation and controls (installed)	9	3	1	5
Piping (installed)	0	7	7	15
Electrical (installed)	0	4	3	8
Buildings	0	2	7	5
Yard improvements	0	1	1	0
Service facilities (installed)	0	0	0	0
Land	0	0	0	0
Indirect costs				
Engineering and supervision	3	3	3	2
Construction expense	0	0	0	0
Contractor's fee	0	0	0	0
Contingency	5	3	3	10

The purchase cost of the rectifier was estimated from the cost of the components and was increased by 19% and 6% to account for manufacturing costs and profit margin, respectively.

6.4.2 Operating Costs, Incomes and Cash-flow

The operating costs associated with the existing plant and the remaining scenarios are detailed in Table 6.4. Due to the novelty of the MEC technology, the following assumptions were adopted regarding the operating costs: (i) One extra plant operator is required to meet the operating requirements of the MEC. (ii) Maintenance, training and insurance costs increase by 10%, 50% and 20%, respectively. (iii) Aerobic sludge production accounts for 4,254 kg d^{-1} in the existing scenario (S0) and 2,187 kg d^{-1} in all three of the other scenarios. Because sludge production in the MEC reactor has been

estimated to be 1,425 kg d^{-1} (see epigraph 6.2.2), the installation of an MEC in the WWTP would help to decrease sludge production by 15%. (iv) The compression of hydrogen requires 2.1 kWh $kg^{-1}H_2$ of electricity. (v) The rectifier has an efficiency of 90%. The electricity prices used were based on the electricity prices and charges established by the Spanish Ministry of Industry, Tourism and Trade (Spain, 2011).

Table 6.4. Operating cost, incomes and cash flow (€/year). Only those items whose associated operating cost varies throughout the different scenarios are included.

Item	SCENARIOS			
	S0	**S1**	**S2**	**S3**
Operating cost				
Labour	180,800	191,750	191,750	191,750
Maintenance	52,031	57,231	57,231	57,231
Training	2,997	4,147	4,147	4,147
Insurances	3,499	4,499	4,499	4,499
Sludge management	98,302	82,261	82,261	82,261
Electricity	172,258	222,891	203,165	188,614
TOTAL	645,269	697,126	677,400	662,849
Difference to S0	**-**	**51,857**	**32,131**	**17,580**
Incomes				
Hydrogen ($I_{H,N}$)	-	111,252	244,754	294,817
Cash flow				
Cash-flow (CF_N)	-	59,395	212,623	277,237

The only income taken into consideration is the sale of hydrogen, and its price was estimated as the mean value of the production costs of different technologies in Europe (Schade et al., 2008) (€3.6 kg^{-1}-H_2), increased by 6% to account for profit margin. Wastewater treatment fees were not considered as an income because they are not dependent on the configuration of the WWTP.

6.4.3 Model Description

An Excel-based spreadsheet model was used to estimate the maximum allowed purchase cost of the MEC. The capital and the yearly operating costs are referred to as $CC_{S,N}$ and $OC_{S,N}$, respectively, for all of the scenarios described in paragraph 6.3. Sub-index N can be 0, 1, 2, or 3, depending on the scenario considered. The estimation of the maximum acceptable purchase price of the MEC units, which is the main objective of this study, was conducted following the steps detailed in Appendix 6.2.

6.5 DISCUSSION

As shown in Figure 6.3, the maximum acceptable purchase price of the MEC units ($CC_{PUR,1}$) in the base scenario (S1) is as low as €22 m_a^{-3}, which corresponds to €0.32 m_a^{-2}. Disregarding manufacturing costs, and assuming that the main elements of the reactor will be manufactured with inexpensive materials, a projected price below €1 m_a^{-2} seems rather unrealistic (for instance, a stainless steel mesh electrode may cost at least €0.85 m_a^{-2} (Wei et al., 2011)). Therefore, if medium- to large-scale dWWTPs are the target applications of MECs within the conditions defined in S1, it is necessary, in some way or another, that this activity be supported by government agencies, or benefit from some type of tax credit.

MECs also provide significant environmental benefits through the displacement of hydrogen production by conventional means (Foley et al., 2010) and through the reduction of CO_2 emissions typically associated with COD removal by aerobic treatment. If small facilities were covered by some type of greenhouse gas emissions trading scheme such as the EU ETS, this reduction in CO_2 emissions would bring additional economic benefits, helping to improve the viability of MEC technology. In addition, hydrogen production in MECs has usually been associated with anodic methane production (Wang et al., 2009). Harnessing and selling this methane represents another way to improve the viability of MECs via improved cash flow. Unfortunately, at the present time it is not possible to offer a confident estimate of how much methane can be recovered from the anode of an MEC using dWW as a substrate.

The MEC purchase price in S1 proved to be highly dependent on the thickness of the MEC units and on the number of MEC units stacked (Figure 6.3). A 20% reduction in the thickness of future MEC units would result in an increase of approximately € 5 m_a^{-3} in the maximum acceptable purchase price. Electricity and power prices also have a significant influence on the MEC purchase price. For instance, a 10% increase in the price of the electricity and a 10% reduction in the price of hydrogen would mean a €10 m_a^{-3} reduction in the $C_{PUR,1}$ (Figure 6.3).

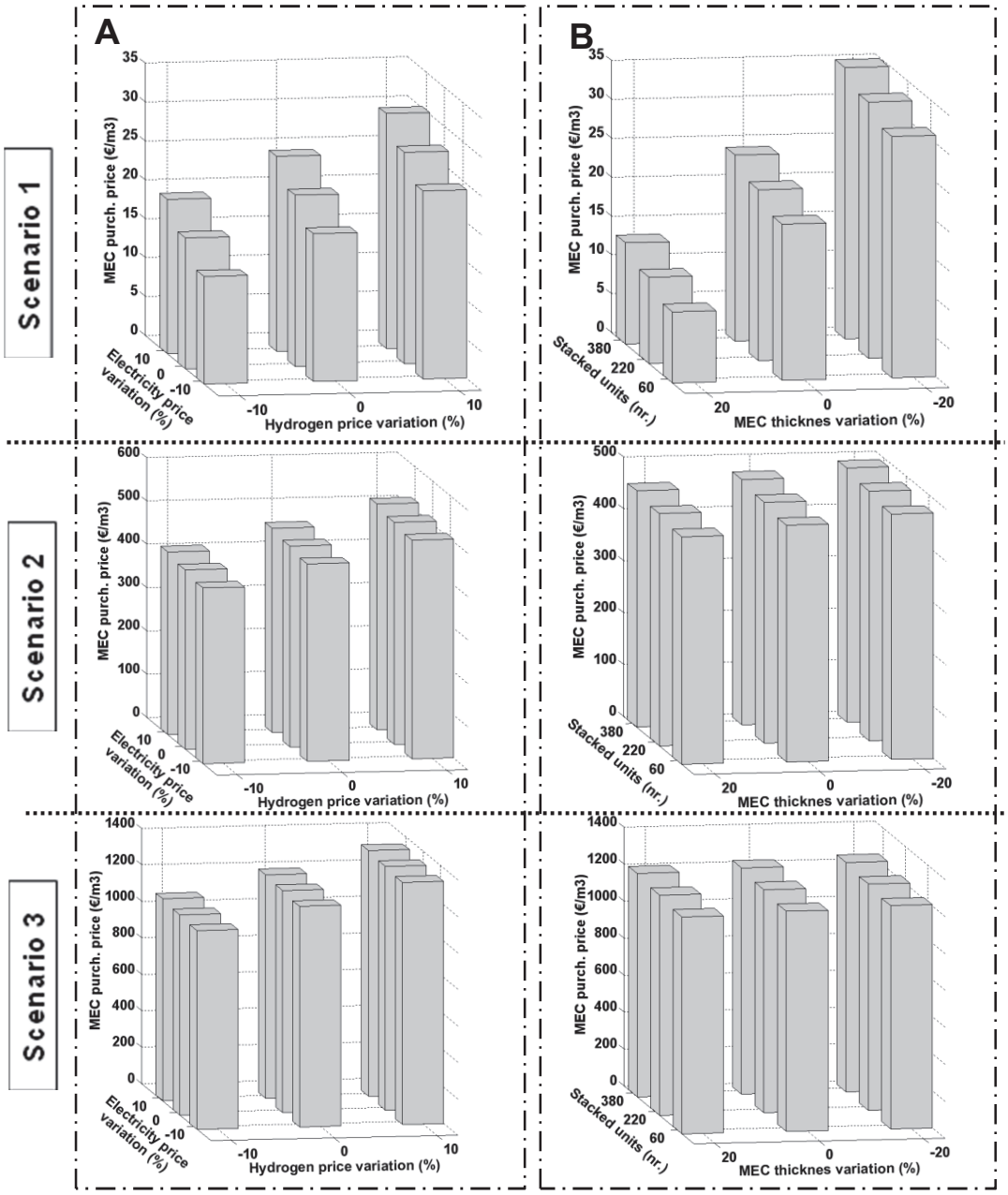

Figure 6.3. A: sensitivity of the maximum acceptable MEC purchase cost ($MEC_{PUR,N}$) to variations in the price of electricity and the price of hydrogen. B: sensitivity of the maximum acceptable MEC purchase price ($MEC_{PUR,N}$) to variations in the number of stacked units (N_U), and the thickness of the MEC units.

In S1, the investment costs of the MEC units ($C_{PUR,1}$) represent less than 20% of the $CC_{MEC,1}$ (capital cost specifically attributable to the MEC, its ancillary equipment and the civil engineering work involved) while the civil engineering work accounts for more than 50% (Figure 6.4). These percentages indicate that within the techno-economic constraints of S1, there is relatively little room for investment in electromechanical

equipment, and the vast majority of the capital costs are attributable to construction issues (i.e., the construction of the vessel to house the MEC reactor).

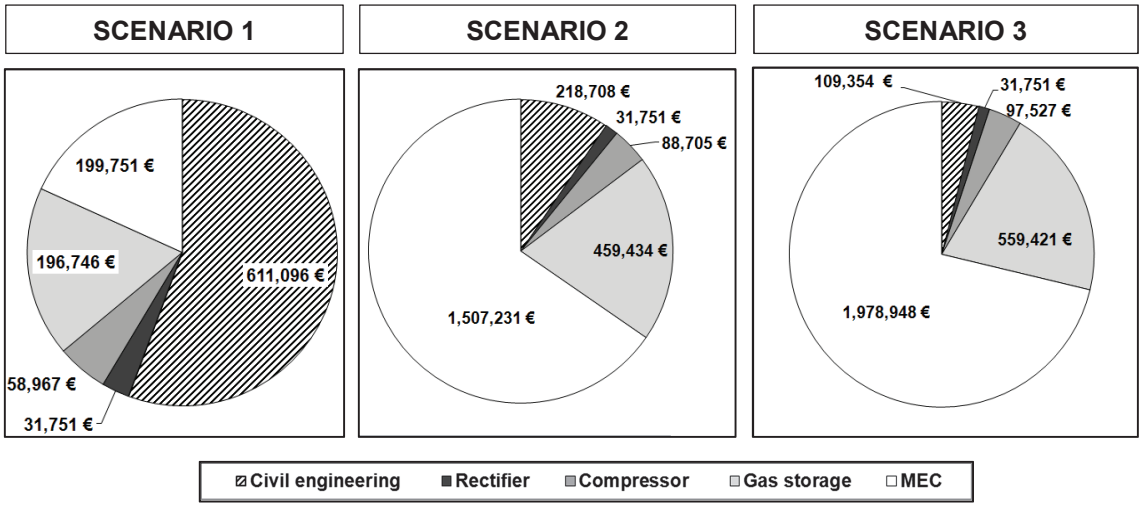

Figure 6.4. Breakdown of the estimated capital cost ($CC_{MEC,N}$) of the MEC plant.

Improved designs and the development of innovative materials may lead to improvements in the current density and other operational parameters, as described in scenario 2 (S2), which would make it possible to raise the purchase price of MEC units ($C_{PUR,2}$) to €465 m_a^{-3} (€7 m_a^{-2}). The use of low-cost materials such as non-platinized activated carbon electrodes, a novel permeable membrane and stainless-steel current collectors allowed Pant et al. (2010) to build a microbial fuel cell with an estimated cost of €1,137 m_a^{-3} (material costs only), which is still well above the maximum allowed in this scenario. Nevertheless, as more units are built and experience accumulates, a reduction in the manufacturing costs might be expected. The phenomenon of cost reduction with increasing manufacturing volume is more pronounced during the first steps of development of a technology because manufactured products tend to decline in costs by 10–30% with each doubling of cumulative production volume (Lipman and Sperling, 2010). Thus, the cost estimates provided above could be further reduced to €1,023-759 m_a^{-3}, which is closer to the range of the purchase prices estimated in S2. However, to increase manufacturing volumes and thereby reduce manufacturing costs, it is essential to find and identify application niches where MEC technology may offer competitive advantages. The treatment of industrial wastewater represents a promising option because of its high energy density (Fornero et al., 2010) and because a bioelectrochemical technology may be competitive in comparison with anaerobic

digestion under certain circumstances (Rozendal et al., 2008; Pham et al., 2006). In fact, the presence of an MEC reactor prior to aerobic treatment is similar to the energy recovery through methane production. However, the AD process is only feasible at influent concentrations above 2,000 g-tCOD m^{-3} (Malina, 1992), while the MEC process may address relatively low-strength influents containing 300-2,000 g-tCOD m^{-3} (Gil-Carrera et al., 2012). In addition, anaerobic reactors are operated at much longer HRTs (Malina, 1992), which increase the system cost and footprint. Overall, by inserting an MEC into the process a dWWTP, we are able to produce a valuable energy carrier, without a significant increase in the size of the treatment system.

In the S2 scenario, the reduction in power consumption diminishes the influence of electricity prices on the feasibility of the MEC, unlike hydrogen prices, which still have a significant influence. The number of MEC units included in one stack and thickness of the MEC units have a limited influence on MEC purchase prices (Figure 6.3).

Further improvements such as those described in scenario 3 (S3) would lead to a maximum acceptable purchase price in the range of ~€1,100-1,350 m_a^{-3} (€16-20 m_a^{-2}), depending on the size of the MEC units and the number of MEC units stacked. These prices seem realistic, particularly if compared with the range of costs estimated by Pant et al. (2011) and Rozendal et al. (2008) (€ 1,137 m_a^{-3} and €3,000 m_a^{-3}, respectively). This result suggests that at current densities above 5 A m_a^{-2} and with energy consumption at approximately 0.9 kWh kg-COD^{-1}, an MEC would begin to become feasible for domestic wastewater treatment. However, to achieve a current density of 5 A m_a^{-2}, the OLR must be kept as high as 17,500 g m_a^{-3} d^{-1} (CE=50%), which may result in a relatively large OLR for a dWW treatment plant. This OLR could be decreased while keeping the same current levels by improving the CE, which can be accomplished by preceding the MEC treatment by a pre-acidification reactor because the CE of bioelectrochemical reactors using easily degradable substrates is usually higher than those fed with more complex substrates (Velasquez-Orta et al., 2011). Nevertheless, this technical solution would increase the biological reactor's volume and the capital cost, thus compromising the viability of the plant. Another option would be to introduce pure cultures capable of increased current density (Yi et al., 2009) or create engineered environments inside the anodic chambers of the MEC units to promote hydrolysis and fermentation rates.

Based on available publications, it appears that a CCE of 90% may also seem unrealistic. CCE values of 50% and less are often reported when complex organic matter is used as a substrate (Ditzig et al., 2007; Wagner et al., 2009). To achieve CCE of 90%, future MEC designs will need to ensure enough tightness to avoid severe gas leaks, find efficient cathode catalysts to achieve high hydrogen production rates and recoveries (Cheng and Logan, 2011), and find methods to control hydrogen consumption by hydrogenotrophic microorganisms (Parameswaran et al., 2011)

As in S2, power prices as well as the configuration of the MEC stacks (i.e., the number of units stacked and their thicknesses) would have a relatively low influence on the MEC purchase price (Figure 6.3). In contrast, the market price of hydrogen would have a significant influence on the feasibility of the plant: an increase of 10% in the price of the hydrogen would make it possible to increase the purchase price of the MEC by approximately 15%.

In S2 and S3, the vast majority of the investment costs in the MEC plant (CC_{MEC}) can be attributed to the acquisition of the MEC reactor (Figure 6.4). In other words, the use of MEC technology in a dWWTP could be feasible even if almost 75% of the CC_{MEC} were attributable to the purchase of the MEC stacks.

Interestingly, to make implementation of MEC-based treatment in a dWWTP feasible, the operating costs (and the structure) of the entire WWTP must be kept almost invariable (with respect to the S0), for all of the scenarios considered (Figure 6.5A).

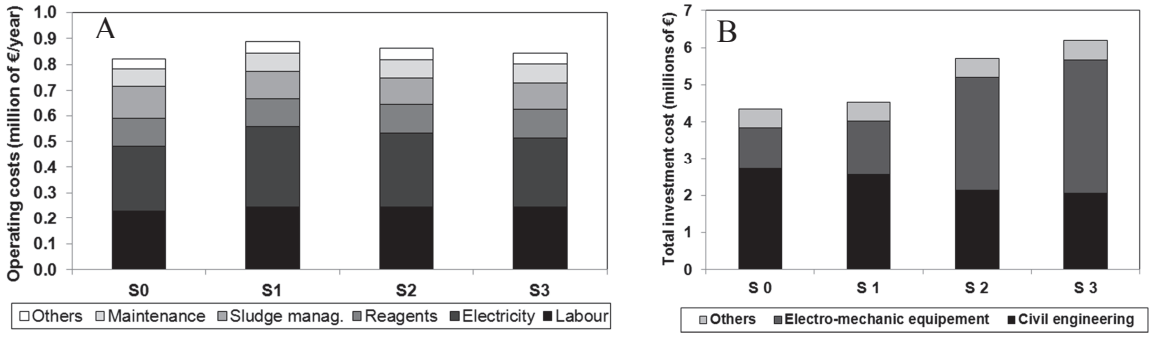

Figure 6.5. A: breakdown of the estimated maximum acceptable operating costs of the entire WWTP. B: breakdown of the estimated maximum acceptable capital cost of the entire WWTP.

With regard to the capital costs of the entire plant, the relatively poor performance of the MEC reactor in S1 makes it necessary to keep the investment of the entire WWTP (and its structure) at the levels of the investment in S0 (Figure 6.5B). In contrast, the improvements in the performance of the MEC assumed in S2 and S3 make it possible to increase the investment in the electromechanical equipment significantly, which in turn makes it possible to increase the investment in the entire WWTP by 45% without threatening the feasibility of the plant.

Although it is difficult to discern which of the operational parameters considered in the scenarios defined have the greatest influence over the maximum acceptable purchase price (mainly because most of these parameters are closely related, e.g., current density depends on OLR, and the energy consumption depends on the current) we offer a rough estimation of their influence on the viability of MEC technology, in the hope that this estimation may help to identify the parameters that require the most research attention.

Figure 6.6 shows the extent to which the maximum allowable purchase price increases by changing from Scenario 1 to Scenario 2 and from Scenario 1 to Scenario 3, modifying the operational parameters considered (current density, OLR, CCE and energy consumption) independently. Cautiously interpreting these results, we can see that the current density has the greatest influence over the MEC purchase price and therefore future research should be focused on maximizing this parameter. This could be accomplished not only by producing pure strains capable of increased current densities (as mentioned above) but also by using real-time voltage control (Tartakovsky et al., 2011) and by improving the catalytic activity in the cathode, which has been identified as an important limiting factor in the performance of bioelectrochemical systems (Rozendal et al., 2006; Dekker et al., 2009). Moreover, the cathode represents a key element in an MEC, not only because most of the total overvoltage is consumed during the hydrogen evolution reaction (Rozendal et al., 2006) but also because the cathode may account for almost 50% of the total capital cost of an MEC (Rozendal et al., 2008). These considerations suggest that further studies conducted to improve cathode performance and develop less expensive materials will pave the way for large-scale MEC application. For instance, it has already been shown that the use of stainless steel, a low-cost material, shows great promise because of stainless steel's high current densities and high energy recoveries (Call et al., 2009).

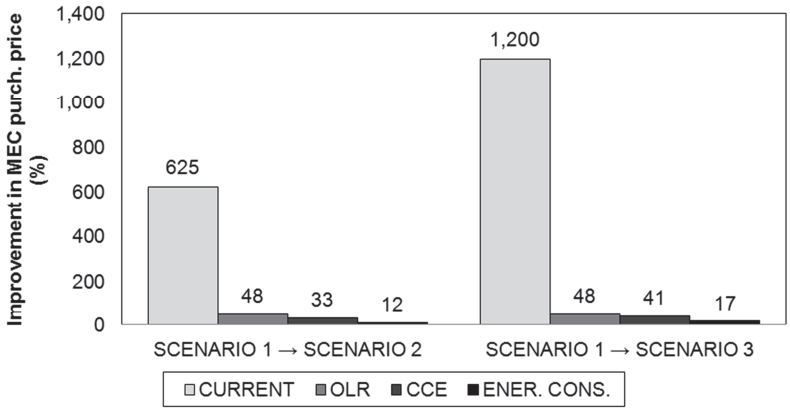

Figure 6.6. Estimated influence of current density, OLR, CCE and energy consumption on the maximum acceptable purchase cost of the MEC (MECPUR,N)

6.6 CONCLUSIONS

The potential inclusion of an MEC in an existing domestic wastewater treatment plant was studied from an economic point of view.

In scenario 1, an MEC can only become economically feasible if its installation is supported by government agencies or benefits from some type of tax credit. Furthermore, this scenario leaves little room for investment in electromechanical equipment (i.e., purchase of the MEC).

In scenario 2 and scenario 3, the size and the arrangement of the MEC and electricity prices have limited influence on the viability of MEC installation, whereas hydrogen prices have a more significant influence.

Overall, if current densities are improved up to 5A m^{-2} and energy consumption is reduced to 0.9 kWh kg-COD^{-1} (scenario 3), a purchase price for MEC units of about €1,350 m^{-3} represents a threshold at which the use of MECs in dWWTPs is economically justified.

Acknowledgements

Funding for this study was provided by the Spanish Ministry of Science and Innovation (Project Number: ENE2009-10395). Spreadsheet help from Diego M. García is greatly appreciated.

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APPENDIX 6.1. MEC reactor size calculation

Calculation methods for the size of aerobic reactors are already well established. In contrast, the current stage of development of bioelectrochemical reactors makes it difficult to establish a robust algorithm to calculate the size of an MEC reactor. Consequently, we have used a simplified algorithm to determine the size of the MEC in scenarios 1, 2 and 3, as described below.

The inputs for the calculation of MEC reactor size are the current density (I_d, [A m^{-2}]), the hourly wastewater flow rate (Q, [m^3 h^{-1}]), the Coulombic efficiency (CE, [%]), the COD of the influent (COD_i, [kgCOD m^{-3}]), the removal efficiency of the MEC (COD_r, [%]), the thickness of the MEC units (δ, [m]), the percentage of the total MEC volume that corresponds to the anodic chamber (r, [%]), and the number of MEC units in one stack (N_U, [-]). The main parameters that define the size and dimensions of the MEC are the following:

The total circulating current (I, [A]):

$$I = \frac{\left(1-\frac{COD_r}{100}\right)\cdot COD_i \cdot Q \cdot CE}{8 \cdot 3.6 \cdot N_U} \quad \text{(A1.1)}$$

The total anode surface area (A_s, [m^2]):

$$A_S = \frac{I \cdot N_U}{I_d} \quad \text{(A1.2)}$$

The total volume of the entire MEC reactor (V_r, [m^3]):

$$V_r = A_S \cdot \delta \quad \text{(A1.3)}$$

The total volume of the anodic chamber (V_A, [m^3]):

$$V_A = V_r \cdot \frac{r}{100} \quad \text{(A1.4)}$$

APPENDIX 6.2. Economic model solution

The economic model presented here makes use of the net present value (NPV) method to estimate maximum acceptable MEC manufacturing costs in an existing domestic wastewater treatment plant to break even at seven years. The NPV method basically requires the selection of an appropriate interest rate (representing the time value of money) and an analysis period, the calculation of the present value of the capital costs, the calculation of the present value of the annual net cash flows, and finally the calculation of the net present value of the investment. The above-referenced manufacturing costs were estimated by the following steps:

(i) The basic inputs to the techno-economic model are the capital and yearly operating costs of the plant associated with the four different scenarios considered (see section 3 for descriptions of the scenarios). These costs will be referred to as $CC_{S,N}$ and $OC_{S,N}$, respectively. Depending on the scenario considered, the subindex "N" takes a value of 0, 1, 2, or 3.

(ii) The capital and yearly operating costs of the plants described in scenarios 1, 2 and 3 are calculated following the methods described in paragraphs 4.1 and 4.2.

(iii) Capital costs specifically attributable to the MEC ancillary equipment (including purchase costs and associated civil engineering work (red lines in Figure 1in the web version)) are denoted as $CC_{MEC\text{-}AN,N}$ and computed as follows (note that the purchase cost of the MEC reactor is not included):

$$CC_{MEC-AN,N} = CC_{S,N} - CC_{S,0} \quad \text{(A2.1)}$$

(iv) Yearly operational costs specifically attributable to the MEC, (including ancillary equipment (red lines in Figure 1)) are denoted as $OC_{MEC,N}$, and computed as follows:

$$OC_{MEC,N} = OC_{S,N} - OC_{S,0} \quad \text{(A2.2)}$$

(v) It is assumed that the sale of hydrogen (I_H) is the only source of income, and thus yearly cash flow (CF) is computed as follows:

$$CF_N = I_{H,N} - OC_{MEC,N} \quad \text{(A2.3)}$$

The net present worth of the annual cash flows (CF'_N) was calculated as follows:

$$CF'_N = \sum_{n=1}^{k} \frac{CF_{N,n}}{(1+d)^n} \quad \text{(A2.4)}$$

where *k* denotes the assumed time period for the recovery of the investment made in the MEC installation (7 years), and *d* indicates the discount rate, which was fixed at 3% in accordance with interest rates established by the Bank of Spain for the last quarter of 2011.

(vi) The present value of the replacement cost of the MEC units at the end of their useful life ($CR_{MEC,N}$) was calculated as follows:

$$CR_{MEC,N} = \frac{CC_{PUR,N}}{(1+d)^l} \quad \text{(A2.5)}$$

where "l" represents the useful life of the MEC units (years).

(vii) The maximum acceptable purchase price of the MEC reactor ($CC_{PUR,N}$) was calculated by solving for $CC_{PUR,N}$ in the following equation:

$$0 = CC_{PUR,N} + CC_{MEC-AN,N} + CR_{MEC,N} - CF'_N \quad \text{(A2.6)}$$

Capítulo 7

Resumen

7.1 AGUAS RESIDUALES Y ENERGÍA.

Las aguas residuales (tanto agrícolas como industriales y domésticas) a menudo consisten en una compleja mezcla de compuestos orgánicos que han de ser eliminados antes de que aquellas sean devueltas al medio ambiente. En 2009, 12.800.974 m3 de agua residual fueron tratados diariamente en España (INE, 2010), lo que se tradujo en un consumo anual de energía de 2.476 GWh (asumiendo que en España 0,53 kWh de energía eléctrica son necesarios para tratar $1m^3$ de agua residual mediante fangos activos (IDAE, 2010)). Comparado con el consumo anual de energía eléctrica en nuestro país, esto representa alrededor de un 1% del total (IEA, 2011).

Por otro lado, los precios de la energía en Europa han mantenido una tendencia alcista creciente durante la segunda mitad de la pasada década (y es muy probable que esta tendencia se mantenga a medida que disminuyen las reservas de combustibles fósiles) desde unos 0,0756 € kWh^{-1} en la UE-27 en 2005 hasta 0,1023 € kWh^{-1} en 2009 (Eurostat, 2010). Esto significa que los costes de operación de las estaciones depuradoras de ARU serán cada vez mayores a pesar de que una parte de los costes de energía se recuperan en forma de biogás procedente de la digestión anaerobia de fangos.

Sin embargo, los costes de operación de estas plantas pueden ser reducidos de manera importante si conseguimos hacer uso del contenido energético remanente de la materia orgánica presente en el ARU. Por ejemplo, en una estación depuradora convencional en Toronto (Canadá), este potencial energético disponible ha llegado a ser 9,3 veces superior al consumo de electricidad en dicha planta (Shizas, 2004), y por lo tanto, las ARUs pueden ser vistas como una materia prima a partir de la cual se pueda obtener diversas formas de energía (Angenent et al., 2004), especialmente energía eléctrica.

7.2 REACTORES BIOELECTROQUÍMICOS.

7.2.1 Pilas de combustible microbianas

La pilas de combustible microbianas (MFC de sus siglas en inglés) representan actualmente uno de los más novedosos enfoques en lo que se refiere a la generación de energía eléctrica. Aunque ya en 1911 Potter (Potter, 1911) observó por primera vez la generación de electricidad asociada a la actividad metabólica de cierto tipo de bacterias, no fue hasta principios de los años 90 cuando, acompañados por el renovado interés en las pilas de combustible convencionales, surgieron nuevos trabajos de investigación en el campo de las MFC's (Allen and Bennetto, 1993). Sin embargo, la operación de este tipo de dispositivos requería el uso de mediadores electroquímicos, lo cual deterioraba en gran medida su viabilidad económica y ambiental.

Un avance significativo tuvo lugar en 1999, cuando se demostró que realmente no era necesaria la adición de estos mediadores electroquímicos, y que los microrganismos electrógenos que intervienen en la generación de electricidad pueden ceder los electrones originados en su metabolismo directamente al ánodo (Kim et al., 1999). Desde entonces, el interés despertado por este tipo de dispositivos no ha hecho más que crecer, lo cual queda reflejado en los numerosos grupos de investigación que a lo largo de todo el mundo dedican su labor investigadora a estos asuntos.

Una pila de combustible microbiana es un dispositivo que convierte la energía química de una amplia variedad de compuestos orgánicos en energía eléctrica, gracias a la acción catalítica de cierto tipo de microorganismos en condiciones anaerobias. La estructura del dispositivo que a tal efecto se despliega (Figura 7.1 izquierda) es análoga a la de una pila de combustible convencional. En el compartimento anódico crecen diversas comunidades bacterianas, que son responsables de la oxidación de un sustrato orgánico. Resultan del proceso de oxidación protones, electrones y CO2. Los electrones son captados por el ánodo y circulan hacia el cátodo a través de un circuito externo dispuesto a tal efecto. Los protones pasan al compartimento catódico, para lo que han de atravesar un separador que impide el contacto eléctrico entre ánodo y cátodo. Es en el cátodo donde se combinan electrones y protones, en presencia de un agente oxidante que habitualmente es el O_2, aceptor final de los electrones.

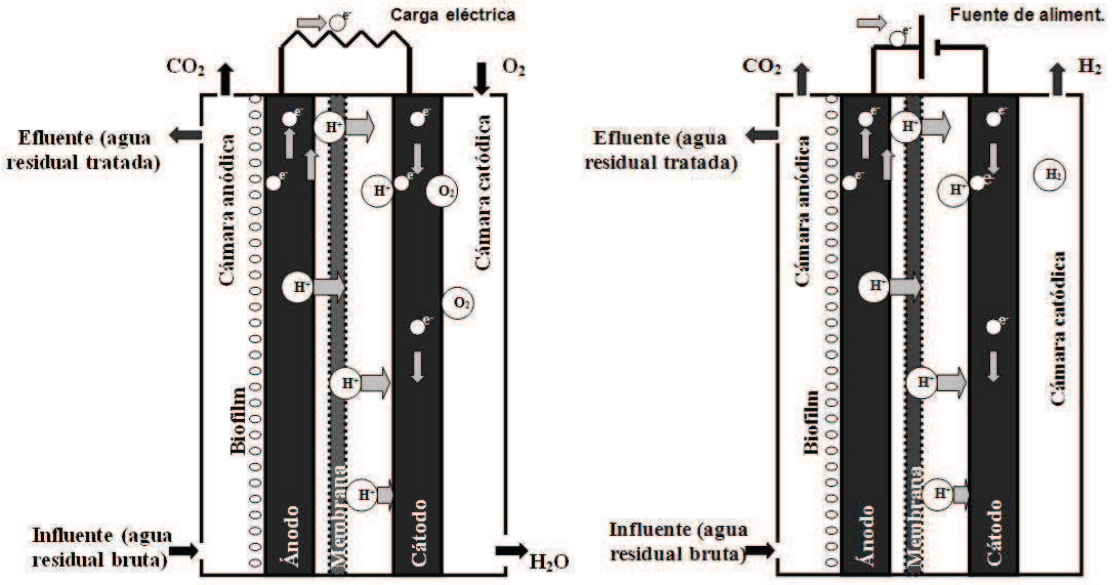

Figura.7.1. Esquemas del funcionamiento de una pila de combustible microbiana (izquierda) y electrolizador catalítico (derecha).

En el compartimento anódico de un MFC existe una gran diversidad de poblaciones bacterias, las cuales pueden metabolizar un amplio rango de sustratos orgánicos, incluyendo azúcares simples, lípidos, proteínas, polisacáridos, y ácidos grasos (He et al., 2005; Huang and Logan, 2008a; Heilmann and Logan, 2006; Huang and Logan, 2008b; Liu et al., 2005a; Min et al., 2005; Rabaey et al., 2003). Gracias a la diversidad de las poblaciones microbianas señalada, las MFC's presentan una cierta versatilidad y flexibilidad a la hora de ser situadas dentro de una línea de tratamiento de aguas.

A pesar de que en las MFC's el aceptor final de electrones sigue siendo el oxígeno, como en el caso de los sistemas aerobios, los procesos que tienen lugar en el ánodo, ocurren en coordenadas termodinámicas cercanas al punto de equilibrio, lo cual deja poca energía libre para el crecimiento bacteriano, lo que finalmente se traduce en una baja proliferación bacteria, y en una menor generación de lodos comparado con los sistemas aerobios convencionales. Esto unido a la potencial producción de electricidad, hace de las MFC's una tecnología atractiva que pueda sustituir el tratamiento secundario de una estación depuradora de aguas residuales, o como pretratamiento para eliminar la mayor cantidad posible de DQO antes de entrar en tratamiento con lodos activos.

7.2.2 Electrolizadores biocatalíticos

La producción de hidrógeno mediante electrólisis biocatalítica (EB) se consigue en cierto modo, invirtiendo el funcionamiento normal de un reactor MFC, de tal modo que en un electrolizador biocatalítico (MEC de sus siglas en inglés), los electrones no circulan libremente hacia el cátodo, y por lo tanto es necesario emplear una fuente de tensión para que la corriente eléctrica pueda circular (Figura 7.1 derecha).

Dado que en un reactor MEC, se impide la entrada de oxígeno en la cámara catódica, los electrones y protones procedentes del ánodo se combinan en el cátodo dando lugar a hidrógeno (H_2). Los procesos tanto biológicos como electroquímicos que tienen lugar en el compartimento ánodico son prácticamente idénticos a los que tienen lugar en el compartimento anódico de una MFC.

Las primeras estimaciones del potencial de producción de H_2 y de reducción de la carga orgánica de los reactores MEC, establecían que para el caso de un sistema electro-biocatalítico que genere 10 Nm^3 H_2 m^{-3} de reactor/día con una eficiencia catódica del 90%, se conseguirían niveles de depuración en torno a 7 kg DQO m^{-3} de reactor/día (Rozendal, 2007). Por el momento, los últimos estudios realizados con aguas residuales reales, tanto domésticas como industriales, ofrecen un rango de producción de hidrógeno de entre 0,2 y ~1 Nm^3 H_2 m^{-3} d^{-1}) (Cusick et al., 2011; Cusick et al., 2010; Wagner et al., 2009; Kiely et al., 2011; Escapa et al., 2012). En lo que se refiere a la tasa de eliminación de DQO, se han alcanzado tasas de depuración con aguas domesticas de hasta el 90% (Ditzig et al., 2007) Es importante citar que empleando un agua residual sintética como sustrato se ha conseguido llegar a producciones de hidrógeno de hasta 17 Nm^3 H_2 m^{-3} d^{-1}) (Cheng and Logan, 2011), lo que pone de manifiesto el hecho de que aun es necesario introducir mejoras importantes en el rendimiento de este tipo de dispositivos.

Uno de los puntos críticos en el diseño de un dispositivo MEC es la presencia de la membrana de intercambio iónico. Este elemento genera diferencias de pH importantes entre cátodo y ánodo, lo cual obliga a elevar la tensión aplicada para producir la misma cantidad de hidrógeno y obtener la misma tasa de depuración. Una posible solución a

este problema es el empleo de electrodos de difusión de gas a modo de cátodo (Logan et al., 2008; Tartakovsky et al., 2008b; Escapa et al., 2009).

Otro de los elementos críticos es el cátodo, y el material empleado en la catálisis de la reacción de producción de hidrógeno(Jeremiasse et al., 2010). En un principio, la mayoría de los investigadores que trabajan en el campo de la bioelectroquímica optaron por el uso de platino como catalizador (Logan et al., 2008; Rozendal et al., 2006; Hu et al., 2008). Sin embargo, las bajas densidades de corriente características de un electrolizador biocatalítico no justifican el empleo de este caro metal. Una alternativa viable pudiera ser el empleo de metales de transición (menos caros) (Selembo et al., 2009; Selembo et al., 2010; Manuel et al., 2010), los cuales han demostrado que es posible conseguir rendimientos de producción de hidrógeno iguales e incluso superiores a los alcanzados con metales nobles, sin mermas en el rendimiento energético del reactor. Otra opción es el empleo de cátodos biológicos, para los cuales habría que solventar problemas similares a los que presentan los ánodos biológicos. En diversos trabajos (Jeremiasse et al., 2010; Rozendal et al., 2008b), se ha demostrado que un cátodo biológico puede operar de una forma más favorable (en términos de sobrepotenciales y densidad de corriente) que aquellos basados en platino, aunque presentan un cierto número de problemas sobre todo derivados de la inestabilidad de las poblaciones microbianas.

Finalmente, otra cuestión a la que se ha de prestar atención son las pérdidas de carácter óhmico. La importancia de este asunto radica en que las pérdidas ohmicas son proporcionales al cuadrado de la corriente y a la resistencia eléctrica de los elementos conductores. Es de esperar que estos dispositivos puedan trabajar a niveles de corriente de varios miles de amperios, con lo cual toda innovación orientada a reducir al máximo la resistencia eléctrica de los conductores y del electrolito redundará en un incremento de la eficiencia del electrolizador. Con el objetivo de minimizar estas pérdidas, resulta muy conveniente la conexión en serie de las diversas unidades o módulos de que constaría el electrolizador.

7.3 OBJETIVOS

El presente estudio se llevó a cabo con el objetivo de estudiar las posibilidades técnicas y económicas de la EB como tecnología potencialmente apta para el tratamiento de aguas residuales. La ventaja principal de la EB sobre los tratamientos aerobios convencionales es que permiten recuperar parte de la energía invertida durante el proceso de depuración en forma de un combustible gaseoso como es el hidrógeno. Por este motivo, en este trabajo la EBC es observada desde una perspectiva eminentemente práctica, haciendo especial hincapié en la evaluación su capacidad de eliminación de carga orgánica contaminante de aguas residuales, y de generación de hidrógeno a partir de la misma.

7.4 EMPLEO DE LA TECNOLOGÍA DE EB PARA EL TRATAMIENTO DE AGUAS RESIDUALES FERMENTABLES

El glicerol es el principal subproducto obtenido durante la producción de biodiesel. En el año 2008 (momento en que se redactó el artículo *"Hydrogen production from glicerol in a membraneless microbial electrolysis cell"* incluido en este trabajo), la creciente producción mundial de biodiesel resultó en una caída importante en los precios del glicerol, convirtiendo este producto en un residuo con un coste de gestión asociado (Yazdani and Gonzalez, 2007).

Varias son las soluciones que se han propuesto para el aprovechamiento energético del glicerol, siendo aquellas orientadas a su conversión en hidrógeno las que han levantado un mayor interés(Valliyappan et al., 2008; Zhang et al., 2007; Adhikari et al., 2008). Así por ejemplo, la descomposición pirolítica de glicerol puede alcanzar rendimientos de conversión cercanos al máximo teórico, aunque a costa de un elevado coste energético derivado de las altas temperaturas necesarias (Zhang et al., 2007; Adhikari et al., 2008). Por otro lado la conversión por vía biológica (fermentación) requiere un aporte energético muy inferior, pero presenta el inconveniente de un menor rendimiento de conversión y de unas bajas tasas de producción de hidrógeno (Liu and Fang, 2007; Ito et

al., 2005). Todo esto condujo a explorar las posibilidades de la tecnología EBC como posible vía para disminuir el consumo energético asociado a la conversión de glicerol a hidrógeno, al mismo tiempo que se mantienen unas tasas de conversión aceptables.

La conversión de glicerol en hidrógeno mediante EBC se puede describir mediante las siguientes semireacciones y reacción global:

$C_3H_8O_3 + 6H_2O \rightarrow 3HCO_3^- + 17H^+ + 14e^-$ (semirreacción anódica) (7.1)

$2H^+ + 2e^- \rightarrow H_2$ (semirreacción catódica) (7.2)

$C_3H_8O_3 + 6H_2O \rightarrow 3HCO_3^- + 3H^+ + 7\ H_2$ (reacción global) (7.3)

Lo cual indica que se puede obtener un rendimiento máximo de conversión de 7 moles de hidrógeno por mol de glicerol consumido.

El cálculo de los potenciales anódico y catódico de equilibrio de acuerdo con la ecuación de Nernst (asumiendo concentraciones de glicerol y bicarbonato de 20 mM y 2mM respectivamente, pH=7, y presión parcial de hidrógeno de 1 atm) muestra cómo el potencial anódico es inferior al potencial catódico. Por lo tanto, teóricamente y en las condiciones mencionadas, la producción de hidrógeno en un reactor tipo MEC podría ocurrir de forma espontánea, y por lo tanto supondría una generación neta de energía. Sin embargo, lo ensayos realizados mostraron que es necesario aplicar un tensión no inferior a 0.5 V para observar un producción de hidrógeno apreciable. Esto puede ser explicado por las pérdidas de energía asociadas a los sobrepotenciales de los electrodos, y el consumo de glicerol por microrganismos fermentadores en lugar de electrógenos. De hecho, los análisis del efluente de la cámara anódica mostraron la presencia de metabolitos originados durante la fermentación del glicerol, lo cual sugiere que son estos metabolitos en lugar del glicerol quienes son utilizados por los microrganismos electrógenos en la producción de la corriente eléctrica.

Por otro lado, y mediante un análisis de materia, se observó que tan sólo entre el 50 y el 70% del glicerol alimentado a un reactor fue recuperado en forma de hidrógeno, metano, 1,3-propanodiol, e iones acetato, propionato, y butirato. Este bajo porcentaje de recuperación puede ser significativo de que no todos los metabolitos originados durante

la fermentación del glicerol fueron tenidos en cuenta en el balance de materia (Yazdani and Gonzalez, 2007; Barbirato et al., 1995).

La resistencia interna del reactor EB dependió en buena parte de la carga orgánica a la cual fue sometido, de tal modo que la mínima resistencia interna fue obtenida a cargas orgánicas de 2,7 g L_a^{-1} d^{-1}. Es importante remarcar el hecho que el sobrepotencial anódico fue mínimo a dicha carga orgánica, lo cual pone de manifiesto la estrecha relación entre la actividad biológica de los microrganismos electrógenos y las propiedades electroquímicas del reactor EB. En base a los resultados arriba mencionados, 2,7 g L_a^{-1} d^{-1} fue considerada la carga orgánica que hace más eficiente, en términos energéticos el funcionamiento de la EB. Por lo tanto, el empleo de un control de realimentación que permita ajustar la carga orgánica en respuesta a modificaciones en las condiciones de operación del reactor, permitiría mejorar de un modo significativo la eficiencia energética del proceso.

En cuanto a la presencia de 1,3-propanodiol en el efluente anódico, se planteó la hipótesis que a parte de su origen biológico(Murarka et al., 2008), también podría ser originado a partir de la reducción del glicerol sobre el cátodo. Sin embargo, la similitud en las concentraciones de 1,3-propanodiol con y sin la presencia de tensión aplicada, y la ausencia de 1,3-propanodiol en condiciones abióticas, lleva a concluir que este metabolito tiene su origen en la actividad fermentativa de las diferentes poblaciones microbianas presentes en el ánodo en lugar de la reducción catódica. Además esto explicaría la elevada concentración de este metabolito cuando se incrementa la carga orgánica de glicerol.

A una carga orgánica media-baja (0,7 g L_a^{-1} d^{-1}), se observó que la eficiencia energética puede ser maximizada fijando la tensión aplicada en 0,5 V. Además, aplicando voltajes superiores a 0,75 V, empeoró la eficiencia en la eliminación glicerol. Sin embargo, a voltajes de 0,75 V y superiores, tanto la tasa de producción de hidrógeno, como la eficiencia de conversión de glicerol en hidrógeno mejoró de forma importante. Por lo tanto, 0,75 V puede ser establecido como una solución de compromiso entre los objetivos de eficiencia energética y de tasas de producción de hidrógeno.

A modo de conclusión se puede decir que el estudio realizado demuestra la viabilidad de la producción de hidrógeno a partir de glicerol empleando reactores de EB. En efecto, la electrolisis con catálisis biológica del glicerol permite superar las barreras termodinámicas asociadas a la conversión biológica resultando en una conversión de casi el 100% de glicerol a hidrógeno. Desde el punto de vista de la producción de hidrógeno, aunque el consumo de energía fue relativamente alto (2-3 Wh L_{H2}^{-1}) fue significativamente inferior a los consumos típicamente asociados a la producción de hidrógeno mediante electrolisis convencional (5 Wh L_{H2}^{-1}) (Liu et al., 2005b). Es de esperar que una disminución del sobrepotencial anódico permita reducir el consumo de energía por debajo de 1 Wh L_{H2}^{-1}, lo cual puede ser conseguido mediante la mejora de las propiedades electroquímicas de los materiales de fabricación de electrodos (Tartakovsky et al., 2008a).

7.5 EMPLEO DE LA TECNOLOGÍA EB PARA EL TRATAMIENTO DE AGUAS RESIDUALES OBTENIDAS EN PROCESOS DE FERMENTACIÓN OSCURA

Los resultados anteriores, han mostrado como empleando como sustrato un residuo industrial sintético y fermentable como es el glicerol, un electrolizador biocatalítico de tipo monocameral, es capaz de extraer hasta 5.4 moles de hidrógeno por mol de glicerol alimentado, lo cual supone rendimiento de conversión del 77%.

Una forma de mejorar las tasas de conversión de materia orgánica en los electrolizadores biocatalíticos es mediante el empleo los productos de la fermentación de compuestos orgánicos complejos como alimentación. Por lo tanto, la inclusión de una etapa previa de preacidificación podría mejorar en buena medida el rendimiento energético y las tasas de producción de hidrógeno del reactor. De hecho, se ha demostrado que una MEC alimentada con ácido acético como fuente de carbono podría alcanzar tasas de producción de hidrógeno de hasta 6 L L_a^{-1} d^{-1} (Tartakovsky et al., 2009) y consumos de energía de tan sólo 0,6 Wh L_{H2}^{-1} (Liu et al., 2005b) a bajas tensiones.

En los ensayos cuyos resultados a continuación se resumen, se empleó como fuente de carbono una mezcla de metabolitos frecuentemente encontrados en los procesos de fermentación (ácidos acético, propiónico y butírico) (Gómez et al., 2006) manteniendo una carga orgánica constante de 6,4 g-DQO L_a^{-1} d^{-1} y variando tanto la tensión aplicada como el tiempo de retención. El objetivo de dichos ensayos fue estimar el impacto que el tiempo de retención hidráulica (TRH) y la tensión aplicada tienen en las tasas de eliminación de materia orgánica, de consumo de energía, de producción de hidrógeno y de generación de metano.

En lo que se refiere a las tasas de producción de hidrógeno, los resultados muestran como la tasa de producción aumenta a medida que aumenta el TRH, y además que dicha tasa de producción es más sensible a modificaciones en el TRH a medida que aumenta la tensión aplicada. De igual modo, un análisis de la influencia de la tensión aplicada sobre la producción de hidrógeno cuando el TRH fue mantenido constante, reveló que incrementar la tensión aplicada a TRH altos es más efectivo que hacerlo a TRH bajos.

Es importante hacer notar que a tensiones por debajo de 0,5 V la cantidad de hidrógeno generado fue poco significativa, y que a medida que se incrementó la tensión, mejoró de forma importante la tasa de producción de hidrógeno, y la eficiencia con la cual se lleva a cabo en el cátodo (eficiencia catódica). Sin embargo, la eficiencia energética se vio afectada de forma negativa, lo cual dificulta la selección de una tensión óptima de operación.

Además de hidrógeno, en la corriente gaseosa del cátodo se detectó un cantidad importante de metano (4-27% v/v) cuyo origen no está claro aunque varios investigadores han aportado pruebas de que este metano se origina mediante la oxidación biológica del hidrógeno generado en el cátodo (Wang et al., 2009; Lee et al., 2009).

Por su parte, el gas generado en el compartimento anódico consistió fundamentalmente en metano y dióxido de carbono. Si se contabiliza el gas generado en ambas cámaras, el metano representa entre el 45 y el 87% (v/v) del total. El análisis de las líneas de tendencia de la producción de dicho gas en el ánodo permite concluir que si el objetivo es reducir la cantidad de metano en la cámara anódica lo más conveniente es operar a

tiempos de retención bajos y tensiones altas lo cual está parcialmente de acuerdo con los resultados obtenidos por otros investigadores (Tartakovsky et al., 2008a). La relativamente alta producción de metano a bajas tensiones podría ser explicada por el hecho de que a bajas tensiones disminuye el potencial eléctrico del ánodo, lo cual puede influir en la competición por el sustrato entre las bacterias electrógenas y las metanógenas, disminuyendo la cantidad de energía que pueden absorber las primeras (Finkelstein et al., 2006).

A pesar de que la tasa máxima de producción de hidrógeno (1,46 L L_a^{-1} d^{-1}) es análoga o incluso superior a las tasa de producción publicadas por otros autores, la elevada proporción de metano en la producción global de gas revela que una cantidad importante de la materia orgánica alimentada al reactor se convierte finalmente en metano en lugar de hidrógeno como sería deseable. Un buen número de trabajos atribuye el origen de gran parte del metano encontrado en reactores MEC a la actividad de microrganismos hidrogenótrofos (Wang et al., 2009; Lee et al., 2009; Lee and Rittmann, 2010) (la reducción electroquímica de CO_2 a metano en la superficie del cátodo ha sido descartada debido a las limitaciones cinéticas de la producción de metano con Ni actuando como catalizador (Hori, 2010)). Por lo tanto, si toda la actividad hidrogenotrofa pudiera ser suprimida y toda la corriente medida fuera recuperada en forma de hidrógeno se podría llegar a alcanzar una tasa de producción de hidrógeno de hasta 2,07 L L_a^{-1} d^{-1}, lo cual representaría un porcentaje sobre el total de hasta el 77% (v/v), lo que a su ver permitiría incrementar sustancialmente la eficiencia energética (desde un 151 a un 235%). Por lo tanto, la actividad metanogénica es un asunto que requiere especial consideración, a pesar de que las estrategias de supresión hasta ahora ensayadas no han permitido encontrar una solución definitiva (Lee et al., 2009; Lee and Rittmann, 2010; Chae et al., 2010; Call and Logan, 2008)

En lo que se refiere a la tasa de eliminación de la carga orgánica, se observó que con un TRH de 8 horas, la tasa de eliminación de materia orgánica fue relativamente baja, lo cual fue debido en gran medida a la baja tasa de conversión del propiónico y del butírico. Cuando el TRH se fijó en 10 h la eliminación de butírico mejoró de forma importante, no así con el propiónico, cuya concentración en el efluente permaneció en valores relativamente altos. La baja tasa de conversión del propiónico puede estar

relacionada con el hecho de que no se consume directamente por los microrganismos electrógenos y en su lugar es empleado por los acetógenos para producir acético (Ha et al., 2008). Un incremento del TRH hasta 12 horas permitió reducir la cantidad de acético y propiónico hasta niveles poco significativos, mientras que el propiónico mantuvo su relativamente escasa tasa de eliminación.

En todo caso, la tasa de eliminación resultó ser proporcional a la tensión aplicada, de modo que una variación de 0.1 V en la tensión aplicada fue más efectiva en términos de eliminación de carga orgánica a bajos TRH que el mismo incremento a con un TRH de 12 h. Este resultado confirma que al menos una parte de la materia orgánica alimentada a la MEC fue consumida por microrganismos electrógenos, a pesar de que la alta producción de metano revela una presencia importante de comunidades metanógenas.

El consumo aparente de energía por kilogramo de DQO eliminado resultó ser tan bajo como 0.11 kWh kg^{-1}-DQO, mientras que el valor más elevado alcanzó 0.84 kWh kg^{-1}-DQO, mostrando una elevada dependencia de la tensión aplicada. Sin embargo el consumo mínimo antes mencionado (0,11 kWh kg^{-1}-DQO) está muy por debajo del límite mínimo teórico de consumo de energía necesario para que la producción de hidrógeno tenga lugar en un reactor MEC (0,47 kWh kg^{-1}-DQO asumiendo una tensión aplicada de 0,11 V). Esta discrepancia puede ser atribuida fundamentalmente a la presencia de otros microrganismos a parte de los electrógenos, que eliminan DQO sin requerir un aporte energético.

La realización un balance de materia reveló que entre un 16% y un 21% de materia no había sido contemplada en el mismo, y que probablemente pueda ser explicado por la presencia en el efluente de metabolitos no analizados y por el crecimiento bacteriano. De hecho, y a pesar de que las tasas de crecimiento microbiano no ha sido estudiadas de forma exhaustiva en reactores bioelectroquímicos, estudios preliminares han ofrecido valores en el rango entre 0,07 y 0,31 g DQO-biomasas g^{-1} DQO-substrato (Rabaey et al., 2003; Freguia et al., 2007). Además, las tasas de crecimiento típicas en entornos anaerobios suelen ser del orden de 0.04 g DQO-biomasas g^{-1} DQO-substrato (Rabaey and Verstraete, 2005). Dado que no sólo microrganismos electrógenos están presentes en el ánodo de la MEC, es de esperar una tasa de crecimiento en el entorno de 0,04-0,31 g DQO-biomasas g^{-1} DQO-substrato, que estaría de acuerdo con la cantidad de materia

que no ha sido tenida en cuenta en el balance. Sin embargo, no se ha tenido en cuenta la presencia de productos solubles, que pueden alcanzar el 11% (Lee and Rittmann, 2010) de la DQO de entrada, por lo que la tasa de proliferación bacteriana pudiera ser incluso inferior a los valores consignados anteriormente.

A modo de conclusión, se puede afirmar que la producción de hidrógeno es más sensible a modificaciones del TRH a tensiones aplicadas altas. De un modo similar, un incremento en la tensión aplicada a tiempos de retención altos resultó ser más efectivo a la hora de incrementar la tasa de producción de hidrógeno. Se alcanzaron tasas de eliminación de DQO superiores al 80% a tensiones aplicadas superiores al 0.8 V y con tiempos de retención por encima de 10 h. Mientras que tanto el butírico como el acético fueron fácilmente degradados, el propiónico mostró un carácter pseudo- recalcitrante.

7.6 EMPLEO DE LA TECNOLOGÍA EB PARA EL TRATAMIENTO DE AGUAS RESIDUALES URBANAS

El tratamiento de aguas residuales urbanas representa un campo de aplicación importante para la electrolisis biocatalítca. Sin embrago, y hasta el momento muy pocos trabajos han sido orientados al estudio de la eficiencia y efectividad de esta tecnología cuando se emplean aguas residuales reales como sustratos (Cusick et al., 2010; Wagner et al., 2009; Kiely et al., 2011). De entre ellos, solamente dos trabajos han sido dedicados al estudio particular de las aguas urbanas (Cusick et al., 2010; Ditzig et al., 2007). En el trabajo realizado por Ditzig et al. (2007) se alcanzaron unas elevadas tasas de eliminación de DQO (91% de eliminación con menos de 7 mg DQO L^{-1} en el efluente). Sin embargo, fue necesario fijar tiempos de retención relativamente altos (30-108 h) y emplear materiales tales como el platino en el cátodo, o una membranas poliméricas de intercambio catiónico, cuyo coste puede hacer prohibitivo el empleo de la tecnología MEC para el tratamiento de aguas residuales (Rozendal et al., 2008a), sin contar con la resistencia interna que introduce el empleo de membranas poliméricas. Siguiendo los esfuerzos realizados por otros investigadores para mejorar el diseño de los reactores MEC y reducir el costes de los materiales empleados (Tartakovsky et al.,

2008b; Tartakovsky et al., 2008a; Zhuang et al., 2009), la membrana de intercambio protónico en nuestro diseño fue sustituida por un material sintético poroso (J-cloth). Sin embargo, esto puede traer consigo que si el hidrógeno no se retira con la suficiente rapidez a medida que es generado en el cátodo, pueda alcanzar el compartimento anódico y ser convertido en metano o incluso dar lugar a corrientes eléctricas parásitas (Kiely et al., 2011; Call et al., 2009).

A parte del diseño del reactor, factores tales como la tensión aplicada y la corriente han de ser estudiados a escala de laboratorio previamente a la implantación de los reactores MEC a escala piloto. La tensión aplicada no sólo influye de forma decisiva tanto en las reacciones anódica y catódica (Liu et al., 2005b), sino que además determina en gran medida el consumo de energía (Tartakovsky et al., 2011), y por lo tanto afecta directamente a los costes de operación. Por otro lado, la densidad de corriente se encuentra íntimamente relacionada no sólo con el tamaño del reactor(Lee et al., 2010) (y por lo tanto con los costes de inversión), sino también con la carga orgánica a la cual está sometido el mismo (Juang et al., 2011). Por lo tanto el estudio del efecto de la tensión aplicada y de la carga orgánica en el tratamiento de aguas residuales mediante tecnología EB ayudará sin duda en el diseño de este tipo de reactores a escala piloto e industrial.

Efecto de la Carga Orgánica

La celda MEC fue alimentada en continuo con agua residual urbana a cargas orgánicas de entra 240 y 3.100 mg –DQO L_a^{-1} d^{-1}. Se observó que la tasa de eliminación de materia orgánica se ve influida de forma moderada por la carga orgánica, de tal modo que un aumento de 1.000 mg –DQO L_a^{-1} d^{-1} en esta última reduce la tasa de eliminación en un 8.4%. La tasa de eliminación de DQO máxima fue del 67%, valor que está de acuerdo con los resultados obtenidos por otros investigadores con aguas industriales (Cusick et al., 2011; Kiely et al., 2011), aunque es inferior a lo alcanzado por Ditzig et al. (2007) (90%) con un reactor MEC operado en batch con agua residual urbana.

Sin embargo, sí se observó un impacto más pronunciado en el consumo de energía, determinándose que éste puede ser reducido notablemente aumentando la carga

orgánica del reactor. Este efecto pudo ser explicado al menos en parte por un descenso en la resistencia interna a medida que aumenta la carga orgánica.

Sólo se observó una producción de hidrógeno significativa a cargas orgánicas por encima de 450 mg-DQO L_a^{-1} d^{-1}, de tal modo que se detectó una dependencia con respecto a la carga orgánica de tipo Monod, con una saturación de 0,462 L_{H2} L_a^{-1} d^{-1}. Asimismo, aguas residuales con una baja concentración de DQO, no produjeron hidrógeno independientemente de la carga orgánica impuesta. Cuando la carga orgánica se fijó en 240 mg-DQO L_a^{-1} d^{-1}, la presión en la cámara catódica se hizo negativa y aumentó de forma importante la concentración de metano en dicha cámara (desde 2% hasta un 16%).

Las eficiencias coulombicas registradas fueron relativamente altas en comparación con aquellas obtenidas por otros investigadores en reactores bicamerales operando con aguas residuales urbanas, lo cual hizo sospechar que en nuestro reactor una parte importante de la corriente registrada pudiera ser debida a la recirculación de hidrógeno entre ambos electrodos. De hecho, se ha estimado que en reactores del tipo al empleado en el presente trabajo, hasta un 70% de la corriente circulante puede ser atribuida a este fenómeno (Lee et al., 2010), lo cual entrañaría que las eficiencias coulombicas so realmente más bajas que las registradas, pudiendo estar en el entorno entre el 5% y el 26%. Esto a su vez revela que una parte importante de la carga orgánica alimentada al reactor MEC fue consumida para otros fines (tales como la formación de biomasa, consumo por parte de microrganismos metanógenos, o la reducción de nitratos y sulfatos (Wang et al., 2009)) más allá de la generación de electricidad. Mediante un balance de materia se llegó a la conclusión de que muy probablemente una parte importante de esta DQO no destinada a la producción de corriente fue convertida en metano, aunque éste no pudo ser detectado presumiblemente por la presencia de una fuga de gas en el compartimento anódico.

En cuanto al consumo de energía, se observó que éste depende en gran medida de la carga orgánica, de tal modo que para cargas orgánicas altas el consumo de energía fue tan bajo como 0,77 Wh g-DQO^{-1}, mientras que a cargas bajas creció hasta 2,20 Wh g-DQO^{-1}, valor éste último que está en el rango de consumo obtenidos en reactores MEC operando con aguas residuales reales empleando platino como catalizador de la reacción

catódica, lo cual sugiere que el uso de metales de bajo coste pueden ser empleados de forma satisfactoria en el tratamiento de aguas residuales.

Mediante la ejecución de una serie de barridos de tensión se persiguió profundizar en la investigación del efecto de la carga orgánica en la eficiencia del reactor. A pesar de que se encontraron diferencias significativas entre los ensayos realizados a cargas orgánicas medias-bajas y aquellos realizados a alta carga, en todos los casos una cantidad de corriente significativa comenzó a circular sólo cuando la tensión aplicada se situó en el entorno de los 0,3-0,4V, lo cual se asocia con el inicio de la actividad bioelectroquímica dentro del reactor (Ditzig et al., 2007; Liu et al., 2005b; Tartakovsky et al., 2011). Por debajo de esta tensión se asume que los potenciales de activación prevalecen sobre el resto de sobrepotenciales (Bagotsky, 2005). La resistencia interna fue calculada a partir del tramo lineal de los barridos observándose que este parámetro desciende a medida que aumenta la carga orgánica, lo cual podría justificar en parte la tendencia en el consumo de energía. Curiosamente, se encontraron resultados similares en los ensayos realizados con glicerol, donde los incrementos de la carga orgánica se correspondieron con reducciones de la resistencia interna. Este comportamiento fue asociado a la actividad de los microrganismos electrógenos, y de las propiedades electroquímicas del reactor. La tensión a partir de la cual las pérdidas por difusión comienzan a prevalecer sobre el resto de los sobrepotenciales depende la carga orgánica a la cual es sometido el reactor. Así, cuando el reactor MEC fue sometido a cargas orgánicas medias bajas, al aplicar tensiones por encima de 0,5 V la reacción bioelectroquímica se ve controlada por difusión. De forma similar, el límite de tensión se fija en 0,7 V para cargas orgánicas altas. A pesar de que la corriente aumentó ligeramente en esta zona de control por difusión se formuló la hipótesis de que el incremento en la tasa de producción de hidrógeno y de eliminación de materia orgánica no justificaría el aumento del consumo de energía derivado de incrementar la tensión. Con el objeto de investigar esta hipótesis, se estudió el efecto de la tensión aplicada a cargas orgánicas medias bajas (493 mg L_a^{-1} d^{-1}).

Efecto de la Tensión Aplicada a Cargas Orgánicas Medias-bajas

Debido a la variabilidad de la concentración en DQO del agua de entrada, para mantener la carga orgánica a valores más o menos constantes, fue necesario emplear dos tiempos de retención: 24 y 10,5 horas.

Curiosamente, y a pesar de que como se ha dicho la carga orgánica se mantuvo en niveles prácticamente constantes, solamente cuando se alimentó agua residual con una alta concentración de DQO, la tasa de eliminación llegó a ser del 76%. Por el contrario, aguas con baja concentración de DQO sólo permitieron alcanzar tasas de eliminación del 32%.

En cuanto al efecto de la tensión, se observó que 0,75 y 0,85 V son las tensiones aplicadas óptimas para aguas con alta y baja concentración de DQO, porque maximizan las tasas de eliminación en sus respectivas condiciones de operación. Sin embargo, este análisis simplificado ha de tener en cuenta el consumo de energía, el cual aumentó de forma importante a medida que aumentó la tensión. De hecho, para aguas con baja concentración de DQO, a pesar que aumento la tensión de 0,5 a 0,75 V supuso aumentar la tasa de eliminación un 15%, el consumo de energía se vio incrementado en un 43%.

En ambos casos, tanto a 0,5 como a 0,75 V, el efluente del reactor MEC, tiene una concentración de DQO superior a lo que permitiría la legislación de vertidos y por lo tanto a escala industrial sería necesario aplicar un postratamiento al efluente con el objeto de eliminar la carga orgánica remanente, cosa que por otro lado ya han sugerido varios autores (Rosenbaum et al., 2010). Si asumimos que la carga orgánica que no es eliminada en el reactor MEC es depurada mediante un sistema aerobio convencional con un consumo de energía asociado de 1,5 kWh kg-DQO^{-1} (Metcalf & Eddy Inc., 2003), el consumo total de energía puede ser estimado como la media ponderada entre el consumo en cada etapa, siendo los coeficientes de ponderación las tasas de eliminación en cada etapa. Por ejemplo, si asumimos que el agua tratada sólo puede ser descargada en los cauces fluviales después de un 95% de eliminación de materia orgánica, el consumo de energía global sería de 1,45 y 1,91 kWh kg-DQO^{-1} a 0,5 y 0,75 V respectivamente. Desde este punto de vista 0,5 V en lugar de 0,75 V sería la tensión aplicada óptima.

A pesar de que la tensión aplicada fue modificada en un amplio rango de valores (0,5-1,2 V), la producción de hidrógeno no experimentó grandes modificaciones, o no fueron suficientes como para compensar el incremento en el consumo de energía lo cual apoya la tesis de que a cargas orgánicas medias-bajas, 0,5 V puede ser establecida como la tensión aplicada que optimiza la operación del reactor. Es interesante remarcar que otros investigadores aplicando otra metodología basada en el seguimiento de las modificaciones de la resistencia interna con la carga orgánica han llegado a conclusiones similares (Tartakovsky et al., 2011).

7.7 ESTIMACIÓN DE COSTES DE LA TECNOLOGÍA MEC

Desde el momento en que la producción de hidrógeno mediante la tecnología MEC fue demostrada por primera vez a mediados de la década pasada (Liu et al., 2005b; Rozendal and Buisman, 2005), sus posibilidades han sido analizadas desde varios puntos de vista, con especial énfasis en asuntos tales como el comportamiento de determinados substratos, (Selembo et al., 2009; Logan et al., 2009), tasas de producción de hidrógeno y eliminación de materia orgánica (Ditzig et al., 2007; Tartakovsky et al., 2009), y el efecto de diversos parámetros operacionales y configuraciones en el funcionamiento del reactor (Rozendal et al., 2007; Hu et al., 2009). Además los reactores bioelectroquímicos han alcanzado un nivel de desarrollo que han permitido llevar a cabo las primeras experiencias a escala piloto (Cusick et al., 2011; Dekker et al., 2009; Logan, 2010; Keller and Rabaey, 2008).

Sin embargo, si se quiere que la tecnología MEC alcance finalmente aplicación a escala industrial, será necesario afrontar otros desafíos de índole tecno-económica tales como: (i) la ausencia de una clara estimación de costes de producción de los reactores MEC y (ii) la necesidad de desarrollar métodos de producción de bajo coste. Estudios preliminares han revelado que al menos desde un punto de vista económico y ambiental, la tecnología BE puede resultar rentable y que además genera numerosos beneficios medioambientales (Cusick et al., 2010; Foley et al., 2010). Sin embargo una estimación de costes con un cierto nivel de precisión es todavía necesaria. Los primeros intentos orientados a estimar estos costes se han basado en el coste de lo materiales empleados y

han llevado a un rango de entre 1.137-3.000 € m^{-3} de compartimento anódico (Rabaey and Verstraete, 2005; Fornero et al., 2010; Pant et al., 2010).

En este trabajo, se ha pretendido ofrecer una respuesta a la primera cuestión formulada en el párrafo anterior cuya respuesta sea además relevante para la segunda de ellas. En particular se intentará estimar el máximo coste admisible de fabricación de una planta MEC ideal que vaya a ser instalada en una planta de tratamiento de aguas residuales prexistente, de tal modo que sea posible recuperar la inversión al cabo de 7 años. Además, se ofrecerá un análisis de sensibilidad del coste de compra de una MEC a variaciones en los precios de la electricidad y del hidrógeno, así como al tamaño y la disposición del reactor MEC.

Descripción de la Planta Objeto de Estudio

La planta donde se pretende estudiar la potencial inclusión del reactor MEC está situada en Jaén (España) y ha sido diseñada para una población equivalente de 55.200 habitantes equivalentes, con un caudal per cápita de 230 litros al día por habitante equivalente. La planta carece de decantador primario, y el agua que entra en el reactor biológico (oxidación prolongada, 16.000 m^{-3}) tiene una DQO de 695 g-DQO m^{-3} y una cantidad de nitrógeno de 48,15 g de nitrógeno Kjeldahl m^{-3}.

A pesar de que en un primer momento se consideró la posibilidad de estudiar la inclusión del reactor MEC como único tratamiento biológico, esta opción fue rechazada ya que con los niveles actuales de eliminación de DQO de los reactores bioelectroquímicos y su incapacidad para eliminar nitrógeno, es poco probable que en un futuro puedan actuar en solitario (Rosenbaum et al., 2010; Rodrigo et al., 2007; Liu et al., 2004; Min and Logan, 2004), y muy posiblemente requieran de un postratamiento de afino . En el presente estudio, y por simplificar, se supondrá que este tratamiento consiste en una oxidación prolongada.

En cuanto a la arquitectura del futuro reactor MEC, y a pesar de que es un factor clave que afecta a la eficiencia del mismo, aun no se ha llegado a un consenso claro en cuanto a sus características. Este diseño, no sólo ha de resultar económico y orientado a la producción en masa (Logan, 2008), sino que además ha de ser capaz de competir con las tecnologías biológicas convencionales. De este modo, el reactor MEC ha de afrontar

al menos tres limitaciones relativas a su huella ecológica, a la composición de las aguas residuales, y otro tipo de limitaciones tecnológicas tales como el modo de conexión de los reactores (Hamelers et al., 2010). Un análisis pormenorizado de cada una de estas limitaciones nos hizo decantarnos por un diseño plano con un grosor de reactor de 2,25 cm, con separación entre electrodos de menos de 1 mm. En cuanto a su conexión, ésta se realizará en serie para limitar la corriente circulante. Debido a que por el momento no está claro cual habrá de ser el grosor óptimo del reactor ni cuántas unidades MEC será necesario colocar en serie, se incluirá un análisis de sensibilidad a ambos factores. En la Figura 7.2 se presenta la configuración y estructura asumidas del reactor MEC.

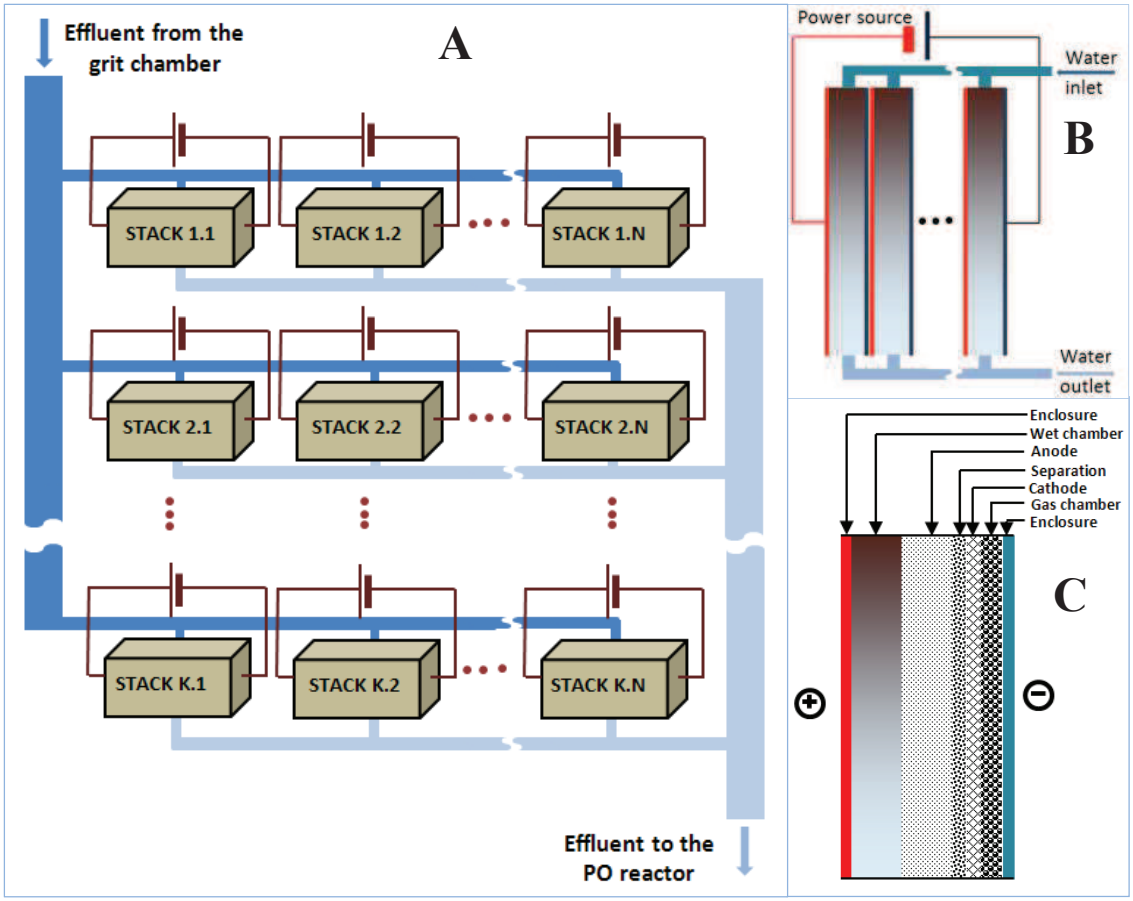

Figura 7.2. A:disposición hidráulica de los "stacks" de unidades MEC. B: sección de uno de los stacks. C: sección de una unidad MEC. El grosor de cada elemento es el siguiente (en mm): cerramiento (2.5), cámara húmeda (10), ánodo (5), separación (0.3), cámara de recepción del gas generado (2), espesor total de la unidad MEC (22.6)

Las condiciones de operación del reactor MEC han sido determinadas a partir de los resultados obtenidos en los ensayos con agua residual real, teniendo en cuenta que el postratamiento aerobio posterior ha de recibir cantidad suficiente de materia orgánica para poder eliminar nitrógeno. De este modo se ha optado por emplear una carga orgánica de 3.100 g-DQO m_a^{-3} d^{-1}, lo cual representa una tasa de producción de hidrógeno de 0,3 L L_a^{-1} d^{-1}, una tasa de eliminación de DQO del 44% y un consumo de energía de 1,15 kWh kg-DQO^{-1}.

El tamaño del reactor aerobio fue calculado de tal modo que la eliminación de DQO y de nitrógeno se pueda realizar de una forma efectiva. EL tiempo de retención hidráulica y de retención de lodos se fijó en 17 horas y 16,5 días respectivamente.

Descripción de Escenarios

Se fijaron 4 escenarios distintos. El primero de ellos (*Escenario 0 [E0]*, o escenario existente) corresponde al escenario de la EDAR que actualmente está implantada. El segundo de los escenarios (*Escenario 1 [E1]*, o escenario base) que se corresponde con los resultados experimentales de laboratorio, en el que además la durabilidad de la celda MEC se ha establecido en 5 años. En el tercer escenario propuesto (*Escenario 2 [E2]*, o escenario moderado), se ha supuesto que la densidad de corriente y la tasa de producción de hidrógeno mejoran hasta 0,6 m^3 m_a^{-3} d^{-1} y 2,5 A m^{-2} y disminuye el consumo de energía hasta 1,00 kWh kg-DQO^{-1}. En el cuarto escenario (*Escenario 3 [E3]*, o escenario optimista) se han asumido mejoras posteriores en la densidad de corriente, tasa de producción de hidrógeno y consumo de energía hasta 0,8 m^3 m_a^{-3} $d^{-1,}$ 5 A m^{-2} y 0,9 kWh kg-DQO^{-1} respectivamente.

Análisis Económico y Estimación de Costes

En la estimación de costes, sólo se han tenido en cuenta aquellos costes que se ven modificados con respecto al escenario de referencia (*E0*). Es decir sólo serán considerados aquellos costes que se ven modificados por la inclusión del reactor MEC, pues sólo las diferencias con E0 serán relevantes para el presente estudio.

En los costes de inversión y de operación relativos a la instalación MEC se han tenido en cuenta los siguientes dispositivos y modificaciones: (i) rectificador, (ii) celda MEC,

(iii) compresor de gas, (iv) tanque de almacenamiento del gas generado, (v) elementos auxiliares, (vi) las modificaciones que es necesario llevar a cabo en la planta original (fundamentalmente en el reactor biológico y demás operaciones de planta asociadas).

En cuanto a los ingresos, sólo se consideran aquellos derivados de la venta de hidrógeno, ya que el canon por tratamiento de aguas se computa como un ingreso idéntico en todos los escenarios. Se ha supuesto un precio de venta del hidrógeno de 3,6 € kg^{-1}, como coste medio de producción de hidrógeno en Europa (Schade et al., 2008) incrementado en un 6% en concepto de beneficio industrial.

Resultados del Estudio. Máximo Coste Admisible Para el Reactor MEC

En el escenario 1, el máximo coste admisible del reactor MEC se estimó en unos 22 € m_a^{-3}, lo cual corresponde con 0,32 € m_a^{-2}. Sin tener en cuenta los costes de manufacturado, un precio de venta por debajo de 1 € m_a^{-2} parece ciertamente poco realista (por ejemplo un cátodo de bajo coste a base de acero inoxidable tiene un precio de 0,85 € m_a^{-2} (Wei et al., 2011). Por lo tanto, en este escenario sería necesario contar con el apoyo de las administraciones públicas para que tecnología MEC llegue al mercado de tratamiento de aguas residuales urbanas. En este escenario (E1), la viabilidad económica de esta tecnología mostraría una gran dependencia de los precios de la electricidad, del hidrógeno y de la configuración y tamaño del reactor.

Un diseño mejorado, y la aparición de materiales con propiedades bioelectroquímicas optimizadas, podrían conducir a una mejora en los parámetros operacionales como la descrita en el escenario 2. Esto permitiría incrementar el precio del reactor MEC hasta los 465 € m_a^{-3} (7 € m_a^{-2}). El empleo de materiales de bajo coste permitió a Pant. et al. (Pant et al., 2010) construir una pila MEC con un coste asociado de 1.137 € m_a^{-3}, lo cual está todavía muy por encima del precio máximo admisible para este escenario.

Si finalmente se actualizara la hipótesis descrita en el escenario 3, un coste del reactor MEC de ~1.100-1.350 € m_a^{-3} (16-20 € m_a^{-2}) dependiendo del tamaño y configuración permitiría hacer rentable la instalación de la tecnología MEC en EDARs . Este precio parece mucho más realista que los obtenidos en los escenarios anteriores, especialmente si se compara con los costes previstos por otros investigadores (1.100-3.000 € m_a^{-3}). Este resultado sugiere que si se alcanzaran densidades de corriente de 5 A m_a^{-2} y

consumos de energía 0,9 kWh kg-DQO^{-1}, con tasas de producción de hidrógeno de 0,8 m^3 m_a^{-3} d^{-1}, la tecnología MEC comenzaría a ser viable al menos desde el punto de vista económico en el tramiento de aguas residuales urbanas, y por lo tanto los parámetros mencionados se pueden establecidos como un objetivo para los reactores MEC.

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Chapter 8

General Conclusion / Conclusiones Generales

8.1 CONCLUSIONS

The high energy consumption usually associated to wastewater treatments is prompting scientist to search new alternatives to conventional technologies. Biocatalized electrolysis (BE) represents a relatively new technology aimed at reducing the energy investment during wastewater treatment. Although large improvements in the reactor performance are still needed, BE was proven to be an effective method for removing part of the organic matter present in certain types of industrial and domestic wastewaters and convert it into hydrogen. The following conclusions can be drawn from the present study:

1. Hydrogen production through BE of glycerol is a feasible process, at least from a technical and biochemical point of view. The rate of hydrogen production was comparable to that observed in the glycerol fermentation process, but the hydrogen yield was significantly higher (77% of the theoretical maximum value) than that associated to dark fermentation of glycerol. In addition, BE allowed to produce hydrogen with an associated energy consumption below 5 Wh L_{H2}^{-1}, the minimum energy consumption required for hydrogen production through water electrolysis.

2. MEC operation at a V_{app} of 0.75 V and an OLR of 2.7 g-COD L_a^{-1} d^{-1}, can be suggested as a compromise between energy efficiency and volumetric performance objectives when glycerol is used as a substrate.

3. When the MEC was fed continuously with a synthetic effluent of a fermentative process, the influence of Vapp and HRT on COD removal and hydrogen production rates were found to be interdependent. Indeed, hydrogen production was more sensitive to HRT changes when the V_{app} is high (1V). Likewise, an increase in the V_{app} was more effective with longer HRTs in increasing hydrogen production.

4. The absence of polymeric membrane in between the two electrodes promoted hydrogen recirculation inside the MEC, what significantly limited its performance in terms of energy consumption.

5. Domestic wastewater treatment efficiency (for COD removal) in a continuously-fed MEC was in the range between 44-76% with energy consumption comparable and even lower to that traditionally associated to conventional aerobic treatments.

6. Hydrogen gas was evolved only at OLR's above 448 mg-COD L_a^{-1} d^{-1} when the MEC was fed with domestic wastewater. Hydrogen production rate followed a Monod-like function, saturating at 0.3 L L_a^{-1} d^{-1} when the OLR was set above 2,000 mg-COD L_a^{-1} d^{-1}. Experimental results also confirmed the hypothesis that the optimum applied voltage was dependent of the OLR.

7. Domestic wastewater treatment by BE may become feasible (from an economical point of view) if the current density, energy consumption and hydrogen production rate could achieve 5 A m^{-2}, 0,9 kWh kg-COD^{-1} and 0,8 m^3-H_2 m^{-3}_a d^{-1} respectively.

8. Within these operational parameters the size of the reactor (volume), its configuration (number of MEC units stacked in series in one module), and the electricity prices have little influence over the MEC feasibility.

9. Domestic wastewater treatment through BE would become feasible only if MEC purchase price were in the range between ~€1,100-1,350 m_a^{-3}.

8.2 FUTURE PERSPECTIVES

Hydrogen generation through BE is a promising technology because it might be able to provide renewable energy to our society with a low carbon footprint. Moreover, when compared with other bio-hydrogen production technologies, hydrogen yields from MEC are quite favorable. However, several challenges need to be overcome before bio-electrolytic hydrogen production can achieve practical implementation. A main challenge of making BE viable is the many energy losses that occur in several parts of the reactor. Another important challenge is the low volumetric production rates which also compromises the feasibility of practical implementation of BE. Overall, it has been estimated that MEC technology will require at least 3-8 years of research and development before it can be practically implemented on a large scale.

From the author's point of view further research is required in two important topics:

1. New electrode materials and new catalysts must be developed, especially for the cathode side and for the cathodic reaction, since most of the bottlenecks of BE are associated to the cathode and the cathodic reactions, namely: low kinetics for the hydrogen evolution reaction (which in turn limits the circulating current and the organic matter removal on the anodic side), hydrogen recirculation (which increases artificially the energy consumption, and biomass proliferation (which converts part of the hydrogen produced into methane). Therefore, these new materials should comply with the following specifications: (i) the hydrogen evolution reaction must be carried-out at relatively low overpotentials, (ii) it should ensure a good diffusion of hydrogen into the gas reception chamber, (iii) it must limit the proliferation of biomass on the cathode surface in contact with the liquid chamber, and (iv) it must be cheap enough to ensure practical implementation in wastewater treatment plants.
2. Architectural and reactor design issues must also be addressed. It is still not clear whether planar designs are preferred over cylindrical designs for wastewater treatment. In addition, manufacturing large MEC reactors (larger than 100 L) does not seem practical, and therefore the application of biocatlyzed electrolysis for wastewater treatment will require the use of arrays of MEC units to fit treatment demands. In this regard, it is still needed to find out which is the optimum arrangement of MEC units, and most important how they must be electrically connected (series vs. parallel).

8.3 CONCLUSIONES

Los tratamientos convencionales de aguas residuales (fundamentalmente aquellos basados en lodos activos) llevan asociado un elevado consumo de energía, lo cual está motivando a científicos e ingenieros de todo el mundo a buscar nuevas tecnologías capaces de reducir la huella energética asociada a la gestión de las aguas residuales. La electrolisis biocatalítica (EB) ha sido objeto de estudio en el presente trabajo, y representa una novedosa alternativa orientada a recuperar, en forma de hidrógeno, parte del contenido energético presente en la materia orgánica disuelta en las aguas residuales. Las siguientes conclusiones generales pueden ser extraídas a partir de los resultados expuestos:

1. La producción de hidrógeno mediante EB a partir de glicerol es un proceso viable, al menos desde un punto de vista técnico y bioquímico. La tasa de producción de hidrógeno obtenida fue similar a las observadas por otros investigadores durante la fermentación oscura del glicerol. Sin embargo el rendimiento de producción fue mucho más elevado, llegando a un 77% del valor máximo teórico. Además, la EB del glicerol asegura la producción de hidrógeno con consumos de energía inferiores a 5 Wh L_{H2}^{-1} (mínimo requerido para la producción de hidrógeno mediante electrolisis convencional).

2. Empleando glicerol como sustrato se proponen cargas orgánicas de 2,7 g-DQO L_a^{-1} d^{-1} y tensiones aplicadas de 0,75 V, como los parámetros de operación que permiten alcanzar un compromiso entre los objetivos de alta eficiencia energética y alta tasa de producción de hidrógeno.

3. Cuando la celda de EB fue alimentada en continuo con un efluente sintético de un proceso de fermentación, se observó que la tensión aplicada y el tiempo de retención influyen de forma interdependiente tanto en la eliminación de DQO como en la tasa de producción de hidrógeno. De hecho, la producción de hidrógeno mostró ser más sensible al tiempo de retención hidráulica (TRH) cuando las tensiones aplicadas fueron altas (1 V). Del mismo modo, un incremento de la tensión aplicada fue más efectivo a TRHs altos (12h) en lo que se refiere a la producción de hidrógeno.

4. La ausencia de una membrana polimérica entre ánodo y cátodo, favoreció la recirculación de hidrógeno entre ambos electrodos, lo cual limitó de forma significativa el rendimiento energético del proceso.

5. La eficiencia del tratamiento (eliminación de DQO) de un agua residual doméstica en una celda de EB alimentada en continuo se situó en un rango de entre un 44 y un 76% con un consumo de energía comparable o incluso inferior al que tradicionalmente se asocia a los tratamientos aerobios.

6. Sólo fue posible generar hidrógeno a cargas orgánicas por encima de 448 mg-DQO L_a^{-1} d^{-1} cuando el reactor de EB fue alimentado con agua residual urbana. La tasa de producción de dicho gas siguió un tendencia similar a la función de Monod, saturando en 0,3 L L_a^{-1} d^{-1} a cargas orgánicas por encima de 2.000 mg-DQO L_a^{-1} d^{-1}. Además, los resultados experimentales confirmaron la hipótesis de que la tensión óptima depende de la carga orgánica.

7. El tratamiento de aguas residuales urbanas mediante EB podría resultar económicamente viable si la densidad de corriente, el consumo de energía, y la tasa de producción de hidrógeno pudieran alcanzar 5 A m^{-2}, 0,9 kWh kg-DQO^{-1} y 0,8 m^3 m_a^{-3} d^{-1} respectivamente.

8. Dentro de los parámetros operacionales referidos en la conclusión anterior, el tamaño del reactor (volumen), su configuración (número de unidades de EB conectadas en serie dentro de un módulo), y el consumo de electricidad tienen relativamente poca influencia sobre la viabilidad económica de la instalación de EB.

9. El empleo de la EB para el tratamiento de aguas residuales estaría justificado desde un punto de vista económico si el precio de compra del reactor de EB estuviera en el rango entre 1.100-1.350 € m_a^{-3}

AGRADECIMIENTOS

Quiero mostrar mi agradecimiento más sincero a mi director de tesis, Antonio Morán, por haber confiado en mí, por su entusiasmo y firme apoyo, y por todo lo aprendido durante estos años trabajando a su lado; a Boris Tartakovsky por su paciencia, su buen talante y su constante apoyo a pesar de la distancia; a Diego M. García por su inestimable e incondicional ayuda, y en general a todos mis compañeros del IRENA y a aquellos que de un modo u otro han hecho posible que este trabajo sea una realidad. Gracias a todos.