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ORGANIC WASTE AND BIOELECTROCHEMICAL SYSTEMS: A FUTURE INTERFACE BETWEEN ELECTRICITY AND METHANE DISTRIBUTION GRIDS

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ABSTRACT

In a very near future, renewable electricity produced by photovoltaic and eolic is destined to be the cheapest form of energy. As these sources can't be constant in time, new industrial research challenges have already been shifted to electricity storage from the grid. Here we present an innovative concept of electricity storage system, based on the field of bioelectrochemical systems. Electromethanogenesis is one of the most recent applications in this field, where methanogenic microorganisms of the Archaea domain can fix CO_2 to methane, under electrical stimulation. In other words, electricity can be efficiently converted into CH_4, i.e. one of the most commonly used fuels, territorially-distributed with a capillary grid in most EU-Countries. What is needed, to implement this process, is a relatively concentrated source of CO_2 in an anaerobic acqueous environment. Currently in our society, huge concentrated streams of CO_2 are released into the atmosphere every day from wastewater and waste treatment facilities, as well as from landfills. To treat sewage and organic waste, organic matter is degraded to inorganic carbon, mainly by microbial oxidation processes, which are strongly energy-intensive. In perspective, every wastewater treatment, anaerobic digestion, organic waste composting facility and controlled landfill could be a key hotspot to transform excess grid electricity into biomethane, while treating waste with the same energy. Biomethane could be injected to the distribution grid and the waste-management facilities would become the interface between the two grids. To achieve this scenario, efforts in scaling up electromethanogenesis systems and new bioelectrodes materials (e.g. electro-active biochar) are needed. Here, we summarize some key steps in this field of research and the constraints that are to be overcome.

1. INTRODUCTION

In the near future, photovoltaics and wind turbines will be considered as primary sources of energy. Their cost and sustainability will soon stably meet the grid parity. Electricity storage capacity will be the real challenge, to buffer intermittent productions and consumptions (Breyer and Gerlach, 2013).

Traditional electricity storage capacities rely mainly on hydropower facilities (pumping). Batteries life cycle and sustainability have already been improving and their costs are also decreasing exponentially. Other technologies and solutions are urgently needed as alternatives to widen the spectrum of possible storage capacity for the electrical grid. Among a range of possible technological solutions, power-to-gas technologies have attracted attention. Water electrolysis to produce gaseous hydrogen as chemical energy vector (power-to-gas, P2G) has been proposed as the solution, to be coupled to fuel cell to reconvert H_2 into electricity. The abiotic electrocatalysis of the reaction $2H^+ + 2e^- \rightarrow H_2$ works theoretically at a cathodic potential of -0.410 V vs Standard Hydrogen Electrode (SHE, pH=7). However, in applications with high current-densities, according to the catalyst and the electrode properties, this reaction may require much lower potentials (-0.7 – 1 V vs SHE), due to consistent overpotentials of both cathodic and anodic reactions (Zoulias and Varkaraki, 2004). Also, safely handling,

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transporting and storing molecular hydrogen is still a technological unresolved challenge and too expensive to think about applications in the near future (Gahleitner, 2013).

An alternative option for more realistic applications is power-to-methane. The conversion of electrical current into methane (i.e. CO_2 methanation) has been for long proposed as alternative, considering that many Countries already count on a capillary methane distribution grid (Zoss et al., 2016). High-temperature and pressure catalytic power-to-methane conversions are the state of the art, but they encounter serious constraints in P2G applications: a) relatively small-scale plants are too expensive; intermittent use, as needed for day-night grid variations, are not viable; and large amounts of high purity CO_2 gas streams are required to avoid hindering the metal catalysts (Götz et al., 2016). Also, the territorially distributed availability of concentrated and pure CO_2 streams is not guaranteed, if we exclude fossil-based power plants.

Biological methanation has been proposed as an alternative for smaller-scale applications (Götz et al., 2016). Several methanogenic microbes of the domain Archaea are known to catalyze the reduction of of CO_2 to methane (autotrophic methanogenesis), in strictly anaerobic environments (Bapteste et al., 2005). Hydrogenotrophic methanogenesis, for example, has been longely known and it is widely used in full-scale anaerobic digestion (AD) facilities as one of the two main metabolic routes towards methane production from biomass (Hara et al., 2013; Premier et al., 2013). Electro-trophic methanogenesis (or electro-methanogenesis) was also recently discovered as an alternative path towards CO_2 reduction (Cheng et al., 2009a). Different innovative biotechnological applications of these biochemical pathway were proposed as options for methane generations by reduction of CO_2 through electrostimulation of methanogenic microbial communities in bioelectrochemical systems (BES) (Blasco-Gómez et al., 2017).

In this article, we discuss the future challenges and potentials of this innovative perspective and we propose a scenario for the integration of such technology in AD process.

2. BIOLOGICAL POWER-TO-GAS

Methanogenic microbes of the domain Archaea can catalyze the conversion of H_2 and CO_2 to methane (hydrogenotrophic methanogenesis), in strictly anaerobic environments. Electrochemical H_2 evolution by water electrolysis and subsequent H_2-sparging in anaerobic digesters (where the environment is saturated with biogenic CO_2) could be a smart solution for P2G at a territorial scale. Today, the EU counts on a year-by-year increasing number of anaerobic digestion plants sufficiently distributed on the territory (EURObserv'ER, 2014). Biogas upgrading to biomethane for injection to the methane grid is also a reality, both under technological and regulatory point of view (EURObserv'ER, 2014). In this scenario, the organic matter contained in waste or wastewater streams would be an inexpensive source of concentrated CO_2, which can be directly converted into biomethane by room-temperature/pressures and easily scalable processes.

Unfortunately, the first step of this transformation chain (i.e. water electrolysis in electrochemical cells, based on abiotic catalysts) is a relatively inefficient process. At cathodic potentials in the range -1 – -1.5 V vs SHE and current densities in the order of 1-10 kA/m^2, the electricity-H_2 conversion efficiency is currently around 4-5 kWh/Nm^3_{H2}. This is due to the high overpotentials of the cathodic electrocatalysis at such high current densities (Zoulias and Varkaraki, 2004). Even considering a stoichiometric conversion of this H_2 to methane:

$$4H_2 + CO_2 \rightarrow 2H_2O + CH_4$$

the electricity-CH_4 conversion efficiency would result of 16-20 kWh/Nm^3CH_4. Additionally, the final conversion efficiency would be even lower due to the low solubility in water of H_2 (Bo et al., 2014).

Also, water electrolysis suffers of poor efficiency in the counter reactions, at the anode. The use of water as electron donor, with O_2 evolution, is definitely not a thermodynamically favorable reaction (+0.82 V vs SHE, pH=7, Figure 1).

3. ELECTROMETHANOGENESIS (OR BIOELECTROCHEMICAL METHANATION)

To overcome these constraints, a new generation of biological methanation process was recently (year 2009) introduced and called Electromethanogenesis (Blasco-Gómez et al., 2017; Cheng et al., 2009b). It results from the integration of electrochemical systems and microbial autotrophic methanogenesis (hydrogenotrophic route). Electroactive microbial communities, grown as biofilms on solid electrodes, were demonstrated to be able of direct electron transfer towards the fixation of inorganic carbon to methane (Cheng et al., 2009b), following the reaction:

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$$

This reaction theoretically happens at a cathodic potential of -0.224 V vs SHE, i.e. it takes half of the energy, with respect to water electrolysis (Rabaey and Rozendal, 2010). This is well represented in Figure 1.

The most common microbial species able to perform this reaction belong to the Archaea domain and are normally found in regular anaerobic sludge in biogas-producing facilities. Direct electron transfers towards inorganic carbon fixation to methane, in fact, was demonstrated as a mechanism that happens in natural anaerobic environments, between different microbial species. The so-called DIET (direct interspecies electron transfer), mediated by membrane bound proteins and conductive extracellular filaments (called e-pili), was demonstrated between acetoclasts (e.g. Geobacter sp., Shewanella sp.) and methanogens (e.g. Methanobacterium sp., Methanosaeta sp., Methanosarcina sp.) (Holmes et al., 2017; Lovley, 2011). In few words, microbes create a network of nanowires to exchange electrons among different species. Where conductive solid materials are present, this connection is favored, as compared to water-suspended cells (Chen et al., 2014).

Additionally, if the electron flow is forced from externally imposed electrochemical potentials, methane

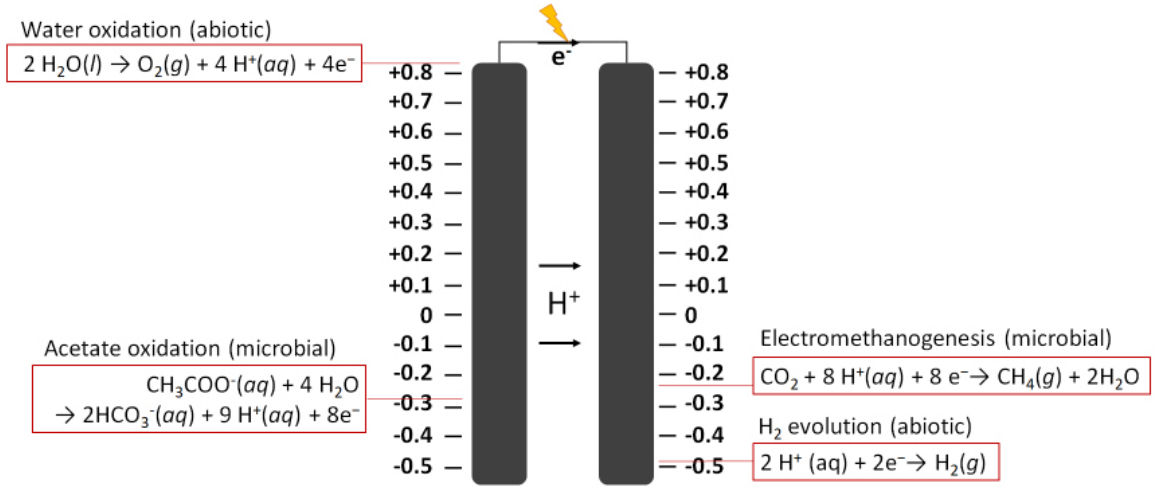

FIGURE 1: Electrochemical reaction standard potentials (E0, V vs standard hydrogen electrode, pH7) for anodic and cathodic main reactions in electromethanogenesis versus water electrolysis.

formation can be favored, even in absence of favorable electron donors, such as organic molecules (e.g. acetate) (Bajracharya et al., 2015). However, the thermodynamics of the system are favored when the electron donor at the anode is an organic molecule (Jadhav et al., 2017; Logan and Rabaey, 2012). In this case, the oxidation reaction is mediated by acetoclastic electro-active microbes, that discharge electrons to the conductive surface of the anode (Andrea Schievano et al., 2016; You et al., 2014). Acetoclastic methanogens were often found in anodic biofilms of bioelectrochemical systems (Rago et al., 2017; Rago et al., 2018) where they compete with electro-active microorganisms for the same electron donor (acetate). For this reason, several studies focused on different strategies for methanogenisis inibition in recent years (Chae et al., 2010, Rago et al. 2015).

4. ORGANIC WASTE AND BIOGENIC CO_2: THE NEW BATTERY

Important agro-industrial sectors by-produce huge amounts of wastewaters that in many cases are cause of environmental concerns and/or imply expensive and energy-consuming purification processes, using traditional technologies. Only in Italy, food-production sectors such as animal production, winery, olive oil and dairy by-produce nearly 200 million m^3 per year of polluted wastewaters (EUROSTAT, 2014). Nowadays, due to the high management costs related to proper disposal and treatment, this amount of polluted water is mainly spread to agricultural land as-it-is and/or, after inefficient purification processes, discharged to superficial/groundwater bodies. In many cases (ex. olive oil and winery wastewaters), the prolonged use of such high organic loads on agricultural soil implies decrease of soil fertility, eutrophication of water bodies and other environmental problems (Carey et al., 2016).

According to various reports, in the EU, as well as in the US, the electrical power consumption dedicated to wastewater treatment and water management is estimated in the range 2-5% of the total electricity consumption (McCarty et al., 2011). This corresponds to typical electrical consumption for aerobic activated-sludge process around 0.6 kWh/m^3 of treated wastewater.

If electromethanogenesis was implemented, in substitution to traditional aerobic treatments, at least half of this amount of energy (the fraction used for organic matter oxidation) could be completely converted into methane. Potentially, even higher amounts of reducing equivalents and CO_2 could be found in all solid organic waste to be treated in anaerobic digestion, composting and landfill plants. All these territorially-distributed hotspots of concentrated streams of biogenic CO_2, could represent a potential interface between the electricity network and the methane grid.

5. NEW CONFIGURATIONS OF ANAEROBIC DIGESTION

Two-stage anaerobic digestion process was suggested as an option to maximize the amount of energy recoverable from biodegradable organic waste in terms of hydrogen (H_2) and methane (CH_4) (Schievano et al., 2012; Venetsaneas et al., 2009). H_2 can be produced from organic materials in a process called dark fermentation (DF) (Manzini et al., 2015). Pre-treatments and a DF step (primary process) can be applied to enhance biomethane productivity of substrates, by increasing the overall biodegradability and equivalent balance. In DF, organic substances are hydrolysed and fermented by anaerobic bacteria to H_2, CO_2, and simple organic molecules such as volatile fatty acids (VFAs). Optimization of DF may lead to improved hydrolysis and therefore higher energetic exploitation of waste materials (Schievano et al., 2014).

The advantages of two-stage digestion systems, if compared to single-stage AD, are typically shorter substrate retention time, enhanced solids degradation efficiencies, enhanced hydrolysis with a subsequently higher CH_4 production and potentially higher organic loading rates (Pognani et al., 2015). In particular, the possibility of such biological process steps towards biogas upgrading (increasing CH_4 concentrations) to high-grade biomethane

for grid injection, rather renovates the interest of this kind of plant configuration. As part of CO_2 is 'stripped' together with H_2 during DF, CH_4 concentrations in a biogas produced by a secondary methanogenic reactor shows tipically higher CH_4 contents, as compared to a single-step AD (Pognani et al., 2015; Schievano et al., 2012).

Therefore, DF should act as primary process to obtain a highly bioavailable hydrolizate (rich in VFA) for secondary bioprocessing, such as bioelectrochemical conversions (A Schievano et al., 2016). Among others, the most interesting possibility is represented by electromethanogenesis (Blasco-Gómez et al., 2017), where CO_2 is fixed to CH_4 by electro-stimulated microbial communities, towards further increase in biogas CH_4 content. In the applications of electromethanogenic processes, CO_2 contained in the biogas is used as electron acceptor: the electron flow is forced from externally imposed electrochemical potentials and methane formation from CO_2 can be favored, either in presence or in absence of favorable electron donors, such as organic molecules (e.g. acetate). This opens two possible scenarios:

a) With O_2-evolution from H_2O as counter reaction, electromethanogenesis could be applied to a concept of bio-electrochemical power-to-gas, where peak electricity from the grid could be converted to methane by fixation of the excess CO_2 contained in the biogas. In this case, the total amount of bioavailable equivalents yielded by the dark fermentation step should undergo methanogenesis in the second stage of AD (Figure 2a), to maximize biogas (CH_4 + CO_2) production. This way, all CO_2 molecules are available to receive reducing equivalents from the electricity grid and be reduced to CH_4.
b) If bioavailable organic matter is sent to the anode, the thermodynamics of the system are favored, and the anodic oxidation reaction is mediated by acetoclastic electro-active microbes, that discharge electrons to the conductive surface of the anode (Schievano et al., 2016; Zhao et al., 2014). In this case, only a fraction of the total bioavailable equivalents yielded by the dark fermentation steps will be sent to the methanogenic AD stage

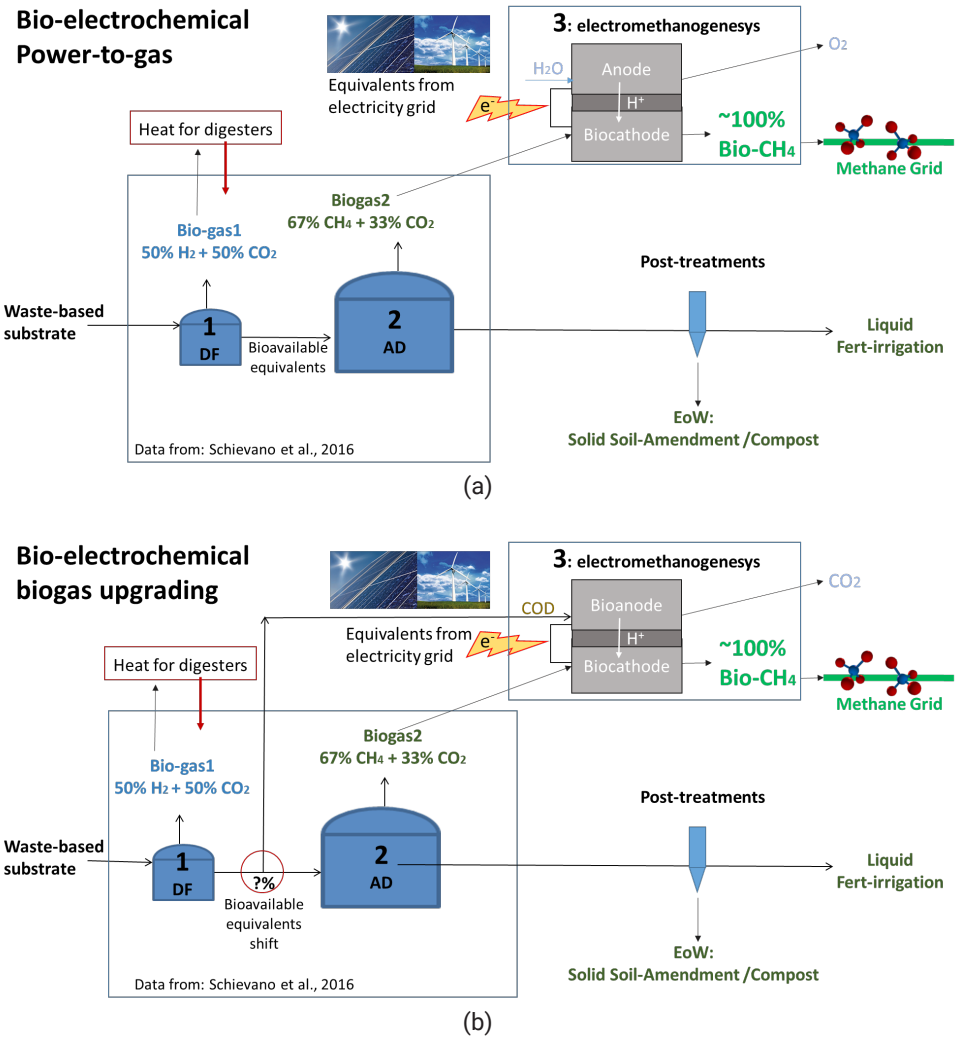

FIGURE 2: The concepts under investigation in this project: a) electromethanogenesis is used as bioelectrochemical power-to-gas system and all bioavailable equivalents yielded from dark fermentation are sent to AD methanogenesys; b) electromethanogenesis acts as bioelectrochemical biogas upgrading system and a fraction of bioavailable equivalents is sent to the bioanodic compartment, as counter-reactive.

TABLE 1: Electrode materials and characteristics of most performing lab-scale electromethanogenesis trials.

	Cathodic poised potential (V vs SHE)	Volumetric surface area m^2/m^3 reactor *	Current density A/m^2 *	Volumetric methane generation rate Nm^3/m^3 reactor day^{-1}	Current capture efficiency	Reference
Graphite fiber brush	-0.5	54	0.3	0.2 ÷ 0.3	96	(Cheng et al., 2009b)
Graphite granules	-0.8 – -0.9	1350	0.07	0.1 ÷ 0.3	75	(Batlle-Vilanova et al., 2015)
Carbon felt	-0.7	104	2.9	0.5 ÷ 1	80	(van Eerten-Jansen et al., 2015)

** total outer active surface area of the cathode, not including pores*

and the rest will serve as electron donors at the anode (Figure 2b). 'The right fraction of the total bioavailable equivalents might change significantly, depending on the type of biomass and the efficiency of both DF and AD. This particular point should be object of future research efforts. Under such conditions, the three-stage AD process can serve as a bio-electrochemical biogas upgrading system, because CO_2 can be fully converted to CH_4, with minimal external power supply. In such systems, the typical electrical power consumption is of 0.1 – 0.2 kWh/kg BOD removed, with cathodic conversion efficiency of power to methane in the range of 0.3 – 0.5 kWh/Nm^3_{CH4} (Blasco-Gómez et al., 2017).

6. LARGE-SCALE BIOELECTRODES: ELECTRO-ACTIVE BIOCHAR?

Typical current densities of electromethanogenic systems are of the order of 0.1 – 1 A/m^2, i.e. 3 – 5 orders of magnitude lower than those of commercial abiotic water electrolysis systems. Finally, the counter reaction at anode (oxidation) can be also bio-electrochemical: as in microbial electrolysis cells, waste organic matter coming from waste and wastewater streams can be oxidized, with much higher thermodynamic gain, as compared to water oxidation to O_2. In such systems, the typical electrical power consumption is of 0.1 – 0.2 kWh/kg BOD removed, with cathodic conversion efficiency of power to methane in the range of 0.3 – 0.5 kWh/Nm^3_{CH4} (Blasco-Gómez et al., 2017). In Table 1, we report the most successful materials used to design electrodes and their main characteristics.

The major challenge to scale up applications of this biotechnology consists in the fabrication of electrodes, with high geometric surface area per volume of bioreactor (of at least 10^2 m^2/m^3). In fact, to counterbalance the low current densities, as compared to abiotic water electrolysis processes, an electrode should have enough surface area where the microbial reactions happen.

New low-cost and biocompatible conductive materials with such characteristics are currently under study (mostly based on graphite and char-coal derived from biomass pyrolysis) in many laboratories. Depending on different properties, such as quinone and aromatic structures, the degree of graphitization, high porosity and the presence of different superficial heteroatoms, biochar can be redox-active and electrically conductive (Kloss et al., 2012). It was recently demonstrated how biochar acts as soil-fertility promoter, not only indirectly by changing the soil structure and chemistry, but also by directly mediating electron transfer processes, i.e., by functioning as an electron shuttle (Kappler et al., 2014). In this experiment, effective biochar stimulated microbial reduction of the Fe(III) oxyhydroxide mineral ferrihydrite by Shewanella oneidensis (a well-known electro-active prokaryote). Meanwhile, Chen et al. demonstrated that biochar act as promoter of direct interspecies electron transfer for different syntrophic associations of microorganisms, thanks to its electrical conductivity and stimulating the capacity of extracellular electron transfer by pili or other direct membrane mediators (Chen et al., 2014). Swarnalakshmi at al. recently prepared a cyanobacterial-biofilmed (Anabaena) bio-fertilizer based on charcoal and soil, containing Azotobacter, Mesorhizobium, Serratia and Pseudomonas strains (Swarnalakshmi et al., 2013). Enhancements of up to 50% of nitrogenase activity were observed, as compared to control experiments.

A recent study, applied biochar to AD, demonstrating how the mere presence of 25 $g/L_{reactor}$ of biochar, derived from pyrolysis (500 – 800°C) of different ligno-cellulose biomass types, significantly improved AD process of food waste fermentate (Cruz Viggi et al., 2017). Other studies reported that several methanogenic communities are favored by the presence of biochar (Lü et al., 2016; Mumme et al., 2014).

Biochars are typically characterized by high BET specific surface areas, in the range of 10-100 m^2/m^3. Depending on the distribution of such area versus pore diameters,

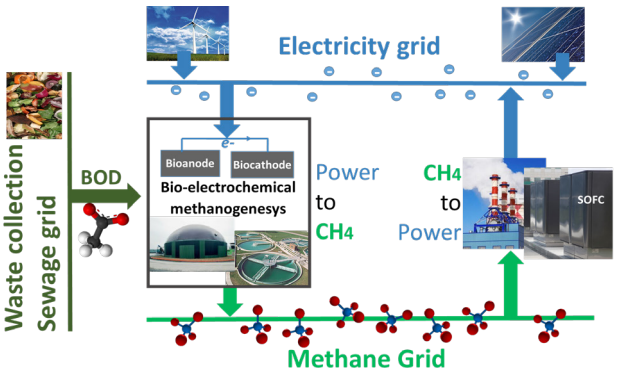

FIGURE 3: Scheme of the potential interface between the electricity and methane distribution grids, based on converting all organic waste/wastewater treatment facilities into Electromethanogenesis units.

this surface might be available to microbes for extracellular electron transfer, and thereby work as a bioelectrode. Deeper studies are needed, to understand the potential use of biochar as low-cost substitute of highly technological materials such as carbon fibers or graphite, for the fabrication of large scale bioelectrodes, to be used in AD systems.

7. PERSPECTIVES AND CHALLENGES

In a near future, every single anaerobic digestion plant, landfilling site, wastewater treatment plant will be a potential spot for a highly efficient interface between the electricity and the methane grids (Figure 3); while treating waste organic matter "for free". This field of research is still in its infancy. However, the results obtained by several studies, even at a real-scale, promise near-future application of this concept. The main issues related to the process scale-up are given by the choice of the electrode materials and the reactor design. The use of electro-active biochar, as material for the development of large-scale high-surface area electrodes, is one of the most promising path of research and development for success in this field.

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