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Microbial fuel cells in bioelectricity production

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ABSTRACT

Bioelectricity production involves generation of electricity by anaerobic digestion of organic substrates by microbes. A microbial fuel cell (MFC) is a device that converts chemical energy released as a result of oxidation of complex organic carbon sources which are utilized as substrates by micro-organisms to produce electrical energy thereby proving to be an efficient means of sustainable energy production. The electrons released due to the microbial metabolism are captured to maintain a constant power density, without an effective carbon emission in the ecosystem. The various parameters involved in MFC technology toward power generation include maximum power density, coulombic efficiencies and sometimes chemical oxygen demand removal rate which evaluates the effectiveness of the device. Application of microbes toward bioremediation at the same time resulting in generation of electricity makes MFC technology a highly advantageous proposition which can be applied in various sectors of industrial, municipal and agricultural Waste Management. Although the efficiency of MFCs in power generation initially was low, recent modifications in the design, components and working have enhanced the power output to a significant level thereby enabling application of MFCs in various fields including wastewater treatment, biosensors and bioremediation. The following review provides an outline about the components involved, working, modifications and applications of MFC technology for various research and industrial objectives.

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1. Introduction

Bioelectricity production is the production of electricity by organisms on account of production of electrons resulting due to their metabolism. These electrons produced can be captured so as to maintain a stable or continuous source of energy production. Bacterial cells when provided a suitable substrate can metabolize the components producing electrons which can be harvested and utilized by connecting them through a circuit. These components can be packed into an assembly called a 'microbial fuel cell' (MFC) proving to be a source of energy. Anaerobic digestion of substrate by the micro-organisms is essential for the production of the electrons occurring due to their metabolism. The above reactions indicate the metabolic reactions carried out by the microbes firstly in the absence of oxygen (1) and then in the presence of oxygen (2) (Moqsud et al. 2013).

2. Microbial fuel cell

A MFC typically consists of several components primarily divided into two chambers, that is, anodic and cathodic chamber containing the anode and cathode, respectively. These chambers are separated by a proton exchange membrane (PEM) (Figure 1). The microbes present in the anodic chamber are provided with a favorable substrate which is anaerobically degraded to release electrons which are transported from the anode to the cathode via external circuit and the protons generated are selectively passed through the exchange membrane. Both these products produced due to the action of the microbes in the anodic compartment travel to the cathode and react with oxygen to produce water (Sharma & Li 2010).

MFCs are devices that can convert chemical energy into electrical energy by the process of oxidation of various carbon sources or even organic wastes

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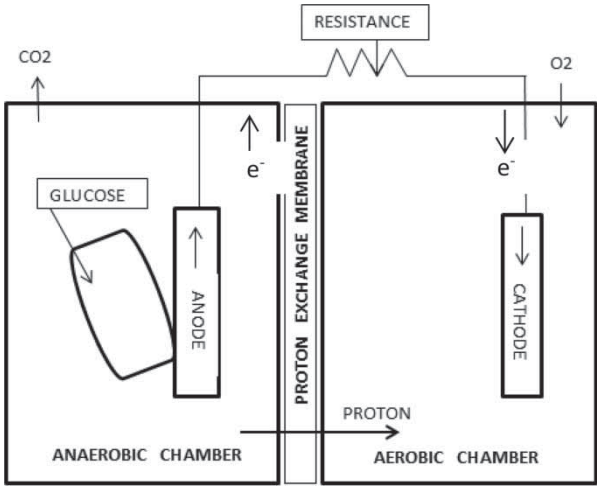

Figure 1. Schematic outline of a typical dual chamber MFC.

carried out by electrochemically active bacteria (EAB) (Angenent et al. 2004; Aelterman et al. 2008; Lovley 2008; Logan 2009). The MFC chambers can be constructed by glass, polycarbonate, as well as plexiglass (Rhoads et al. 2005). Materials such as carbon cloth, carbon paper, graphite and graphite felt can be used as anode electrode (Zhang et al. 2011; Zhou et al. 2011; Wei et al. 2011; Sangeetha & Muthukumar 2013). An air cathode is used to maintain the aerobic nature of the electrode and this can be made up of materials such as platinum (Pt) or Pt-black catalyst materials. The anode chamber consists of the organic substrates which are to be utilized by the microbes to produce electrons which flow through the external circuit to the cathode ultimately accepted by the solution present in the cathodic chamber. The protons generated pass from anode to cathode via the ion exchange membrane (Wang et al. 2013). Ferricyanide ($[Fe(CN_6)]^{3-}$) or permanganate (MnO_4^-) solutions can act as effective catholytes but are not sustainable (Pham et al. 2004; Wei et al. 2012).

3. Micro-organisms

Geobacter (Lovley et al. 1993; Rotaru et al. 2011; Nevin et al. 2008) and *Shewanella* (Gorby et al. 2006; Watson & Logan 2010; Wang et al. 2013) *species* account for the majority of the microbial population that have been utilized in MFC technology. Photosynthetic bacteria can also be used effectively in a MFC for electric power generation. One particular advantage of using photosynthetic bacteria in MFCs is the elimination of carbon dioxide from the atmosphere due to photosynthesis coupled with bioelectricity generation (Rosenbaum et al. 2010). Previously, cyanobacterial strains of *Anabaena* and *Nostoc* also have been used as biocatalysts in MFCs (Tanaka et al. 1985; Yagishita et al. 1997, 1998). Another idea that can be used in MFCs is the synergistic relationship between photosynthetic bacteria and heterotrophic bacteria for electricity generation. The relationship works on the symbiotic functioning involving utilization of organic matter synthesized due to photosynthesis by the heterotrophic bacteria. *Pseudomonas aeruginosa* strains have also been used along with manipulation of NAD co-factor thereby increasing the metabolic rate and potential of the bacteria toward enhanced biofuel production. Anaerobic acidogenesis of cattle dung revealed *Clostridium* sp., *Pseudomonas luteola* and *Ochrobactrum pseudogrignonense* to be the most dominant groups present responsible for the electricity generation process (Zhao et al. 2012). Algal species of *Leptolyngbya* sp. JPMTW1 have also been used for coupled biofuel and bioelectricity production (Maity et al. 2014). Mixed cultures of microbial population have also been used in MFCs, for example, natural microbial community, domestic wastewater, sediments from marine and lake as well as brewery wastewater (Logan 2005; Rabaey et al. 2005; Feng et al. 2008).

4. Substrates

A range of organic substrates can be used for anaerobic digestion by the microbes in bioelectricity production. Domestic wastewater can be used for continuous electricity production (Choi & Ahn 2013). Min et al. (2005) demonstrated production of maximum power density using swine wastewater as a substrate in single-chambered MFC. Oil wastewater can also be used for bioelectricity production (Jiang et al. 2013; Choi & Liu 2014). Waste sludge also has been demonstrated to be an effective substrate in bioelectricity generation coupled with hydrogen production (Ge et al. 2013; Choi & Ahn 2014). Fruit and vegetable wastes were employed as a substrate for microbes isolated from high Andean region in a single-chambered MFC (Logroño et al. 2015). Choi and Ahn (2015) reported use of food waste leachate obtained from bio-hydrogen fermentation as a potential substrate toward enhanced electricity generation. In a study, simple substrates such as glucose, acetate, propionate and butyrate have been

used as substrates in MFCs toward power generation (Ahn & Logan 2010). The power density measured in this study for the different substrates was in the order of acetate > butyrate > propionate. This is of particular importance because acidogenic degradation of organic wastes produce a range of volatile fatty acids which depending upon their affinity toward the microbes influence the electricity generation (Choi & Ahn 2015).

5. Design

There are different designs for the construction of a MFC depending upon the number of chambers, the mode of operation, etc. These types primarily include:

5.1. Two-chamber MFC

This design is the classical design of a MFC consisting of dual chambers separated by an ion exchange membrane. These typically run in batch modes but can function in continuous mode as well and are currently only used in laboratories (Du et al. 2007).

5.2. Single-chamber MFC

A single-chamber MFC involves only the anodic chamber coupled with an air cathode to which the protons and electrons are transferred. Various designs have been proposed for the construction of a single-chamber MFC such as Table 1.

5.3. Stacked MFC

A stacked microbial fuel is a collection of MFCs connected with each other in series or in parallel connection (Aelterman et al. 2006).MFC can be stacked by achieving different configurations of both electrode as well as hydraulic flow. These can be of four types such as (i) series electrode connections in parallel flow mode, (ii) parallel electrode connections in parallel flow mode, (iii) series electrode connections in series flow mode and (iv) parallel electrode connections in series flow mode (Choi & Ahn 2013). Choi and Ahn (2013) obtained an overall increase in chemical oxygen demand (COD) removal, Coulombic efficiencies and maximal power densities in parallel electrode connection (series flow mode) while treating wastewater which was attributed to a higher stability of the oxidation–reduction potentials in overall cells. Aelterman et al. (2006) reported a six times higher voltage and current output when connected in parallel as compared to series thereby implying an overall higher biochemical reaction rate. Thus, these studies imply a possible innovative modification in MFC technology which could assist in increasing the power output thereby contributing toward one of the application of MFCs.

6. Proton exchange membranes (PEM)

In MFC technology, electro-neutrality between the two chambers is a very important pre-requisite for its efficient operation achieved by the PEM on account of the transfer of protons across the membrane (Rozendal et al. 2006). PEM are a very important component of the MFC assembly assisting in separation of the anode and cathode chambers as well as facilitating transfer of protons to the cathode to sustain the electric current (Chae et al. 2007). The ideal characteristics of a PEM include the following criteria:

(i) cost effective
(ii) increased proton conductivity
(iii) good segregational properties
(iv) increased mechanical strength
(v) endurance against heat and chemicals
(vi) electronically resistive.

PEM surface area plays a contributive role in MFC power generation. Oh and Logan (2006) reported that

Table 1. Reports on designs proposed for the construction of a single-chamber MFC.

Design	Anode	Cathode	Reference
Rectangular	Mn^{4+} graphite anode	Fe^{3+} graphite cathode	Park and Zeikus (2003)
Cylindrical	Carbon paper without wet proofing	Carbon electrode/PEM assembly or rigid carbon paper without PEM.	Liu and Logan (2004), Liu, Cheng et al. (2005), Liu, Grot et al. (2005) and Cheng et al. (2006)
Tubular	Granular graphite matrix	Ferricyanide solution	Rabaey et al. (2005)
Concentric design	Graphite	Air porous made up of carbon/Pt catalyst	Liu et al. (2004)
Flat plate	Carbon paper	Carbon cloth	Min and Logan (2004)

the PEM surface area limits the power output when its surface area is smaller than the electrodes due to internal resistance. PEM that have been used in MFC technology include Nafion (Bond & Lovley 2003), Ultrex (Rabaey et al. 2005; Taskan et al. 2014) and salt bridge (Nair et al. 2013). Nafion a Dupont product has been widely used in MFC technology (Jana et al. 2010). Nafion is a sulfonated tetrafluroethylene copolymer made up of a hydrophobic fluorocarbon backbone ($-CF_2-CF_2-$) attached to hydrophilic sulfonate groups (SO_3^-) (Mauritz & Moore 2004). Although widely used application of Nafion has encountered some complications, which include increase in the pH of the cathode and decrease in anodic pH ultimately resulting in reducing the working efficiency of the MFC (Gil et al. 2003). The cause of these complications is the transfer of other cationic species other than the protons across the membrane resulting in accumulation of cations and increased conductivity in the cathode chamber (Rozendal et al. 2006). Chitosan membranes cross-linked in sulfuric acid were also considered as a possible candidate and, therefore, were evaluated through various parameters for their utilization as a PEM. Chitosan is an N-deacetylated derivative of chitin which is a polysaccharide in various organisms. Water absorption of chitosan membranes has been found to be more efficient than Nafion 117 but thermally less stable (Mukoma et al. 2004). Sulfonated polyimides have also been casted into membranes and evaluated for their ability as a PEM to be used in MFC technology (Genies et al. 2001). Styrene and its derivatives have also been used as a core molecule in the construction of a PEM which have been produced commercially as BAM from Ballard and SEBS (sulfonated styrene-ethylene-butylene-styrene) from Dias Analytics (Hickner et al. 2004). One of the major factors governing the efficiency of any PEM is its water absorbing ability as well as conductivity. Water absorption influences the passage of protons across the membrane required for the functioning of the fuel cell, but at the same time affects the mechanical properties of the membrane. Both these factors are a function of the concentration of ion conducting units (Hickner et al. 2004).

Cation exchange membranes (CEM) are separators containing negatively charged groups present on them such as $-PO_3^-$, COO^- and $C_6H_4O,^-$ which facilitate the passage of positive ions across them conversely restricting the negative ions (Rahimnejad et al. 2015).

Anion exchange membranes (AEM) are membranes containing positively charged groups such as NH_3^+, NHR_2^+, NR_2H^+, NR_3^+, PR_3^+ and SR_2^+ attached to the membrane matrix and allow passage of negatively charged groups through them inhibiting the anions (Peighambardoust et al. 2010). Kim et al. (2007) constructed multiple MFCs using different membranes which included AEM, CEM and three different ultrafiltration membranes having different molecular cut-offs. These MFCs were then examined for their production of power densities, Coulombic efficiencies (CE). It was found out that the MFC constructed with the AEM produced the largest power density and CEM as compared to the others, which was attributed to the proton charge transfer facilitated by phosphate anions mostly present in MFCs and lower internal resistance (Kim et al. 2007). Thus, this provides a conclusion stating that the positively charged groups present on the AEM matrix assist in transferring the protons (phosphate anions) across the membrane and with a particular advantage over CEM by inhibiting passage of excess cations across the chambers thereby enhancing electricity generation.

Bipolar membranes consist of two monopolar membranes, that is, CEM and AEM mounted together with a transition space between them as illustrated in Figure 2. The main reason for conduction of ions across bipolar membranes is due to the water spitting reaction which occurs at the interface of AEM and CEM in turn resulting in formation of protons and hydroxide ions which travel through the CEM and AEM, respectively (Harnisch et al. 2008). Bipolar membranes have been combined with ferric ion reduction in graphite cathode using ferric iron chloride and ferric iron sulfate as catholytes to monitor its effect on the efficiency of the MFC assembly (Ter Heijne et al. 2006).

The salt bridge is the simplest form of PEM that could be used in an MFC. The salt bridge consists of an ionic salt such as KCl or NaOH which is melted with agar and poured in a cylindrical cast and allowed to solidify. Upon solidification the bridge is placed between the two chambers of the MFC thereby acting as a PEM and facilitating the transfer of protons. Sevda and Sreekrishnan (2012) concluded that 5% concentration of salt in the salt bridge produces maximum power density of 84.99 mW/m^3. Nair et al. (2013) varied the concentration of agarose in a salt-bridge MFC

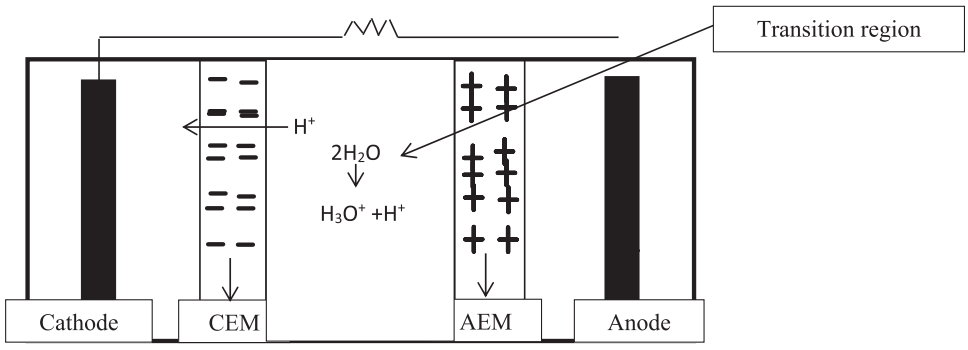

Figure 2. Structure of a bipolar membrane.

to find out that 10% of agarose concentration acts as optimum for current and voltage generation.

7. Mediators

The electrons produced by the micro-organisms on account of anaerobic degradation of the substrate require a mediator to be transferred to the electrode (Fultz & Durst 1982). A mediator is a compound having low redox potential which is added to the growth media at specific concentration extracts the electrons from the metabolic reactions of the microbes in and supplies those electrons to the anode electrode (Sevda & Sreekrishnan 2012). An ideal mediator present in a MFC should possess the following characteristics (Park & Zeikus 2000):

(i) should form a reversible redox couple at the electrode
(ii) should link to NADH and have a high negative E^{0-} value
(iii) should be stable in both oxidized and reduced form
(iv) soluble in aqueous systems.

The compound 2-hydroxy-1,4-naphthoquinone has been previously used as a mediator in a MFC using cyanobacterium *Synechococcus* sp. UTEX2380 as the microbial biocatalyst (Yagishita et al. 1997). Thionine is one of the compounds which have been extensively used as an electron mediator in MFCs utilizing *Escherichia coli* (Roller et al. 1984; Rahimnejad et al. 2012). Methylene Blue has also been used as an electron mediator to increase power production in MFC (Zuo et al. 2007). Babanova et al. (2011) reported the order of mediators as Bromocresol Blue < Neutral Red < Methyl Red < Methyl Orange < Methylene Blue in terms of power generation in MFC.

The electrons generated by the bacteria upon substrate utilization anaerobically are transferred to the anode either by an exogenous electron carrier compound (potassium ferricyanide, thionine, neutral red, methylene blue (Delaney et al. 1984; Park & Zeikus 2000; Rabaey, Boon, Dendf et al. 2004, Rabaey, Boon, Siciliano et al. 2004; Zhou et al. 2007; Babanova et al. 2011) or directly from the enzyme involved in bacterial respiration to the electrode or with or without (Bond and Lovley 2003; Chaudhuri and Lovely 2003; Gil et al. 2003) the help of mediators. Exogenous chemical compounds used as mediators in MFC have certain demerits such as toxicity and their expensive nature (Bond & Lovley 2003; Gil et al. 2003). Mediator-less MFCs have also been developed and consequently applied in power generation using wastewater sewage (Gil et al. 2003; Liu et al. 2004). Another alternative to the mediators is the utilization of a salt bridge which is made up of agar and sodium chloride salt (Sevda and Sreekrishnan 2012). Nair et al. (2013) analyzed the power generation capacity of a dual chambered MFC using sewage wastewater as a substrate with varying concentrations of agarose in the construction of salt bridge. The optimal concentration of agarose was found out to be 10% as it showed maximum power density of 78.21 mW/m^2.

8. Cathode performance

The cathode is the electrode where the protons along with electrons and oxygen combine to form water. Cathodes usually used in MFCs are either Pt-coated carbon electrodes immersed in water of just plain carbon electrodes in ferricyanide solution (Oh et al. 2004). Carbon cloth is most commonly used as

material for electrode in MFC along with Pt as catalyst but are expensive in nature. Other materials which can be used include graphite granules, granular activated carbon and graphite fiber brush electrodes. Cathode surface area is one of the factors that influences the power generation in MFC. Non-precious metal catalysts such as Cobalttetramethoxyphenylporphyrin (CoTMPP) is one of the compounds that can be used for coating the cathodic surfaces which has been used in conjunction with brush anodes and shown to achieve a power generation value of 18 W/m^3 (Zuo et al. 2007). Zuo et al. (2008) compared the performance of two cathodes constructed from two AEM and CEM along with another cathode constructed from ultrafiltration membrane coated with graphite granules and using a catalyst CoTMPP. It was observed that the best performance was obtained using the AEM cathode having a maximum power density of 449 mW/m^2 and Coulombic efficiency of 70%. Application of graphite granules and the catalyst to the membrane resulted in increase of surface area of the cathode as well as making it electrically conductive. Oh et al. (2004) have compared the characteristics and performance of two cathodes (Pt-coated carbon electrode and plain carbon electrode) using a two-chambered MFC. Air- cathode MFCs are also used in which the cathode is exposed to air on one side and water on the other side mainly to provide the aeration factor thereby achieving high power densities (Logan et al. 2006).

9. Anode performance

The materials which can be mostly used for anode in MFC include carbon in different formats such as granules, rods, plates and also as fibrous materials (felt, foam, mesh, cloth, paper and fibers) (Logan et al. 2006). The surface area of the anode plays a contributive role in power generation in MFC. A three dimensional anode would prove to be more effective toward electricity generation as it would provide more surface area for attachment of microbes (Di Lorenzo et al. 2010). The current conductivity of the different materials which can be used for anode was studied and reported in the order of carbon felt > carbon foam > graphite (Chaudhuri & Lovely 2003). Another modification are the graphite brush anodes consisting of graphite fibers wound around a metal core were used in a cube air-cathode MFC which was observed to produce a maximum power density of 2400 mW/m^2 and a maximum Coulombic efficiency of 60% (Logan et al. 2007). The power density production can be directly attributed to the increased surface area of the graphite brush anodes accounted by the cumulative surface area of individual graphite fiber and the elimination of clogging due to the design as compared to other carbon materials such as carbon foam (Chaudhuri and Lovely, 2003). The small size of individual graphite brushes and their low resistance enables them to be a prime candidate for their utilization in MFC for various applications (Logan et al. 2007). Di Lorenzo et al. (2010) constructed a single-chamber MFC using packed bed of graphite granules as the anode. The current output was measured and found out to be increasing with increasing levels of anode thickness and the overall surface area. Graphite granules when packed into a bed provide increased surface area as compared to other materials which proves to be proportional to the electrical output. Cheng and Logan (2007) treated the MFC anode with ammonia gas at high temperature which resulted in an increased power production. The result of this treatment was due to increased amine groups on the anode surface which facilitates better attachment by the bacteria which are negatively charged (Silhavy et al. 2010). Better attachment in turn influences better electron transfer (Terada et al. 2006). Further, functionalization of dimethylaniline groups on carbon cloth anode was done by using the compound 4(*N*,*N*-dimethylamino)benzene diazonium tetrafluoroborate to increase the nitrogen groups present on the surface and this functionalization individually was also varied as well as compared with that by ammonia gas treatment (Saito et al. 2011). It was noted that lowest amount of dimethylaniline provided maximum power production and that excess or no functionalization can result in impedance of MFC performance. Thus, one of the factors that influences MFC performance could be attributed to the nitrogen content of the anode.

10. Types of MFCs

10.1. Mediator-less MFC

Some mediators are inorganic in nature and pose a potential toxic nature toward the microbial flora employed in the MFC system. Therefore mediator-less MFCs have been developed thereby eliminating the potential use of mediator compounds. Thus, in

this type of MFCs biofilm formation on the anode surface by electrochemically active microbes leads to the utilization of the substrate producing electricity (Niessen et al. 2004; Schröder 2007). This type of MFC employs a class of microbes namely EAB which mediate the transfer of electrons from the substrate (electron donor) to the electrode in primarily two possible ways: directly through membrane bound proteins such as pili, c-type cytochromes and filaments, or indirectly through mediators (Wang & Ren 2013). Bond and Lovley (2003) found out that the Geobacter genus are capable of forming highly conductive networks of filaments (pili) along with c-type cytochrome OmcS mediating electron transfer. *Shewanella* genus have been found out to produce bacterial nanowires which have been proposed to mediate transfer of electrons from bacterial cells to solid phases located at distances (Gorby et al. 2006). A mediator-less MFC was constructed with artificial wastewater used as the substrate which produced highest power density of 0.56 W/m^2 (Moon et al. 2006). Gil et al. (2003) constructed a mediator-less MFC which was evaluated and optimized for its various operational parameters such as pH, resistance, electrolyte used and dissolved oxygen concentration in the cathode compartment. It was observed that an optimum pH of 7, lower resistance, buffer with NaCl solution, and increased aeration rate were the parameters ideal for efficient mediator-less MFC operation.

10.2. Membrane-less MFC

PEM serve as a means of transporting protons produced as a result of microbial degradation to the cathodic chamber. Membrane-less MFC eliminate the usage of PEM, which creates a transmembrane potential difference in turn leading to resistance to the flow of ions in electrolytes (Du et al. 2007). Membrane-less MFCs are mostly preferred in cases of wastewater treatment applications as the membrane acts as an electronic insulator and inevitably will result in fouling due to suspended solids and soluble contaminants (Jang et al. 2004). Due to the absence of a membrane, ohmic losses in electrolytes can be diminished by decreasing the distance between electrodes (Du et al. 2007). This same parameter was evaluated by Ghangrekar and Shinde (2006) when they constructed a membrane-less MFC utilizing wastewater and studied the power density production at different electrode distance. Maximum power densities of 10.9 and 10.16 mW/m^2 were obtained at an electrode spacing of 20 cm. Jang et al. (2004) constructed a novel mediator-less and membrane-less MFC which employed wastewater for current generation and COD removal but proved not much efficient due to the design of the MFC which assisted in passage of oxygen from cathode to the anode. Jadhav et al. (2013) constructed a dual chambered membrane-less MFC designed to treat synthetic wastewater producing a maximum current and power density of 3.8 mA/m^2 and 0.52 mW/m^2.

10.3. Catalyst coated electrode MFCs

There are certain chemicals which are coated on the surface of the electrodes to increase their efficiency. These chemicals mostly include conductive polymers such as polyaniline which could assist in the transfer of electrons to the electrode. Niessen et al. (2004) examined the ability of fluorinated aniline polymers toward their efficiency as an electrode modifier. They also depicted that the polymers could improve the catalytic activity of Pt toward formed hydrogen as well as protect it from poisoning. Another polymer polytetrafluroethylene (PTFE) has also been used in MFCs wherein it was composed (30%) with a graphite anode generating a power density of 760 mW/m^2 (Zhang et al. 2007). Carbon nanotubes/polyaniline composite structure was also illustrated as a possible anode modification which could enhance the MFC efficiency (Qiao et al. 2007). Ammonia pretreatment of the anode can also increase the power density due to the presence of functional groups on the surface (Cheng & Logan 2007). Similar to the anode, the cathode undergoes oxygen reduction reaction on its surface which has slow kinetics on plain graphite, and therefore a catalyst is required to expedite this reaction. Potassium ferricyanide and Pt are the most commonly used catalysts that are employed in the cathodic chamber in MFCs (Rahimnejad et al. 2015).

10.4. Sediment-type MFCs

The concept of this type of MFC involves insertion of one of the electrode (anode) in anaerobic sediment which constitutes of both, the organic substrates and the microbial community. This electrode is connected to the cathode which is placed in aerobic water.

Thomas et al. (2013) constructed a sediment-type MFC which was linked to a wireless telecommunication device and was able to power the device for considerable time without any external control. Sediment-type MFC can further be coupled with various modifications thereby differentiating them depending upon the type of microbial catalyst involved as well as the process of electron generation and transfer (Rosenbaum et al. 2010).

11. Applications

11.1. Production of bioelectricity

The main feature of a MFC is the utilization of organic carbohydrate substrates from biomass obtained from agricultural, industrial and municipal wastes for the production of bioelectricity. MFCs involve another added advantage of direct conversion of fuel molecules into electricity without the production of heat, the Carnot cycle which limits the efficiency for thermal energy conversion is avoided thereby enabling achievement of a higher conversion efficiency ($>$ 70%) (Du et al. 2007). Although MFCs are not currently an economical method for power production, the last few years have proved to be a progressive arch for MFCs in power generation. Power output of 10–50 and 250–500 mW/m^2 have been generated using substrates such as domestic wastewater and glucose, respectively (Logan 2004). Rabaey et al. (2003) generated a power density of 3.6 W/m^2 using a simple substrate like glucose and a mixed consortium of microbial community (Rabaey et al. 2003). Chaudhuri and Lovely (2003) reported the utilization of a novel micro-organism *Rhodoferax ferrireducens* which can oxidize glucose to CO_2 without the need of electron mediators to shuffle them to the anode. Thus, this eliminates the requirement for an electronic mediator thereby providing a way for future modifications in the MFC design increasing its efficiency. Stacked MFCs are another idea that could be implemented for increased power generation thereby applying at the same time through various other applications. Aelterman et al. (2006) connected six individual MFC units in a stacked configuration which produced a maximum hourly averaged power output of 258 W/m^3. Although the power production by MFC falls short when compared with that by other fuel cells, for example, methanol drivel FCs but the variation in terms of substrate utilization adds an incentive feature to the technology (Rabaey & Verstraete 2005). Also a self-sustained phototrophic MFC has been created which eliminates the usage of substrate, that is, organics or nutrients and gives continuous power output under illumination thus if upgraded could prove to be an efficient alternative source of sustainable energy (He et al. 2008). Rosenbaum et al. (2005) constructed a MFC utilizing the metabolic activity of *Rhodobacter sphaeroids* for *in situ* oxidation of photo-biological hydrogen for the generation of electricity. Therefore, this MFC technology can be applied as a potential utilization of sustainable source of energy. MFC technology can also be applied toward a concept of Bio-battery which is able to recharge appliances and devices requiring small voltage. Different modifications have been inculcated into the primary and basic design of a MFC thereby providing a base for further construction of new ideas and applications.

11.2. Bio-hydrogen production

Usually in MFCs the bacteria act as catalysts and oxidize the substrates present in the anodic chamber thereby producing electrons and protons which are transferred to the cathode via the wire (externally) and through the PEM, respectively. Both of them combine to form water thereby eliminating any chances of hydrogen production. The final electron acceptor for the bacteria in the anodic compartment during substrate oxidation can either be the electrode which results in power generation or produce reduced metabolites such as methane or hydrogen gas (Rabaey, Boon, Siciliano et al. 2004). External application of potential in a MFC resulted in overcoming the thermodynamic barrier to form hydrogen at the cathode by the combination of electrons and protons. This provides a possible modification to the MFC functioning as to direct it toward bio-hydrogen production. Rabaey, Boon, Siciliano et al. (2004) enriched microbes harvested from anodic chamber of a MFC which consisted of microbial consortia which when identified were known to contain some hydrogen producing species as well. In this study, the hydrogen production rates initially up to 43 $\pm$ 5%, fell below the detection limit with an increase in the electron transfer rate. Thus, this study indicates that electricity generation and hydrogen production are not influenced or

caused by each other in MFCs and highly unlikely to occur simultaneously.

11.3. Wastewater management

Wastewater effluent from industrial, municipal and other sources acts as a prime source for energy harvesting and simultaneously proving to be a suitable substrate toward bioremediation. Microbial fuel technology proves to be an ideal solution to the long lasting question of wastewater management. The primary three parameters on which the efficiency of MFC technology works are maximum power density, Coulombic efficiencies and COD. Maximum power densities obtained as a result of usage of pure substrates such as acetate, glucose and sucrose by MFC technology are always higher (494 mW/m^2) as compared to a complex substrate like wastewater (146 mW/m^2) (Feng et al. 2008). Wastewater from different sources have been tested using MFCs for power generation which include domestic wastewater (Liu et al. 2004), swine wastewater (Min et al. 2005), meat packing wastewater (Heilmann & Logan 2006), food processing wastewater (Kim et al. 2004), hydrogen fermentation reactor effluent (Oh & Logan 2005) and brewery wastewater (Feng et al. 2008). As compared to the pure substrates, complex organic substrates such as wastewater residues from different sources may produce potential problems interfering with electricity generation such as toxicity due to high concentration of ammonia or due to volatile acid production during hydrolysis and substrate fermentation (Min et al. 2005).

11.4. Biosensors

MFCs can be widely used in the field of biosensors for evaluating the pollutant level of several wastewater effluents. MFC technology can be utilized as a means of measuring the biological oxygen demand of different treatment plant effluents. This ability of MFCs is due to the proportional relationship between the Coulombic yield with the biological strength of wastewater (Kim et al. 2003).

11.5. Other applications

The production of bioelectricity technology is being used for its various applications both at industrial and research levels. MFC technology utilizing microbes for electricity generation involve degradation of various substrates which can be applied at an industrial level coupled with biofuel production. One such example is the complete degradation of Acid Orange-7 dye using a MFC integrated with an aerobic bioreactor (Fernando et al. 2014). Thus, this technology achieves wastewater treatment for Acid Orange-7 dye along with simultaneous production of bioelectricity. In another study, soil MFCs were used to degrade a toxic refractory pesticide called hexachlorobenzene along with electricity generation (Cao et al. 2015). Both of the above examples signify the importance and application of MFC technology being efficiently used for bioremediation coupled with bioelectrogenesis. Different organisms such as micro-algae can also be used in MFCs for wastewater treatment owing to their ability to degrade organic and inorganic pollutants present in the water. *Leptolyngbya* sp. JPMTW1 was used in a MFC coupled bioreactor for biofuel, bioelectricity production and wastewater treatment (Maity et al. 2014). The anodic compartment present in the MFC is the region of inhabitation for the microbes along with the process of degradation. Several improvements in the anodic compartments especially the bioanode can definitely enhance the efficiency toward electricity production. These include use of carbon or graphite materials, their dimensions (due to increase in surface area), low resistivity and also the design of the compartment. Along with this the operational conditions of the bioanode also influence the efficiency. These parameters include anode potential, pH, medium composition and feeding mode (Pham et al. 2009). Thus, these systems responsible for the production of electricity can have a number of applications such as efficient harvesting of solar energy (Wang et al. 2013), oxidation and degradation of organic and inorganic pollutants in wastewater and microbial utilization of substrates for production of useful products (Pham et al. 2009).

MFC technology on account of its power generation ability, sustainable energy generation and biosensor application can be targeted toward a future application in space technology.

12. Advantages and disadvantages

One of the most important merits of MFC technology is its environment friendly nature as compared to other energy production technologies which involve methanogenic anaerobic digestion, fossil fuels, etc.,

resulting in emission of carbon dioxide and global warming (Du et al. 2007). As aforementioned the various applications of MFC technology include production of bioelectricity from various organic sources such as solid waste biomass, food waste, domestic and other wastewaters, etc. Thus, inclusion of these waste products as substrates in MFC technology makes it a more potent means of sustainable energy generation. Industrial and domestic wastewaters namely sewage, cattle, swine and brewery wastewaters have been employed as potential substrates in MFC technology generating efficient results (Min et al. 2005; Feng et al. 2008; Zhao et al. 2012). Upgrading these models to a larger scale would aim to decrease the energy expenditure in terms of their treatment (Logan et al. 2006). Another implication of MFC technology is the alternate production of hydrogen and methane (Rabaey, Boon, Dendf et al. 2004). Hydrogen production is achieved by external application of potential to the MFC system which contributes to overcome the thermodynamic barrier leading to formation of hydrogen (Liu, Cheng et al. 2005; Liu, Grot et al. 2005). Thus, basically MFC technology aims to induce generation of clean energy from waste products generated in the society through efficient conversion by employing microbes. This technology as opposed to the means of renewable sources of energy recycles the waste and energy generated by our society and makes it replenishes it back to us eliminating the harmful side effects of environmental endangerment.

There are a number of restrictions that MFC technology faces in terms of its utilization and application in energy production. One of the most important demerits is the inability to scale up MFC models on a large and commercial scale (Singh et al. 2010). Any bioreactor model when scaled up has to deal with quantities tenfold and hundredfold of the original and accordingly proportionate the components concurrently maintaining similar efficiency to validate the process. Most of the MFC models do provide efficient energy production but pose a question mark on the efficiency when scaled up. The electricity production by MFC technology as of currently when compared with methanogenic anaerobic digestion falls short of economical (Logan 2004). The operating temperature also acts as a limitation for MFC technology as microbial reactions cease at temperatures below 20°C (Shantaram et al. 2005). There are several factors involved in determining the efficiency of MFC technology namely, technical factors such as internal resistance, electrode potential and oxygen availability, which act as a hindrance in elevating the potential of MFC technology on a commercial and economical basis (Logan & Regan 2006). Continuous power generation by MFCs is largely dependent on its reliance on biofilm formation by the microbes to facilitate transfer of electrons from the biofilm to the anode for which the development of various microbial catalysts need to be found and employed (Angenent et al. 2004). Although, several microbial strains such as *Geobacter* and *Shewanella* have been introduced in MFC technology for their ability to self-mediate the transfer of electrons (Chae et al. 2009; Bond & Lovley 2003), other microbes employed involve assistance from electron mediators which inadvertently decrease the efficiency of the MFC system. The pre-requisites involved in MFC technology are expensive and fragile and do present a question about execution of these materials on a large scale. Certain materials such as carbon cloth, paper and rods are not conducive to scale up due to their lack of durability and strength (Logan & Regan 2006).

13. Recent developments

Zhang, He, Yang et al. (2016) have reported utilization of nitrogen doped ionothermal carbon aerogel which is coated on the surface of the cathode to achieve a maximum power density production of 2300 mW/m^2. This power density generation in 1.7 times greater as compared with that obtained by most commonly used Pt/C cathodes. Certain modifications in the electrodes such as development of air cathode have been proved to enhance the efficiency of the MFC system (Feng et al. 2008; Choi and Ahn 2013; Di Lorenzo et al. 2014). Air-cathodes are basically constructed with three basic layers: a catalyst, current collector and a diffusion layer (Zhang, He, Zhang et al. 2016). As compared to the traditional Pt coated cathodes, air-cathodes have emerged as promising alternatives. These are traditionally made by brushing a catalyst (Pt) with a binder (mostly Nafion) onto carbon cloth/mesh with PTFE used as a diffusion layer on the air side of the cathode (Cheng et al. 2006). Zhang et al. (2009) constructed an activated carbon air cathode by cold-pressing the activated carbon with a PTFE binder around a Nickel mesh current collector. The maximum power density produced by the activated carbon air cathode was higher than the traditional Pt-catalyzed

electrode indicating a higher activity for oxygen reduction in case of the former. Wei et al. (2011) compared the efficiency of granular semi-coke and granular activated carbon as electrode materials for a biocathode in an MFC system and the power density obtained was compared with two commonly used biocathode materials graphite and fiber-felt. It was observed that the power density generated in case of the two former materials was higher than the two latter materials. MFC technology involves proximate association of micro-organisms with the anode (bioanode) through which the electrical current generated is being transferred. There are number of factors affecting the performance of the bioanode namely mass transfer, ohmic losses, activation losses and electron quenching reactions (Pham et al. 2009). A number of studies have been carried out evaluating the bioanode performance with respect to its structural and chemical properties which can be enhanced by utilization of different models of electrodes, application of various electron mediating compounds such as catalysts. Adjoining these factors, certain other parameters such as compartment design and microbiology also influence the power generation capability of the MFC system (Rabaey et al. 2005; Li et al. 2008). Metabolic and genetic engineering of the microbial strains that are employed in MFC technology is one of the major routes toward increasing the efficiency of the system. Yong et al. (2014) achieved enhanced bioelectricity production through over-expression of NAD synthetase gene by genetic engineering.

14. Conclusion

Thus, bioelectricity production technology can be applied through various modes achieving different goals ranging from energy production to biofuel production as well as bioremediation. Bioelectricity production from microbes can very well act as a sustainable source of energy minimizing the utilization of fossil fuels resulting in green energy. Also, anaerobic digestion of waste products, pollutants and chemicals can prove to be an effective way of maintaining environmental purity and production of renewable energy.

Disclosure statement

No potential conflict of interest was reported by the authors.

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