Review Paper:

Review selection criteria of microbial fuel cell types and applications

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Abstract
The world's energy consumption has increased enormously due to increase in energy demand, therefore research is focused on alternate eco-friendly energy sources. Microbial fuel cell (MFC) is a bio-electrochemical device that transposes the chemical energy present in organic and inorganic compounds into electricity by using microorganism as biocatalysts. The major classification of MFC is based on design/construction such as single chambered, double chambered, up flow and stacked cell; parameters affect the function of a cell such as substrate mediator, inoculum, membrane and electrode design, microorganisms in aqueous medium and as biofilm at electrode.

The applications of MFCs are bioelectric and bio-hydrogen generation, industrial effluent/wastewater treatment, bioremediation of toxic compounds and biosensors. The major advantage of MFC is generation of electricity at low temperature which significantly helps to reduce the pollution for creating clean environment. The major obstacles are microorganism culture, high cost of electro catalyst and membrane. This review elaborately discusses on selection criteria to choose right kind of MFC for specific application.

Keywords: Fuel cell, Bioelectricity, Biocatalyst, Microorganism.

Introduction
In this world, contribution of machines to work is major key for the day to day progress of activities. The machines require adequate amount of energy. In recent years, the utilization of energy drastically increased; the increased utilization of energy has led to a tremendous decrease in the availability of non-renewable sources of energy, which are now being used for energy generation.

Hence, in this energy dependent era, researchers are looking for an alternate energy which is nonpolluting and eco-friendly. According to researchers and scientists, we may soon find ourselves using fuel cells to generate electrical power. A fuel cell is a device which converts chemical energy to electrical energy[1-5]. In a typical fuel cell, hydrogen acts as fuel and oxygen/air acts as an oxidant to generate electricity through an electrochemical process. The fuel cells are classified into different types based on the ion transfer as follows: (i) Proton exchange membrane fuel cell (ii) Anion exchange membrane fuel cell and (iii) Solid oxide fuel cell. A special type of fuel cell that uses the microbes to generate electricity by treating the different industrial waste/effluent is called a bioelectrochemical or microbial fuel cell.

The microbe takes in the organic compounds present in industrial waste/effluent and releases electron. Microbial fuel cell (MFC) is capable of operating at low temperature. Typical microbial fuel cells are mainly compressed of anode/negative terminal and cathode/positive terminal, proton exchange membrane and external circuit. The electrons are released through the oxidation process at anode and travel to cathode via external circuit[6,7].

The proton exchange membrane has been used to permeate the protons and reaches the cathode electrode where the reduction reaction occurs with the electrons from the outer circuit[8-11]. The aspiration of this review is to study the types of microbial fuel cells, their applications and limitations.

Additionally, various microbes used in fuel cell and their culture techniques are also studied. The advantages of MFC are generation of energy out of bio waste /organic matter, direct conversion of substrate energy to electricity, emission of gas treatment, aeration, bioremediation of toxic compounds and the disadvantages of MFC are high initial cost, activation losses, ohmic losses and bacterial metabolic losses. The overall review gives us an idea to choose the type of fuel cells for specific application with right kind of microbes.

Principle of microbial fuel cells: Microbial Fuel Cells (MFCs) are electrochemical devices that could be utilized for bacteria as a biocatalyst to oxidize fuels and generate electricity by direct or indirect methods, through a mediator. The mediator is used for transferring electrons to the electrode[1-5].

The electrons produced are transferred from the anode / negative terminal to the cathode / positive terminal connected to conductive material containing a resistor load. The anode holds bacteria and the organic compounds in an anaerobic environment. The cathode holds the conductive salt water solution in a double chambered type MFC or air in the case of single chambered MFC.

Not all bacteria are capable of producing electrons directly. So in order to alter the bacteria nature to produce electrons, the artificial chemical mediators are used such as neutral red or anthraquinone-2, 6-disulfonate added to the system to produce electricity[9,13]. The bacteria grow in the anode by oxidizing matter and release electrons as they break down substrate molecules. Bacteria that require some special type of bio-films are called as exoelectrogens[14].

Anodic reaction: $$CH_3COOH + 2H_2O \longrightarrow 2CO_2 + 8H^+ + 8e^- \quad (1)$$

Cathodic reaction: $$8H^+ + 8e^- + 2O_2 \longrightarrow 4H_2O \quad (2)$$

Overall reaction: $$CH_3COOH + 2O_2 \longrightarrow 2H_2O + 2CO_2 \quad (3)$$

Materials of construction: The basic and main components of MFC are anode, cathode, proton exchange membrane, substrate and electrode.

- Proton Exchange Membrane – widely used Nafion has the least resistance.
- Substrate – any organic matter is used as source of energy for microorganisms e.g. wastewater.

Bacteria – exoelectrogens, mostly suited for MFC application.

Anode: In general, fuels used at anode are industrial effluents/wastes which contain acetate, cellulose, glucose, starch, anibiotics and chitin. Microorganisms used are *Esherichia coli K12, Candida melibiosica*, cellulose degrading bacteria helping in reakdown/disintegrate/ degrade the fuel to remove the pollutant/ harmful/heavy metal present[15]. A good anodic material must have high conductivity, surface area, porosity, thermal and electrochemical stability and should be biocompatible in the reactor solution. The metal anodes are made of noncorrosive material but copper is not appropriate in view of toxicity. Generally, carbon is used as electrode material which is available in different form such as graphite plates, rods or as granules and as glassy carbon[16-18].

To maintain high surface area, compact materials like reticulated vitreous carbon are used which are available with many pore sizes or by layers of carbon granules or beds. The high porosity will prevent the clogging. To increase performance of the cathode, neutral red is used as a mediator at anode, electro catalytic materials like Pt are used to direct the oxidation of microbial metabolism[19,21].

Decrease in electrode spacing increases the power density[22] which has been achieved using reticulated vitreous carbon in an up-flow type MFC or in a granular anode reactor with ferricyanide cathodes. Flow through an anode has also been used in reactors using exogenous mediators. The produced proton at the anode chamber travels towards cathode through proton exchange membrane. The generated electron at the anode is passed to the cathode via external circuit.

Cathode: The cathode chamber of electrode is subjected to catholyte of an oxidizing agent in solution. The oxidizing agent is reduced as it receives electron and proton from anode through external circuit and membrane[23]

$$H_2 \longrightarrow 2H^+ + 2e^- \quad (4)$$

$$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O \quad (5)$$

The concentration, proton availability, electrode structure all may have an effect on the performance of cathode. The suitable catalyst can lower the activation energy and enhance the rate of the reaction[24,25]. The oxygen acts as an electron acceptor at the cathode owing to the accessibility, intense oxidation potential and producing non-poisonous product[16]. Some of the commonly used cathode materials are discussed in table 2.

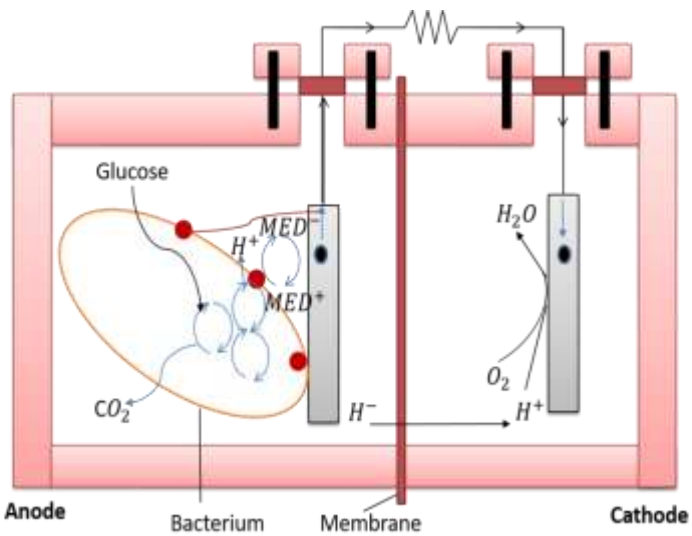

Figure 1: Schematic representation of MFC

Table 1
Reaction mechanism at anode and cathode electrode

	Reaction	E_0(v)	Conditions	E_{MFC} (V)
Anode	$2HCO_3^- + 9H^+ + 8e^- \longrightarrow CH_3COO^- + 4H_2O$	0.187	HCO_3^- = 5 mM CH_3COO^- = 5 mM pH=7	-0.296
Cathode	$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$	1.229	pO_2 = 0.2 pH=7	0.805
	$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$	1.229	pO_2 = 0.2 pH =10	0.627
	$O_2 + 2H^+ + 2e^- \longrightarrow H_2O_2$	0.695	pO_2 = 0.2 H_2O_2 = 5mM pH=7	0.328
	$MnO_2(s) + 4H^+ + 4e^- \longrightarrow Mn^{2+} + 2H_2O$	1.23	Mn^{2+} = 5mM pH=7	0.470

Table 2
Material of construction of components for MFC[1-25]

Components	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, Plexiglass
Cathodic chamber	Glass polycarbonate, Plexiglass
Proton Exchange Membrane	Naflon, Ultrex, Polyethylenepoly (styrene-co-divinylbenzene); salt bridge, porcelain septum or solely electrolyte
Electrocatalyst	Pt, Pt black, MnO_2, Fe^+, polyaniline, electron mediator immobilized on anode

For an anaerobic condition the anodes are affected by K_3 [Fe $(CN)_6$], which get through with the anode chamber proton exchange membrane. The advantage of Ferricyanide is through potential on carbon electrode[26,29]. Most frequently used catalyst platinum is engaging the cathodic reaction but due to its poisoning sensitivity the platinum is not suitable as a catalyst in MFCs[30].

To amplify the performance of the Microbial Fuel Cell, alternative oxidants are used i.e. an artificial electron as redox mediators, in a cathode chamber such a potassium permanganate[32,33]. Moreover potassium permanganate shows a lower concentration as an oxidizing agent and has a vast potential to increase the power and voltage in MFC[34]. The possible cathodic reactions are conferred in table 1 with different pH. Since anode is enhancing the surface area material for example by using graphite material, the efficiency of the cathode is increased in power generation meanwhile decreases the expenses.

Electrolyte/ion transfer membrane: The produced proton is transferred from anode to cathode chamber through a permeable membrane called proton exchange membrane. Membrane acts as a separator between anode and cathode which prevents short circuit[48]. These separators are generally made of ultrafiltration by typical ion exchange membrane. The membrane matrix is made of two types the cation exchange membrane and anion exchange membrane [49-51]. In few cases the MFCs are naturally separated as in sediment MFC and are completed by burying anode in anaerobic mud. Generally used cation exchange membrane is nafion and readily available, an alternate to conventional nafion is Ultrex.

Besides the advantages of a separator, they may also be unfavorable to the reaction[52]. In addition to increasing and reducing pH in the cathode and anode chamber respectively and they decrease the stability of the system[53-58]. To overcome these types of problems, different separators are established such as salt bridges, bipolar membrane, glass fibers, microfiltration membrane, porous fabrics and other pour filters[59-65].

Voltage generation in MFC: The overall reaction is thermodynamically favorable. The reaction can be investigated in terms of Gibbs free energy and used to calculate the maximum amount of work that can be derived from a reaction[66] as follows:

$$\Delta G_r = \Delta G_r^0 + RTln(\Pi) \quad (6)$$

where ΔG_r (J) is the Gibbs free energy, ΔG_r^0 (J) is the Gibbs free energy at standard temperature (298.15 K), pressure (1 bar), for 1 M concentration of all species, R (8.31447 J $mol^{-1}K^{-1}$) is universal gas constant, T (K) is the absolute temperature and Π is the reaction quotient calculated by the ratio of the activities of the products and activities of the reactants.

The standard reaction Gibbs free energy is calculated from energy of formation of products in water[35-37]. it would be most convenient to estimate the reaction in terms of the overall cell electromotive force (emf) E_{emf} is defined as the potential difference between the cathode and anode in Volt. This is related to work W is measured in Joules, produced by the cell, or

$$W = E_{emf}Q = -\Delta G_r \quad (7)$$

where Q = nF is the charge transferred during the reaction expressed in Coulomb (C), which is determined by the number of electrons exchanged in the reaction, n is the number of electrons per reaction mol and F is Faraday's constant (9.64853×10^4 C/mol).

Combining two equations (6) and (7)

$$E_{emf} = -\Delta G_r/nF \quad (8)$$

If all reactions are evaluated at standard conditions, Π, then

$$E_{emf}^0 = -\Delta G_r^0/nF \quad (9)$$

Therefore, use the above equations to express the overall reaction in terms of the potentials as:

$$E_{emf} = E_{emf}^0 - RT/nFln(\Pi) \quad (10)$$

For the reaction to occur spontaneously, the E_{emf} value should be positive and directly produce emf for the reaction. This calculated emf provides an upper limit for the cell voltage. The actual potential derived from the MFC will be lower due to various polarization losses occurring during the operation.

The reactions taking place in the MFC can be studied with respect to the half-cell reaction at anode and cathode[33]. For example, if acetate is oxidized by bacteria at the anode, then reaction can be written as:

$$2HCO_3^- + 9H^+ + 8e^- \longrightarrow CH_3COO^- + 4H_2O \quad (11)$$

The standard potentials are reported relative to the Normal Hydrogen Electrode (NHE) and have a potential of zero at standard conditions {(298 K, pH=2), 1 bar, $[H^+]$ 1M}. To obtain the theoretical anode potential, under specific conditions, using (10) with the activities of different species assumed to be equal to their concentrations, we therefore have

$$E_{An} = E_{An}^0 - \frac{RT}{8F} ln\left(\frac{[CH_3COO]}{[HCO_3]^2[H^+]^9}\right) \quad (12)$$

For the theoretical cathode potential, consider the case where oxygen is used as the electron acceptor for the reaction, then:

$$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O \quad (13)$$

$$E_{cat} = \pi r^2 = E_{cat}^0 \frac{RT}{4F} ln\left(\frac{1}{pO_2[H^+]^4}\right) \quad (14)$$

The voltage variation occurs in the cell majorly due to the change in the catholytes. Instead of oxygen catholyte, one can use manganese oxide and ferricyanide as an alternative which leads to change in pH of catholyte. The overall cathode potential is affected due to pH of the cathode solution. The overall cathode potential can be calculated using (14) and standard tabulated potentials are available for inorganic compounds for several different conditions[33], the theoretical cathode potential for these different catholytes ranges from 0.361 to 0.805 V. The cell electromotive force is calculated as:

$$E_{emf} = E_{cat} - E_{an} \quad (15)$$

where the negative sign is a result of the anode potential as reduction reaction, even though oxidation reaction is taking place in a cell and pH at anode and cathode are equal. Different levels of power output are received while using the same anode in a system with different conditions. The power produced by an MFC based on selection of cathode depends on the choice of cathode and this should be taken into account when comparing power densities achieved by different MFCs.

Open Circuit Voltage (OCV) - The cell emf may be a thermodynamic value that does not consider the internal losses of cell during operation. The Open Circuit Voltage (OCV) is the cell voltage that is measured by considering internal losses during the cell operation. Theoretically, the OCV approaches the cell emf but practically, OCV is substantially less than the cell emf due to various potential losses. This loss is usually mentioned as over potential or the difference between equilibrium potential and actual potential.

Types of MFCs

Single Compartment MFC: In single chambered MFC, anode compartment is present and the cathode is exposed to the atmosphere. Oxygen supply to the cathode chamber is not necessary since it is directly exposed to air. Since the design is simple, scale up process is viable. Additionally, operating in batch as well as continuous mode is easy and cost effective in terms of design[67,68]. The nonconductive polycarbonate plate is used to construct the cell with the dimensions of 15cm x 15 cm x 3 cm (L x B x H). The serpentine path is created for wastewater retention with the total surface area of about 55 cm^2 and volume of about 22 cm^3. The plates are sealed using screw and bolt system. Porous carbon paper and carbon cloth impregnated with platinum catalyst of dimension 10 cm x 10 cm are used as anode and cathode electrode respectively. Nafion membrane is used to transfer the protons form anode to cathode and copper wire is used to complete the electrical circuit by connecting both the electrodes[69].

Two compartment MFC: Anode and cathode compartment are separated by the membrane which is used to transfer the ion from one end of the electrode to the other side. The schematic representation of the double chambered MFC is shown in figure 1. In anode chamber microbes and media are present along with electrode. At cathode fresh water and oxygen supply are maintained with corresponding electrode. Anaerobic condition is obtained by the supply of nitrogen at the anode compartment. H type cell is the basic model of two chambered cell[71]. It can be constructed using two borosilicate glass bottles. The glass bridge between two chamber is made by clamp system and separated by proton exchange membrane.

Usually Nafion membrane is used. The carbon paper of dimension 2.5 X 4.5 cm is used as anode and cathode. But the cathode was impregnated with platinum catalyst (0.35 mg/cm^2). The lake sediment is used as the inoculum. The microorganisms are grown in mineral salts medium (MSM) and stored in 4 ºC for further use. The maximum power density obtained is 19mW/m^2 which increased to 39mWm^2 by increasing the concentration of cysteine (0.77g/L)[71].

Up- flow MFC: Up-flow MFCs are used for the waste water treatment where the wastewater is pumped into the system from the bottom and the effluent flows out from the top of the system in a continuous mode[72]. A typical up-flow MFC works without a proton exchange membrane. The MFCs are tubular in shape with a total height of 100 cm and diameter 10 cm and made with polyacrylic plastic. Graphite felt (196 g) anode material (53.3 g) was used as the cathode. In between anode and cathode series of layers of glass beads and glass wool are used and the sample ports are situated throughout the length of the reactor. The total area of the anode is 465 cm^2 and cathode is 89 cm^2.

The fuel (artificial wastewater containing glucose and glutamate) is supplied at the rate of 0.28 $mL.min^{-1}$ from the bottom of the reactor and the effluent is taken out from the top. The aerators are used to aerate the cathode layer and platinum wire (resistance 10 Ω) is connected with the electrodes to an external circuit. The main advantages of this design are the absence of proton exchange membrane and the continuous mode of operation which reduces the cost.

The main disadvantage of this method is the substantial energy utilized to pump the wastewater in comparison to the energy generated. Hence, it is possible to use treat wastewater where electricity generation is not a first priority[72].

Stacked MFC: The stacked MFCs are combined either in series or parallel connection to obtain high power density. Stacked MFCs are designed as six individual continuous MFC connected together[73]. Graphite granules are used as anode and cathode which provide maximum surface area for microbes to transfer electrons. The volume of one MFC is 60 mL and the overall volume is 360 mL. The proton exchange membrane is Ultrex CMI7000 utilized to sepárate the anode and cathode. It is observed that the performance of parallel MFC is better than series connection due to higher efficiency and chemical oxygen demand removal[73].

Parchment paper is used for fabricating the MFC and acts as an H^+ ion transfer membrane which is cheap, chemical free and disposable. The graphite particles are deposited on the paper using four different strokes of pencils which act as an electrode. The crayon is added to the corners to make it hydrophobic. The microbes are added to the anode chamber along with few microliters of media. The air cathode is used where electrons are accepted byO_2. The microorganism used is *Shewanellaoneidensis.* The maximum voltage and current generated were found to be 300 mV and 11 µA respectively[74].

Biocathodes: Biocathodes are advantageous over abiotic cathodes for several reasons. Preliminary the construction and operation cost of MFCs may be lowered. Metal catalysts or artificial electron mediators could be made superfluous in MFCs with biocathodes due to catalytic function of microorganism.

Furthermore, the microorganisms such as algae produce oxygen through photosynthetic reactions with specified conditions and excluding the cost for an external oxygen supply. Secondary, biocathodes should be able to improve MFC sustainability, since sulphur poisoning with the platinum or consumption and restore of electron mediator will be removed. Tertiary biocathodes can be used to produce valuable products or eliminate unwanted compounds in the microbial metabolism.

Effect of mediator in MFC: In MFC, anolyte/catholyte microorganism forms a biofilm which contains both exoelectrogenic bacteria and non-exoelectrogenic bacteria. Exoelectrogenic bacteria have a potential of transferring electrons from cell surface to the electrode surface. Non exoelectrogenic bacteria can be used mediator for transfer of the electrons.

A mediator is a substance used to transfer the electrons form cell to the electrode surface. The substance ediators are listed in the table 4 which can be added externally or produced by the microbe itself. The list of microbes and the corresponding microbe are given in the table 4.[76-78]

Factors affecting MFC performance: There are several factors that affect the performance of MFCs as shown in figure 2[83]. The metabolism of the microbes is the main parameter in determining cell potential. Either microorganisms or enzymes might be utilized in MFCs. Enhancing the efficiency and commonly used microbes in industries are *Saccharomyces* species and *Escherichia coli.* These microorganisms allow multiple enzymes and substrate. The MFCs can be inoculated by mixed cultures of bacteria which are very advantageous for waste water treatment. The substrate concentration is another factor which must be considered. Increase in substrate concentration increases the power output from 0.2-1.2Wm^{-3}. The effect of microbes for sodium acetate as a substrate has been listed in table 3.

The high pH in the cathode chamber can substantially reduce the current generation because potential of the oxygen reduction increases with a decrease in pH. Therefore, the low operational pH is advantageous for the oxygen reduction and subsequently to achieve higher current. Bacteria need neutral pH for their optimum growth and count for the variation in internal and external pH by regulating their activities.

The bacterial activity decreases with the lower pH in the analyte and also affects the biofilm formation and current generation. However, the pH ranging from 6 to 9 is appropriate for microbial growth and achieving comparatively higher power. The air-cathode can be operated with an anolyte of pH range between 8 and 10.

Table 3
Effect of microbes used for sodium acetate as substrate[15,17-19]

Cathode	Anode	Substrate	Microbes at anode	OCV (mV)	Power density (mWm^2)
RGO-AcOH	Carbon brush/ammonia	Sodium acetate	*Esherichia coli K12*	727	1683
N/RGO	Carbon felt	Sodium acetate	*Candida melibiosica*	160	1150
GO/MgO	Carbon felt	Sodium acetate	*Cellulose derading bacteria*	568	755
rGO/SnO_2	Carbon felt	Sodium acetate	*Escherichia coli*	~500	80
NG-MFCs	Carbon fiber brush	Sodium acetate	*Preacclimated bacteria from an active MFC -*	555	1350±15

Table 4
Mediator needed for microbes to generate electricity through MFCs[15,18,33,72]

Microbe	Mediator
Proteus mirabilis	Thionine
Erwiniadissolven	Ferric chelate complex
Lactobacillus plantarum	Ferric chelate complex
Streptococcus lactis	Ferric chelate complex
Desulfovibriodesulfuricans	Sulphate/sulphide
Actinobacillussuccinogenes	Neutral red or thionine
Gluconobacteroxydans	HNQ, resazurin or thionine
Escherichia coli	Methylene blue
Pseudomonas aeruginosa	Pyocyanin and phenazine-1-carboxamideas
Klebsiella pneumonia	HNQ
Shewanellaoneidensis	Anthraquinone-2,6-disulfonate(AQDS)

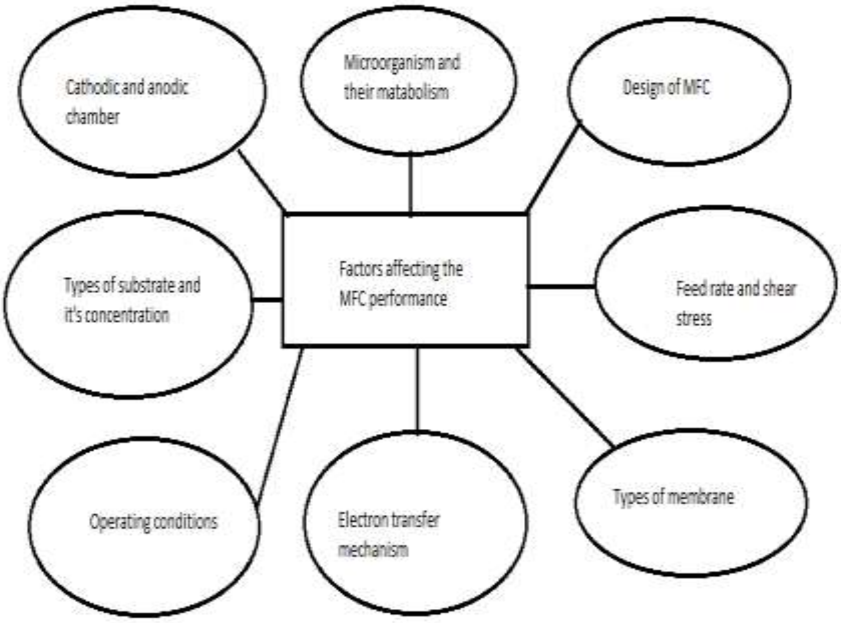

Figure 2: Factors affecting the performance of MFC

Temperature is important factor that affects the kinetics of the whole system, large deviation in the temperature during the operation may affect its performance. It mainly affects the microbial metabolism, mass transfer and thermodynamics. A study found that the temperature ranges between 30 to 45^0C are more beneficial for the operation of MFCs to obtain higher power because the bacterial biofilms showed maximum catalytic activity between the mentioned temperature range above which the microorganism starts to decay.

Applications of MFC

Hydrogen production: MFC can be used for hydrogen production apart from current generation. In conventional method, the anode and cathode (two chambers) are bifurcated by proton exchange membrane and proton passes through this membrane whereas electrons pass through the external circuit. The proton combines with oxygen and electron in cathode chamber to form water. If the cathode chamber is maintained in an anaerobic condition and a small amount of external potential (to break thermodynamic barrier) is provided, a thermodynamically reaction takes place in the cathode chamber.

The protons (H^+) combine with electrons (e^-) to form hydrogen molecules (H_2). Theoretically, only 110 mV is required to break the thermodynamic barrier whereas practically about 1210 mV is required to split the water molecules (electrolysis). Approximately about 8 to 9 mol of H_2 are generated from 1 mol of glucose which is 2 times greater than conventional fermentation methods where about 4 mol of H_2 are generated for each mol of glucose[79].

Methane production: MFC technology using methanogen bacteria could be possible to generate methane other than hydrogen and electricity generation. The design contains two compartments (anode and cathode) split by Proton Exchange Membrane which is quite similar to those used for hydrogen and electricity generation but the mode of operation varies. A small power is supplied for splitting of water in anode compartment under anaerobic condition without microbes. The cathode compartment is supplied with Co_2 and the protons produced near the anode pass through Proton Exchange Membrane, react with carbon dioxide to form CH_4 and H_2O. The methane produced is pure and can be utilized directly[80,81].

Biosensors - MFCs are commonly used as biosensors to detect the level of pollutants in the environment. The correlation between wastewater strength and coulombic yield is utilized to sense biological oxygen demand[82], the current increases linearly with increase in Biological Oxygen Demand. Biological Oxygen Demand sensors are more reliable when compared to other Biological Oxygen Demand sensors because of their stability and accuracy. MFCs Biological Oxygen Demand biosensors have more lifespan without maintenance when compared to other sensors.

Wastewater treatment: Treating wastewater is a major problem today which has to be solved in a cost-effective manner[81]. Wastewater could be from any source such as municipal, domestic, industrial, medical and agricultural wastewater. Out of these, it is found that the municipal wastewater is very difficult to treat because of its most diversified composition.

Apart from being treated, wastewater can also be used as an energy source for generating electricity. It is also found that this leads to the generation of less solid waste (50 – 90% less) by converting acetate, butyrate and propionate etc. into Co_2 and H_2O before disposal and this has been widely discussed in table 5.

Table 5
Effect of MFC's for various treatments[19,41,60,63,67,68,70,80,82]

Substrate	**Source**	**Anode**	**Cathode**	**Microorganism**	**Power density at 600 mV mWm^{-2}**
Acetate	Food industry	Graphite	Copper, Zn	*Bascilliussphaericus*	--
Glucose (Monosaccharide)	Biogas production	Carbon cloth/graphite cloth	Aluminum foil	*Methanobacterium*	2160 +/- 1
Lignocellulosic (polysaccharide)	Paper recycling	Zn, KOH	Li, Al, Ca, Fe, Mg	*Pseudoanabaena and chroococcus*	4.9 +/- 0.01
Starch	Air cathode and beer industry	Graphite rods & bushes, carbon cloth & paper	Carbon or graphite	*Yeast-Saccharomcescerevisiae*	0.528
Glucose	Swine waste water treatment	Nitrogen gas	$KMnO_4$	*Aspergillusniger*	261
Protein	Meat industry	Zinc or Lithium	Aluminum foil	*Lactobacillus*	80 +/- 1
Anaerobic granule (sludge)	Municipal wastewater	Carbon cloth	Ni-Co	*Bascillus*	116
Cellulose	Paper industry	Zinc	Lithium	*Pseudoanabaena and chroococcus*	20
Dye	Effluent of textile industry	C/TiO_2	Carbon	*Penicilliumoxalicum-(red)*	--
Glucose	Ethanol production	Co/Fe/N/CN	Carbon paper	*Saccharomyces cervisiae*	751
Glucose	Sugar	rGO/Pt/Co	Carbon cloth/acid/heat	*Escherichia coli*	1378

Conclusion

This review elaborately discussed about different types of MFCs, their applications and limitations. The importance of thermodynamics on MFC was explained since the microbial reactions are significantly affected by various conditions such as pH and mediator due to which the reactions taking place at anode and cathode differ for the same process. The effects of microbe and mediator on different substrate were studied. Many Microbial Fuel Cells are designed alternatively to maintain the consistency of energy generation and to reduce the cost of proton exchange membrane.

The MFCs provide a potential to sensor remote to trace which is unable to be achieved by batteries. It is a great task to enhance the efficiency of the MFC in terms of power density which is low when compared to conventional power sources. In future it is expected to increase the power density, efficiency and output power, so it can be used as a power source but one of the main draw backs of the MFCs is insufficient input power. It is evident that bio cathodes are a best choice for the replacement of metals and composites.

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References

1. Berk R.S. and Canfield J.H., Bio electrochemical energy conversion, *Appl. Microbial*., **12**, 10-12 **(1964)**

2. Rao J.R., Richter G.J., Von Sturm F. and Weidlich E., The performance of glucose electrodes and the characteristics of different biofuel cell constructions, *Bioelectrochem. Bioenerg.*, **3(1)**, 139-150 **(1976)**

3. Davis J.B. and Yarbrough H.F., Preliminary experiments on a microbial fuel cell, *Sci*., **137(3530)**, 615-616 **(1962)**

4. Cohen B., The bacterial culture as an electrical half-cell, *J. Bacterial*, **21**, 18-19 **(1931)**

5. Santoro C., Arbizzani C., Erable B. and Ieropoulos I., Microbial fuel cells: From fundamentals to applications, *A Rev. J. Pow. Sour.*, **356**, 225-244 **(2017)**

6. Rabaey K., Boon N., Siciliano S.D., Verhaege M. and Verstraete W., Biofuel cells select for microbial consortia that self-mediate electron transfer, *Appl. Environ. Microbial*., **70(9)**, 5373-5382 **(2004)**

7. Rabaey K., Boon N., Hofte M. and Verstraete W., Microbial phenazine production enhances electron transfer in biofuel cells, *Environ. Sci. Technol.,* **39(9)**, 3401-3408 **(2005)**

8. Cao Y., Mu H., Liu W., Zhang R., Guo J., Xian M. and Liu H., Electricigens in the anode of microbial fuel cells: pure cultures versus mixed communities, *Microbiol. Cell Factor*, **18**, 39 **(2019)**

9. Ezziat L., Elabed A., Ibnsouda S. and El Abed S., Challenges of Microbial Fuel Cell Architecture on Heavy Metal Recovery and Removal From Wastewater, *Front. Energy Res*., **7**, 1 **(2019)**

10. Gorby Y.A., Yanina S., McLean J.S., Rosso K.M., Moyles D., Dohnalkova A., Beveridge T.J., Chang I.S., Kim B.H., Kim K.S., Culley D.E., Reed S.B., Romine M.F., Saffarini D.A., Hill E.A., Shi L., Elias D.A., Kennedy D.W., Pinchuk G., Watanabe K., Ishii S., Logan B.E., Nealson K.H. and Fredrickson J.K., Electrically conductive bacterial nanowires produced by Shewanellaoneidens is strainMR-1and other microorganisms, PNAS, 11358-11363 **(2006)**

11. Reguera G., McCarthy K.D., Mehta T., Nicoll J.S., Tuominen M.T. and Lovley D.R., Extra cellular electron transfer via microbial nanowires, *Nature*, **435**, 1098-1101 **(2005)**

12. Bond D.R., Holmes D.E., Tender L.M. and Lovley D.R., Electrode reducing microorganisms that harvest energy from marine sediments, *Sci.,* **295**, 483-485 **(2002)**

13. Park D.H. and Zeikus J.G., Utilization of electrically reduced neutral red by Actinobacillussuccinogenes: physiological function of neutral red in membrane-driven fumarate reduction and energy conservation, *J. Bacteriol*., **181(8),** 2403-2410 **(1999)**

14. Logan B.E., Extracting hydrogen and electricity from renewable resources, *Environ. Sci. Technol*., **38(9),** 160-167 **(2004)**

15. Park I.H., Christy M., Kim P. and Nahma K.S., Enhanced electrical contact of microbes using FE3 O4/CNT Nano composite anode in mediator-less microbial fuel cell, *Biosen. Bioelectron*., **58**, 75-80 **(2014)**

16. Logan B.E., Hamelers B., Rozendal R., Schro¨der U., Keller J., Freguia S., Aelterman P., Verstraete W. and Rabaey K., Microbial fuel cells: methodology and technology, *Environ. Sci. Technol.*, **40(17)**, 5181-5192 **(2006)**

17. Wu L.C., Wang G.H., Tsai T.H., Shih-Yu Lo S.Y., Chiu-Yu Cheng C.Y. and Chung Y.C., Three-Stage Single-Chambered Microbial Fuel Cell Biosensor Inoculated with Exiguobacterium aestuarii YC211 for Continuous Chromium (VI) Measurement, *Sensors*, **19**, 1418(1-13) **(2019)**

18. Meenu P.C., Sreelekshmy B.R., Basheer R., Sadasivan S.M., Ramakrishnan R.M.V. and Shibli S.M.A., Development of a high-performance mediatorless microbial fuel cell comprising a catalytic steel anode, *ACS Appl. Bio Mater.*, **1(4),** 1124-1133 **(2018)**

19. Sudirjo E., Buisman C.J.N. and Strik D., Marine Sediment Mixed with Activated Carbon Allows Electricity Production and Storage From Internal and External Energy Sources: A New Rechargeable Bio-Battery With Bi-Directional Electron Transfer Properties, *Front. Microbiol.,* **10**, 934 **(2019)**

20. Niessen J., Schroder U., Rosenbaum M. and Scholz F., Fluorinated polyanilines as superior materials for electro catalytic anodes in bacterial fuel cells, *Electrochem. Commun.,* **6(6)**, 571-575 **(2004)**

21. Schroder U., Niessen J. and Scholz F., A generation of microbial fuel cells with current outputs boosted by more than one order of magnitude, *Angew. Chem., Int. Ed. Engl.*, **42(25)**, 2880-2883 **(2003)**

22. Cheng S., Liu H. and Logan B.E., Increased power generation in a continuous flow MFC with advective flow through the porous anode and reduced electrode spacing, *Environ. Sci. Technol.,* **40**, 2426-2432 **(2006)**

23. Angelaalincy M.J., Krishnaraj R.N., Shakambari G., Ashokkumar B., Kathiresan S. and Varalakshmi P., Biofilm Engineering Approaches for Improving the Performance of Microbial Fuel Cells and Bioelectrochemical Systems, *Front. Energy Res.*, **6**, 63 **(2018)**

24. Kim K., Nakashita S. and Hibinoa T., Enhanced power performance of an in situ sediment microbial fuel cell with steel-slag as the redox catalyst: I. electricity generation, *Sustain. Energ. Fuels*, **4(3)**, 1363-1371 **(2020)**

25. Zhou M., Yang J., Wang H., Jin T., Hassett D.J. and Gu T., Bio electrochemistry of microbial fuel cells and their potential applications in bioenergy, *Bioenerg. Res. Adv. App.*, DOI:10.1016/B978-0-444-59561-4.00009-7, 131-152 **(2013)**

26. Gil G.C., Chang I.S., Kim B.H., Kim M., Jang J.K., Park H.S. and Kim H.J., Operational parameters affecting the performance of a mediator-less microbial fuel cell, *Biosens. Bioelectron.*, **18**, 327-334 **(2003)**

27. Yasri N., Roberts E.P.L. and Gunasekaran S., The electrochemical perspective of bioelectrocatalytic activities in microbial electrolysis and microbial fuel cells, *Environ. Microbiol*., **5**, 1116-1136 **(2019)**

28. Franks A.E. and Nevin A., Microbial fuel cells, a current review, *Energies*, **3**, 899-919 **(2010)**

29. Logan B.E. and Regan J.M., Microbial fuel cells-challenges and applications, *Environ. Sci. Technol*., **40(17),** 5172-5180 **(2006)**

30. Park D.H. and Zeikus J.G., Improved fuel cell and electrode designs for producing electricity from microbial degradation, *Biotechnol. Bioeng.,* **81(3)**, 348-355 **(2003)**

31. Oh S.E., Min B. and Logan B.E., Cathode performance as a factor in electricity generation in microbial fuel cells, *Environ. Sci. Technol*., **38(18)**, 4900-4904 **(2004)**

32. Chang I.S., Moon H., Jang J.K. and Kim B.H., Improvement of a microbial fuel cell performance as a BOD sensor using respiratory inhibitors, *Biosens. Bioelectron*., **20(9)**, 1856-1859 **(2005)**

33. Najafpour G., Rahimnejad M. and Ghoreshi A., The enhancement of a microbial fuel cell for electrical output using mediators and oxidizing agents, *Energy Source*, **33(24)**, 2239-2248 **(2011)**

34. Lefebvre O., Ooi W.K., Tang Z., Abdullah-Al-Mamun M.D.H.C., Chua D.H.C. and Ng H.Y., Optimization of a Pt-free cathode suitable for practical applications of microbial fuel cells, *Bioresource. Technol.*, **100(20)**, 4907-4910 **(2009)**

35. Fornero J.J., Rosenbaum M., Cotta M.A. and Angenent L.T., Microbial fuel cell performance with a pressurized cathode chamber, *Environ. Sci. Technol.*, **42(22)**, 8578-8584 **(2008)**

36. Huang L., Regan J.M. and Quan X., Electron transfer mechanisms, new applications and performance of biocathode microbial fuel cells, *Bioresource Technol.*, **102(1)**, 316-323 **(2011)**

37. Rahimnejad M., Najafpour G.D., Ghoreyshi A., Talebnia A., Premie G., Bakeri G.H., Kim J. and Oh S., Thionine increases electricity generation from microbial fuel cell using Saccharomyces cerevisiae and exoelectrogenic mixed culture, *J. Microbiol.*, **50**, 575-580 **(2012)**

38. Izadi P., Fontmorin J.M., Fernández L.F.L., Cheng S., Head I. and Yu E.H., High Performing Gas Diffusion Biocathode for Microbial Fuel Cells Using Acidophilic Iron Oxidizing Bacteria, *Front. Energy Res*., **7**, 93 **(2019)**

39. Kumar P., Chandrasekhar K., Kumari A., Sathiyamoorthi E. and Kim B.S., Electro-Fermentation in Aid of Bioenergy and Biopolymers, *Energies*, **11(2)**, 343 **(2018)**

40. Yazdi H.R., Carver S.M., Christy A.D. and Tuovinen O.H., Cathodic limitations in microbial fuel cells, *J. Power Sources*, **180**, 683-694 **(2008)**

41. Zhou M., Wang H., Hassett D.J. and Gu T., Recent advances in microbial fuel cells and microbial electrolysis cells (MECs) for wastewater treatment, bioenergy and bio products, *J. Chem. Technol. Biotechnol*., **88(4)**, 508-518 **(2013)**

42. Zhang G., Zhao Q., Jiao Y., Lee D.J. and Ren N., Efficient electricity generation from sewage sludge using biocathodemicrobial fuel cell, *J. Chem. Technol. Biotechnol.*, **46(1)**, 43-52 **(2012)**

43. Ghasemi M. et al, Nano-structured carbon as electrode material in microbial fuel cells, *J. Alloy Compound*, **580**, 245-255 **(2013)**

44. You J., Rimbu G.A., Wallis L., Greenman J. and Ieropoulos I., Living architecture: toward energy generating buildings powered by microbial fuel cells, *Front. Energy Res*., **7**, 94 **(2019)**

45. Deng D., Li X., Zuo J., Ling A. and Logan B.E., Power generation using an activated carbon fiber felt cathode in an up flow microbial fuel cell, *J. Power Sources*, **195**, 1130-1135 **(2009)**

46. Ghasemi M., Daud W.R.W., Rahimnejad M., Rezayi M., Fatemi A., Jafari Y., Somalu M. and Manzour A., Copper phthalocyanine and nickel nanoparticles as novel cathode catalysts in microbial fuel cells, *Int. J. Hydrog. Energy*, **38(22)**, 9533-9540 **(2013)**

47. Park D. and Zeikus J., Impact of electrode composition on electricity generation in a single-compartment fuel cell using Shewanella putrefaciens, *Appl. Microbiol. Biotechnol.*, **59(1)**, 58-61 **(2002)**

48. Rahimnejad M., Jafari T., Haghparast F., Najafpour G.D. and Goreyshi A.A., Nafion as a nanoproton conductor in microbial fuel cells, *Turkish J. Eng. Environ. Sci*., **34(4)**, 289-292 **(2010)**

49. Heijne A.T., Hamelers H.V.M., De Wilde V., Rozendal R.A. and Buisman C.J.N., A bipolar membrane combined with ferric iron reduction as an efficient cathode system in microbial fuel cell, *Environ. Sci. Technol.*, **40(17)**, 5200-5205 **(2006)**

50. Kim J.R., Cheng S., Oh S.E. and Logan B.E., Power generation using different cation, anion and ultrafiltration membranes in microbial fuel cells, *Environ. Sci. Technol*., **41(3)**, 1004-1009 **(2007)**

51. Harnisch F. and Schro¨der U., Selectivity versus mobility: separation of anode and cathode in microbial bioelectrochemicalsystems, *Chem Sus Chem*., **2(10)**, 921-926 **(2009)**

52. Qiao Y., Li C.M., Bao S.J. and Bao Q.L., Carbon nanotube/polyaniline composite as anode material for microbial fuel cells, *J. Power Sources*, **170(1)**, 79-84 **(2007)**

53. Liu H., Cheng S. and Logan B.E., Power generation in fed-batch microbial fuel cells as a function of ionic strength, temperature and reactor configuration, *Environ. Sci. Technol.*, **39(14)**, 5488-5493 **(2005)**

54. Watanabe K. and Biosci J., Recent developments in microbial fuel cell technologies for sustainable bioenergy, *J. Biosci. Bioeng.*, **106(6)**, 528-536 **(2008)**

55. Oh S. and Logan B.E., Proton exchange membrane and electrode surface areas as factors that affect power generation in microbial fuel cells, *Appl. Microbiol. Biot.*, **70**, 162-169 **(2011)**

56. Sami G.A., Flimban S.G.A., Ismail I.M.I., Kim T. and Sang-Eun Oh S.E., Overview of Recent Advancements in the Microbial Fuel Cell from Fundamentals to Applications, *Energies*, **12(17),** 3390 **(2019)**

57. Min B., Cheng S. and Logan B.E., Electricity generation using membrane & salt bridge microbial fuel cells, *Water Res.*, **39(9),** 1675-1686 **(2005)**

58. Rabaey K., Lissens G., Siciliano S.D. and Verstraete W., A microbial fuel cell capable of converting glucose to electricity at high rate and efficiency, *Biotechnol. Lett.*, **25**, 1531-1535 **(2003)**

59. Rabaey K., Clauwaert P., Aelterman P. and Verstraete W., Tubular microbial fuel cells for efficient electricity generation, *Environ. Sci. Technol*., **39(20),** 8077-8082 **(2005)**

60. Mohan S.V., Raghavulu S.V. and Sarma P., Biochemical evaluation of bioelectricity production process from anaerobic wastewater treatment in a single chambered microbial fuel cell

(MFC) employing glass wool membrane, *Biosens. Bioelectron.*, **23(9)**, 1326-1332 **(2008)**

61. Zhang X., Cheng S., Wang X., Huang X. and Logan B.E., Separator characteristics for increasing performance of microbial fuel cells, *Environ. Sci. Technol.*, **43(21),** 8456-8461 **(2009)**

62. Zuo Y., Cheng S., Call D. and Logan B.E., Tubular membrane cathodes for scalable power generation in microbial fuel cells, *Environ. Sci. Technol.*, **41(9)**, 3347-3353 **(2007)**

63. Sun J., Hu Y., Bi S. and Cao Y., Improved performance of air cathode single-chamber microbial fuel cell for wastewater treatment using microfiltration membranes and multiplesludge inoculation, *J. Power Sources,* **187(2)**, 471-479 **(2009)**

64. Fan Y., Hu H. and Liu H., Enhanced columbic efficiency and power density of air-cathode microbial fuel cells with an improved cell configuration, *J. Power Sources*, **171(2)**, 348-354 **(2007)**

65. Zhuang L., Zhou S., Wang Y., Liu C. and Geng S., Membrane-less cloth cathode assembly(CCA) for scalable microbial fuel cells, *Biosens. Bioelectron*., **24(12)**, 3652-3656 **(2009)**

66. Singh A. and Yakhmi J., Microbial fuel cells – Applications for generation of electrical power and beyond, *Criti. Rev. Microbiol*., **42(1),** 1-17 **(2014)**

67. Min B. and Logan B.E., Continuous Electricity Generation from Domestic Wastewater & Organic Substrates in a Flat Plate Microbial Fuel Cell, *Environ. Sci. Technol*., **38(21)**, 5809-5814 **(2004)**

68. Fornero J.J., Rosenbaum M. and Angenent L.T., Electric power generation from municipal, food and animal wastewaters using microbial fuel cells, *Electroanalysis*, **22(7-8)**, 832-843 **(2010)**

69. Park D.H. and Zeikus J.G., Improved fuel cell and electrode designs for producing electricity from microbial degradation, *Biotechnol. Bioeng*., **81(3)**, 348-355 **(2003)**

70. Logan B., Cheng S., Watson V. and Estadt G., Graphite Fiber Brush Anodes for Increased Power Production in Air-Cathode Microbial Fuel Cells, *Environ. Sci. Technol*., **41(9)**, 3341-3346 **(2007)**

71. Logan B.E., Murano C., Scott K., Gray N.D. and Head I.M., Electricity generation from cysteine in a microbial fuel cell, *Water Res.*, **39(5),** 942-952 **(2005)**

72. Jang J.K., Pham T.H., Chang I.S., Kang K.H., Moon H., Cho K.S. and Kim B.H., Construction and operation of a novel mediator- and membrane-less microbial fuel cell, *Process Biochem*., **39(8)**, 1007-1012 **(2004)**

73. Aelterman P., Rabaey K., Pham H., Boon N. and Verstraete W., Continuous electricity generation at high voltages and currents using stacked microbial fuel cells, *Environ. Sci. Technol*., **40(10)**, 3388-3394 **(2006)**

74. Lee S.H., Ban J.Y., Oh C.H., Park H.K. and Choi S., A solvent-free microbial-activated air cathode battery paper platform made with pencil-traced graphite electrodes, *Sci. Rep.*, **6**, 28588 **(2016)**

75. Lovley D.R., Dissimilatory Fe(II) and Mn(IV) reduction, *Rev. Microbiol.*, **55(2)**, 259-287 **(1991)**

76. Logan B.E., Exoelectrogenic bacteria that power microbial fuel cells, *Nature Rev. Microbiol*., **7**, 375-381 **(2009)**

77. Rhoads A., Beyenal H. and Lewandowski Z., Microbial fuel cell using anaerobic respiration as an anodic reaction and bio mineralized manganese as a cathodic reactant, *Environ. Sci. Technol.,* **39(12),** 4666-4671 **(2005)**

78. Ieropoulos I.A., Greenman J., Melhuish C. and Hart D.J., Comparative study of three types of microbial fuel cell, *Enzyme Microbiol. Technol.,* **37(2)**, 238-245 **(2005)**

79. Liu B.E., Grot S., Logan H., Liu H., Grot S. and Logan B.E., Electrochemically assisted microbial production of hydrogen from acetate, *Environ. Sci. Technol*., **39(11),** 4317-4320 **(2005)**

80. Wagner R.C., Regan J.M., Oh S.E., Zuo Y. and Logan B.E., Hydrogen and methane production from swine wastewater using microbial electrolysis cells, *Water Res.*, **43(5),** 1480-1488 **(2009)**

81. Habermann W. and Pommer E.H., Biological fuel cells with sulphide storage capacity, *Appl. Microbiol. Biotechnol*., **35**, 128-133 **(1991)**

82. Wang X., Cheng S., Feng Y., Merrill M.D., Saito T. and Logan B.E., Use of carbon mesh anodes and the effect of different pretreatment methods on power production in microbial fuel cells, *Environ. Sci. Technol.,* **43(17)**, 6870-6874 **(2009)**

83. Shanmuganathan P, Rajasulochana P. and Murthy R., A, factors affecting the performance of microbial fuel cells, *Int. J. Mech. Engn. & Technol*, **9(9),** 137-148 **(2018)**.

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