

CONTRIB SCI 11:127-134 (2015)
doi:10.2436/20.7010.01.220

Students' Prize of the Catalan Society for Technology for 2014

Microbial fuel cells implemented in constructed wetlands: Fundamentals, current research and future perspectives

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Summary. A microbial fuel cell (MFC) is a device that generates electricity from the microbial degradation of organic and inorganic substrates. Constructed wetlands (CWs) are natural wastewater treatment systems that constitute a suitable technology for the sanitation of small communities. The synergy between MFCs and CWs is possible because of the presence of organic matter in CWs due to wastewater characteristics and the naturally generated redox gradient between the upper layer of CWs treatment bed (in aerobic conditions) and the deeper layers (completely anaerobic). As a result of MFC implementation in CWs (MFC-CW), it is possible not only to produce an energy surplus while wastewater is treated but also to improve and monitor the overall treatment process. Moreover, the implementation of MFCs may exert other beneficial effects on CWs, such as a decrease of surface treatment requirements, reduction of greenhouse gas emissions or clogging. Finally, MFCs implemented in CWs would be also a suitable bio-electrochemical tool for the assessment of treatment performance without any additional cost involved in the process. Overall, though considered to be at an infancy stage, MFC-CW represents a promising synergy between technologies that may reduce energy costs and enhance treatment performance and monitoring while wastewater is treated. The envisaged main challenges for maximizing the synergy between both technologies are linked to the optimization of both operational and design criteria in CW and MFC cell architecture and materials. [Contrib Sci 11:127-134 (2015)]

The fundamentals: Microbial fuel cells technology

Microbial fuel cells (MFCs) are bioelectrochemical devices that generate current by means of electrochemically active microorganisms as catalysts [29]. In an MFC, organic and in-

organic substrates are oxidized by exoelectrogenic bacteria and the electrons are transferred to the anode from where they flow through a conductive material and a resistor to a higher redox electron acceptor, such as oxygen, at the cathode [29,37] (Fig. 1). So far, there are two well-known bacterial genera which present exoelectrogenic activity, i.e., *She-*

Keywords: constructed wetlands · microbial fuel cells · treatment efficiency · clogging · biosensors

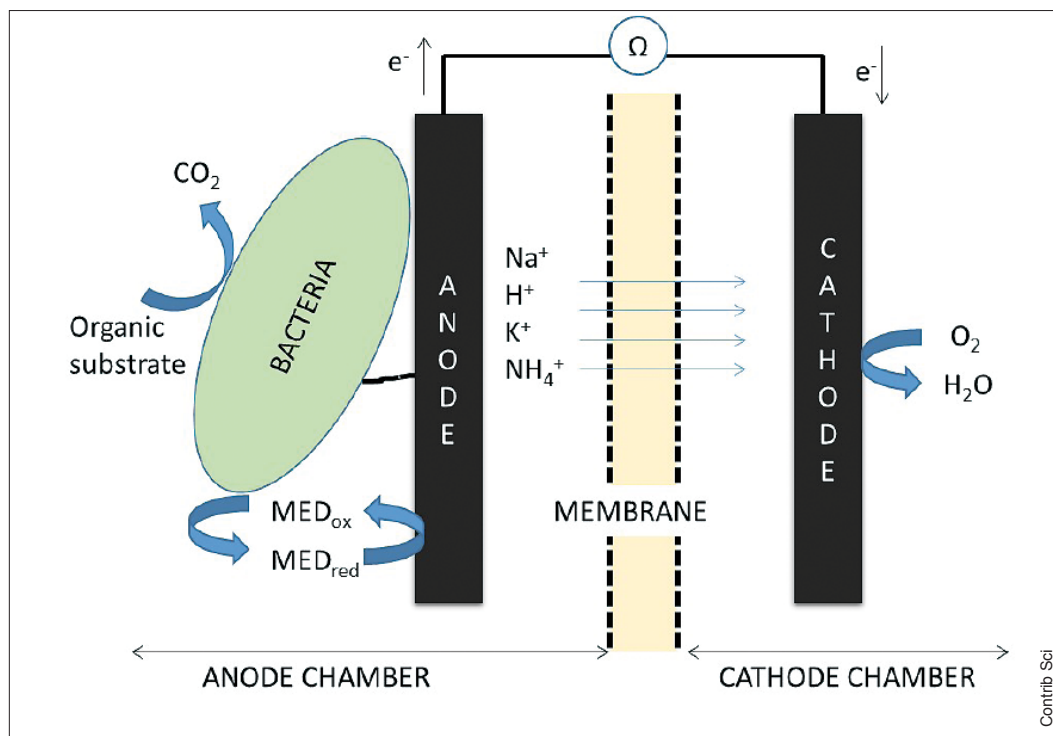


Fig. 1. Scheme of a microbial fuel cell (MFC) and its main processes.

wanella [41] and *Geobacter* [22]. Moreover, *Geobacter* species are not only able to perform direct electron transfer but they have also the potential to transfer electrons through the biofilm by means of electrically conductive pili (indirect electron transfer) [40].

Compounds oxidized at the anode are mainly simple carbohydrates such as glucose or acetate that can be already present in the environment or derived from the microbial degradation of complex organic substrates such as organic sediments or wastewater [31,36,39]. MFCs are, therefore, an alternative technology to harvest energy directly from wastewater in the form of electricity [13,26,31]. In order to ensure the use of the anode as the final electron acceptor by electrochemical active microorganisms, no acceptor with higher redox potential should be present in their vicinity. Consequently, the electromotive force of the cell will depend on the potential of the anode and the cathode and therefore, on the redox gradient between electrodes [29,37].

In order to provide a redox gradient between the anode and the cathode of an MFC, two different strategies may be applied. The first strategy is to use a proton exchange membrane (PEM) between the electrodes that enables the existence of an electromotive force between

the electrodes by only allowing the transfer of charges between the anode and the cathode zones. Another strategy is to exploit the natural redox gradient existing between surface waters and organic sediments in natural or semi-natural environments. The later MFC design is generally known as sediment or benthic microbial fuel cell (sMFC). Implementing a PEM between the electrodes allows us to have a greater cell force between electrodes, yet it results in a more expensive set up (of difficult scalability) when compared to MFC operated without a PEM (sMFC configuration).

Regardless of the MFC configuration (either with or without a PEM), MFC performance is influenced by biological, chemical and electrical factors. Accordingly, parameters defining MFCs performance are listed as [38]: (a) substrate conversion rate; (b) overpotentials at the anode; (c) overpotentials at the cathode; (d) proton exchange membrane related factors; and (e) internal resistance of the MFC. However, operational variables such as the concentration of chemical oxygen demand (COD) in the anodic chamber, pH or temperature, together with the surface area of electrodes and electrode materials and their relative distance, have also been reported as influencing factors [19].

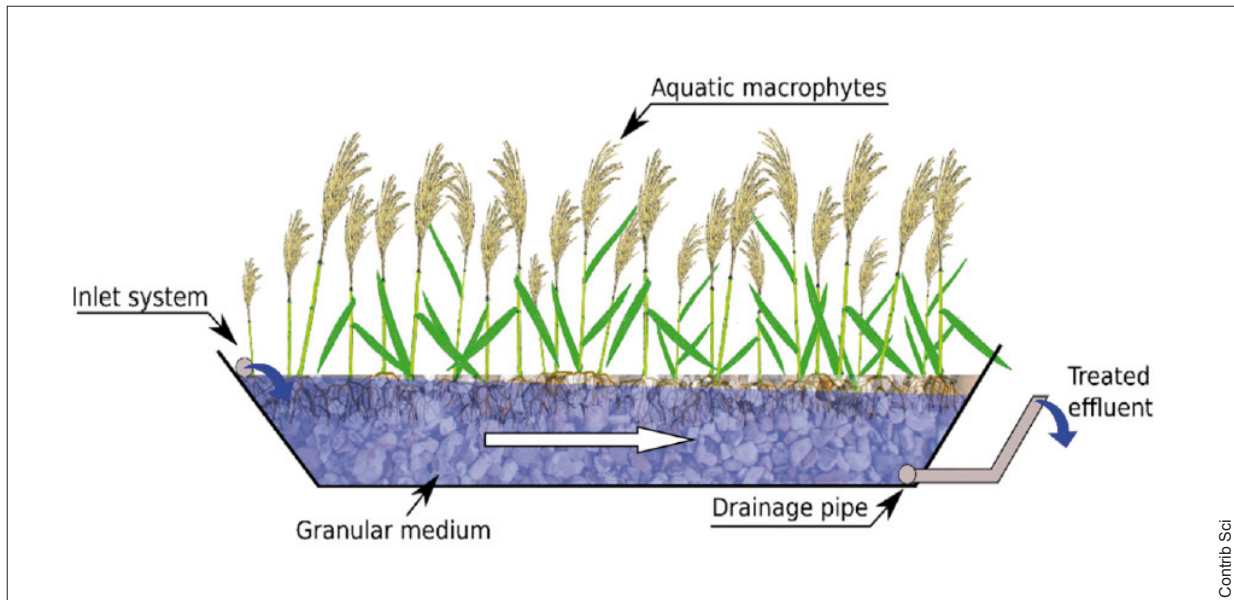


Fig. 2. Scheme of a horizontal subsurface flow constructed wetland (adapted from [42]). Note: the arrow indicates the direction of the water flow.

Constructed wetlands technology

Constructed wetlands (CW) are natural wastewater treatment systems where wastewater is treated by means of physical, chemical and biological processes taking place inside the treatment bed [17]. They consist of shallow lined basins filled up with a filter media (generally gravel) and planted with aquatic plants (macrophytes). CWs treat wastewater from a wide range of origins such as urban, industrial or agricultural wastewaters. They are also characterized by being low energy demanding systems and easy to operate and maintain. As a consequence, they have become an alternative to conventional intensified systems for the sanitation of small communities [16,35].

The CWs configuration most widely used is that of horizontal subsurface flow constructed wetlands (HSSF CWs). In HSSF CWs, water flows horizontally and below the surface of the granular medium (see Fig. 2). HSSF CWs are operated under saturated conditions and are, generally, shallower than other type of wetlands, with water depth being generally between 0.3 and 0.6 m. Removal rates of most of the contaminants in HSSF CWs are affected by design parameters such as the organic loading rate, the width to length aspect ratio, the granular medium size and the water depth.

Due to its anaerobic nature, HSSF CWs have relatively large surface requirements when compared to intensive technologies (such as activated sludge-based treatment sys-

tems), which is one of its major drawbacks. Over the past years, research in HSSF CWs has focused on the improvement of treatment performances and the reduction of surface requirements. Accordingly, forced (or active) aeration has been suggested as an efficient way to improve removal of organic matter and reduced nitrogen species [3,48]. Since the 1990s, active aerated systems have shown interesting results, leading to more than ten-fold increase of removal rates when compared to passive systems [33], resulting in the reduction of the required treatment surface. However, active aeration results in a significant increase in energy consumption during operation when compared to traditional HSSF CWs designs.

Organic matter removal in wetlands is simultaneously carried out by means of aerobic respiration, denitrification, sulphate reduction, fermentation or methanogenesis [17]. Therefore, greenhouse gases such as methane (CH_4) or nitrous oxide (N_2O) are emitted to the atmosphere. Methane is among the most relevant gases in terms of greenhouse effect not only since it has increased by ca. three times since pre-industrial times but also because its global warming potential is about 25 times higher than CO_2 [18]. Greenhouse gases emission from wetlands is highly related to both environmental and operational parameters such as redox conditions, temperature, organic loading and primary treatment applied [5,17,30,43].

Moreover, HSSF CWs are subjected to a progressive reduction of its hydraulic conductivity and porosity. This process

is generally known as clogging. Clogging of HSSF CWs occurs due to different processes [20,24]: (a) deposition of inert (mineral) suspended solids; (b) accumulation of refractory organic material (resistant to microbial degradation); (c) deposition of chemical precipitates; (d) biofilm growth (d) root system growth. Therefore, clogging is, at least partially, a consequence of solids accumulation and amongst the most significant drawbacks of the technology [20]. The composition and the quantity of accumulated solids depend not only on the load applied to the CWs [24] but also on other environmental conditions. In this regard, a positive relationship between the quantity of solids accumulated and both TSS and COD loading rates [4] has been reported. Furthermore, clogging is not a homogeneous phenomenon along the length or the depth of the wetland. Accordingly, several authors have described greater solids accumulation at the inlet zone due to higher organic matter concentrations [24] and higher sludge deposition at the bottom of the treatment bed [34].

In order to delay/alleviate clogging two strategies are currently envisaged [32]: preventative strategies and restorative strategies. Intermittent operation, multiple influent distribution or minimization of the inlet cross-sectional loading would be some of the preventative strategies most widely applied, while excavation and replacement of the gravel, washing and reuse of the gravel or application of chemicals are among most widely applied restorative strategies. However, addressing the management of the clogging leads to an increase in maintenance costs in HSSF CWs. In fact, it is assumed that inlet zone maintenance, conducted every 5 years, may account for up to 15% of construction costs [20]. Therefore, finding a cost-effective solution to clogging phenomena is of capital importance for increasing the lifespan of HSSF CWs and improving the economical management [20].

Benefits of MFC implementation in constructed wetlands

MFC can be implemented in HSSF CWs not only because of the presence of organic matter (OM) in the system (wastewater) but also because there is a naturally generated redox gradient of about 0.5 V between the upper zone (in contact with the atmosphere and therefore in aerobic conditions) and the deeper zone (in completely anaerobic conditions) of the treatment bed [6].

The implementation of the MFCs in constructed wetlands not only provides an energy surplus while wastewater is treated but also contributes to the improvement and moni-

toring of the overall treatment process. MFCs electricity production would be of special interest within the constructed wetlands scenario, since one of the major advantages of this technology is the low energy input necessary for wastewater treatment ($<0.1 \text{ kWh}\cdot\text{m}^{-3}$) [20]. Accordingly, the implementation of MFCs in constructed wetlands can result in the generation of enough electricity to cover part of the energy requirements of the system or to power low input devices in remote locations (such as water quality sensors).

Moreover, MFCs implemented in constructed wetlands may have other benefits such as a significant improvement on treatment capacity, and reduction of both clogging and methane release to the atmosphere. By implementing MFCs within the treatment systems, organic matter degradation can be fostered by increasing the availability of electron acceptors in such anaerobic conditions [9]. Accordingly, it is also described that the presence of MFCs in a sulfide-rich environment may accelerate the organic matter oxidation rates by means of the regeneration of SO_4^{2-} as an electron acceptor, which is only possible in the presence of an anode [45]. MFCs may also reduce the clogging phenomenon by enhancing the mobilization of organics contained in filter media, which can rarely be hydrolyzed under anaerobic conditions. Moreover, exoelectrogenic bacteria use acetate as a substrate, which decreases the availability of the carbon source for methane producing bacteria. Competition between exoelectrogenic bacteria and methane producing bacteria may result in a significant decrease in methane emissions during wastewater treatment under anaerobic conditions.

MFCs implemented in CWs would be also a suitable bio-electrochemical tool for the assessment of treatment performance without any additional costs involved in the process. MFC implementation in constructed wetlands results in the optimization of the treatment process and reduction of its environmental impact.

Current research on sMFC

Some research groups have already addressed the implementation of MFCs on marine sediments [39], planted systems [44,46], rice paddy fields [21,10] and recently also constructed wetlands [6,14,47,49]. The implementation of MFCs in constructed wetlands is a topic scarcely addressed in current literature and only a few lab experiences are currently available (Fig. 3). The majority of these experiences did not use real wastewater and most of them were based on the application of lab-scale systems simulating constructed wet-

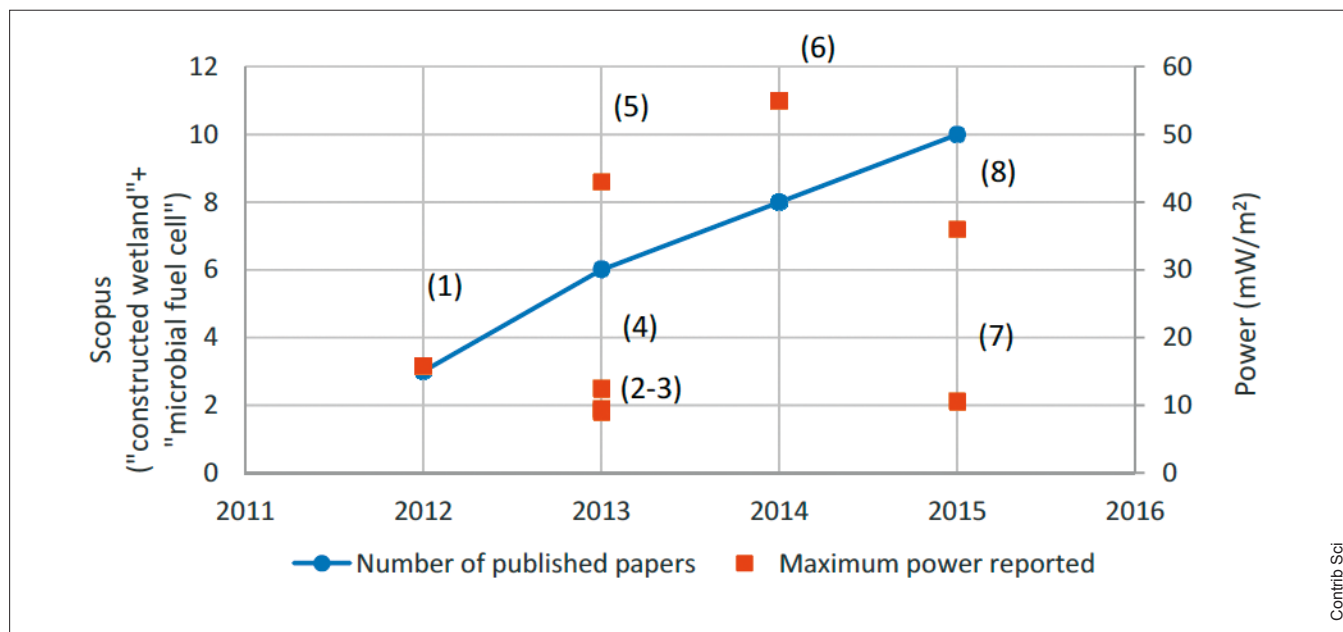


Fig. 3. Published papers on the “constructed wetlands” + “microbial fuel cells” topics. Note: Data has been collected by using Elsevier, Scopus and ISI data bases. From: (1) [49]; (2) [14]; (3) [50]; (4) [27]; (5) [47]; (6) [28]; (7) [12]; (8) (unpublished results of our research group). Note: some of the bibliography could not be included in the secondary axis due to the lack of information to calculate the power density in relation to electrodes’ surface.

lands. Only one author described the implementation in a pilot-scale constructed wetland [47].

MFC implementation in full scale CWs is currently hampered by the lack of successful adaptation of classical cell architectures to a very complex scenario. In order to successfully implement MFCs in CWs it is of capital importance to address design aspects related to electrode and materials, position or dimensions [12,28,50]. The influence of plants on MFC performance has been also currently addressed, yet not in the context of constructed wetlands [6,27,28]. Plants influence CW performance by their ability to release oxygen or easily biodegradable substrates through the root system. Plants also influence the redox conditions within the treatment bed due their ability to evapotranspire water that, in turn, causes significant water level variations within the treatment bed. To this extent, water level fluctuations driven by plants evapotranspiration has been described as influencing MFC performance to a high extent [7]. The effect of plants on MFC voltage pattern is shown in Fig. 4. From Fig. 4 it can be seen that once the effect of plants was removed (by covering them), MFC voltage pattern drastically changed from a very marked daily fluctuation (when plants were not covered) to a more stable MFC signal when they were covered. As mentioned above, plants evapotranspiration in wetlands may cause significant water level variation and, thus, may influence oxygen availability at the cathode. To this extent, cur-

rent results evidence that oxygen availability at the cathode under periods of low water level variation (during periods of low evapotranspiration due to conditions such as winter) may increase MFC efficiency by 66% due to lower internal resistances in the system [8].

Beyond plants influence, other wetlands’ operational conditions such as hydraulic retention time, flow regime or aeration mode have been also linked to MFC performance in current literature [6,12,50]. Even though the synergy between CWs and MFCs may have several potential benefits, current research is mostly focused on energy production. Figure 3 shows the power produced with MFCs implemented in CWs. However, the authors of the current study wish to point out that direct comparison between MFC performance reported in current literature on the subject must be undertaken carefully due to significant differences between studies (such as different set-up dimensions and configurations, different electrode materials, type of wastewater or external resistances). In addition to the above-mentioned differences, energy production data reported in current research shows that this can range from ca. 9 mW/m² [14] to 55 mW/m² [28].

From data shown in Fig. 3, the total amount of power produced via MFC implementation in a CW was estimated. With this aim, an ideal scenario was defined: (i) the entire wetland surface would be suitable for MFC implementation; (ii) power could be produced continuously during the day; (iii) the ex-

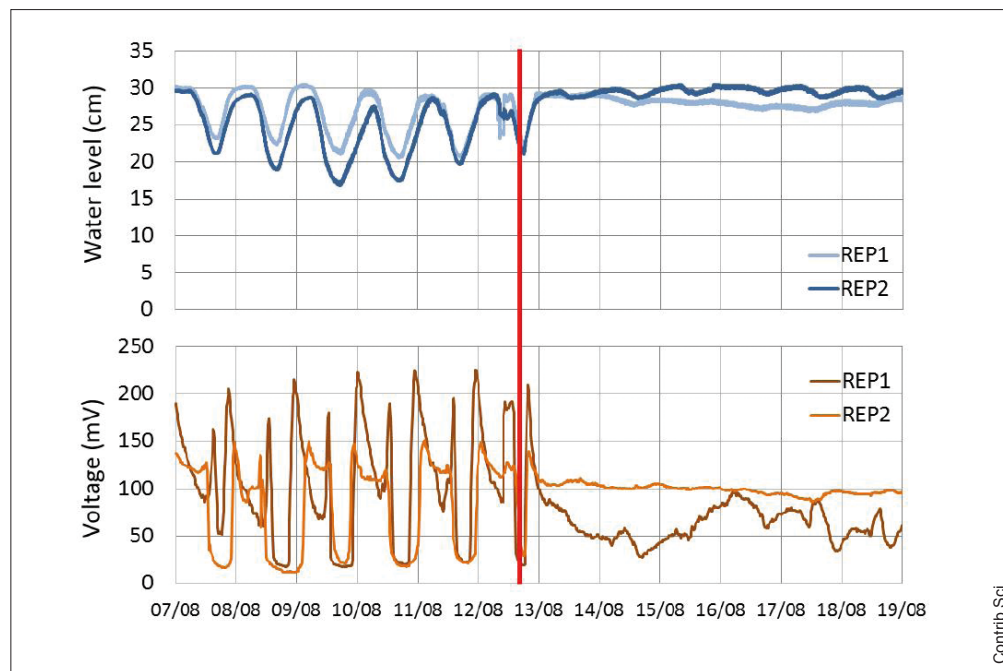


Fig. 4. Influence of water level variation caused by macrophytes evapotranspiration on MFC cell voltage. Red line indicates the moment when plants were covered. Adapted from [7].

trapolated power output would be calculated on the basis of a full-scale HSSF CW treating wastewater from a population of 2,000 PE and finally, (iv) the surface ratio for a horizontal subsurface-flow CW (HSSF CW) would be considered to be 5 m²/PE [20]. By taking into account these assumptions, it can be estimated that the total power produced for the 10,000 m² HSSF CW would range from 2.2 kWh/day to 13.2 kWh/day (considering the maximum and minimum power produced from Fig. 3). Therefore, in terms of power produced nowadays, MFCs implemented in CWs could be only used to power low energy input devices. Furthermore, if the current generated by bioelectrochemical systems is compared with other equivalent energy-producing technologies (such as chemical batteries or chemical fuel cells) [2] the conclusion is that economically feasible applications of MFCs in the near future shall be based on sustainable environmental applications rather than on energy production alone.

Future challenges for the environmental application of MFC in CW

As previously stated, CW technology can be improved via MFC implementation. Accordingly, MFCs implemented in CWs may increase not only CW treatment capacity but also

would be of use as a biosensor tool to monitor treatment performance and operational conditions (such as influent organic matter concentration). Organic matter concentration is currently determined by means of analysis of the biochemical oxygen demand (BOD) after five days (BOD₅) or the chemical oxygen demand. Despite the fact that these methods are universally used, BOD₅ has a limitation in terms of being time consuming, and is not suitable for online process monitoring. COD is a faster procedure for assessing organic matter concentration in wastewater, yet it is quite costly and produces toxic reagents that might pose a threat to the environment. In the context of wastewater treatment plants based on CWs, the organic matter content is among the most important water quality parameter and therefore, the possibility of developing an online technology for its estimation is of great value for wastewater treatment plant management. In this regard, there are several studies currently available on the use of MFC as a biosensor tool for the assessment of wastewater organic matter concentration in terms of BOD [11,23,25].

However, most of these studies were conducted with conventional MFCs (MFC with a PEM), and the potential application of MFCs in CWs as a biosensor tool for organic matter assessment is clearly under-addressed in current research. Furthermore, most studies published up to the present date which deal with the application of MFCs in CWs have failed

to describe a strong correlation between COD concentration and MFC signal [15,47,50].

Overall, the synergy between CWs and MFCs has been so far mostly based on optimization for energy production. Besides the interest that an energy surplus can have in the context of CW technology, further research shall be focused on the optimization of both technologies to fully address other benefits of MFC implementation in CWs such as treatment efficiency improvement, process monitoring and the reduction of clogging or methane emissions. ■

Acknowledgements. This research was funded by the Spanish Ministry of Science and Innovation (MICINN) (project CTM2010-17750). Clara Corbella kindly acknowledges her PhD scholarship (2014 FI_AGAUR, Generalitat de Catalunya).

Competing interests. None declared.

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