Ecological Engineering 107 (2017) 1–7

Contents lists available at ScienceDirect

Ecological Engineering

journal homepage: www.elsevier.com/locate/ecoleng

Research paper

# The salinity effects on the performance of a constructed wetland-microbial fuel cell

J. Villaseñor Camacho[a,*], L. Rodríguez Romero[b], C.M. Fernández Marchante[c], F.J. Fernández Morales[a], M.A. Rodrigo Rodrigo[c]

[a] *Chemical Engineering Department, Institute for Chemical and Environmental Technology (ITQUIMA), University of Castilla-La Mancha, Avenida Camilo José Cela S/N, 13071, Ciudad Real, Spain*
[b] *Chemical Engineering Department, School of Civil Engineering, University of Castilla-La Mancha, Avenida Camilo José Cela S/N, 13071, Ciudad Real, Spain*
[c] *Chemical Engineering Department, Faculty of Chemical Science and Technology, University of Castilla-La Mancha, Avenida Camilo José Cela S/N, 13071, Ciudad Real, Spain*

ARTICLE INFO

*Article history:*
Received 11 September 2016
Received in revised form 24 June 2017
Accepted 27 June 2017
Available online 7 July 2017

*Keywords:*
Constructed wetland
Microbial fuel cell
Bioelectrogenic
Salinity

ABSTRACT

The objective of the present work is to study the influence of the wastewater salinity concentration on the performance of a Constructed Wetland-Microbial Fuel Cell (CW-MFC) for simultaneous water pollution control and electricity generation. The work has been carried out under the hypothesis that increasing the salinity may improve the electricity production because of a lower internal ohmic resistance, although it could damage the microbiological processes or the plants. A pilot-scale horizontal subsurface flow CW, modified to function as an MFC, was operated under a continuous operation mode over five consecutive experimental periods of approximately 2 months each. The wastewater salinity was increased in each new period by steeply increasing the NaCl concentration in the synthetic wastewater from 0.51 to 9.51 $g\,L^{-1}$. The CW-MFC performance was monitored during every stationary period. The increasing salinity first improved the cell voltage, and the resultant maximum voltage (130 mV) under continuous operation corresponded to a salinity concentration between 4 and 5 $g\,L^{-1}$. However, subsequently higher salinity levels caused the opposite effect. The maximum voltage was obtained in an unstable condition, as microbiological inhibition in the anode zone appeared early, at approximate salinity levels of only 3 $g\,L^{-1}$. Batch experiments confirmed the results, and higher cell voltage values up to 600 mV were obtained if longer retention times were allowed. The wetland plants (*Phragmites australis*) were only damaged at a salinity concentration of 9.51 $g\,L^{-1}$.



## 1. Introduction

Microbial Fuel Cells (MFCs) are electrochemical devices that can obtain electricity from organic matter by means of the activity of bioelectrogenic microorganisms. As conventional fuel cells, they also have two chambers, with electrodes working under a difference of electric potential. However, what makes MFCs unique is the fact that active microorganisms in the anode chamber are capable of oxidizing the organic matter using electric current instead of oxygen by various complementary mechanisms, becoming the real biological catalyst of the electrochemical device. MFCs have been extensively studied, and many scientific papers and books have been published in recent years. Because organic waste can be used as fuel for MFCs, this technology has been proposed for environmental remediation purposes, and the concept of bioelectrochemical wastewater treatment is currently receiving significant attention (Gude, 2016).

In this context, currently, a very promising variety of MFCs is being studied, consisting of integrating MFC technology into natural ecosystems or low-cost environmental remediation technologies. There are currently three of these technologies, including the Sediment Microbial Fuel Cells (SMFCs), also called Benthic MFCs; the Plant-type Microbial Fuel Cells (PMFCs); and MFCs coupled to Constructed Wetlands (CW-MFCs), and they all are based on the redox potential differences that naturally exist between the top water-air interface and the anaerobic bottom of these ecosystems. There is also a large amount of literature on the subject. All of these technologies have been described in a recent review (Fernandez et al., 2015).

* Corresponding author.
*E-mail address:* jose.villasenor@uclm.es (J. Villaseñor Camacho).

http://dx.doi.org/10.1016/j.ecoleng.2017.06.056
0925-8574/

One of the most interesting options of these low-cost technologies for wastewater treatment are constructed wetlands (CWs). These systems are wetlands, isolated from the underground below them, that receive wastewater. Wastewater treatment in CWs is the result of a combination of natural physical, chemical, and biological phenomena (Zhi and Ji, 2012). There are different types of CWs; subsurface flow wetlands are one of the most implemented types (García et al., 2010). Basically, they consist of a wastewater subsurface flux flowing through a porous gravel bed, which includes macrophyte plants growing on the top surface and a mixed microbial population in the form of biofilms attached to the gravel and roots.

The study of the combination of CWs and MFCs is recent. The first work was published by Yadav (2010), and although the number of papers is still low, it is increasing exponentially in the last 5 years (Doherty et al., 2015a). The works studied the influence of the type or concentration of the organic pollutants (Corbella et al., 2015; Fang et al., 2015; Liu et al., 2014; Srivastava et al., 2015; Wu et al., 2015a), the role of plants and the effect of the position of the roots (Corbella et al., 2014; Fang et al., 2013; Liu et al., 2014), the water flow configuration (Corbella et al., 2014; Corbella et al., 2015; Doherty et al., 2015b), the type of cathode (Liu et al., 2014; Srivastava et al., 2015) and the distance between the electrodes (Doherty et al., 2015b; Doherty et al., 2015c). The works usually aimed to improve the cell efficiency through maintaining a high redox potential between the electrodes and reducing the internal resistance.

To the authors' knowledge, wastewater salinity may be an important aspect influencing the CW-MFC performance, and its effect has not yet been studied. Initially, wastewater salinity is expected to have a contradictory effect on the two main processes (biological and electrochemical) occurring in the device: negative in the biological process and positive in the electrochemical process. Regarding the possible biological effects, constructed wetlands have been extensively applied for industrial wastewater treatment (Gao et al., 2015; Wu et al., 2015b), and there are some works focused on high salinity wastewater treatment by CWs (Gao et al., 2015; Karajić et al., 2010). Klomjek and Nitisoravut (2005) reported that some plant species used in CWs were adversely affected by high salinity in wastewater. Gao et al. (2015) tested twelve different plants species and detected a salinity level at which the treatment efficiency begins to fall. Regarding the microbial role in wetlands, Gao et al. (2012) reported that the increase in salinity strongly reduced the microorganism concentration, while Lin et al. (2008) reported inhibition of the microbial activity.

Regarding the electrochemical performance, Logan (2008) and Rozendal et al. (2008) described the expected positive effect of increasing the wastewater salinity in an MFC and explained it in terms of the increase in the electrical conductivity of the electrolyte, which reduces the internal ohmic resistance and results in an ohmic drop of the fuel cell. However, they also stated the expected negative effect in the microbial activity at high salinity levels. Likewise, Lefebvre et al. (2012) reported increased power and decreased internal resistances using increasing salinity levels but found a drastic power reduction at a NaCl level of 20 g/L because of the inhibition of microbial growth.

In this context, it could be considered that the wastewater salinity could be an important factor to be tested in the performance of the combined CW-MFC system, and this paper aims to describe and discuss the results of the study of a pilot-scale CW-MFC treating wastewater with a steeply increasing salinity. Until now, this subject has not been tested, and it is hypothesized that a moderate salinity could produce a positive effect on the fuel cell performance, although it could also negatively affect the role of plants or microorganisms in the subsurface system. Because of the complexity of the CW-MFC mechanisms, the global effect and the salt tolerance limit are still unknown. The results could be of great relevance because of their potential applicability to the treatment of high salinity industrial wastewater. For instance, leachate from domestic landfills, or washing effluents from agro-food industries could be suitable for such combined CW-MFC technology.

## 2. Materials and methods

The materials, experimental procedures, and analytical methods have been described thoroughly elsewhere (Villaseñor et al., 2013; Villaseñor Camacho et al., 2014). The following subsections only describe the important details.

### 2.1. Constructed wetland – microbial fuel cell microcosm

The experimental installation consisted of a pilot-scale horizontal subsurface flow CW for wastewater treatment, modified to function as an MFC (Fig. 1).

The installation was located in the greenhouse facility of the Institute for Chemical and Environmental Technology of the University of Castilla La Mancha, Ciudad Real (Spain). The wetland consisted of a 115 cm × 47 cm plastic channel with a bed depth of 50 cm, and it was filled with gravel with an average particulate diameter of 9 mm and bed porosity of 0.4. Sampling points were placed along the wetland, and they made it possible to introduce temperature or dissolved oxygen probes. *Phragmites australis*, which was purchased from a commercial greenhouse, was planted in the wetland in autumn 2011 (20 plants $m^{-2}$), although this work was performed in the period February-October 2014, and the plants were completely developed during the experimental work.

Regarding the MFC elements, rectangular (each was 70 cm × 15 cm and 3 cm thick) graphite plate electrodes were located in the gravel bed, and the distance between them was 26 cm. The anode plate was located 12 cm above the bottom of the wetland, and an identical graphite cathode plate was also located 12 cm below the wetland surface. Both electrodes were located in the subsurface water flow. The anode and cathode were connected by a 120 Ω resistor.

A 2-cm-thick layer of calcium bentonite (*Bentonil A*, from *Süd-Chemie*) separated the anode and cathode compartments in order to limit the growth of roots to the upper area only, where the cathode was located. The raw wastewater flow passed through the anode compartment, and subsequently, the outlet flow was pumped to the cathodic compartment via horizontal subsurface flow and finally left the wetland.

### 2.2. Synthetic wastewater

The synthetic domestic wastewater composition included glucose (175 mg $L^{1}$), $CH_3COONa{\cdot}3H_2O$ (175 mg $L^{-1}$), $NaHCO_3$ (144 mg $L^{-1}$), $KH_2PO_4$ (58 mg $L^{-1}$), $MgCl_2{\cdot}6H_2O$ (48 mg $L^{-1}$), $CaCl_2{\cdot}2H_2O$ (39 mg $L^{-1}$), $(NH_4)_2SO_4$ (146 mg $L^{-1}$), and $(NH_4)_2Fe(SO_4)_2{\cdot}6H_2O$ (109 mg $L^{-1}$). The resulting main inlet wastewater parameters of this synthetic wastewater were as follows: total suspended solids (TSS): 0–5 mg $L^{-1}$, chemical oxygen demand (COD): 300 mg $L^{-1}$, inorganic salt concentration: 515 mg $L^{-1}$, and electrical conductivity: 0.9 mS $cm^{-1}$. Over the course of the experiment, the salinity concentrations were modified as described later in this paper. It was considered that the COD level was high enough, but not excessive, to perform the experimental study, and it was always maintained constant.

### 2.3. Experimental procedure

A start-up period was not necessary because the wetland had been continuously working since autumn 2011, using synthetic