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Vertical redox profiles in treatment wetlands as function of hydraulic regime and macrophytes presence: Surveying the optimal scenario for microbial fuel cell implementation

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HIGHLIGHTS

- Redox gradients are maximal between the surface and the bottom of the wetland.
- Plants increase the redox gradient in constructed wetlands.
- Continuous hydraulic regime increases the redox gradient within the wetlands.
- Estimated energy production is that of 16 mW/m^2.

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ABSTRACT

Sediment microbial fuel cell (sMFC) represents a variation of the typical configuration of a MFC in which energy can be harvested via naturally occurring electropotential differences. Moreover, constructed wetlands show marked redox gradients along the depth which could be exploited for energy production via sMFC. In spite of the potential application of sMFC to constructed wetlands, there is almost no published work on the topic. The main objective of the present work was to define the best operational and design conditions of sub-surface flow constructed wetlands (SSF CWs) under which energy production with microbial fuel cells (MFCs) would be maximized. To this aim, a pilot plant based on SSF CW treating domestic sewage was operated during six months. Redox gradients along the depth of SSF CWs were determined as function of hydraulic regime (continuous vs discontinuous) and the presence of macrophytes in two sampling campaigns (after three and six months of plant operation). Redox potential (E_H) within the wetlands was analysed at 5, 15 and 25 cm. Results obtained indicated that the maximum redox gradient was between the surface and the bottom of the bed for continuous planted wetlands (407.7 ± 73.8 mV) and, to a lesser extent, between the surface and the middle part of the wetland (356.5 ± 76.7 mV). Finally, the maximum redox gradients obtained for planted wetlands operated under continuous flow regime would lead to a power production of about 16 mW/m^2.

1. Introduction

Sub-surface flow constructed wetlands (SSF CWs) are used for the wastewater treatment in small communities worldwide (Puigagut et al., 2007; García et al., 2010). Low cost operation and maintenance, low energy requirements and good landscape integration are some of the most attractive advantages of this technology compared to conventional treatment systems (García et al., 2003; Rousseau et al., 2008). Contaminant removal efficiency in SSF CWs depends, among other factors, on redox potential (E_H) conditions (Caselles-Osorio and García, 2007; Pedescoll et al., 2011). Accordingly, E_H in SSF CWs is subjected to great spatial and temporal variation, which is caused, in turn, by several factors including the presence of plants, fluctuations in the water level due to evapotranspiration, light intensity and temperature (Wießner et al., 2005; Dušek et al., 2008; Biaolwiec et al., 2012; García et al., 2010). In general terms, E_H variation in SSF CWs is accepted to be of great intensity (fluctuation of several hundreds of millivolts within few hours) (Dušek et al., 2008) in depth rather than across the length of the bed (García et al., 2003), and especially pronounced within the morning hours (Bialowiec et al., 2012). SSF CWs can be designed, by changing operational and design parameters, to favour a desired range of redox conditions targeting a specific pollutant removal pathway (Faulwetter et al., 2009) or, more recently, to produce energy through microbial fuel cell (MFC) implementation (Yadav et al., 2012).

To this regard, in an MFC bacteria oxidize an electron donor (organic matter), with an anodic electrode as the electron acceptor. The electrons flow from the anode through an electrical circuit toward a high redox electron acceptor, such as oxygen, at the cathode. Furthermore, a sediment microbial fuel cell (sMFC) represents a variation of the typical

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configuration of a MFC in which energy can be harvested via naturally occurring electropotential differences (Whitfield, 1972; Reimers et al., 2001). So far, sMFC have been successfully implemented in rice paddy fields (Kaku et al., 2008) and marine environments (Whitfield, 1972; Reimers et al., 2001; Bond et al., 2002; Tender et al., 2002; Holmes et al., 2004; Ryckelynck et al., 2005; Lowy et al., 2006; Rezaei et al., 2007), and just one work has been published on the implementation of sMFC to constructed wetlands (though it is a laboratory study using dye wastewater and operated in batch mode) (Yadav et al., 2012).

To the best of our knowledge, there are no current studies addressing the influence of operational and design parameters in SSF CW (such as hydraulic regime and macrophytes presence) on redox profiles with the aim at describing the best scenario for sMFC implementation. Therefore, the potential use of SSF CW for energy production remains unaddressed in current literature. The hypothesis behind the work is that constructed wetlands are a suitable technology for energy production via microbial fuel cell implementation.

The objective of the present work was to determine the influence of flow regime and macrophytes presence on redox conditions along the depth of SSF CWs. The analysis of redox gradients along the depth of SSF CWs will be used to describe the optimal scenario to maximize the energy production with sMFC.

2. Materials and methods

2.1. Pilot plant

The experimental plant was located in Barcelona, and treated urban wastewater directly pumped from a municipal sewer. It was built in 2011 at the Department of Hydraulic, Maritime and Environmental Engineering of the Universitat Politècnica de Catalunya and was set in operation in March 2011.

The wastewater was coarsely screened and subsequently stored in a 1.2 m^3 plastic tank, which was continuously stirred in order to avoid sedimentation of solids. This tank was equipped with level buoys that controlled the operation of the feeding pumps. Wastewater retention time in this tank was approximately 5 h. From the storage tank, the wastewater was pumped to 4 cylindrical PVC static settlers. Two settlers of 14 L fed the wetlands working under continuous flow regime, while the other two settlers (of 7 L each) fed the wetlands working under discontinuous flow regime.

From settlers, wastewater was conveyed to the secondary treatment which consisted of six SSF CWs of 0.4 m^2 each, fed with 21 L day^{-1} of primary settled domestic sewage. Wetlands were constructed in plastic containers 0.75 m long, 0.55 m wide and 0.39 m high. A uniform gravel layer (40% initial porosity) was used which provided a wetland depth of 0.35 m. The water level was kept 0.05 m below the gravel surface to give a water depth of 0.30 m.

All the wetlands were operated at 2.5 days of hydraulic retention time (HRT) and at an organic loading rate (OLR) of about 5 $gBOD \cdot m^{-2}$ day^{-1}. Four of the six wetlands were fed under continuous flow regime (cf SSF CW) and the two wetlands remaining were fed discontinuously (3 times per day) (df SSF CW). cf SSF CW received a flow of 0.875 L h^{-1}, while df SSF CW was fed three times a day with a flow of 7 L per pulse by means of electrovalves. Furthermore, two of the cf SSF CW and the df SSF CW were planted with common reed (*Phragmites australis*) in March 2011 at an initial density of 16 plants m^{-2}. Each experimental condition was addressed by means of two replicates. After secondary treatment, effluent was discharged into a graduated tank of 22 L capacity. Measuring the influent and effluent flow allowed us to calculate wetland efficiency on a mass balance basis. Overall, the influence of the presence of macrophytes on redox conditions within the wetlands was addressed by comparing the planted and unplanted wetlands operated under continuous flow regime, whereas the effect of flow regime was addressed by comparing the planted wetlands operated under continuous or discontinuous flow regime.

2.2. Redox potential monitoring

Redox conditions within the wetlands were monitored in two sampling campaigns during sampling periods of 24 h for each wetland. The first sampling campaign was conducted in June 2011 (after three months of plant operation) and the second campaign was conducted in September 2011 (after six months of plant operation). It is worth mentioning that the root system was approximately 20 cm deep during the first sampling campaign whereas it reached the bottom of the wetland (approximately 30 cm) during the last sampling campaign. Vertical redox profiles were obtained by means of three redox probes (Digimed TH-404) equipped with a platinum electrode (Ag/AgCl reference system — accuracy: ± 10 mV). Redox probes were inserted at each wetland at 5, 15 and 25 cm depth and connected to a data logger (DATA TAKER DT50 series 3) that recorded redox values every 10 s for periods of 24 h. Redox data was transformed to express the results in terms of the standard hydrogen electrode (E_H).

2.3. Physical and chemical analyses

The systems were analysed from March to October 2011 for their efficiency on contaminant removal. Surveyed water quality parameters were soluble COD, total COD, ammonia nitrogen and nitrate nitrogen. Analyses were carried out once a week according to Standard Methods (APHA-AWWA-WEF, 2005).

2.4. Power production estimation

According to Logan et al. (2006), the electromotive force of the MFC (in volts), which is actually the maximum attainable voltage, can be expressed as (Eq. (1)):

$$\mathrm{E_{emf}} = E_{cat} - E_{an}. \tag{1}$$

According to Logan et al. (2006), the measured cell voltage (E_{cell}) is usually lower than the electromotive force of the cell (E_{emf}) due to a number of losses such as anode and cathode overpotentials (η_a and η_c, respectively) and ohmic losses (IR_Ω) (Eq. (2)):

$$\mathrm{E_{cell}} = \mathrm{E_{emf}} - \left(\sum \eta_a + \left|\sum \eta_c\right| + \mathrm{IR}_\Omega\right). \tag{2}$$

For the purposes of this paper the cell voltage (E_{cell}) will be considered the 50% of the electromotive force of the MFC (E_{emf}) (Logan et al., 2006). Accordingly, a decrease in cell voltage is considered to be about 50% since, as has been previously reported by Logan et al. (2006), the maximum attainable E_{emf} is that of 1.1 V, whereas maximum E_{cell} described in current literature is that of 0.62 V. Although it is just a roughly estimation on the actual cell voltage that could be obtained in SSF CWs, authors believe that it is a good approximation to address which is the potential power production of MFC implemented in SSF CWs.

Furthermore, according to Logan et al. (2006), the theoretical power produced by the implementation of a microbial fuel cell is that of (Eq. (3)):

$$P = I \cdot \mathrm{E_{cell}}. \tag{3}$$

Normally the voltage is measured across a fixed external resistor (R_{ext}), while the current is calculated from Ohm's law (Eq. (4)):

$$I = \frac{\mathrm{E_{cell}}}{\mathrm{R_{ext}}}. \tag{4}$$

Thus, power is usually calculated as (Eq. (5)):

$$\mathrm{P} = \frac{\mathrm{E^2{}_{cell}}}{\mathrm{R_{ext}}}. \tag{5}$$