**Constructed wetland integrated microbial fuel cell system: looking back, moving forward**
Yae Wang, Yaqian Zhao, Lei Xu, Wenke Wang, Liam Doherty, Cheng Tang, Baiming Ren and Jinhui Zhao

**ABSTRACT**
In the last 10 years, the microbial fuel cell (MFC) has been extensively studied worldwide to extract energy from wastewater via electricity generation. More recently, a merged technique of embedding MFC into a constructed wetland (CW) has been developed and appears to be increasingly investigated. The driving force to integrate these two technologies lies in the fact that CWs naturally possess a redox gradient (depending on flow direction and wetland depth), which is required by MFCs as anaerobic anode and aerobic cathode chambers. No doubt, the integration of MFC with a CW will upgrade the CW to allow it to be used for wastewater treatment and, simultaneously, electricity generation, making CWs more sustainable and environmentally friendly. Currently, published work shows that India, China, Ireland, Spain, Germany and Malaysia are involved in the development of this technology although it is in its infant stage and many technical issues are faced on system configuration, operation and maximisation of electricity production. This paper aims to provide an updated review and analysis of the CW-MFC development. Focuses are placed on the experience gained so far from different researchers in the literature and further research directions and proposals are discussed in great detail.

**Key words** | constructed wetland, electricity generation, microbial fuel cell, review, wastewater treatment

**INTRODUCTION**
Historically, carbon (organic matter) in wastewater has been considered as a pollutant and treatment plants expend significant energy to oxidize it to harmless by-products, carbon dioxide, and water. Continuing this practice is not sustainable. In order to cope with the practical realities of the 21st century and beyond, a truly cyclic economy must be established. An alternative method for wastewater treatment is to extract the energy from it. Actually, wastewater has potential energy, and anaerobic digestion of high strength industrial wastewater and excess sludge from municipal wastewater treatment plants (WWTPs) is well known and widely practiced to produce biogas.

Microbial fuel cells (MFCs) have undergone long-term development since the early 20th century, among which, major attention has been paid to two aspects: intrinsic improvement of the power production, and the development of some treatment platforms based on the core of MFCs. In terms of electricity production, significant improvements have been achieved to reach orders of magnitude with higher power density compared to their primary configuration (Ge et al. 2016). Considering the treatment platforms’ development, one of the promising directions is the exploration of some sustainable or energy-positive wastewater treatment platforms. Within this scope, many novel technologies were successfully developed with the integration of MFCs into traditional wastewater treatment processes, for instance, membrane bioreactors and the activated sludge process (Wang et al. 2013a; Gajaraj & Hu 2014).
recently, researchers also found that the naturally existing stratified redox gradients in constructed wetlands (CWs) are highly consistent with the conditions in MFCs, i.e. aerobic zone at the air–water interface and anaerobic area in the inner/lower part. With the implanted electrodes in the respective area, a new merged technique was formed which has been termed CW-MFCs (Yadav 2010; Doherty et al. 2015a).

As a robust and environmentally friendly technology, CWs have been widely applied worldwide for treating various wastewaters. However, their efficiency in nutrient removal still needs to be improved to meet the stringent discharge standards. It was proved that nutrient removal efficiency can be further enhanced through the synergy effects between CWs and MFCs (Fang et al. 2013; Srivastava et al. 2015). More importantly, green energy can be simultaneously extracted from wastewater during the treatment process, which is highly consistent with the aim of sustainability, showing a promising updating choice against traditional CWs.

In addition, rather than targeting improving the treatment efficiency, CW-MFCs have large potential in the energy and sensor market. Since a CW has its unique character in scaling up with low operation and maintenance expenditure, abundant energy could be harvested if an efficient energy capture system can be applied. Moreover, it is undoubted that the power densities of CW-MFCs will be gradually enhanced along with its development, which will further consolidate its status in energy production. In terms of the bio-sensor developments, it is clear that the operation of MFCs relies on the metabolism of the exoelectrogens; thus any external factors which can influence the activities of these exoelectrogens can be reflected by monitoring the changes of voltage/current that the system produces, providing the basis to build CW-MFCs based sensors.

Therefore, in order to explore the potential of CW-MFCs, perspectives related to these already published works are reviewed in this paper. Furthermore, expectations on the development tendency of CW-MFCs in the near future are discussed and proposed.

**CURRENT STATUS OF CW-MFCS**

After the early attempts with CW-MFCs (Yadav 2010; Yadav et al. 2012; Zhao et al. 2013), an increasing number of researchers showed interest in this field (Doherty et al. 2015b). Most of them were focused on the following three aspects: (1) testifying or verifying the feasibility of this integration, which includes trials on both vertical flow and horizontal flow CWs (Table 1); in addition, different types of feeding waters varying from synthetic wastewater to real polluted water (swine water or urban wastewater) were studied (Table 1); (2) utilizing the electrode reactions for specific pollutant removal or nutrient removal enhancement; Fang et al. (2015) found that an overall 15.9% improvement in decolorization was achieved with ABRX3 concentration of 150 mg/L, and later work conducted by Wei et al. (2015) also revealed the improvement of benzene and MTBE removal efficiency with MFC engaged in a CW system; (3) attempts to increase the power production; methods such as flow regime adjustments or electrode optimizations were adopted in the previous studies (Table 1).

**CW-MFCs for enhanced wastewater treatment**

One of the main purposes of MFC integration in traditional CWs is that the produced electricity can promote pollutant removal in wastewater. Regarding organics, the anode electrode can serve as the electron acceptor during the oxidation processes, while those electrons can be transported to the cathode to complete the reduction reactions, such as oxygen reduction. This kind of synergy effect between organics oxidation and electricity production of MFCs provides CW-MFCs with an important role in enhanced wastewater treatment compared to traditional CWs.

Turning our attention to the published work in the literature, chemical oxygen demand (COD) was typically used to prove that MFC integration can further improve COD removal from wastewater. Srivastava et al. (2015) found that the MFC integration contributes to a 12–20% COD removal (0.5–0.75 g/L glucose load) in a hybrid system, while this value in another work by Fang et al. (2013) is 12.6% (using a bio-recalcitrant azo dye (ABRX3) as the substrate with a COD of 180 mg/L). In addition, Doherty et al. (2015b) showed that 33% of the total COD is removed at the anode chamber which only occupies 13.6% of the liquid volume of the system. Overall, although the pathways between those recalcitrant and bio-degradable organics are different, i.e. one as electron acceptor while another as electron donor, the studies showed that MFC integration can be used to enhance the wastewater treatment.

However, while most of the attention was paid to the anode chamber, research about cathode influences on pollutant removal remains to be done. When using the most common electron acceptor (oxygen) to participate in the reduction reactions occurring on the cathode, hydrogen...
<table>
<thead>
<tr>
<th>Objective</th>
<th>Operation regime</th>
<th>Feeding water</th>
<th>Scale and HRT</th>
<th>Descriptions</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Certification or verification</td>
<td>Batch mode</td>
<td>Synthetic wastewater with methylene dye</td>
<td>Total volume of reactor: 5 L; HRT: 96 h</td>
<td>75% COD removal with 1,500 mg/L dye. MPD of 15.73 mW/(m² anode area)</td>
<td>Yadav et al. (2012)</td>
</tr>
<tr>
<td></td>
<td>Batch mode and continuous upflow</td>
<td>Swine wastewater</td>
<td>Net volume of wastewater: 3.7 L; HRT: batch mode 10–11 d, continuous mode, 0.9–1.25 d</td>
<td>76.5% COD removal with peak PD of 9.4 mW/(m² anode area) under continuous mode; influent COD: 3,190–7,080 mg/L</td>
<td>Zhao et al. (2013)</td>
</tr>
<tr>
<td>Continuous horizontal subsurface flow</td>
<td>Synthetic wastewater</td>
<td>Reactor scale: 1.15 × 0.47 × 0.5 (L × W × H, m); HRT: 3.2 d</td>
<td>90–95% COD removal with MPD of 43 mW/(m² anode area) and CE between 0.27 and 0.45%; influent COD: 560 mg/L</td>
<td>Villasenor et al. (2013)</td>
<td></td>
</tr>
<tr>
<td>Continuous horizontal subsurface flow</td>
<td>Urban wastewater</td>
<td>Cell scale: 0.05 × 0.4 (Φ × H, m) HRT: 2.6 d</td>
<td>61% COD removal with MPD of 36 mW/(m² anode area); influent COD: 323 mg/L</td>
<td>Corbella et al. (2015)</td>
<td></td>
</tr>
<tr>
<td>Pollutant removal efficiency enhancement</td>
<td>Upward continuous flow CW-MFC</td>
<td>Synthetic wastewater with azo dye</td>
<td>Net volume of wastewater: 12.4 L; HRT: 3 d</td>
<td>An overall 15.86% improvement in decolorization was achieved with ABRX3 concentration of 150 mg/L; with MPD of 0.302 W/(m² working volume of anode)</td>
<td>Fang et al. (2015)</td>
</tr>
<tr>
<td></td>
<td>Upward continuous flow CW-MFC</td>
<td>Synthetic wastewater with azo dye</td>
<td>Reactor scale: 0.3 × 0.5 (Φ × H, m); HRT: different</td>
<td>A highest decolorization rate of 95.6% and MPD of 0.852 W/m³ (CE of 1.89%) was achieved when the COD concentration was 300 mg/L and the ABRX3 proportion was 30%</td>
<td>Fang et al. (2015)</td>
</tr>
<tr>
<td></td>
<td>Horizontal subsurface flow</td>
<td>Contaminated groundwater</td>
<td>Reactor scale: 2.01 × 0.05 × 0.6 (L × W × H, m); HRT: 15 d</td>
<td>Contribute to more than 15 and 60% removal of benzene and MTBE respectively; initial concentration: benzene, 12 mg/L; MTBE, 3 mg/L; with MPD of 1.74 mW/(m² anode area)</td>
<td>Wei et al. (2015)</td>
</tr>
<tr>
<td>Improvements of power production</td>
<td>Upward continuous flow CW-MFC</td>
<td>Synthetic wastewater</td>
<td>Net volume of wastewater: 1.4 L; HRT: 3 d</td>
<td>Increased from 1.76 mW/(m² cathode area) of SSM bio-cathode to 55.05 mW/(m² cathode area) of GAC-SSM bio-cathode</td>
<td>Liu et al. (2014)</td>
</tr>
<tr>
<td></td>
<td>Different flow pattern</td>
<td>Swine wastewater</td>
<td>Net volume of wastewater: 8.1 ± 0.12 L; HRT: 1 d</td>
<td>MPD increased from 0.163 to 0.276 W/m³ when using simultaneous upflow–downflow regime</td>
<td>Doherty et al. (2015b)</td>
</tr>
<tr>
<td></td>
<td>Upward continuous flow CW-MFC</td>
<td>Synthetic wastewater</td>
<td>Net liquid volume: 1.5 L; HRT: 1 d</td>
<td>MPD increased from 36.58 to 87.79 mW/(m² anode area) with the addition of 10% PAC in anode chamber</td>
<td>Xu et al. (2016a)</td>
</tr>
</tbody>
</table>

HRT: hydraulic retention time; PD: power density; CE: coulombic efficiency; MTBE: methyl tert-butyl ether; SSM: stainless steel mesh; GAC: granular activated carbon; PAC: powdered activated carbon.
peroxide can be simultaneously produced (Wang et al. 2013b). Hydrogen peroxide is a strong oxidizing substance which is widely used in advanced oxidation technology. Thus, the potential for in situ utilization of the produced hydrogen peroxide in CW-MFCs to enhance the treatment efficiency should be taken into consideration in future studies. Another potential usage of the cathode is for heavy metal element removal and/or recovery (Wang & Ren 2014). By accepting electrons from the cathode, metal ions existing in wastewater with appropriate reduction potentials could be reduced and then precipitated on the surface of the cathode. Nitrate is another potential target which can be used as the electron acceptor in CW-MFCs, as has been revealed by many works in which both nitrification and denitrification processes could be stimulated by MFCs (Yan et al. 2012), thus providing an alternative method for enhanced nitrogen removal in CWs.

Overall, CW-MFC is a promising choice in upgrading traditional CWs for enhancing treatment efficiency. With appropriate use of anode and cathode reactions, respectively, there is no doubt that more advantages of CW-MFCs against CWs, beyond those aspects referred to above, will be discovered gradually in the near future.

Towards a higher energy output

As an extension of pure MFCs, higher power density is certainly another concern that should be investigated. The MFC itself has already experienced long-term development and the maximum power density (MPD) increased from several W/m³ to several thousand W/m³ during this period. However, most of the MFC studies were conducted at a millilitre scale which is far smaller than a CW-MFC scale (normally litre scale), which resulted in a 2–3 orders of magnitude lower MPD compared to MFCs at this stage. Figure 1 shows the comparison of power densities between pure MFCs and CW-MFCs based on the published studies. It is clear that the power densities of CW-MFCs tend to be lower than most pure MFC values (gathered at the lower right corner within the range). This significant difference between CW-MFCs and MFCs is mainly a result of large ohmic losses (due to the internal resistance increment) and electrode potential losses (activation losses). Considering this, in order to obtain a higher power density, the most direct way would be the reduction of internal resistance. By reducing the spacing between the anode and cathode electrode, Doherty et al. (2013b) showed a decrement of 41% of internal resistance from 508 to 300 Ω. Moreover, Deng et al. (2014) also revealed that both substrate and overlying water depth can significantly influence the internal resistance of the system.

Electrode modification is another option to study for enhancing the power production. In terms of the anode, instead of using genetic engineering techniques on anode biofilm to improve its electron conductivity and thus the reduction of overall energy losses (Leang et al. 2013), more simple methods, such as using an Fe/ferric oxide modified anode (Fu et al. 2014) or amending colloidal iron oxyhydroxide into the anode substrate (Zhou et al. 2014) should be considered in later study. Some efficient current collectors should also be considered. For example, a 3D macroporous shape can be used (Xie et al. 2012). Regarding the cathode, since inexpensive material should be adopted in CW-MFCs, exploring more effective cathode materials in oxygen reduction is the major task in developing a higher energy output system, for example, carbon based materials (Watson et al. 2013). Certainly, other potential electron acceptors with higher reduction potential, which can be easily utilized in cathode reactions, can also be an option. In addition to these, bio-cathode developments will be a promising direction for stable and practical cathode developments in CW-MFCs (Wang et al. 2013c).

Considering the impossibility of using an ion exchange membrane in CW systems, the design of the MFC-CW configuration and the operation regime of the system are also two challenges that need to be addressed in future works in order to achieve an optimized output. In our previous study, a simultaneous upflow–downflow feeding regime contributed to a 70% higher power density (Doherty et al. 2013b) while the different configuration of the system can also bring significant differences in terms of the internal resistance and thus the output (Doherty et al. 2013b).
PROSPECTS AND FURTHER RESEARCH DIRECTIONS

The global trend for wastewater treatment is directed toward energy self-sufficiency, rather than energy consumption, i.e. an energy-positive process. Based on recent practice in a municipal WWTP, a net energy production of 0.002 kWh/m³ was gained through a tubular MFC (Zhang et al. 2013). Actually, the potential energy in medium strength wastewater is over three times higher than the energy required in maintaining its operation (Xu et al. 2016b). Thus a net-positive energy balance is conceivable in MFC integrated techniques. However, with CW-MFCs, energy acquirement should not be the sole objective during its development, since it is unrealistic to use expensive electrode materials or catalysts in the CW configuration. Instead, fine and inexpensive materials, for example, granular graphite or activated carbon, should be chosen as the electrode materials.

Noting that the electricity is produced with simultaneous treated wastewater, more attention should be paid on how to utilize the synergism between this integration. This might include: (a) improving the nutrient removal efficiency of COD or nitrogen as referred above; (b) targeting the enhanced treatment of some specific organic pollutants, like dyes, pesticides and pharmaceutical and personal care products; (c) heavy metal ion removal and recovery.

Scaling up CW-MFCs to field scale is an inevitable procedure to fulfill their practical application and it is vital to effectively and efficiently scale up this hybrid system. Studies in our laboratory revealed that a proper size of electrode will gain the highest power density and a comparative small current collector can obtain a higher power density. Thus, a parallel system with several relatively small electrodes should be considered in the future studies in terms of scaling up CW-MFCs. However, in spite of the in situ utilization of the produced energy for some specific pollutant removal enhancement, there is still a long way to a CW-MFC becoming an ultimate power unit, which can supply electricity to the main grid.

Since the theoretical voltage of MFCs is in the order of 1.1 V and the open circuit voltage is usually less than 0.8 V in the laboratory trials, due to a number of losses (Logan et al. 2006), after the scaling up, one of the major issues that should be considered is how to capture produced energy. Multiple methods have been developed during the last few years on pure MFCs, one of which is using the power management systems to stabilize and amplify the low voltage to a pre-set higher value, and then it is used to support the operation of electronics (Thomas et al. 2013).

In addition, a supercapacitor based charging–discharging system is worth trying in CW-MFCs systems. As shown by Kim et al. (2011) an eight-supercapacitors engaged electronic circuit can be used to alternatively charge and discharge the electrons produced from MFCs for continuous power production.

We should acknowledge that many of the CW-MFC applications are presently restricted due to their low power production. Developing a CW-MFCs based bio-sensor is another more promising research area since the fluctuation of the produced electricity signals can be used to reflect the parameter changes within the system. Actually, a few studies were carried out in this area by using pure MFCs as the sensor for on-line monitoring of water quality (COD and cadmium) (Di Lorenzo et al. 2014). An early work conducted by Zhang & Angelidaki (2012) also showed the potential of MFCs in dissolved oxygen monitoring, which could be an effective and economical method when adopted in CW systems. Other potential uses (like being a toxicity sensor or used to reflect the activity of those related exoelectrogens) deserve to be explored in CW-MFC systems.

Overall, study on CW-MFCs is still in its infant stage. Far more possibilities can be explored within the scope of sustainability (Figure 2). More attention should be paid to the strategies for in situ utilization of the produced power from MFCs at this stage and it is believed that an extension of other functions based on this versatile platform will be gradually uncovered.

Figure 2 | Future directions of CW-MFCs study (PMS: power management system; MEC: microbial electrolysis cell).
CONCLUSIONS

MFC integrated technologies possess a promising future, and CW-MFCs have unique advantages; among others, for example, they are easy to construct and have low operation and maintenance expenditure. Here, already published works are briefly presented and discussed. From the literature so far, it is understandable that the energy harvesting should not be the main target in future exploration of CW-MFCs. Accordingly, other synergetic effects between MFCs and CWs should be gradually explored. In addition, the in situ bio-sensor development is a very promising direction in future investigation/development related to CW-MFCs. It is hopeful that this brand new integration will become a mature technology in the near future.

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