LONG TERM FEASIBILITY STUDY OF IN-FIELD FLOATING MICROBIAL FUEL CELLS FOR MONITORING ANOXIC WASTEWATER AND ENERGY HARVESTING

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1. Abstract

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 In the present work different prototypes of floating MFCs have been tested in anoxic water environments of wastewater plants in Italy, over a period of 3 years. Several configurations of horizontal (flat) and vertical (tubular) MFCs were assembled, using low-cost and light-weight materials, such as plastic lunch boxes, polystyrene or wood to keep the systems afloat, and ceramics for the MFCs. Untreated carbon cloth or veil were used for both anode and cathode electrodes. Felt (flat MFCs) or clay (tubular MFCs) was used as the cation-exchange separator. Single flat MFCs generated power up to 12 mW/m² while a 32 cylindrical MFC stack generated up to 18 mW/m². The testing lasted for more than two years and there was no inoculation other than exposing the MFCs to the denitrification environment. The cathodes of the flat MFCs were spontaneously colonized by algae and plants, and this did not affect the stability of the systems. Natural light increased the power output of the flat MFCs which were smaller than 50x50cm. Diurnal oscillation of temperature and periodic water flow did not significantly affect the performance of the MFCs. The largest flat MFC produced the highest absolute power, although in a disrupted way. A new, simple low-energy remote monitoring system, based on LoRa technology was used for data transmission over distances of >500m. This is a piece of hardware that could potentially be suitable for remote monitoring as part of a network, as it can be directly powered by the deployed MFCs.

Index Term: Floating Microbial fuel cells, long term field operation, wastewater monitoring, low-energy remote data transmission.

Highlights:

- Prototypes of floating MFCs producing power for energy harvesting in anoxic wastewater
- 0.4 3 mW (0.2-0.6 V) was generated by the MFCs connected to a DC/DC converter
- More than two years continuous operation of tubular MFCs set in floaters
- Large flat MFCs more productive than a set of smaller flat MFC of equivalent electrodes surface
- 38 Light cycle strongly influences the productivity of small flat MFCs
- 39 Floating MFCs as energy autonomous sensors of biodegradation for remote monitoring systems

2. Introduction

The biotechnological purification of wastewater is based on complex and strictly interconnected physicochemical and biological processes. The efficiency of the process is achieved only through careful and correct control of crucial parameters, such as nutrient content, organic loading and aerobic/anaerobic conditions. Therefore, regular measurement of physicochemical parameters such as temperature, water flow, dissolved oxygen, organic load is regularly carried out in wastewater treatment plants (WWTPs). The concentration of biodegradable organic matter is the most important parameter of the process, which would require closer monitoring. The frequency of analysis is governed by the instability of the system operation, which is normally more pronounced in smaller treatment plants where the demand for a greater number of controls is often challenged by the availability of resources (human and technical ones). On-line monitoring devices are often used in modern WWTPs, depending on their dimensions, practice and available resources (Bourgeois

et al. 2001), whereas the strict control of the water treatment in emerging economies is often unsustainable, if at all supported. Nevertheless, sensing is becoming increasingly important as a function performed to protect and preserve natural ecosystems, whether in developed or emerging economies.

There are currently numerous sensing technologies that are being used for monitoring different environmental parameters, many of which can operate for prolonged periods. The cost however, could be disproportionately high for those WWTPs also requiring strict maintenance regimes, high energy and plenty of consumables. In this context, Microbial Fuel Cells (MFCs) are a promising technology with the dual purpose of harvesting energy and sensing aquatic environments, especially but not exclusively wastewater. Several sediment MFCs have been previously investigated (Reimers et al. 2001) and a MFC-powered rowing float (called Row-bot) has also been recently reported for wastewater environments (Philamore et al. 2015), which is based on the EcoBot principle of operation (Ieropoulos & Melhuish 2005; Ieropoulos et al. 2010)). Several other laboratory experiments confirmed the possibility of using MFCs as sensors for biodegradation in the water (Tront et al. 2008; Kim et al. 2003). The challenge however remains as one of scale up for selfpowering MFC sensors for water quality and establishing real environmental (even remote) monitoring networks, where electricity may not be available. More recently floating systems (Schievano et al. 2017; Martinucci et al. 2015) have also been proposed, with promising results. The low concentration of biodegradable organic matter (10's of mgL⁻¹ COD) dissolved in the water of the anoxic tank strongly limits the power production of this kind of MFC (Martinucci et al. 2015). The scaling up of such simple systems, based on microbial catalysis at anode and cathode, would be needed in order to be performing well enough for the desired objectives (power and sensing), optimizing the cell geometry and connecting in series parallel several MFC units (Ieropoulos et al. 2008).

In the present study, the performance of floating MFCs suitably designed for anaerobic water environments was tested both for energy harvesting and sensing purposes, in long-term experiments (more than three years) in denitrification tanks of WWTPs, as part of a longer term study (Martinucci et al, 2015). A particular focus was the selection of low cost and readily available materials, parts, electronic components and open-source software, for the purpose of wastewater monitoring and for a possible development of monitoring networks, acknowledging the sense of emerging "citizen science" of the industrialized world (Wildschut 2017). Different designs and geometries of flat and tubular cells were investigated, with electrodes assembled in horizontal and vertical configurations, using plastic lunch boxes or polystyrene to keep the system afloat in contact with the anoxic wastewater. The MFC configuration was based on carbon electrodes avoiding any chemical catalysts or pretreatment, and a simple inert separator (polypropylene or ceramic) between anode and cathode (Figure 1). Experiments were carried out in two Italian WWTP, at the Milano-Nosedo WWTP (2014-2018) and subsequently at the Carimate WWTP (2017-2019). Milano-Nosedo is the largest WWTP serving a population of 1.25 million in the city of Milan, whereas Carimate is one order of magnitude smaller, but with similar aerobic and anoxic treatment processes. Previous work performed with the same flat MFC configuration at the same Milano-Nosedo WWTP demonstrated the possibility to produce energy from such MFC configurations (Martinucci et al. 2015) and higher power densities were achieved reducing the electrode area from 0.125 m² (40 x30 cm) to 0.03 m² (20 x 15 cm). The present study was conducted with the aim of in situ assessing such MFC systems in producing power and sensing, whilst exposed to the elements (diurnal cycle, weather conditions) and water parameters (temperature, flow, organic content, etc.). A new generation of low-energy remote data logging system (LoRa) was also developed and integrated into the electronic circuitry, to utilise the generated power from MFCs and transmit signals over long distances; the near-term vision is that such systems become an integral part of a full MFC sensing package for remote area access and telemetry.

3. MATERIALS AND METHODS

Experiments

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Several flat MFCs units of different dimensions were operated in a denitrification anoxic pool at the Milano-Nosedo WWTP during a trial period of more than three years (2014-2017). Some flat MFCs units were operated as individual units and the output was monitored through a resistance of $100~\Omega$ while other units, usually the better performing, were occasionally disconnected from the resistance and connected in parallel with other units, to harvest the generated energy (data not shown). A schematic representation alongside photos to illustrate the system are shown in Figure 1A and 1B. Another long term testing of 6 flat MFCs with small electrodes and anodes short-circuited all together was operated in the anoxic basin of a different WWTP located at Carimate (Milano, Italy) since June

2017, for about one year. The generated electricity from these MFCs was also monitored through a connected 100Ω electrical resistance.

Several tubular MFCs inserted in a polystyrene frame shaped as a boat were also tested close to the flat ones in the same denitrification anoxic pool at Milano-Nosedo WTTP (Fig. 1C-E). The tubular ceramic MFC units shown in the picture and diagram of Fig. 1C were connected in two different floating stacks, one with 16 MFC units (Small boat, Figure 1D) and the other with 32 MFC units (Big boat, Figure 1E). All the MFCs units of each boat were electrically connected in parallel using stainless steel wire and terminal blocks and an external resistance of $100~\Omega$ was connected between them. The small boat (16 tubular MFCs) was introduced into the Milano-Nosedo WTTP since 2014, close to the flat MFCs of various geometries and was removed in 2018, after more than three years of continuous operation. The big boat (32 tubular MFCs) started to operate at the beginning of March in 2016 and was removed with all the other MFCs in 2018. The different geometries of flat MFCs were operated in the same period.

The trends of power generated in long time experiments by the different flat and tubular MFCs, summarized in Table 1, are discussed in this work. The flat MFC geometries tested at Milano-Nosedo WWTP are named: Flat-large (one, with 50x50 cm electrodes), Flat-medium (four, with 18x18 cm electrodes) and Flat-small (six, with 10x13 cm electrodes). Six more Flat-small MFCs with anodes electrically connected together were the ones tested at the Carimate WWTP.

Table 1. Characteristics of the MFCs types

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Type, materials	Electrodes Geometry	Name	Number
Flat, carbon cloth electrodes and PPE felt (1cm)	50 x 50 cm	Flat-large	1
Flat, carbon cloth electrodes, PPE felt (1cm)	18 x 18 cm	Flat-medium	4
Flat, carbon cloth electrodes, PPE felt (1cm)	10 x 13 cm	Flat-small	6
Flat, carbon cloth electrodes, PPE felt (1cm)	10 x 13 cm	Flat-small	6
anode shorted all together			
Tubular, terracotta (thickness=0.2cm L=7cm,	Anode: 280 cm ²	Small boat	16
d=1.5cm), filled with activated carbon	Cathode: 20 cm ²		
(cathode); anode in carbon fiber outside			
Tubular, terracotta (thickness=0.2cm L=7cm,	anode of 280 cm ²	Big boat	32
d=1.5cm), filled with activated carbon	cathode of: 20 cm ²		
(cathode); anode in carbon fiber outside			

A detailed description of the Milano-Nosedo WWTP, one of the largest plants in Europe, for 1,250,000 Population equivalent (PE) and water parameters, has been reported previously (Martinucci et al, 2015) . In brief, the anoxic water is characterized by an incoming BOD₅ of around 170 mgL⁻¹ reduced through biodegradation for 99% (< 5 mgL⁻¹ outlet); an incoming COD of about 300 \pm 100 mgL⁻¹ and COD less than 15 mgL⁻¹ in the outlet. The residual COD concentration in the anoxic tank is around 20 mgL⁻¹ measured on a filtrated (0.45 μ) sample, excluding the activated sludge.

The Carimate WWTP is a smaller waterworks facility and serves about 70,221 inhabitants in an area close to Milan, producing about $5.000.000 \, \text{m}^3/\text{y}$ of wastewater. Part of the treatment is for industrial wastewater, which is about $1,000,000 \, \text{m}^3/\text{y}$ and which corresponds to $4,000-5,000 \, \text{m}$ more population equivalent, (as BOD_5). The dissolved COD in the anoxic wastewater of this plant is a little higher than in Milano-Nosedo plant, usually ranging between $10-80 \, \text{mgL}^{-1}$.

Flat MFCs fabrication

Schematic diagrams for the flat MFC are presented in Fig. 1A. The two electrodes of each MFC had the same area and were placed parallel to each other at a distance of 1 cm, separated by a polypropylene (PPE) felt. The cathode and anode were both made of carbon cloth, which was free of any chemical catalyst (cod. SCCT-8, SAATI, Legnano, Italy). An electrical resistance of $100~\Omega$ was connected in the external circuit of each MFC, between anode(s) and cathode.

Tubular ceramic MFCs building

Tubular MFCs were assembled using terracotta cylinders (L=7 cm, d=1.5 cm, thickness 0.2 cm) that were sealed at one end with a plastic stopper. The anodes were made from carbon fiber veil (280 cm² per MFC) that was folded, wrapped around the cylinder and secured with stainless steel wire (Figure 1C). The cathodes

made of activated carbon as previously described (Gajda et al. 2015) were inserted into the cylinders and connected with stainless steel crocodile clip to the wire. A 10 mL plastic syringe was attached to the top of the ceramic cylinder in order to fit the MFCs into the floating 'boat'-like polystyrene material. In this way, the activated carbon is exposed to air through the open top connected to the syringe in the floating part of the boat.

Data acquisition and transmission

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For each tested flat MFC, the voltage V through the R ($100~\Omega$) resistance was recorded every 10 min, using a multichannel data logger made with Arduino hardware and open source software, as described in Supporting Information (Figure 1S). The generated power P (V x I), where I is the current flowing through the external resistance R, was calculated using Ohm's low (V=I x R). The data acquired were then transmitted using a LoRa low energy transmission system described in Figures 1S and 2S, which was set up and tested for data transmission over distances of >500 m.

RESULTS AND DISCUSSION

Both the flat MFCs and the tubular MFCs types were immersed in the denitrification tank without prior inoculation. The electrode facing the anoxic water quickly developed a biofilm fueled by the residual organics dissolved into the water in contact with the electrode. In the case of the flat MFCs whose electrodes were separated though a porous PPE felt, without any electrolytic membrane, biofilm grew also on the cathode sustaining the catalysis of the cathodic reaction (biocathode). Previous works on laboratory based systems reported that the air breathing biocathode of single chamber and membraneless MFCs using the same anoxic wastewater from Milano-Nosedo plant quickly become anaerobic developing a biofilm rich of bacteria of the sulfur and nitrogen cycles (Guerrini et al. 2014; Rago et al. 2017). The same microrganisms differently enrich the anode and the cathode, but alone or in synergy with other microorganisms, such as Spirochetes and photosynthetic anaerobic bacteriaare able to sustain a good cathodic catalytic activity using atmospheric oxygen just as the end-terminal electron acceptor (Cristiani et al. 2013). This mechanism allow the flat floating MFCs to perform in the anoxic tank. The development of the biofilm at the cathode was inhibited in the case of tubular ceramic MFCs, as the ceramic porosity does not allow the passage of bacteria (Rago et al. 2018), but also due to the fact that the internal cavities of the ceramic cylinders were not directly exposed to the anoxic water. The cathodic operation in this case was facilitated by the activated carbon, whose cathodic catalytic properties, which are higher than the plain carbon cloth, have been well documented (Anon 2017; Dong et al. 2012; Gajda et al. 2014; Wei et al. 2012).

MFC power performance

The power output from the flat and tubular MFC systems (boats) floating in anoxic wastewater, over a long period of time, is shown in Figures 2-7. The lack of data in Figure 2 (May 2016) is due to technical issues with the data acquisition system and is not an indication of the MFCs ceasing to work. The data shown represent significant parts from the whole 3-year operational period. After approximately 2 weeks from the initial immersion, all the MFCs reached a maximum voltage, varying between 0.2 - 0.5 V depending on type. In the case of the small boat, a peak voltage of 0.7 V (about 2 mW of power) was produced within the first month of operation (Figure S1 of supplementary information). Output levels suddenly dropped, before stabilizing, possibly due to humidity, which would have caused short-circuiting and the uptake of atmospheric oxygen. The small boat had been generating power in the range of 0.04 - 0.31 mW, showing power density up to 9.6 mW/m² especially during the first period of the operation, although not continuously. Performance however dropped continuously in the second year, when the Big boat was put side by side (Figure 2), which outperformed the smaller boat. The big boat MFCs, swiftly reached a power output of 1.15 mW in November 2015 and reached about 0.9 mW (Figure 2), corresponding to a power density of 14 mW/m² and continued to generate power with a similar trend during the whole experimental period. The better performance of the big boat, compared to the smaller one, is not simply due to the higher number of MFCs connected in series/parallel (32 instead of 16) alone, but also due to the fact that the MFCs in the small boat had probably undergone cathode clogging due to moisture penetration and sludge accumulation resulting from water splashes, as it was operating for a longer period of time. Hence, the decrease in the oxygen supply to the cathode had probably caused the decrease of MFC performance.

The flat MFCs required slightly longer periods to start power generation, but all reached a peak in less than one month from the immersion. The Flat-large MFC produced higher absolute power, with peaks of 3 mW (Figure 3) corresponding to a density of 12 mW/m², which were more evident over weekly rather than

daily periods. Nevertheless, a minimum of approximately 0.4 mW was consistently generated. Oscillation trends were already shown in previous experiments (Martinucci et al. 2015), and it was particularly highlighted in smaller flat MFCs (Figures 4-7).

Figure 4 shows the trend of power produced by 4 identical flat-medium MFCs during about 4 months of continuous operation. The maximum peak power (1.5 mW) was almost half compared to Flat-large MFC with a similar power density (12 mWm²), since the total electrode area (1296 cm²) was approximately half. On average, the performance was generally inferior. The inferior performance, more marked in the case of the Flat-small MFCs, can be attributed to a high variability of the power produced by the single MFCs (Figure 2S of supplementary information). Indeed, the performance between the four MFCs was inconsistent with some producing less power than others, in this way negatively affecting the power density. The power trend produced from 6 of this MFC type is shown in Figure 5. The power produced peaked at 0.5 mW, corresponding to a power density of 6.4 mWm², which was inferior to the larger ones.

Figure 6 shows three (out of six) of the better performing Flat-small MFCs, which produced 13.6, 9.4 and 4.6 mWm² respectively. These results point to a severe concern regarding the achievement of a stable power from the smaller MFCs for energy harvesting. In fact, the problem of spatial distribution and stability affected these flat MFC more than the others, especially in cases of storms and pronounced changes of water flow. The increased rate between perimeter and area characterizing the electrodes of the smallest flat MFCs resulted in the anaerobic conditions becoming rate limiting for the anode, which operated next to the water surface. Consequently, the possibility of polarity reversal of the cells has to be taken into account for these MFCs, causing the decay of produced power. A phenomenon such as this is reported in Figure 6, documented in the power trends of the six Flat small MFCs operating in the Summer of 2017.

MFC output vs temperature and water flow

The generated power by the tubular MFCs on the boat and the relationship with temperature and water flow (Q) measured at the plant inlet during the same period of time is reported in Figure 2. The variation of power appears to be affected by the large variation of flow rate that was consistent with the adverse weather events (mainly rainfall and storms) which diluted the incoming wastewater whilst increasing the flow causing temporary decreases. No direct correlation of power with the water temperature is noticeable, neither for the diurnal cycle, nor for the whole experimental period. Nevertheless, the MFC performance decreased to very low levels during winter time, when the environment temperature generally dropped below 15°C impacting on the temperature of the first layer of water. This result is consistent with mesophilic bacterial metabolism, which has an optimum between 20 – 35°C, in the context of the Arrhenius law of temperature. The daily oscillation of power from both Small and Big boats were negligible, like in the case of the flat MFC with much larger cathodes (Figure 3). In fact, cylindrical cathodes of the boats were not exposed to light since they are positioned inside the terracotta cylinder and immersed in water. The observed increases in power can be consequently, correlated with the diurnal cycle and also with the concentration of organic substance through the anodes. Also the power oscillations of Flat-large MFC are only marginally dependent on the temperature and water flow as for MFC boats (Figure 3). In fact, the decay in performance was mainly coinciding with periods of intense rain and other events that significantly diluted the dissolved organic substance, changing organic load in the stream.

The daily power oscillations of Flat-medium MFCs are evidenced in Figure 4, which is also highlighted in the zoomed graph of the power trends of the single MFCs during ten days of June 2015. This graph shows for all the four MFCs a daily variation of power much more pronounced than the weekly or multi-day variation, which results synchronized with the sun hours and the variation of flow rate rather with the temperature variation. The same oscillating behavior was noticed for Flat-small MFCs (Figures 5-7). Daily power trends of Flat-small MFCs (three of six) and of both boats during a single day are shown in Figure 6 with Temperature, Q and COD concentration of the wastewater sampled at the plant inlet (20-21 June 2017). The graphs show that the MFC performance improves concurrently with daytime, the increase of the COD dissolved and the increase of water flow. A noticeable power peak for the Flat-small MFCs is, in fact, in advance of hours with respect to the water temperature variation.

It could be inferred that the cathode electrode was limiting in the case of small size MFCs, not able to sustain the anodic oxidation, especially when anodes are exposed to very low levels of substrate (10-20 mg/L COD). The presence of microalgae could favor the local increase in the concentration of oxygen on the cathode resulting in higher power output (Gajda et al., 2015) when exposed to light, and higher power over the long term. Also a contribution of photosynthetic microorganisms in producing the power could be responsible for MFCs performing well during the hours of solar radiation. Several microorganisms as well

cyanobacteria could be involved, as reported in the literature (Rosenbaum et al. 2010; Huarachi-Olivera et al. 2018). For instance, purple non sulfur bacteria were frequently detected in biocathodes of single chamber microbial fuel cells (Cristiani et al. 2013) during previous tests performed at laboratory level using the same wastewater from the nitrification tank of the Milano-Nosedo WWTP (Cristiani et al. 2013; Rago et al. 2017). This aspect deserves further investigation in any future analyses.

It may be finally noted that the black color of the material used for the cathode electrode could increase the temperature oscillation in it, affecting the intensity of the MFC response due to sun exposure. Nevertheless, a test performed with a thermoresistance (PT 100) placed on the electrode surface of a flat MFC exposed to the sun demonstrated that the temperature variation during insulation did not vary more than 2-3°C with respect to the temperature of the water bulk, thereby excluding the immediate effect of temperature.

MFC output vs environmental factors

Figure 6 shows the trend of the six floating cells immersed in the anoxic basin of the Carimate WWTP, with electrodes measuring 10 x 13 cm and anodes short-circuited. In this way, the different output of the single cell is due to the cathode performance and not to the (common) anode. The figure show daily oscillating power trends as already registered for the smallest flat MFCs operated at Milano Nosedo WWTP. Therefore, power limit, in this case as in the case of the other small flat MFCs, is underlined with the underperforming cathodes. The graph shows a strong daily variability especially during the first months. At the end of November, the cathodes were variously covered by a layer of mud that strongly limited the exchange with the oxygen of the air as well as impeding, to some extent, the arrival of light on the cell. In that period, the power, and also the daily variation, were much more contained, although a direct relationship of power production with sun irradiation and meteorological events was still maintained. The presence of photosynthetic anaerobic bacteria producing hydrogen in such condition could played a relevant role, enhancing the cathodic reaction in synergy with the rich anaerobic pool (Cristiani et al. 2013; Rago et al. 2015). This phenomenon deserve further investigation to be confirmed. Figure 6 shows also a zoom of the voltage trend of the six flat cells immersed in the anoxic tank of the Carimate WWTP with the solar irradiation measured with a commercial solarimeter (Futura electronics, code 8220-DVM1307). Rain precipitation, expressed as mm of water, is also reported in the graph. The rain causes the dilution of the wastewater, and consequently a reduction of the organic content. This phenomenon can be easily correlated with the power drop.

MFC output vs COD concentration

The trend of COD concentration measured by colorimetric method (Hatch Lange kits and instrumentation) every hour at the inlet of the (Milano–Nosedo) WWTP during one day (20-21 June 2017) with power trends of the Flat-small MFCs and of both the boat MFCs immersed in the same anoxic tank is reported in the Figure 7. The graph shows a significant difference in the trend of the different MFC types.

The correlation between the increase in the signal and the period of light is evident for the Flat-small MFCs, even if, in this period, it is not the sole phenomenon that determines the intensity of the power.

In fact, the COD fluctuation in the denitrification tank also affected the MFC power production of each type and size. The larger boat output could be better correlated to the COD level than the others exposed to the light and also the small boat, as it was not performing well during that period. The dynamic behavior of nutrient concentration could then be monitored via on-line signal, and the treatment could be more efficiently controlled, and therefore cost effective in the long term (Tanwar et al. 2008).

Energy harvesting and data transmission

The simple low-energy remote system (LoRa) that was set for the MFC data transmission is described in Supplementary information (Fig. S3, S4). It was successfully tested over a distance of 500 m, between the transmitter and the receiver installed at the WTTPs. This system requires a minimum tension of 3.3 V and 0.3 mA (about 1mW) to operate in sleeping mode and consumes about 130 mA (during the data transmission, that lasts only about 70 μs .

Based on the results achieved, it could be concluded that a single Flat-large MFC which produced continuously an average between $0.4-3\,$ mW $(0.2\text{-}0.6\,\text{V})$ connected to a DC/DC converter in an harvesting circuit, like those described in previous works (Schievano et al. 2017), is able to supply enough power for

the transmitter. For a two time a day message, the additional power of 858 mW for 140 µs is needed, which is, in term of energy (0.12 mWs), negligible with respect to the sleeping mode consume.

In case of Big boat, the minimum requested power of 0.4 mW is not produced in continuous mode. Therefore, the number of MFCs for the future construction of the boat should be increased.

In both cases, due to the variability of the produced power in time, the connection of two or more MFC systems should be recommended to reliably power the LoRa transmitter.

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- Post operation observation of flat MFCs
- Image of immersed flat and cylindrical reactors in a MFC boats during operation are reported in Figure S5 322 and S6 in Supplementary information. Post operation observation of flat MFCs are reported in Figure S7. 323
- The flat MFCs were quickly covered by photosynthetic organisms (Figures S7, supplementary information). 324
- As time progressed, spontaneous vegetation of grass, herbs and shrubs grew on the cathode of these MFCs 325
- (top surface, exposed to air), somewhat demonstrating a wetland phenomenon, whose root system gently 326
- 327 covered the electrode without damaging it, allowing the oxygen to reach cathode and preventing its
- permeating through (Figure 6S in Supplementary information). This phenomenon probably allowed Flat-328
- 329 large MFC to outperform other set-ups in long time. For the tubular configuration in the boats there were no
- vegetation growth on the cathodes. Differently, activate sludge can excessively accumulate on the cathodes, 330
- inhibiting the power production. The tubular cathodes, i.e. internal cathodes, suffered for sludge incoming 331
- 332 which obstructed aeration, especially the ones in the small boat as they operated for a longer period of time
- (since 2014). This last phenomenon in particular resulted critical and have to be prevented for using small 333
- 334 size of both kinds of MFC.

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4. Conclusions

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Both the tested floating MFCs types (flat and tubular) were demonstrated to be able to provide electric power for years, although with oscillations, despite the low concentration of organic matter in the wastewater of the denitrification tanks. They clearly demonstrated the viability of the MFC system as an energy harvester in a real environment.

The dissolved COD in the wastewater as well as the meteorological conditions (sun irradiation and rainfall), mainly caused the oscillation in MFC's output. The daily temperature and water flow variations had a negligible effect.

Floating MFCs reached a power peak in about two weeks from the installation and do not need maintenance during the whole experimental period. Photosynthetic species (bacteria, microalgae and plants) growing on the floating MFCs have a positive effect, both as visual impact and in avoiding mud encrustation on the cathodes. These aspects allowed a long time operation of the MFCs. On the contrary, sludge accumulation on the cathodes of both tubular and flat MFCs resulted in a much reduced output and most critically required prevention in future designs of MFC's as sensors and energy harvesters. A new, simple low-energy remote transmission system (LORA) successfully tested, shows great promise for a cost effective way of data transmission that could be implemented in monitoring and controlling water quality based on floating MFCs.

A single unit of Flat-large MFCs and boats are able to guarantee energy enough for a daily remote transmission of signals from the tested system, although not continuously.

The simplicity in setting up such a monitoring system lends itself well towards the development of citizen science and for remote environmental control.

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Figure captions

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Figure 1. Scheme of a flat MFC (A) and set-up of six MFC elements in a frame ready for the immersion in wastewater (B). Single tubular MFC element and its scheme (C). Tubular MFC elements integrated into a styrene boat: Small boat with 16 elements (D); Large boat with 32 elements (E).

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- Figure 2. Power trends of the Small boat and Large boat MFCs during more than one year (April 2016-July 2017) in an anoxic tank (Milano-Nosedo WWTP); trends of temperature and wastewater flow incoming in the plant is also reported.
- Figure 3. Power trend of the Flat-large MFC (50 x 50 cm) operated from January to July 2017 (Milano-Nosedo WWTP); trends of temperature and wastewater flow incoming in the plant is also reported.
- Figure 4. Power trends of the Flat-medium MFCs (18 x 18 cm) operated from April to July 2017 (Milano-Nosedo WWTP); trends of temperature and wastewater flow incoming in the plant is also reported. The graphs on the bottom are ten days zoomed.
- Figure 5. Total power and single voltage trends produced by 6 Flat-small MFCs (10 x 13 cm) during one month operation (June-July 2017) at Milano-Nosedo WWTP. Wastewater temperature and flow are also reported.
- Figure 6. Power trend of 6 Flat-small MFCs (10 x 13 cm) with shortened anodes (Carimate WWTP). A detail of power trend (November-December 2017) with meteorological measurements (sun irradiation and rain) is also reported.
- Figure 7. One day (20-21 June 2017) power trends of three Flat-small MFCs and of the two boats.

 Temperature, flow and COD concentration in the wastewater sampled at the inlet of the Milano-Nosedo WWTP is also reported.

Acknowledgment

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