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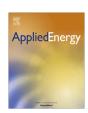
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## Low pH, high salinity: Too much for microbial fuel cells?

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#### HIGHLIGHTS

- Microbial fuel cells fed by solid organic waste.
- Harsh environmental conditions in the MFC feedstock.
- Power production even at very low pH and high salinity.

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#### ABSTRACT

Twelve single chambered, air-cathode Tubular Microbial Fuel Cells (TMFCs) have been filled up with fruit and vegetable residues. The anodes were realized by means of a carbon fiber brush, while the cathodes were realized through a graphite-based porous ceramic disk with Nafion membranes (117 Dupont). The performances in terms of polarization curves and power production were assessed according to different operating conditions: percentage of solid substrate water dilution, adoption of freshwater and a 35 mg/L NaCl water solution and, finally, the effect of an initial potentiostatic growth.

All TMFCs operated at low pH (pH =  $3.0 \pm 0.5$ ), as no pH amendment was carried out. Despite the harsh environmental conditions, our TMFCs showed a Power Density (PD) ranging from 20 to 55 mW/m<sup>2</sup> kg<sub>waste</sub> and a maximum CD of 20 mA/m<sup>2</sup> kg<sub>waste</sub>, referred to the cathodic surface.

COD removal after a 28-day period was about 45%.

The remarkably low pH values as well as the fouling of Nafion membrane very likely limited TMFC performances. However, a scale-up estimation of our reactors provides interesting values in terms of power production, compared to actual anaerobic digestion plants. These results encourage further studies to characterize the graphite-based porous ceramic cathodes and to optimize the global TMFC performances, as they may provide a valid and sustainable alternative to anaerobic digestion technologies.

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#### 1. Introduction

The quest for sustainable and efficient energy sources has been the object of great research efforts in the last decades [1,2]. Along with the increasing need of a more sustainable waste management, new approaches able to combine waste treatment with energy recovery can contribute to the establishment of a green economy [3–6]. Generally, waste-to-energy technologies based on incineration, gasification or anaerobic digestion are recommended for large-scale plants, to produce thermal energy or to convert waste in biogas, syngas and other secondary fuels [3,4,7]. Nevertheless,

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the large part of these processes do not require the selection of incoming waste, with a consequent, unavoidable production of pollutants, toxic leachate, ash and greenhouse gases [8]. The treatment of such pollutants makes the management and control of these processes complex and expensive [9,10].

In this context, bio-reactors based on natural processes like fermentation and/or methanogenesis, can play an important role towards the establishment of a more sustainable waste management. Microbial Fuel Cells (MFCs) are based on the ability of microorganisms to use inorganic compounds as electronic acceptor to obtain electric power directly from microbe metabolism, without any combustion. Recent researches confirm the potential of such systems in turning "waste" into a "resource", by treating different types of substrates and even recovering by-products with a non-negligible economic potential [6].

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As biomass-based systems, MFCs (like other Bioelectrochemical Systems) are considered carbon neutral: the bio-transformation of organic matter into chemicals through microbial metabolism, in fact, prevents the primary production of CO<sub>2</sub> emissions. Moreover, MFCs do not involve CH<sub>4</sub> production and combustion, as opposed to traditional anaerobic digestion plants. Thus, this newborn technology is characterized by remarkable features: the direct electrical power production, the conversion of the chemical energy contained in any form of biomass [11], low environmental impact, low operating temperatures and simple architectures [12]. All these characteristics, together with the environmental advantages ingrained with this technology are supposed to largely overcome the costs for MFC development and implementation [6].

However, even though a wide number of papers deals with the set-up and the study of MFCs fed with wastewaters, few attempts to apply this innovative technology to solid organic waste treatment have been carried out. In 2011, Mohan & Chandrasekhar studied the operational factors affecting the performances of MFCs fed with canteen food waste, focusing on electrodes distance and feedstock pH [13]. After this seminal work, other researchers started working on the application of MFCs to the Organic Fraction of Municipal Solid Waste (OFMSW) using different approaches, but all confirming the effectiveness of MFC technology as tool for energy recovery and organic load removal from OFMSW [6]. MFCs, in fact, represent a valid alternative to achieve small-scale, distributed and efficient conversion of organic waste into electricity [14], even in developing Countries, where solid waste is often dumped rather than landfilled.

Nevertheless, the industrial implementation of this technology is still challenging [15,16]. The use of solid or liquid food waste in MFCs generally leads to anodic environmental conditions highly unfavorable for bioelectricity production, due to low pH and high salinity and, as a consequence, high ionic strength [11,17–19].

Thus, the scale-up of reactors, necessary for industrial power applications, is limited by several issues, so that further research is required to improve the reactor geometry, the economic feasibility and the response of the system to unfavorable conditions. In our previous works, we assessed the possible adoption of MFC technology for the treatment of OFMSW, highlighting the importance of appropriate reactor layout and electrode design, in order to minimize the internal resistance [20–23].

In this work, we explored the efficiency of tubular single-chambered, air-cathode MFCs (TMFCs) fed by a feedstock composed of vegetable and fruit slurry. All MFCs were provided with Nafion membranes adhering to the cathode, which was realized by means of a graphite-based porous ceramic disk: this innovative material was ad hoc designed and realized in order to be used in scaled-up MFCs, as well. Power production was studied as a function of different parameters, such as solid substrate inoculum, liquid-to-solid ratio, salinity of amending solution and the adoption of a preliminary potentiostatic growth phase. An ad hoc measurement set-up has been realized to test the MFC reactors in order to prove evidence of their feasibility and reliability in standard and also harsh anodic environment.

#### 2. Materials and methods

#### 2.1. TMFC assembly

Twelve tubular MFC bioreactors, adapted from [24,25,20], were realized by using standard 50 mL polypropylene Falcon test tubes, supplied by BD Corning Inc. (Tewksbury, USA), sterile and suitable for biological cultures. Two 20 mL Falcon tubes were used to sample the organic feedstock and to monitor pH (see Fig. 1).



Fig. 1. Layout of the tubular MFC, realized by means of one 50 mL and two 20 mL Falcon test tubes.

The electrodes were made by carbon-fiber anode brush, realized with a high strength carbon fiber from FIDIA s.r.l. (Perugia, ITALY) and unpolished stainless steel wire (ASTM A313) with 0.5 mm section, while for the cathode a porous ceramic disk was developed starting from graphite powder type GK 2 Ultra-fine, by AMG Mining AG (Hauzenberg, Germany). The brush anode had an estimated surface area of 0.22 m²/g while the cathode disk had a surface area of 60.75 m²/g [24], (Fig. 2(b)). The electrodes were placed at a distance of  $\sim 3$  cm. A standard Nafion 117 membrane by DuPont Inc. (Richmond, USA [26]) was used to seal the porous cathode.

#### 2.2. Data acquisition system

The data collection hardware was based on the Arduino board MEGA 2560 [27], composed by a load array (for polarization curve acquisition) with 6 resistors, ranging from  $\sim 10^6~\Omega$  to  $\sim 10~\Omega$ . The software for data acquisition was developed with LabVIEW Interface For Arduino, (LIFA) package. Fig. 3 sketches the acquisition system and the measurement chain.

#### 2.3. Experimental setup

Apples, pumpkins, chickpeas and zucchini in a 1:1:1:1 ratio were used to prepare a slurry by mechanically mixing the vegetable residues with water (see Table 1 for the details of water composition).

In order to verify the effect of salt concentration on TMFC performances, six reactors were filled with a slurry prepared using fresh water; in the other six cells, a NaCl solution (35 mg/L NaCl) was added to improve the slurry conductivity and test TMFC performances in presence of high Na<sup>+</sup> concentration, as salts concentration can increase, in leachate, along with the organic matter degradation [11,17–19].

The Liquid-to-Solid ratio, and the specific conditions used in each cell are reported in Table 2. Cells 4, 5 and 10, 11 have been added with spent substrate (10% of the overall feedstock) from TMFC reactors filled with the same organic substrate and previously operated for a 28-day period.

Cells 1, 2, 3, 6, 7, 8 and 9 were filled with 30 g of solid waste and 30 g of water, while cells 4, 5, 10, 11 and 12 were filled by 15 g of solid waste and 45 g of water, to obtain the desired Liquid-to-Solid

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