

Microbial Fuel Cells (MFC) for Energy Production from Wastewater: A Review

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Abstract: Much energy is stored in wastewaters. How efficiently capture this stored energy is of great significance for meeting the world's energy needs and increasing the sustainable electrical energy from wastewater. The microbial fuel cell (MFC) is a recently developed promising technology for electrical energy recovery from the organic pollutants in wastewaters. MFCs also have great promise for sustainable wastewater treatment. However, at present there is still much research needed before the MFC technique can be practically implemented in the real world. In this review, analyze the opportunities and key challenges for MFCs to achieve sustainability of energy from wastewater. Specially the problems and challenges for scaling up the MFC systems; this is the most critical issue for realizing the practical implementation of this technique. In order to achieve sustainability, MFCs may also be combined with other new techniques to yield high quality of waste from waste water. However, research in this area is still on-going and many problems need to be stable before real-world application. Advances are required in respect of efficiency, economic feasibility, system stability, and reliability.

Keywords: Microbial fuel cell (MFC), Sustainability, Scale up

1. Introduction

Wastewater is actually a huge “energy storage tank”[1]. Recently, Microbial Fuel Cells (MFCs) have emerged as a promising technology for harvesting electrical energy from organic pollutants [2]. MFCs use micro-organisms as the catalysts for directly converting the chemical energy available in the biomass into electricity. Only those microorganisms are capable of transferring electrons outside the cell to insoluble electron acceptors (such as iron and other metal oxides, or to solid electrodes), called exo-electrogens, contribute to electricity generation in MFCs [2]. A typical MFC system consists of an anode compartment and a cathode compartment with or without a proton exchange membrane (fig 1).

through electrolyte and membrane in order to achieve electron detachment. At the cathode, a terminal electron acceptor, such as oxygen, nitrate, or sulfate, accepts the electrons and combines with protons to produce new products. MFCs can generate electricity from all most all sources of biodegradable organic matter in wastewater, including simple molecules such as acetate, ethanol, glucose, and polymers such as polysaccharides, proteins, and cellulose [3].

The MFC technology has great challenges from low power output, high capital cost, and other system limitations exist and need to be overcome. In this perspective will focus on the important opportunities and challenges of MFCs for sustainable electrical energy.

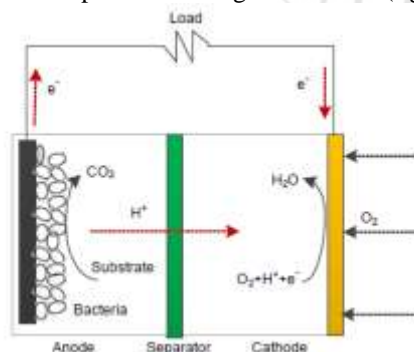


Figure 1: Schematic diagram of the working principle of MFCs for electricity production

In the anode, organic substrates (electron donors) are oxidized by exoelectrogens, generating electrons and protons. The electrons are transferred to the anode material and then passing through an external electric circuit to the cathode. At the same time, protons diffuse from the anode to the cathode

2. MFCs for Sustainable Energy from Wastewater: Opportunities and Challenges

A sustainable energy from wastewater essential features: neutral-energy operation, minimal adverse environmental impact, balanced investment and economic output, stable treatment performance, high waste quality to meet energy recovery and reuse requirements, little resource consumption, and good social equity[4]. Energy from domestic wastewaters using conventional processes, such as activated sludge approach, membrane bioreactor and anaerobic digestion, is usually hard to achieve sustainability, because of their high organic pollutants consumption, adverse environmental impacts and low waste quality. For example, conventional activated sludge process requires 0.3 kWh/m³ for aeration [5] and generates 0.4– 0.8 g-VSS (volatile suspended solids)/g-COD. Membrane bioreactors demand a high energy input of 1 to 2 kWh/m³ for an appropriate

efficient energy and high waste quality[6]. Although anaerobic digestion of sludge has achieved energy neutrality by producing biogas (methane), its sustainability is limited due to the requirement for a high organic load (>3 kg organic matter per m^3) and warm temperature (>20 °C), resulting in low waste quality, and high operational cost [6].

First, MFCs are theoretically energy profitable, based on their low energy consumption and direct electricity generation. MFC can consider as an energy saving technology due to their needless of aeration or temperature maintenance, and their low excess sludge generation compared to the conventional activated sludge process[7]. Only about 0.024 kW or 0.076 kWh/kg-COD on average (mainly for reactor feeding and mixing) was estimated to be consumed in MFCs[8], compared to about 0.3 kW or 0.6 kWh/kg-COD for the activated sludge based aerobic process[5]. More importantly, MFCs are capable of directly producing electricity from the organic matter in wastewater with a high energy conversion rate, whereas the conversion of biogas (e.g., CH_4 or H_2) into electricity causes a significant energy loss of more than 60% [9].

Second, MFCs have a less adverse impact on the environment. MFCs are capable of efficiently removing a large variety of pollutants from wastewaters, such as nutrients [10], unmanageable cellulose [11], dyes[12], leachates[13], volatile fatty acids[14], metals[15] and nitrate and sulfur compounds[16]. A good waste quality with $COD < 20$ mg/L can be achieved by MFCs with an improved reactor configuration and operating condition[17]. Moreover, the low energy consumption of MFCs results in low fossil related carbon dioxide production. MFCs also have a less sludge production of about 0.1 g-VSS/g-COD, which is much lower than that produced in activated sludge systems (0.4–0.8 g-VSS/g-COD) [18]. Therefore, the secondary pollution risks and extra energy consumption associated with sludge disposal are greatly reduced.

Third, MFCs have theoretically a better operational stability and low operational cost. The microbes in MFCs have a good resistance to toxic substances and fluctuations in pH[19]. MFCs can also operate over several different temperature ranges, ranging from ambient temperatures (15–35 °C) to both high temperatures (50–60 °C) and low temperatures (<15 °C) [20].

The biggest challenge is the relative low power production level of MFCs, especially for those at larger scales. This makes it little hard to realize the energy. Although a maximum volumetric power density of 2.87 kW/ m^3 (normalized to the fuel cell volume) has been achieved in a 30 ml MFC with a cloth electrode assembly configuration [21], the value decreased substantially (typically to less than 35 W/ m^3) when the fuel cell size was increased from milliliter scale to liter scale [22]. It has been suggested that MFCs should have to be able to produce at least 400 W/ m^3 to be competitive with traditional anaerobic digestion[23] and to have an output of 1 kW/ m^3 (at an organic loading rate of 10 kg-COD/(m^3 ·d)) to

achieve energy self-sufficiency[24]. It is clear that there is much area for the MFC technology to improve its power production level. In addition to low power production, other factors, such as high capital cost, less power harvesting efficiency and poor long-term system stability.

During the past decades, much laboratory work has been conducted on milliliter-scale MFCs[25], which provides valuable guidance for the future development of commercial MFCs. The components of wastewaters are complex and may contain some un-degradable or even toxic substances which will obstruct the electrochemical activity of anodic microorganisms. Wastewaters are usually poorly buffered which will lead to an accumulation of H^+ in the anode and OH^- in the cathode region; the conductivity of real wastewaters is usually too low to maintain a low internal resistance; in many regions the ambient temperature may change dramatically at different times of the day and in different seasons of the year, which makes it hard to always maintain a high performance of the anode bacteria.

Large-scale MFCs can act as a standalone technique for energy production, or they can be combined with other processes to form a synergic system. This strategy is capable of realizing many specific purposes, e.g., for a high waste quality or for recovering more commercial value from wastewaters, and thus has been proposed as a more promising way for future energy production[26]. However, with a continuing improvement in both technique and material aspects, it is also possible in some instances to achieve sustainable energy from wastewater by using the MFC technique alone.

3. Scaling Up MFCs to A Practical Level

It would be ideal to get a practical level of efficient energy output when the reactor size of MFC is enlarged from milliliter to liter or cubic meter scale. However, limitations such as low power output, high capital cost, power management problems, and reduced long-term stability of the system are challenging the scaling up of MFCs. Only some of the studies on overcoming these limitations have been done. To manage the critical factors limiting the scaling up of MFCs and the challenges explained in the following section.

3.1 Increasing Power Output

There are two approaches for making large-scale MFCs for energy production from wastewater: enlarging the size of an individual reactor and combining MFC units as a stack.

3.1.1 Enlarging reactor size

When the MFC is scaled up to several liters or more, the volumetric power density can be 2–4 orders of magnitude lower than that of laboratory-scale MFCs[27]. Previous scaling up efforts provide a valuable information for understanding the reasons for this low power output from large-scale MFCs, which should be considered in for future reactor design. It has been proposed that one of the main

reasons for power loss upon scaling up of MFCs is the increase in internal resistance [28]. Internal resistance can be reduced by decreasing the spacing of the electrodes or by increasing the solution conductivity [29]. A close distance between the anode and the cathode is very important for reducing the solution resistance and pH gradient in large-scale MFC systems [30]. However, possible short circuits and increased oxygen diffusion to the anode reduction in power output when the electrodes are too close. So a separator which prevents electrode contact and oxygen diffusion is recommended to keep the electrodes spaced and the internal resistance small. However, the separator can also prevent proton transfer and lead to pH gradients between the electrode chambers thus increasing the internal resistance. The balancing needs of reducing oxygen transport but facilitating proton transport make it difficult to design separators. Low-cost cloths have been recommended to replace expensive membranes as an effective separator for large-scale applications. A cloth-electrodes assembly configuration has proved to enable reducing the anode-cathode spacing to 0.6 mm while greatly improving power generation [21]. However, cloths may be gradually degraded by the microorganisms in the system, thus impairing the long-term stability of MFCs. Non-biodegradable and low cost separators with low oxygen permeability and high proton transmission rates need to be developed.

Cheng and Logan demonstrated that in a 1.6 L air-cathode MFC, doubling the cathode size can increase power output by 62% with domestic wastewater, but doubling the size of the anode increased power output by only 12%. The volumetric power density of MFC was linearly related to the specific surface area of the cathode, and autonomous of the fuel cell size or configuration.

When the MFC becomes large, it may not be easy to maintaining "homogeneity" in the reactor. The "inhomogeneity" in large-sized MFCs is revealed by different substrate concentrations. An un-even distribution of substrate can affect the mass transfer rate, electrochemical reaction rate and finally electricity production. Increasing the mixing intensity by increasing the hydraulic retention time, the internal recirculation flow rate and the aeration flow rate will be useful in achieving a homogenous distribution of the substrate for large-sized MFCs [13]. However, adverse effects such as anodic biofilm detachment and less pollutant removal efficiency may occur when the flow rate is too high. Hence, it is necessary to design an optimal flow rate, at which the substrate is equally distributed; the system is not extremely disturbed.

3.1.2 MFC stacks

A variety of challenges exist in the scaling up of individual MFCs, which may prevent the reactor size being as large as the existing energy harvesting systems. An alternative, which may be a more possible option for MFC scaling-up, is to construct stacks of moderately scaled MFC units. In order to implement practically MFCs as an energy source, one can connect MFC units in parallel to produce a higher current or in

series for a higher voltage. Aelterman and et.al, connected six MFCs in parallel, which results in a current equal to the sum of the individual MFCs, while the voltage was similar to the average of the individual MFCs. Furthermore, the maximum power density of parallel connected MFCs can be several times greater than that of the single MFC unit [31]. For Series Connection, it would be ideal that the output voltage equals to the sum of the voltages of the individual MFCs, and the current would be at the average of the individual reactors. However, MFCs may experience cell voltage reversal and ionic short circuits, making the series stack efficiency as low as 38%–41% [31]. Voltage reversal results from un-equal electrode potentials between the unit cells, possibly due to inadequate distribution of the substrate [32]. Voltage reversal can be prevented by using air cathodes of high parallelism in performance, maintaining similar catalytic activity of anode bio-films, and increasing the homogeneity of substrate distribution in different unit cells. However, much work is still needed to turn these strategies into real time. The ionic short circuit occurs when the same anolyte or catholyte is shared by different MFCs in series connection [33]. Separating the anolyte of the unit cells may be useful to prevent ionic short circuits, but it will increase the costs of reactor construction and maintenance. A promising development way for the MFC stack is to create an electrical group to multiply connect the MFC units both in series and in parallel. In this way, both the cell voltage and current can be boosted and the substrate can be properly degraded. However, researches in this aspect are still few, and research effort is required to better understand the interaction between distinct MFC units, to enhance the connection mode for the maximum power output, and to maintain the stable complex stack system.

3.2 Reducing capital cost

Another critical problem is the large-scale application of MFC and its high capital cost, which mainly arises from the expensive construction materials. Reducing the capital cost can be accomplished by using highly efficient, scalable and less-expensive anode, cathode and separator materials. Electrodes containing current collectors are now considered a suitable configuration, due to their simple structure and effective current collection. For the anode, one of the most promising electrode structures is a graphite fiber brush, which is made by incorporating graphite fibers into a non-corrosive metal core (certain stain-less steels or titanium). Metals such as tungsten and stainless steel can also be used in brush form. Another promising anode material is Activated Carbon (AC) granules, particularly when linked to a metal mesh current collector. An anode chamber stacked with AC has a high specific surface area (area per mass) for bacterial growth and electricity production. However, much remains to be known about the distribution of microbes and the proton and electron transfer mechanisms inside the AC stack, and the fuel cell configuration needs to be improved for a better performance.

The price of cathode materials has high percentage (47%–75%) of the MFC capital cost. The most promising cathode form for future MFCs is that using oxygen in the air as the

terminal electron acceptor (the air-cathode), based on the readily available nature of oxygen in the air and the absence of a need for solution aeration. Reducing the cost of the air-cathode can be achieved by developing inexpensive current collection materials, diffusion layer materials, binders, and catalysts. Promising current collection material is the metal mesh, such as a stainless steel mesh and nickel foam, which is low cost and highly-conductive. Low-cost poly-tetra-fluoro-ethylene (PTFE) and poly-di-methyl-siloxane (PDMS) can be used as the oxygen diffusion layer and catalyst binder instead of the expensive Nafion. Low cost catalysts with non-precious metals, such as CoTMPP, MnPc, β -MnO₂, Co-OMS-2, MnO_x, and Co/Fe/N/CNT [34] can be used instead of the expensive Pt. An especially interesting catalyst is AC, which is low cost and has a high catalytic activity. However the mechanism of activated carbon catalyzes oxygen reduction remains unclear [35]. Another difficulty in reducing the cost of cathode;s is the requirement of a complex gas-liquid-solid three-phase interface for oxygen reduction, which makes the selection of cathode material and design of cathode structure more challenging.

The separator is another costly component of MFCs. Even though it has been proved that the absence of a separator in small MFCs favors low internal resistance and low capital cost[36], in large sized MFCs it is usually necessary to construct close electrode spacing for a low internal resistance, and thus a separator is essential to prevent electrode contact and oxygen crossover to the anode. From the economic point of view, expensive membranes, such as ion exchange membranes, ultra filtration membranes, and forward osmosis membranes are not suitable for use in large-scale MFCs. A promising low cost separator material is non-woven cloth [21], but its mechanical strength and long-term stability still need to be improved. The development of low cost, proton transferable, and long-term stable separator materials is very important for large-scale MFCs in the future.

3.3 Managing Output Power

Efficient electrical energy harvest is a difficult issue in the scaling up of MFCs. It is challenging for an MFC to directly support a practical load, even at the maximum power generating point, due to the low voltage and current level[32]. Thus, a Power Management System (PMS) is needed to be incorporated into MFCs to make the feasible energy for powering electrical devices. e.g., wireless sensors to monitor the environment[37]. Although using an optimum resistor (resistance value equal to the internal resistance) makes MFCs capable of producing their maximum power density, resistors cannot harvest energy because the generated electricity is dissipated as heat instead of being utilized or stored. For effective harvesting and use of MFC energy, a DC/DC voltage

boost converter and various electric -storage capacitors have been tested. DC/DC voltage boostconverters can extract energy from MFCs by a high frequency switching operation [38]. Park and Ren have demonstrated that the operating voltage of MFCs can be easily maintained at the maximum power point and the output voltage can be boosted to a standard level of 1.5 V or 3.3 V using a separate boost converter to support electronic loads. By use of metal oxide semiconductor field effect transistor to replace the traditional diode of the converter, the harvesting efficiency of the synchronous boost converter can reach 75.9% [38]. Optimization of the electronic circuit of the converter and developing a maximum power point tracking technique [39] can be promising strategies for this purpose. When a capacitor is connected to a MFC it stores energy from the MFC and waits until a preferred amount of energy is stored, then discharges the energy. It has been reported that connecting a capacitor to a Sediment Microbial Fuel Cell (SMFC) enabled the SMFC to produce 2.5 W powers which can be used to operate a wireless sensor [37]. Another study showed that parallel charging of multiple capacitors can avoid potential voltage reversal and discharging the capacitors in series produced up to 2.5 V with four capacitors [32]. A great challenge for capacitor energy harvesting is that capacitors can only passively capture the energy from the MFC, so the system's performance may not be stable. Another challenging problem is that a continuous high-level power output cannot be realized by using capacitors. To overcome these drawbacks, developing more efficient capacitors by optimizing electrode materials and control systems, or designing different combination modes between the capacitor and the MFC might prove useful.

For large-sized MFCs, it is also critical to consider the great power loss from the large ohmic resistance of large-sized electrodes. This is because the distance between the points where electrons are generated and the leading-out/in terminals where current flows in/flows out of the electrode increases with the increase of the size of the electrodes [40].

3.4 Increasing long-term stability

Long-term stability is important for the energy balance and economic feasibility of the MFC system. A failing performance of MFCs during long-term operation has been detected in many studies [41]. Reasons for this performance weakening depends on many factors, such as the decrease of electrochemical activity of anodic biofilm, the deterioration of cathode performance, fouling and deformation of separator materials, and clogging of the system by excessive bio-mass and solid pollutants in wastewaters.

Table 1: Comparative study of voltage, current and current density by recent researches

Authors	Results obtained (current, voltage and current density)	Type of Reactor	Different dilution condition used
Zhang et al. (2015)	Maximum current density 1.8 A/m ²	Double Chamber MFC	Effect of 6.6 % dilution of raw distillery wastewater on power generation
Debajit et al. (2013)	Maximum voltage 69mV	Double Chamber MFC	
Jang et al. (2004)	Maximum current 3.2mA	Double Chamber MFC	Effect of 8.3 % dilution of raw distillery wastewater on power generation
Ashutoshpatra (2008)	Maximum voltage 590mV and current 0.78mA	Single Chamber MFC	
Sam and Mercy (2012)	Maximum voltage 400mV and current 4.5mA	Double Chamber MFC	Effect of 10 % dilution of raw distillery wastewater on power generation
Banik et al. (2012)	Maximum voltage 435mV and current 2.1mA	Double Chamber MFC	
Yongtae and Logan (2013)	Maximum voltage 450 mV	Double Chamber MFC	Effect of 6.6 % dilution of raw sugar wastewater on power generation
Martha et al. (2014)	Maximum voltage 580mV and current 0.4mA.	Double Chamber MFC	
Vignesh et al. (2012)	Maximum current 275 μ A	Double Chamber MFC	Effect of 13.3 % dilution of raw sugar wastewater on power generation
Debajit et al. (2013)	Maximum voltage 690mV	Double Chamber MFC	
Der Fong Juang (2012)	Maximum voltage 90mV	Double Chamber MFC	Effect of 20 % dilution of raw sugar wastewater on power generation
Zain et al. (2011)	Maximum voltage 630mV and current 0.27mA	Double Chamber MFC	

4. Conclusions

MFCs have great promise for sustainability of electrical energy from wastewater. At present, the real-world large-scale application of this latest attractive technology is still in progress. Scientists and engineers from all over the world are giving great efforts to develop large-scale MFCs and to settle the problems limiting the scaling up of MFCs, such as the low power output, high capital cost, low energy harvesting efficiency, and poor system stability. Studies regarding the integration of MFCs with other techniques to give high waste quality or for recovering energy rich or highly valuable chemicals have just emerged, and challenges in the electricity production efficiency, effectiveness, economic feasibility, and system stability need to be overcome for the practical application of these techniques. Great efforts from experts in reactor design, material engineering, system optimization, and biological manipulation are required in the future to realize sustainable energy production from wastewater by MFCs.

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