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Review

Challenges in the application of microbial fuel cells to wastewater treatment and energy production: A mini review

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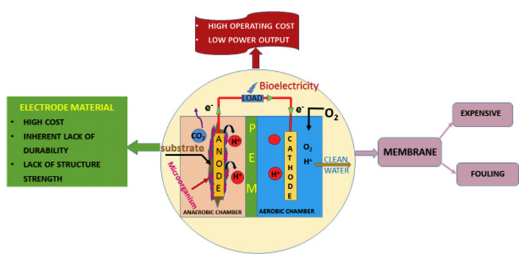
HIGHLIGHTS

- MFCs are a promising technology for wastewater treatment and energy production.
- Costs of MFC material fabrication and electricity production are challenged.
- Current instability and high internal resistance are also problematic issues.
- Membrane fouling and low rate of growth of microbes limit the MFCs' application.
- Practical version of tonne scale MFC is proposed and tested with real wastewaters.

GRAPHICAL ABSTRACT



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ABSTRACT

Wastewater is now considered to be a vital reusable source of water reuse and saving energy. However, current wastewater has multiple limitations such as high energy costs, large quantities of residuals being generated and lacking in potential resources. Recently, great attention has been paid to microbial fuel cells (MFCs) due to their mild operating conditions where a variety of biodegradable substrates can serve as fuel. MFCs can be used in wastewater treatment facilities to break down organic matter, and they have also been analysed for application as a biosensor such as a sensor for biological oxygen which demands monitoring. MFCs represent an innovation technology solution that is simple and rapid. Despite the advantages of this technology, there are still practical barriers to consider including low electricity production, current instability, high internal resistance and costly materials used. Thus, many problems must be overcome and doing this requires a more detailed analysis of energy production, consumption, and application. Currently, real-world applications of MFCs are limited due to their low power density level of only several thousand mW/m^2. Efforts are being made to improve the performance and reduce the construction and operating costs of MFCs. This paper explores several aspects of MFCs such as anode, cathode and membrane, and in an effort to overcome the practical challenges of this system.

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Contents

1. Introduction

Wastewater is now recommended as a vital resource for water reuse and saving energy. Conversely, traditional treatment technologies such as conventional aerobic activated sludge (CAAS) require large amounts of energy and generated residuals; there is also the problem of not recovering enough or any potential resources available in wastewater (He et al., 2017). Currently, anaerobic digester (AD) technology is widely accepted as a vital treatment strategy in that it saves energy sources and is highly effective in converting organic chemicals into methane (CH_4) gas. This in turn can be changed into electricity by CH_4-driven engines or chemical fuel cells. However, some research indicates that treated wastewater does not always meet stringent regulatory standards, and more technical advances are demanded for the post-treatment scenario. Despite these problems, water reuse has already been widely implemented especially in some dry areas. However, it invariably requires more energy for treatment, principally arising from the increased water quality requirements for reuse (Venkata Mohan et al., 2011).

Microbial fuel cells (MFCs) have been recognized as an encouraging and challenging technology in saving energy and simultaneous wastewater treatment, overcoming environmental problems (Pandey et al., 2016). This is particularly the case in isolated areas that are supplied with biosensors, bio hydrogen production, as well as in-situ power sources for bioremediation and wastewater treatment (He et al., 2017; Surya Ramadan and Purwono, 2017).

In recent years, the number of papers on MFCs being published in journals has markedly increased. The Web of Science ™ database searching with keyword of "microbial fuel cell" on December 25, 2016 leaded to a total of 6198 papers, in the field of "biotechnology applied microbiology" (1896), "energy fuels" (1664), "electrochemistry" (1154) and "environmental sciences" (1006) (Hu et al., 2017). In the last few years, MFCs as a new source of bioenergy have been extensively reviewed with different emphasis, such as designs and configurations, electrodes and electrode surface modifications, microbial communities, operation conditions for performance and biofilm formation, challenges and possibilities, fundamental electron transfer mechanisms and applications (Pandey et al., 2016; Surya Ramadan and Purwono, 2017).

He et al. (2017) indicated there are many reasons why MFCs are more sustainable when applied to wastewater treatment. The first advantage is their ability to directly convert substrate energy into electricity. Second, using MFCs allows wastewater processes to reduce activated sludge compared to anaerobic digestion and CAAS processes. The third advantage is insensitivity to the operational environment. The fourth one is that MFCs do not require any treatment for gas because of the recycling and conversion. Much more energy can be saved by MFCs without any energy input required for aeration. Fifth and finally, MFCs can be used widely in locations where there is insufficient electrical infrastructure.

Despite of the fact that, MFCs technology is an innovation strategy for improving waste/wastewater treatment and energy product. However, many challenges must be addressed including electron transfer mechanism, the microscales with biofilm formation and associated transport process, and the macro-scales with electrodes and separators in bioanode (Kim et al., 2015).

Despite the MFCs' application at lab level, researchers have proved their suitability in industrial contexts such as the reactor volume operational time and wastewaters investigated in MFCs (He et al., 2017).

With these possibilities in mind, this study aims to discuss the MFC concept and its practical application for wastewater treatment and energy production. By introducing a wide range of MFCs and looking at each one in detail, the challenges of MFCs are highlighted. Moreover, the combination of MFCs with other treatment processes is explained in terms of practicality and effectiveness. Furthermore, the challenges and opportunities for scaling up and future applications of MFC in wastewater are also discussed in this paper.

2. General features of microbial fuel cells

Recently, a type of technology using microbial fuel cells (MFCs) that converts the energy stored in chemical bonds in organic compounds into electrical energy has been achieved through the catalytic reactions generated by microorganisms. This process has aroused considerable interest among academic researchers since the early 1990s (Allen and Bennetto, 1993; Choi et al., 2003; Gil et al., 2003; Moon et al., 2006). Microbial fuel cell technology has become an innovation renewable energy resource by degrading organic pollutants in wastewater (Mustakeem, 2015; Wang et al., 2015).

Microbial fuel cells (MFCs) are devices that use bacteria as catalysts to oxidize organic and inorganic matter and generate electrical current. Microbes in the anodic chamber of an MFC oxidize added substrates and generate electrons and protons in the process. Carbon dioxide is produced as an oxidation product. However, there is no net carbon emission because the carbon dioxide in the renewable biomass originates from the atmosphere in the photosynthesis process. The bacteria on the anode decompose organic matter and free H^+ ions and electrons. Electrons produced by the bacteria from these substrates are transferred to the anode (negative terminal) and flow to the cathode (positive terminal) linked by a conductive material containing a resistor, or operated under a load, i.e., producing electricity that runs a device (Hernández-Flores et al., 2015; Surya Ramadan and Purwono, 2017). The H^+ ions flow through the semi-permeable membrane to the cathode. This process is driven by the electrochemical gradient resulting from the high concentration of H^+ ions near the anode. The electrons from the cathode combine with dissolved oxygen and the H^+ ions to form pure water (Brown, 2012).

Microbial fuel cells are being constructed using a diverse range of materials and in a variety of configurations. Fig. 1 is a schematic diagram of a typical MFC for producing electricity. It consists of anodic and cathodic chambers partitioned by a proton exchange membrane (PEM).

Electrode reactions are shown below using acetate as an example substrate.

Anodic reaction:

$$CH_3COO^- + 2H_2O \rightarrow CO_2 + 7H^+ + 8e^-$$

Cathodic reaction:

$$O_2 + 4e^- + 4H^+ \rightarrow 2H_2O$$

The overall reaction is the breakdown of the substrate to carbon dioxide and water with a concomitant production of electricity as a by-product. Based on the electrode reaction pair above, an MFC bioreactor can generate electricity from the electron flow originating in the anode and going to the cathode in the external circuit. Based on the transfer of produced electrons by active microorganisms from media to anode electrode, MFCs can be divided into two different types: firstly, MFCs with a mediator, where electron shuttles or mediators are added into the system; and secondly, mediator-less MFCs where no mediator needs to be added (Rahimnejad et al., 2015).

There are various factors that affect the performance of MFCs and its energy production in wastewater treatment such as microorganims, substrates which can be utilized as the source of electron donors, operating conditions in terms of pH, temperature, electrode surface area, material and construction of the anode, cathode and membrane could have a markable impact on electricity generation (Aghababaie et al., 2015).

Due to the ability to convert chemical energy into electrical energy, MFCs have many potential applications, for example electricity generation, bio hydrogen production, wastewater treatment and biosensor (Parkash, 2016; Santoro et al., 2017).

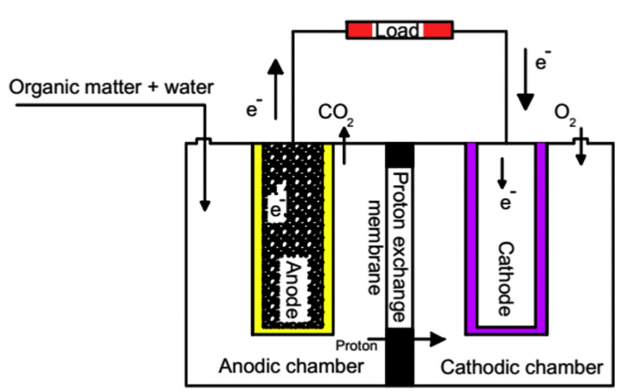

Fig. 1. The MFC system consists of anode and cathode compartments.

2.1. MFCs' configuration

The most essential requirement for MFCs is that they have been appropriately designed. MFCs are built according to a range of architectural requirements, and various kinds of MFCs are usually appraised by power output, Coulombic efficiency, stability, and longevity (Parkash, 2016). Apart from that microbial fuel cell can be optimized in two types on the basis of number of compartments of chambers.

2.1.1. Two-chamber microbial fuel cell

Research by Logan et al. (2006) shows that MFCs can have many different configurations. A widely used and inexpensive design is a two-chamber MFC built in a traditional "H" shape, usually consisting of two bottles connected by a tube containing a separator which is normally a cation exchange membrane (CEM) such as Nafion or Ultrex or a plain salt bridge, to allow protons to move across to the cathode while blocking the diffusion of oxygen into the anode. The compartments can function in various practical shapes such as cylindrical, rectangular and miniature. The two-chamber design of MFCs is frequently operated in batch mode and fed-batch mode. A typical MFC consists of an anodic chamber and a cathodic chamber separated by a PEM as depicted in Fig. 2.

2.1.2. Single chamber microbial fuel cell

A standard single chambered MFC is illustrated in Fig. 3. In this design the anode and cathode are not placed in different compartments. They are both in a simple anode compartment where there is no definitive cathode compartment and may not contain proton exchange membranes as shown in Fig. 3 (Lee et al., 2015). A porous cathode which is located on one side of the wall of the cathode chamber utilizes oxygen from atmosphere and lets protons transfer through them. Single compartment MFCs offer simpler designs and are cheaper (Das and Mangwani, 2010).

Besides these two common designs, several adaptions have been made in MFC design and structure; many single chambered MFC designs are available for different construction methods.

In order to achieve the high power densities in MFCs, the main issue is the system architecture, not the composition of the bacteria community (Logan and Regan, 2006a). Indeed, many studies have indicated that the performance of MFCs with mixed inoculation would be better than that with pure culture inoculation in terms of both power density and efficiency in removing contaminations. The commercialization of MFCs can be achieved by employing an appropriate design, efficient scaling up, manageable costs, ensuring high performance and being conveniently combined with existing wastewater treatment facilities. Currently, MFCs are still at the laboratory level stage of analysis and evaluation, but some ingenious designs have been developed to incorporate MFCs into other wastewater treatment processes.

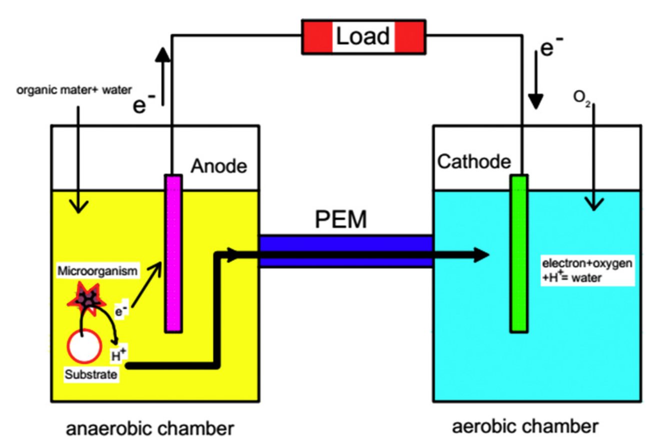

Fig. 2. Two-chamber MFC.

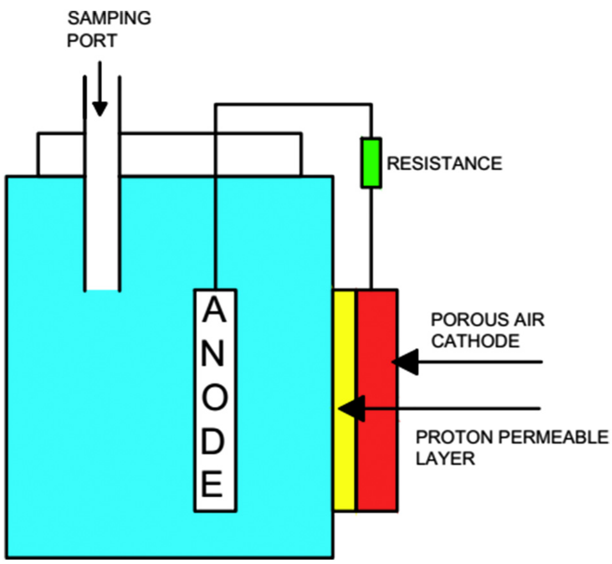

Fig. 3. A single chamber microbial fuel cell without an air cathode.

2.2. Electrode material of MFCs

Electrode material is ideal for the performance of MFCs in terms of bacterial adhesion, rate of electron transfer and electrochemical efficiency. To implement MFC technology in a real world scenario, the cost of materials must be reduced and power densities must be maximized. Furthermore, the cathode materials should have catalytic properties for oxygen reduction (Mustakeem, 2015). There are some differences when selecting materials for the anode and cathode, however, both should have the following properties: (Aelterman, 2009) surface area and porosity; (Aghababaie et al., 2015) electrical conductivity; (Ahn and Logan, 2010) stability and durability; and (Allen and Bennetto, 1993) cost and accessibility. Table 1 below summarizes the MFC components and materials used to construct them (Bullen et al., 2006; Logan and Regan, 2006b; Lovley, 2006; Rabaey et al., 2006).

2.2.1. Anode material

The anaerobic anode compartment is a major part of a MFC. It is filled with substrate, mediator or no mediator, and the microorganisms and anode electrode function as electron acceptors. Various factors affect the performance of MFCs such as electrode material and equipment configuration (Logan et al., 2006; Oh et al., 2004). One of the most effective factors is anodic microbial electron transfer, which amplifies the microbial electron transfer rate, through miscellaneous applications such as adding electron mediators and optimizing cell design and electrode. Ideally, electrode material should have the following features: (i) good electrical conductivity and low resistance; (ii) strong biocompatibility; (iii) chemical stability and anti-corrosion; (iv) large surface area; and (v) appropriate mechanical strength and toughness. The most popular utilized materials in anode are made of carbon materials containing graphite fiber brush, carbon cloth, and graphite rod (Logan et al., 2006). The simplest materials for anode electrodes are graphite plates or rods since they are inexpensive, easy to handle, and have a defined surface area. Table 2 summarizes different materials used for anode electrodes with their respective advantages and disadvantages.

Table 1
Basic components of a microbial fuel cell.

Items	Materials
Anode	Graphite, graphite felt, carbon paper, carbon cloth, Pt, Pt black, reticulated vitreous carbon (RVC)
Cathode	Graphite, graphite felt, carbon paper, carbon cloth, Pt, Pt black, (RVC)
Anodic chamber	Glass, polycarbonate, Plexiglas
Cathodic chamber	Glass, polycarbonate, Plexiglas
Proton exchange system	Nafion, Ultrex, polyethylene.poly (styrene – co – divinylbenzene), salt bridge, porcelain septum, or solely electrotyle
Electron catalyst	Pt, Pt black, MnO_2, Fe^{3+}, polyaniline, electron mediator immobilized on anode

2.2.2. Cathode material

The cathode materials play an important role on the power capacity of MFCs, which have a high redox potential, easily to capture protons. Most of the materials used as an anode can be used as a cathode. Currently, graphite, carbon cloth and carbon paper are the common cathode materials (Zhou et al., 2011). To improve performance of MFC, utilizing Pt at the cathode is one of the innovation technologies in order to reduce the cathodic reaction activation energy and increase the reaction rate. Moon et al. (2006) created an MFC that used graphite felt including Pt as the cathode. The power density reached 150 mW m^{-2}, which was three times higher than that for the pure graphite cathode. However, Pt is an expensive metal, so it can effect to the MFC' application (Logan et al., 2006). Many efforts have been made to reduce the cathode cost by reducing Pt loading or finding a new types of inexpensive catalyst. Recently, noble- metal free catalysts that utilize pyrolyzed iron (II) phthalocyanine or CoTMPP have been proposed as MFCs cathodes (Cheng et al., 2006).

2.3. Microbes used in microbial fuel cells

The key to understanding the theory of how MFCs work is the anodic electron transfer mechanism in them. Microbes transfer electrons to the electrode through an electron transport system that includes a series of components in the bacteria extracellular matrix and together with electron shuttles are dissolved in the bulk solution (Du et al., 2007). Many microorganisms possess the ability to transfer electrons derived from the metabolism of organic matters to the anode. A list of them is shown in Table 3 together with their substrates.

According to Logan et al., a MFC utilizes bacteria to catalyze the conversion of organic matter into electricity by transferring electrons to a developed circuit (Bond et al., 2002; Logan and Regan, 2006a; Logan and Regan, 2006b). Logan et al. (2006) suggest that microorganisms can transfer electrons to the anode electrode in three ways: firstly, exogeneous mediators (external to the cell) such as potassium ferricyanide, thionines, or neutral red; secondly, using mediators produced by the bacteria; or thirdly, by direct transfer of electrons from the respiratory enzymes (i.e., cytochromes) to the electrode.

Bennetto (1990) suggests that these mediators can divert electrons from the respiratory chain by entering the outer cell membrane, becoming smaller in size, and then leaving in a reduced state to shuttle the electron to the electrode. Marine sediment, soil wastewater, freshwater sediment and activated sludge are all rich sources for these microorganisms (Du et al., 2007). Studies earlier this century have discussed: firstly, the screening and identification of microbes; and secondly, the construction of a chromosome library for microorganisms that are able to generate electricity by degrading organic matter (Holmes et al., 2004; Logan et al., 2005).

As shown in Fig. 4, bacteria use the electrons to produce energy by way of the electron transfer chain. The microbial fuel cell breakdowns the electron transfer transport chain using a mediator molecule to shuttle electrons to the anode. The electrons transport chain begins with NADH, a biological transport molecule, releasing a high energy electron (e^-) and a proton (H^+). The electron follows the red path through the proteins in the mitochondrial membrane. As the electron passes through each protein, it pumps hydrogen ions (H^+) through the membrane. In a normal bacterial cell, the electron continues along the dotted

Table 2
Different types of materials used for MFC anode.

Anode material	Advantage	Disadvantage	References
Carbon cloth	– Large relative porosity – Higher specific area and mechanical strength	– Relative expensive	(Ishii et al., 2008)
Carbon paper	– Easy-to-connect wiring – Relative porous	– Fragile – Expensive	(Kim et al., 2007)
Carbon Felt	– High porosity, high electrical conductive – Relative low cost – Wide surface area	– Large resistance	(Kim et al., 2002)
RVC	– High electrical conductivity	– Large resistance, fragile	(He et al., 2005)
Stainless steel (plate/mesh/foam or scrubber)	– High conductivity – Relatively cheap – Easy accessibility	– Low surface area – Biocompatibility issue – Corrosion	(Dumas et al., 2007)
Graphite rods/plate	– Good electrical conductivity and chemical stability – Relative inexpensive – Easy accessibility	– Difficult to increase surface area	(Liu et al., 2005a)
Graphite fiber brush	– High specific area – Easy construction	– Clogging	(Ahn and Logan, 2010)

red path where it combines with oxygen to make water. In a microbial fuel cell, the electron continues along the solid red path where it is picked up by a mediator molecule and taken to the anode.

2.4. Proton exchange membrane

The proton exchange membrane (PEM) plays an important role to the configuration and operation of the MFCs (Hernández-Flores et al., 2015). Du et al. (2007) indicated that proton exchange membrane can affect to the internal resistance and concentration polarization loss of the MFC and they in turn influence the power output of the MFC. The functions of the PEM in MFCs are to: (i) separate two chambers: anode and cathode; (ii) reduce the substrate flux from the anode to cathode and to minimize back diffusion of oxygen to the anodic chamber; (iii) increase the Coulombic efficiency (CE); and (iv) ensure an efficient and sustainable operation over time.

The most commonly used PEM is Nafion due to its highly selective permeability of protons. Despite Nafion being expensive it is still the best choice. Alternatives to Nafion such as Ultrex CMI – 7000 (Membranes International Incorp, Glen Rock, NJ. (Logan et al., 2006) also are well suited for MFC applications and are considerably more cost-effective than Nafion. Active research on replacing Nafion separators by other membranes has been carried out in recent years and such analyses include: ultrafiltration and microfiltration membranes, sulphonated polyether ether ketone membrane, anion and cation exchange membranes, bipolar membrane, and forward osmosis membrane.

Other researchers reported that they prepare interpolymer cation exchange membranes with polyethylene by sulfonation with a solution of chlorosulfonic acid in 1,2 – dichloroethane (Grzebyk and Poźniak, 2005). Ayyaru and Dharmalingam (2011) developed a sulphonated polyether ether ketone (SPEEK) for employment in a MFC instead of NF. When using PEM, it is important to realize that it might be permeable to chemicals such as oxygen, ferricyanide, other irons, or organic matter used as the substrate. The market for the ion exchange membrane is constantly growing, and more systematic studies are necessary to evaluate the effect of the membrane on performance and long-term stability (Rozendal et al., 2006).

Table 3
Summary some of the MFCs utilized for wastewater treatment.

Type of MFC	Electrode	Inoculum and substrate	Results	Reference
Two chamber MFC	– Anode: Graphite cylinder with total surface 20 cm^2. – Cathode: porous graphite bar with total surface 20 cm^2	Municipal wastewater inoculated by activated sludge	Maximum power 25 mW m^{-2}, the removal efficiency of COD was 30.0%	(Rodrigo et al., 2007)
Single-chamber air cathode MFC	– Anode: graphite fiber brush. – The cathodes (3,8 cm diameter, 7 cm^2 total exposed surface area)	Domestic wastewater plus olive mill wastewater	Total COD and BOD_5 was reduce of 65.0% and 50.0%, respectively, recovering 29% of the coulombic efficiency	(Sciarria et al., 2013)
MFCs with single-chamber air cathode and two chamber with an aqueous cathode	The electrodes 2.5 × 24.5 cm were made of Carbon paper	Agriculture wastewater	The maximum power density was 45 mW/m^2 and the removal efficiency of COD and ammonia were 86.0% and 83.0%, respectively	(Min et al., 2005)
Two chamber MFC	– Anode: carbon paper (6 cmx 8 cm). – Cathode: Carbon paper (4 cm × 5 cm) with 40% platinum	Agriculture wastewater (human feces wastewater)	Total COD, soluble COD, and NH_4^+ were reduced by 71.0%, 88.0%, and 44.0% respectively.	(Fangzhou et al., 2011)
Annular single chamber MFC	– Anode: graphite-coated stainless steel mesh. – Cathode: carbon cloth type B	Dairy wastewater (COD of 1000 mg/L) inoculated by activated sludge from dairy wastewater treatment plant	Maximum power density: 20.2 W/m^3. Maximum columbic efficiency of 26.87%. 91% COD removal	(Mahdi Mardanpour et al., 2012)
Granular activated carbon single-chamber microbial fuel cell (GAC-SCMFCs)	– Anode: a graphite rod inserted into the GAC bed. – Cathode: platinum--coached carbon cloth	Domestic wastewater was used as inoculums and supplemental sodium acetate was added to domestic wastewater to achieved the designated COD concentrations of 100–1500 mg/L		(Jiang and Li, 2009)

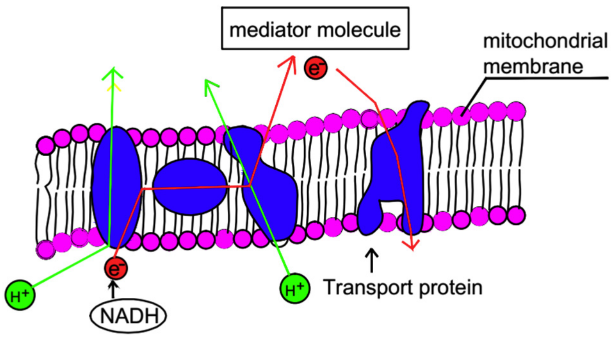

Fig. 4. The electron transfer chain.

2.5. Substrates used in MFCs

Liu et al. (2009) indicated that substrate is a critical factor affecting the generation of electricity. Various kinds of substrate can be utilized in MFCs for producing electricity such as pure compounds and complex mixtures of organic matter present in wastewater. MFC performance depends on many variables such as operating conditions, surface area and type of electrodes and various kinds of microorganisms being utilized.

Researchers use different units to explain and describe the performance of MFCs. Current density is considered to be one of the most common units. It acts as the current generated per unit area of the anode surface area (mA/cm^2) or current generated per unit volume of the cell (mA/m^3). Bond et al. (2002) assert that acetate is a simple substrate and it is extensively used as a carbon source to induce electroactive bacteria. Aelterman (2009) contends that in order to create new MFC components, reactor designs or operational conditions, acetate commonly serves as a substrate because of its inertness towards alternative microbial conversions at room temperature. Glucose is another commonly used substrate in MFCs. In one study, the performance of a MFC containing *Proteus vulgaris* depended on the carbon source in the initial medium of the microorganism. It was discovered that glucose initiated cells in MFC ran for a short period of time compared to galactose (Kim et al., 2000).

3. Application of MFCs in wastewater and energy product

3.1. Wastewater treatment

MFCs technology was first considered for use in treating wastewater in the early 1990s (Habermann and Pommer, 1991). Recently, He et al. (2017) have shown that MFCs are a promising technology for various kinds of wastewater treatment in municipal, agricultural and industrial contexts. For an efficient treating system, high operational sustainability and low material costs are worthwhile characteristics. MFCs are also applied on field scale to monitor remote areas and combined with other treatment unit to treat wastewater. Although electricity production is still in allow level (maximum power production efficiency is ±60%), but this issue is regarded as a challenge for researchers to improve MFCs performance (Surya Ramadan and Purwono, 2017). Table 3 summarizes some of the MFCs utilized for wastewater treatment.

Scientists have indicated that to remove nitrogen and organic matter from leachate, biological treatment is popularly used as a reliable and highly cost effective strategy (Mehmood et al., 2009). MFCs using certain microbes have a special ability to remove sulfides as required in wastewater treatment (Rabaey et al., 2005). MFCs can enhance the growth of bio-electrochemically active microbes during wastewater treatment, thus confirming they have good operational stabilities. Up to 90% of the COD can be removed in some cases and a Columbic efficiency as high as 80% has been reported (Kim et al., 2005).

The ability of MFC technology to simultaneously generate electricity and remove salinity from Se-containing wastewater was observed, leading to the conclusion that at higher serenity concentration both power output and Columbic efficiency are lower (Rahimnejad et al., 2015). Kim et al. (2008) showed that MFC-based technology increases the speed of removing odor if the electricity production reaches 228 mW/m^2. Furthermore, biodegradable organic matter and electricity generation with high nitrogen and salinity content can be treated by biofuel cells using landfill leachate (Puig et al., 2011). Continuous flow and single compartment MFCs and membrane-less MFCs are preferred in wastewater treatment due to concerns in scaling up these kinds of operations (He et al., 2005; Jang et al., 2004; Moon et al., 2005).

Corbella and Puigagut (2018) illustrated that constructed wetlands operated as MFCs is a promising strategy in order to improve domestic wastewater treatment efficiency. Researchers set up 6 lab –scale membrane- less MFCs and loaded in batch mode with domestic wastewater for 13 weeks. The results showed that 220 Ω was the best operation condition for the highest MFCs treatment efficiency (Corbella and Puigagut, 2018).

Conventional anaerobic digestion wastewater treatment has been considered as a green technology due to its low-cost. However, there has some barriers including low temperature and low organic concentrations have exited in anaerobic wastewater treatment (Chen et al., 2016; Lu et al., 2016; Sadhukhan et al., 2016).

Indeed, anaerobic treatment and MFCs are quite different treatment technologies with generating clean energy in wastewater. Anaerobic digestion and MFC technologies can be considered as implementary technology. MFCs have limitation in energy conversion efficiency and capital investment, however, the effluent from MFCs is better than that from anaerobic digestion. In comparison with conventional anaerobic digestion, the MFC technology has some specific advantages, such as its applicability for the treatment of low concentration substrate at temperatures below 20 °C, where anaerobic digestion generally fails to function. Moreover, volatile fatty acids, like acetate and butyrate, can be effectively degraded by MFCs, even at low concentration, but in anaerobic digestion the volatile fatty acids are metabolic products, and their accumulation would have a passive effect on the treatment process (Oh et al., 2010). Pham et al. (2006) showed a list of critical comparison between the anaerobic digestion and MFCs as shown in Table 4.

In order to overcome the MFCs' limitation, expand the application and commercial its operation, numerous researchers have indicated that it was necessary to integrate MFCs with conventional wastewater treatment process, which are classified as sediment MFCs (SMFCs), constructed wetland MFCs (CW-MFCs), membrane bioreactor MFCs (MBR-MFCs), desalination MFCs (DS-MFCs) and others. These combinations can not only enhance the treatment efficiency, but also has the ability to be a self-sustained or even net energy producer (Fang et al., 2015; Ren et al., 2014; Wang et al., 2011). Table 5 summarizes the combination between MFCs with other wastewater treatment.

3.2. Generation of bio-electricity

Microbial fuel cells can convert the chemical energy stored in the chemical compounds in a biomass into electrical energy by microorganisms. (Chaudhuri and Lovley, 2003) showed that R. ferrireducens can generate electricity with an electron yield as high as 80%. An extremely high Coulombic efficiency of 97% was reported during the oxidation of formate with the catalysis of Pt black (Rosenbaum et al., 2006). MFCs are especially suitable for powering small telemetry systems and wireless sensors that have only small power requirements for the purpose of transmitting signals such as temperature to receivers in remote areas (Ioannis et al., 2005). In addition, bioelectricity was successfully created utilizing orange peel waste as a renewable carbon source in a dual chamber mediator-less microbial fuel cell. High reproducibility in terms of voltage generation (max. = 0.59 ± 0.02 V at 500 Ω) was achieved for batches fed with different forms of orange peel waste

Table 4
Comparison of conventional anaerobic digestion technology with microbial fuel cells technology.
(Adapted from Pham et al., 2006.)

Items	Anaerobic digestion technology	Microbial fuel cells technology
Configuration	– Upflow Anaerobic Sludge Blanket (UASB) reactor – Anaerobic Migrating Blanket Reactor (AMBR) – Expanded Granular Sludge Bed (EGSB) and Internal Circulator (IC) reactors	– Two chamber – Single chamber – Cylindrical reactors – Tubular system – Stacked MFC
Biocatalyst	A complex "food chain" type microbial consortium catalyzes the process	The microbial catalysts can be an axenic culture or a mixed culture
Power input	Can application for both high and low concentration COD biomass at temperatures about 30 °C.	Can be utilized rather low strength influents containing glucose, sucrose or acetate at temperatures below 20 °C.
Power output types	– Produces methane or hydrogen. – Usually 1/3 of the biogas produced is converted with a high energy level (producing 220 Volt electricity) and the remaining 2/3 with a low energy level (producing 60–80 °C heat), which can be used to heat the digester	– Convert energy available in biomass directly to electricity. – The energy produced by single MFCs is at a low level since the voltage generated per MFC amounted to approx. 0.5–0.7 Volt.
Power output units	– Anaerobic digestion allows 1 kg of COD to be converted to an energy amount of roughly 1 kWh – The power density obtained is about 400 W/m^3 when the technology is applied to treat about 5 to 25 kg of COD per m^3 of the reactor per day.	– 1 kg of COD can be converted to 4 kWh of electrical energy. The current has not exceeded 0.1 A. – The average power density of MFCs is about 40 W/m^3. Recently, stacked configurations of MFCs have reached power densities of 250 W/m^3
Advantages	– Removal of higher organic loading. – Low sludge production and high pathogen removal, methane gas production. – Low energy consumption	– Less excess activated sludge compared to the process of AD. – Intensive to operation environmental. – No require gas treatment. – Widespread application in location with insufficient electrical infrastructures.
Disadvantages	– Difficult to store biogas. – High cost to remove H_2S. – Approximately €100,000/ton of COD treated per day. – low cost of the current non-renewable energy sources	– Limited effectivity of the open-air cathodes. – High cost of electrode materials and proton exchange membrane.

namely powdered, filtered and unfiltered peel waste (Miran et al., 2016).

Another element - Ferric iron can affect the current generation of MFCs. Researchers shows the response of microbial electrode communities to insoluble ferric iron at different concentrations in MFCs. The results illustrate that a low concentrate of Fe^{3+} facilitated the power output of MFCs and shaped community structures of the electrode biofilm (Liu et al., 2018).

Logan proposed that MFCs can be used as a practical energy source because the power density reported in MFC studies rose from 0.1 W/m^2 to 6.9 W/m^2 during the period 1999 to 2008 (Fan et al., 2008). In order to turn MFCs into practical energy production units, larger reactors with enough energy output should be promoted (Hu et al., 2017).

Oh and Logan (2006) have shown that two-chambered MFCs can operate with variously sized anode and cathode, and PEM with three different surface areas (3.5, 6.2, 30.6 cm^2). The power density normalized to the anode surface area increased according to the PEM size. PEM surface area was shown to limit power output when this surface area was smaller than that of the electrodes due to an increase in internal resistance. They also suggest that increasing the ionic strength and using ferricyanide at the cathode also increased power output (Oh and Logan, 2006). In other research, Liu et al. (2005a, b, c) examined the effect of the solution's ionic strength, electrode spacing, and temperature on power generation in a single chamber, membrane–free MFC. The researchers showed that power output will rise when increasing the solution ionic strength by adding NaCl. It was also shown here that by moving the anode closer to the cathode (to within 2 cm), power density could be increased by 67%. Liu et al. (2005a, b, c) also indicated that power output rose by 68% when the cathode was replaced by a carbon cloth cathode containing the same Pt loading. However, the power output fell by 9% when the temperature fell from 32 to 20 °C (Liu et al., 2005b).

3.3. Biohydrogen production

MFCs can be readily modified to produce hydrogen instead of electricity. Hydrogen can be accumulated for later applications (Du et al., 2007). Under normal operating conditions, protons released by the anodic reaction migrate to the cathode to combine with oxygen to form water. The generation of hydrogen from the protons and the electrons produced by the metabolism of microbes in an MFC is thermodynamically unfavorable.

Table 5
Integration MFCs with other wastewater treatment process.

Type of MFCs	Inoculum and substrates	Power density	Removal efficiency of COD and VFA	Reference
Sediment microbial fuel cells (SMFCs)	Domestic sewage and fermented- distillery wastewater	211.14–224.93 (mA/m^2)	86.67% and 72.32%	(Venkata Mohan et al., 2011)
Wetland-MFCs (CW-MFC)	Swine wastewater	9.4 mW/m^2 anode area under continuous mode	76.50% under continuous mode	(Zhao et al., 2013)
Upward continuous flow CW-MFC	Synthetic wastewater with azo dye	0.852 W/m^3 working volume of anode, with HRT 3 days, 300 mg COD/L (30% dye)	85.66% with HRT 3 days, 135 ± 10 mg COD/L (25% dye)	(Fang et al., 2015)
Membrane-less biocathode MFCs integrate sequencing batch reactor (SBR-MFC)	Synthetic wastewater	2.34 W/m^3	18.7%	(Xian-Wei et al., 2011)
Batch mode MBR-MFCs	Domestic wastewater	14.5 W/m^3	>97% for both soluble COD and NH_3-N)	(Malaeb et al., 2013)

MFCs can produce about 8–9 mol H_2/mol glucose compared to the typical 4 mol H_2/mol glucose achieved in conventional fermentation(Liu et al., 2005). To generate hydrogen gas in a typical MFC, anodic potential must be increased with an additional voltage of approximately 0.23 V or more. As well the oxygen in the cathode chamber should be removed (Rabaey et al., 2005).

In bio hydrogen production using MFCs, oxygen is not necessary in the cathodic chamber. This has enabled MFC's efficiencies to improve because oxygen leaking to the anodic chamber is no longer an issue. Another advantage is that hydrogen can be generated and stored for later application. Therefore, MFCs supply a renewable hydrogen source that can be donated to the overall hydrogen demand in a hydrogen economy (Holzman, 2005).

3.4. Biosensor

Another application of MFC technology is in sensor pollutant analysis and in situ process monitoring and control (Feng et al., 2013). MFC technology has been applied to constructing biosensors for fast BOD estimation, in which a biological sensing element and a transducer are combined. The MFC-based sensors are advantageous in that they have long-term stability and can be utilized continuously for online wastewater monitoring. However, the higher BOD concentration means the longer response time it takes, since the Coulombic yield can be calculated only after the BOD has been depleted unless a dilution mechanism is in place (Moon et al., 2004).

4. Challenges of MFCs in wastewater treatment and energy production

The advantage of MFC technologies is its ability to directly convert chemical energy into electrical energy by biological pathways, therefore allowing it to biologically adapt to treating various chemical substrates at diverse concentrations. One positive impact has been the fact that numerous research groups are utilizing MFC technology to understand microbial, biochemical, electrochemical and material surface reactions under specific, controlled conditions. They are investigating how these can be influenced by the choice of materials, feedstock substrates and chemical compounds among others (Santoro et al., 2017). On the other hand, an emerging problem is the fact that the technology has never been considered a serious contender in the wastewater treatment field or in the renewable energy sector. This is despite the fact it is perhaps the only example of a technology that can generate rather than consume energy from the cold oxidation of waste organic matter and under certain conditions inorganic carbon as well.

The MFCs have both advantages and disadvantages regarding their applications in the field. The operational problems comprise high operating costs and low power output, and these should be resolved before commercializing the MFC technology. The capital cost of the MFC, on average, is 30 times higher than that of traditional activated sludge treatment systems for domestic wastewater, due to its configuration and treatment (He et al., 2017). Normally, the high-level capital cost in an MFC is mainly caused by the use of expensive electrode materials such as current collector, catalyst and separator materials. Power created by the cell might not be enough to run a sensor or a transmitter continuously. This is the main issue with utilizing microbial fuel cells. It can be treated by increasing the electrodes' surface area or using a suitable power management program because the data are transferred only when enough energy is stored. This occurs when an ultra-capacitor is used (Rahimnejad et al., 2014). The other limitation of MFCs is that they cannot operate at low temperatures because microbial reactions are slow at low temperatures (Shantaram et al., 2005).

In the last two decades, many efforts have been made in the development and modification of electrode material in order to promote MFCs' performance. However, many problems in current MFCs technology still have to be resolved if industrial application is to be successful. Firstly, the cost of electrode material is still a key factor limiting their practical application. Their prices are nevertheless expensive even though relatively high output power can be generated using carbon cloth and carbon paper. Secondly, the long-term stability of electrode materials is also a very crucial problem in wastewater treatment technology. However, most studies have paid much more attention to the output power, not fully discussing the stability of the electrode materials, which would not provide a valuable guideline for their long-term service in industrial applications.

Presently, practical applications of traditional carbon-based materials are limited by high capital cost. Researchers also indicated that the development of low-cost, high-current-output, carbon-rich anode materials from waste tires for use MFCs would therefore be significant. This work was to use carbonized waste tires as anode materials in MFCs, not only to avoid the secondary pollution caused by waste tires, but also to provide a new source of anode materials for engineering applications of MFCs (Chen et al., 2018). To reduce the inhomogeneity of flow and concentration fields in a large-scale MFC, multiple electrodes in individual chambers may constitute a novel design (Lee et al., 2015). On this issue of electrodes, the cost of electrode materials used to construct MFCs is the main factor when implementing MFCs technology in the large-scale context.

In order to support biofilm, large surface areas are required, and the structure must be able to bear the weight of the water and biofilm. The basic materials used for electrode include carbon cloth, carbon paper, graphite rods, plates and RVC. Some materials are not expected to be adaptable to scaling up due to their inherent lack of durability or structure strength or cost such as carbon paper or graphite rods. Future researchers should focus on conductive coatings for supporting material structure. Cathode materials might also be extended to carbon fibers being linked to noncorrosive substances such as nickel and titanium (Hasvold et al., 1997). Modification of anode electrode could be useful in promoting the MFC's performance by utilizing nanoengineering techniques that help the electron be more easily transferred (Scott et al., 2007).

Apart from this, to improve the power density and enlarge the capability of electron to accept heterogeneous fabrication, other methods and modification strategies involving nanomaterials have been tried (Zhou et al., 2011). Qiao et al. (2007) highlighted that carbon nanotubes (CNTs) can amplify the electron transfer capability and electrode surface area using carbon nanotubes/polyaniline nanostructure composite as anode.

Researchers are paying more attention to MFCs for wastewater treatment because they can recover energy from waste and reduce the production of excess sludge. However, fouling at the membrane is the major factor that limits the MFCs' application in wastewater treatment. It should also be noted that membranes are expensive and they constitute the over-arching cost when constructing a MFC. In particular, biofouling leads to a decline in MFC performance because of the interruption of proton migration and completion for substrate utilization (Choi et al., 2011; Xu et al., 2012). Therefore, a membrane-less MFC has the ability to reduce the problem of expense when treating wastewater. Membrane-less MFCs are now being widely researched since their construction costs are less than the basic two-chamber MFC (Zhang et al., 2016).

Nonetheless it is difficult to contain all fed organic matter in the anodic chamber without cross-over owing to the ionic membrane's absence. Furthermore, because of the no membrane design configuration, electrolyte mixing on both sides of the anode and cathode commonly occurs because of migration, convection and diffusion (Tartakovsky and Guiot, 2006). This problem will affect the performance of membrane-less MFCs due to oxygen and substrate cross-over to the anode and cathode, causing a low Coulombic efficiency and power density. Kim et al. (2016) applied dual anode in membrane-less MFC to supply a larger reaction surface to prevent the pollution of the organic cross-over, and this consequently enhanced the MFCs' performance.

Liu et al. (2013) showed that membrane fouling was mitigated significantly in the membrane bioreactor (MBR). An innovation membrane bioreactor was combined with an inserted bio-electrochemical cell including iron anodes, microbes and conductive membrane modified by polypyrrole, which allowed to keep all benefits of MBR as well as generated constant electrical potential for cathode membrane fouling reduction As mentioned above, MFCs have overcome the deficiencies in existing technologies and can now save more energy, produce less sludge and create more energy. While researchers have made significant efforts to improve the performance of MFCs by developing novel structure designs, electrode materials, catalytic, and microorganisms, MFCs are far from ready for commercial applications. Their energy output is still too low to make an energy-neutral operation feasible at the practical scale, and both capital and operational costs are high. Long-term stability is another huge challenge for researchers along with finding solutions for power output and expense (Rahimnejad et al., 2015).

Currently, MFCs are still at the laboratory stage of investigation and experiment, but some ingenious designs have been developed to incorporate MFCs into other wastewater treatment processes. For example, integration with anaerobic digestion will make up the deficiency of individual technology and improve the water quality of effluent with membrane technology (He et al., 2017). Liu et al. (2017) revealed that combining MFCs with FO and anaerobic acidification (AAFO-MFC) was a novel process, enhancing bio-electricity and water recovery from low-strength wastewater. In treatment process using membrane modules fouling becomes an emerging issue. However, it has been illustrated that the integration of MFCs in membrane bioreactor (MBR-MFCs) systems helps to reduce membrane fouling (Li et al., 2014; Liu et al., 2013; Ren et al., 2014).

Rashid et al. (2013) has been illustrated that using algae biomass with activated sludge as a substrate in MFC can produces much higher power density than other reported substrates. Among test concentrations of dry algae biomass, 5000 mg COD/L produced the highest voltage of 0.89 V and power density of 1.78 W/m^2 under 1000 Ω electric resistance. The use of algae biomass with activated sludge served dual purpose, the waste mitigation and electricity generation.

Although some basic and important knowledge has been generated due to intensive MFC research, much still has to be learned in the scaling up of MFCs for large-scale applications. The power densities for larger-scale MFC reported in recent literature are of the order 100 mW/m^2, five orders of magnitude lower than the chemical FC (10^4–10^5 W/m^2). Hence it is not practical to use MFC as an alternative for chemical FC. When working with full-scale MFCs, the external mass transfer resistances produced by incomplete mixing and inhomogeneous biofilm structures developed on electrodes and other scale-up factors will reduce the power density when compared to their mini-sized counterpart.

5. Future perspectives

MFCs are regarded as a new trend in wastewater treatment, and therefore future research should focus on the following issues. Firstly, there is the topic of metabolic mechanism, in that to further understand metabolic mechanism, electrochemically active microorganisms will contribute to selecting high electrochemical activity microorganisms. This means constructing a conductive thick biofilm and optimizing the operating conditions. Secondly, the design and architecture of the reactor for MFCs will directly decide their application in wastewater treatment. Thirdly, MFC stacks are important due to voltage reversal and ionic short circuit still existing as huge barriers to practical application. This is due to biocatalyzed electrode reactions in the MFC. Fourthly, power collection and utilization need to be investigated in more detail, given that the development of a power collection and utilization system will accelerate the commercial application of MFCs. Fifthly and final, there is the possibility of synergy with other wastewater treatment technologies to consider, given that a combined technology may accelerate the application and effectiveness of MFCs in wastewater treatment (He et al., 2017).

6. Conclusion

Wastewater is recognized as making a major contribution to environmental pollution. Current wastewater treatment technologies have energy- and cost-related limitations and therefore wastewater recovery is difficult to achieve and sustain. Microbial fuel cells (MFCs) have been researched and are now recognized as an innovative technology that has certain advantages especially in the field of wastewater treatment. The general features of Microbial fuel cell such as design and architecture were described in this research. Some unique features make MFCs superior to other wastewater treatment methods and these include anaerobic digestion (AD). MFCs save energy, result in less sludge production and produce more energy. Despite the fact that in recent years the amount of power generated from MFCs has improved considerably and reached the level of primary power target at least in small lab-scale systems, scaling up is still a big challenge. Moreover, the high cost of cation exchange membranes, the potential for biofouling and associated high internal resistance restrain the generation of power and limit the practical application of MFCs.

Many other studies have indicated that MFCs are capable of effectively removing several kinds of contaminants. Some aspects of MFCs regarding wastewater treatment technology should be the focus of more analysis in the future, such as cost and power requirements. Further research should also pay attention to new MFC materials in order to make wastewater treatment more effective. Finally, it is necessary to better understand the nature and function of electrode materials. Multiform wastewaters can be significantly degraded by advancing MFCs alone or integrating them with other processes.

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