



# Maximizing the energy harvest from a microbial fuel cell embedded in a constructed wetland



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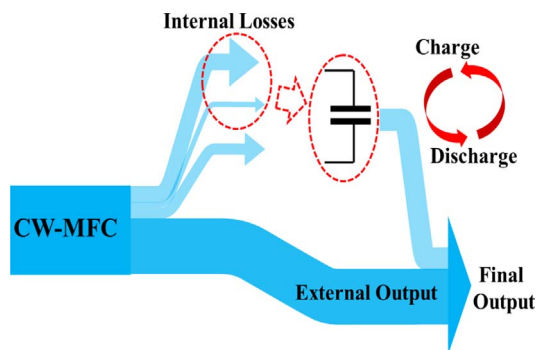
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## HIGHLIGHTS

- A novel strategy was developed to harvest energy from CW-MFC.
- CDC strategy performs better than DC or traditional CL mode.
- Low D value contributes to more electrons' capture and higher  $\text{NRR}_{\text{COD}}$ .
- CDC strategy takes an advantage in higher internal resistance system.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Direct energy harvesting from the newly established constructed wetland-microbial fuel cell (CW-MFC) offers it a competitive position compared with traditional constructed wetlands (CWs) to allow the CWs for wastewater treatment and concomitantly achieve power generation. However, the integration of MFC into CWs always faces a large portion of energy losses due to the existence of higher internal resistance. This paper reports tests of a novel strategy, namely a capacitor engaged duty cycling (CDC) strategy, to harvest energy from an open air bio-cathode CW-MFC. Results show that with duty cycle value of 31.6% ( $D = 31.6\%$ ), the effective charge obtained from CDC strategy is 19.81% higher than the conventional continuous loading (CL) mode within the same discharging time. With a lower D value of 20% ( $D = 20\%$ ), the total charge harvested increased about 25.0%. The CDC operation mode shows advantages over the higher internal resistance system and contributes to a higher normalized COD removal rate. This operation strategy can minimize the energy losses with a suitable D value. It is a simple but effective way to maximize the energy harvesting from the CW-MFC system.

## 1. Introduction

Worldwide, the consumption of energy is accelerating because of

increased electrification and the development of information systems. The annual report of British Petroleum (BP) shows that an overall increment of 37% in primary energy consumption will be reached in 2035

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compared to 2013 [1]. Attention now switches from fossil fuel resources to technologies which are renewable and carbon-free and which have a light environmental footprint. Among these, microbial fuel cell (MFC) technology has shown the ability to extract energy as electricity directly from wastewater streams during the treatment processes without any unfriendly by-products [2,3]. This unique feature makes MFC the core of many integrated wastewater treatment processes [4–6], as well as the solid-waste-based MFCs [7,8] in recent years. A novel option is to combine the MFC with the traditional constructed wetland (CW): a constructed wetland-microbial fuel cell (CW-MFC). This enhances the traditional treatment wetland, producing both treatment efficiency and extra energy output as electricity [9–12].

So far, studies of CW-MFC have mainly focused on two areas: pollutants and/or enhanced removal of nutrients [13–16] and energy output improvements [12,17–19]. The higher energy output is owing to the efficient harvest of electrons from the anode (electrically related oxidation) which can then be consumed on the cathode (normally for oxygen reduction) within a certain time. The CW-MFC systems are always facing severe energy losses from different causes, however, and thus the output power is always considerably lower than expected. Electrode modification is commonly used in MFCs to obtain higher electrical performance [20,21]. Alatraktchi et al. [22] showed that with gold nanoparticles sputtered on the electrode, a maximum power density (MPD) of  $461.6 \text{ mW/m}^2$  was achieved, which is 1.88 times higher than that from the plain electrode. Unfortunately, such methods cannot be used in CW-MFC because of the high cost or complex manufacturing required. In contrast, the bio-cathode could be a promising approach for CW-MFC purposes. The bio-cathode's electrical performance compares well with that of the platinum catalyst electrode [23]. For instance, the white-rot fungus was used to inoculate the bio-cathode, which achieved a significant improvement of its MPD ( $320 \pm 30 \text{ mW/m}^2$ ) compared to the abiotic control ( $50 \pm 10 \text{ mW/m}^2$ ) [24].

Another approach for efficient energy extraction is through external circuit optimizations. Wang et al. [25] gave a detailed description of these updated power management system (PMS), an advance in energy harvesting on the ordinary MFC. The capacitor-based PMS among these is a wiser system for energy storage and release. As shown by Kim et al. [26], when using two sets of four capacitors for alternatively charging and discharging, a 67% coulombic efficiency was obtained compared to only 38% when using individual MFC with a fixed resistance. These authors showed later [27] that it was possible to use the energy released from these capacitors through linking the MFC to microbial electrolysis cells (MEC). Liang et al. [28] did related work which showed that an alternatively charging discharging (ACD) mode could produce 22–32% higher average current than an intermittent charging (IC) mode.

As for the IC mode, Ren et al. [29] reported that the charge and discharge frequency is a key factor, which has a significant influence on current output, COD removal efficiency and charge recovery efficiency. In addition, an 18.4% higher power density can be achieved ( $1238 \text{ mW/m}^2$ ) through the transient-state regulation than through the steady state mode ( $1045 \text{ mW/m}^2$ ) [30]. Furthermore, Walter et al. [31] also revealed that the intermittent loading strategy can improve the output of an MFC system; although this strategy actually failed when using the cation exchange membrane rather than the ceramic membrane. Walter et al. [31] claimed that the capacitance-like effect was occurring when using a ceramic membrane. They also stated that the faster exchange/consumption rate of the accumulation of organic acids in a ceramic system contributed to its higher output. This presented the possibility of using an external capacitor to improve the overall output of the MFC system, performing functions like those of the internal capacitance.

Actually, the duty cycling strategy was already used in an environmental MFC system with a shared cathode and multi-anodes [32]. The authors posited that in order to achieve a maximum charge transfer, it is necessary to replenish the depleted electron donors within

the anodic biofilm and the surrounding diffusion layer. In addition, a shorter "OFF" time (open circuit) could make anode potential recovery impossible. This implies that there should be a minimum "OFF" time with the duty cycling strategy, since the unrecovered situation can lift the anode potential and then lower the charge transfer efficiency on the anode.

So far, there is no work reported in CW-MFC on energy collection and use. Therefore, in order to improve the feasibility of the newly emerged CW-MFC system this preliminary work presents the use of different working strategies in CW-MFC. Results showed that with the combination of external capacitors, more energy could be harvested within each cycle. This resulted in a higher chemical oxygen demand (COD) removal rate in the CW-MFC system (normalized to the same discharge time, "ON" time). This work gave a promising direction for scaling a multi-electrodes CW-MFC system, to achieve both higher energy recovery and improved treatment efficiency.

## 2. Materials and methods

### 2.1. CW-MFC system and operation

A lab scale vertical flow CW, with the dimension of 15 cm in internal diameter and 32 cm in height, was set up in this study. The main wetland substrate was dewatered alum sludge (DAS), collected from Ballymore Water Treatment Plant, Ireland, which treats reservoir water using aluminium sulphate as coagulant. DAS is a promising CW substrate developed by our group [33–35]. It has no potential risks in either aluminium or organics releases [36,37]. Further, DAS can alleviate pH changes within the CW-MFC system [37,38], which could also be potentially used in solid-waste-based MFC to achieve higher electrical performance because of the restriction from the low pH [39,40]. The average particle size was 10–15 mm. The average porosity was around 0.4, which resulted in a net liquid volume of about 2.0 L. The bottom held gravel with average diameter of 5 mm to a depth of 30 mm. This acted as a support and improved the distribution of wastewater in the system. The anode electrode consisted of a piece of stainless steel mesh (SSM, thickness of 1 mm, 5 Mesh) buried in a layer of 30 mm graphite gravel. The open air bio-cathode was an SSM net (with average pore size of about  $150 \mu\text{m}$ ) sandwiched with a layer of 10 mm particle activated carbon. The cathode was located at the very top of the system, which connected with the anode inside the system by insulated copper wire through the external circuit with a resistor ( $1000 \Omega$ ). The electrode spacing between cathode and anode electrodes (two parallel systems with different electrode spacing) is about 7 cm and 12 cm, respectively (termed as System 1 and System 2). Both systems were inoculated with active sludge sourced from Malahide Wastewater Treatment Plant, Dublin for three weeks. Prior to the tests, the CW-MFC systems operated under the continuous upflow mode (with HRT of 12 h) for several months and both had achieved a very stable power output before the electrical tests. In order to certify our operation strategy, synthetic wastewater consisting of  $\text{CH}_3\text{COONa}$ , 0.642 g/L;  $\text{NH}_4\text{Cl}$ , 114 mg/L;  $\text{K}_2\text{HPO}_4$ , 18.23 mg/L;  $\text{CaCl}_2$ , 11.5 mg/L;  $\text{MgSO}_4$ , 12 mg/L; and trace element solution 10 mL/L [41] was used throughout the experiment, so as to eliminate the influence of feeding water on electrical performance. This was necessary because the characteristics of different wastewater streams can affect the voltage output of the MFCs and therefore the CW-MFC system [42]. The trial of the CW-MFC systems was conducted at room temperature ( $20 \pm 2^\circ\text{C}$ ).

### 2.2. Circuit and operation strategy design

The circuit consisted of three parallel connected  $4700 \mu\text{F}$  super-capacitors and a relay switch module (5VDC/1A SPDT Micro Relay, RadioShack) which were controlled by a programmable micro-controller (UNO, Arduino, Italy). The relay switches controlled the duty cycle. Fig. 1 shows the equivalent circuit. In the CW-MFC unit,  $C_1/C_2$

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