Microbial Fuel Cell Functioning, Developments And Applications-A Review

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Abstract: Development of any country highly depends upon the generation of energy and efficiently using it in industries and agricultural sector. Country such as India which is still developing has a major problem ahead of it in terms of generating energy which is sufficient. With the present crisis and environmental issues government has to look beyond carbon based sources and look towards sustainable energy sources. Microbial fuel cell (MFC) is such technology which can be used to treat wastewater as well as be a power source at large scale. Here the crucial role is of researchers who can make this technology feasible as well as efficient enough to be undertaken. Researchers all over the worlds have researched on each and every major aspect of the MFC and still are optimizing it In order to use in its best possible way. This paper shows MFCs functioning, Developments and application which are currently in existence, like Wastewater treatment, Desalination, Hydrogen production and as Biosensors. The paper allows reader to understand all the development in the field of MFC.

Index Terms: Minimum Anode, Biosensors, Cathode, Cation Exchange Membrane, Desalination, Proton Exchange Membrane, Microbial Fuel Cell, Wastewater treatment.

1. INTRODUCTION

One of the major challenges which mankind faces is the exponentially growing demand for energy. This energy demand results in the continuous use of fossil fuels. Still, the majority of total energy generated in the world is fulfilled by Fossil fuels. This results in not only depletion in their deposits at an alarming rate but they also generate CO2 which results in Global warming. India solely will produce 1905 Terawatt by 2022, which will make India as the Fifth largest consumer and producer of electricity [1]. Alternate renewable sources are in progress such as solar, wind and tidal. But waste management remains a big bottleneck in the commercial sector. This makes Microbial Fuel cell (MFC) a sustainable alternative source of renewable energy. MFC is a device that is an electrochemical technology that is being to recover electricity from wastewater [2][3][4]. It has great potential as an alternative to conventional power sources as it has applications in various fields like Wastewater Treatment [5][6][7][8], Implantable devices in medical fields [9] & Biosensors [10][11][12]. The original conceptualization of generating electricity from the decomposition of organic compounds was proposed by M.C. Potter in 1911. Due to low power generation, the idea was not appreciated [13]. The first major breakthrough came in 1931 when Barnet Cohen produced 35 volts with the number of microbial half fuel cells connected in series. This drew the attention of researchers towards MFC. The next fifty years comprised of understanding basic concepts of MFC and various experiments. The second and major breakthrough was the mediator less MFC. After this only optimization of various components is been done till today for better performance [14]. India alone produces about 36,400 million liters per day of wastewater. This wastewater has resulted in the development of MFC's because of its multipurpose application of production of electricity with treating wastewater or production of hydrogen which can be further used as fuel. Indian scientific community has also contributed to the MFC field and will be doing furthermore work as MFC has great potential in India [15].

2 FUNCTIONING OF MFC

MFC structurally consists of two chambers, Anode chamber where oxidation occurs and Cathode chamber where reduction occurs [16][17][18][19]. Anode chamber consists of Anode, Substrate (organic material) and the bacteria. The bacteria decompose the substrate in to form electrons (e^-) and protons (H^+)[20][21]. These electrons are transferred from bacteria to Anode (Electrode) by membrane-bound quinones and by cytochromes in electrogenic bacteria which does not require any mediator for electron transfer or by mediators such as Methylene blue or neutral red. These electrons are transferred from the anode chamber to the cathode chamber by external circuit providing the current while the protons are transferred through the salt bridge or Proton exchange membranes (PEM) [22]. Reduction takes place in the cathodic chamber mostly in the presence of oxygen. The transferred electron from the anode and the protons which are transferred from the PEM combine to form water in the cathode compartment. The bacteria form CO_2 and H_2O when it decomposes substrate in the presence of oxygen. But the presence of oxygen is found inhibitory so Anode chambers are made Anaerobic. In anaerobic conditions, the bacteria decompose the organic matter into only CO_2. As cathode compartment can be aerobic, the cathode chamber can be eliminated which results in single-chamber MFC. The reactions while using acetate as a substrate are given below [15]. Figure 1 shows the schematic diagram of the MFC.

Anodic Reaction:
$C_2H_4O_2 + 2H_2O = 2CO_2 + 8e- + 8H+$ (1)
Cathodic Reaction:
$2O_2 + 8e- + 8H+ = 4H_2O$ (2)

Performance of MFC can be outlined by the power density, electric current generated and the electric efficiency which are dependent on many parameters. Thus MFC is a complex system that is evident from the multidisciplinary subjects and would require many experts from various fields to optimize to its full potential. However, in the scope of this paper we would discuss the basic function of MFC, various aspects in design of MFC like electrode materials, Substrates used in MFC, Different electrogenic microorganisms, the designs in MFC and Various application of MFCs.

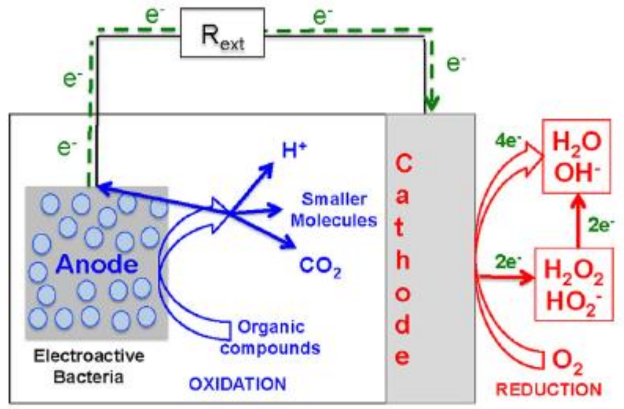

Fig. 1 *Schematic of MFC [26]*

3. ESSENTIAL PARTS IN MFC

Basic MFC contains single or dual chamber with anodic and cathodic chamber constructed by different materials, separated by different membranes and filled with different substrates and microorganism. This paper provides review of role of each part in MFC and the different materials used to construct electrode, membranes materials and microorganism used. Components of MFC are described below.

3.1 Anode

The anodic chamber is one of the important parts of the MFC because it is the place where decomposition of biomass occurs in the chamber with the help of bacteria. Anode electrode is the key element in transferring the electron and hence is an electron acceptor. There are various factors that influence the working and efficiency of the MFC like electrode material, bacteria, and proton transfer membranes. One of the major influential systems is the anodic electron transfer mechanism. Thus much work is being done to optimize the mechanism in to get best results. Electrical conductivity, Chemical stability, resistance to corrosion, high surface area, high mechanical strength and low cost for being feasible are the most important properties for materials as anode electrode [23][24]. Carbonaceous metal-based materials are used mostly in MFC because it comprises of all the above qualities required. Copper-based materials are not used due to the corrosion issues [25]. Carbonaceous based materials like carbon veil, carbon paper, carbon rod, carbonized cardboard, carbon cloth, and reticulated vitreous carbon materials are used [26]. Carbon cloth is the most often used anode material in MFC because of the high strength and high porosity for high surface area [27][28][29][30][31]. Nickel sheet, Copper sheet, stainless steel plate, silver sheet, titanium plate & gold sheet were used as anode materials [32]. Researchers have also utilized electrocatalytic materials like polyaniline (PANI) in to improve the current generation as the combination results in better electrical conductivity and environmental stability. Utilization of Pt one electrodes has been useful as it enhances electrocatalysis, however, the cost of Pt has been one of the major drawbacks for MFC. Alternates such as tungsten carbide have shown comparable results such as Pt [23]. Properties like high strength, large surface area, ductility, and stability have made carbon nanotubes (CNTs) one of the major materials which can be utilized as an electrode. Research conducted by Qiao et al [33] reported the use of CNTs and PANI in combination to form anode electrode which enhanced the performance of MFC by the enhanced electron transfer system. Scott et al [34] conducted experiment by modifying graphite felt electrodes by C/PANI, carbon nanofibres and nitric acid carbon activation. The results suggested that modified electrodes performed better when compared to normal graphite felt electrodes. This occurred due to an increase in surface area which leads to more sites where microbial colonization could occur. CNTs have shown great results in terms of better performance compared to normal electrodes but the cost of CNTs and the expertise required to manufacture it has made it not feasible for its application in MFC till now. But we expect as the demand goes up and mass production of CNTs would bring down the cost and would be feasible enough in future to be utilized in MFCs.

3.2 Cathode

Cathode plays an important role in the performance of an MFC. Cathode should have high redox potential and properties to easily transfer protons. Initially, commercially available carbon electrodes were predominantly used, Graphite in particular due to properties like a wide electrochemical window, low residual current, recyclability, reusability and sufficient electrical conductivity [35]. Apart from graphite, cathode materials are similar to anode materials like Carbon veil, carbon cloth, carbon rod and carbon paper which are carbon-based and materials like nickel, titanium which are metal-based [36]. But as these materials were used a rod or single sheet which decreased productivity as it lacked a higher surface area which is a must for better growth of microbial activity. After various experiments by Marshall and his team concluded that using granular graphite as cathode would result in higher volumetric acetate production from CO_2. This experiment was backed by the results of electron micrographs which showed the better attachment of bacteria over electrodes [37][38]. Various catalysts are added with cathode electrode for better electron transfer and are divided into three categories which are based on the presence/absence of platinum and the presence/absence of earthly based metals. These three categories are platinum-based (PGM-based), carbonaceous-based (metal-free) and platinum group-metal free (PGM-free) [26]. These catalysts are incorporated into the cathode electrode by various techniques like spraying technique, Doctor blade technique, drop-casting, pressing and rolling. Among them, PGM-based based catalyst has been one of the most common and effective catalysts when compared to metal-free and carbonaceous catalyst. But the economics of using a PGM-based catalyst in the cathode electrode is hindering the development of MFC which is feasible enough to be mass-produced. Cheng et al [39] studied the variation in potential when the Pt catalyst load is varied from 2 to 0.1 mg cm^{-2}. They concluded that the maximum decrease in potential was about 19% which was viable keeping in mind the cost-effectiveness of using less Pt. Carbonaceous based material are the more viable due to feasibility, relatively high and stable performance [40]. Carbonaceous materials comprise of graphene, carbon nanotubes, carbon nanofibers, and modified carbon black. Carbonaceous catalyst are found to have better oxidation-reduction reactions in neutral media compared due to high surface area and nanometric pores. Activated carbon is the most used carbonaceous material catalyst [41]. Techniques like rolling [42] [43] and pressing [44] [45] are used to incorporate catalysts on cathodes in the case of carbonaceous catalyst. Apart from this the third type of catalyst which are PGM-free catalyst is one which is under a lot of research and has the attracted attention of researchers all around the world. These catalysts are based on transition metal along with carbon and nitrogen. These metals comprise of Mn, Fe, Co and Ni. Various test of Mn-based [46][47][48][49], Ni-based [50][51] and Fe based [52][53][54][55][56][57][58][59][60] cathode catalysts have been demonstrated.

3.3 Membrane Materials

Membrane plays a critical role in the performance of MFC as it the component through which the proton transfer takes place. Membranes are used to physically separate the anodic and the cathode chamber. Though it is found that membrane-less single-chamber MFC has higher power density but an increase in oxygen and substrate diffusion causes a decrease in columbic efficiency of the MFC [61]. To overcome this spacing between electrodes was considered and the experiments showed higher internal resistance and due to the high rate of substrate diffusion, the cathode electrode faced rapid deactivation [62]. Thus it was sufficient to use membrane as separators in MFC for efficient and sustainable performance. There are basically three main drawbacks which are caused due to usage of membranes, they are: a) Increase in internal resistance b) pH splitting (increase in pH levels in the cathodic chamber and decrease in anodic) c) Increases initial cost [16] [63]. Membrane materials are generally classified as cation exchange membrane (CEM), anion exchange membrane (AEM), bipolar membrane (BPM), ultrafiltration microfiltration, salt bridges, porous fibers and glass fibers.

CEM is the one which is widely used because they can easily transfer protons. CEM such as Nafion, Zirfon, Ultrex CMI 7000 are the most common ones. Out of them, all Nafion is the most widely used because of the negatively charged hydrophilic sulfonate group attached to hydrophobic fluorocarbon. The major drawback of CEM is the pH splitting, high initial cost, and formation of biofilm on CEM are inevitable which limits the use of CEM in MFC in long term operations. AEM is found to have a better proton transfer rate when compared to CEM due to the usage of phosphate or carbonate. Apart from better proton transfer rate, pH is more balanced in MFC with AEM due to phosphate anions [64]. The study showed that AEM performed better when compared to CEM during similar conditions [65]. Usage of phosphate buffer in MFC where AEM is used for better performance makes it costly and not feasible for treating wastewater. Bipolar membranes are the combination of two monopolar membranes, i.e AEM and CEM. The advantages of using bipolar membranes are that it allows the transfer of both protons and hydroxide ions which are formed by water splitting at the membrane interface [66]. Although it allows better transportation of protons and hydroxide ions, the fundamental issue of pH splitting is not solved. BPM's are gaining attention by researchers who are working on Microbial Desalination Cells (MDC's), as it allows ions to transfer easily into the electrode chambers which would be helpful for them as MDC have similar structure like MFC and have high salt content water for treatment [67]. Apart from this much research is going on in order to find membrane materials that are inexpensive and have desired characteristics [68]. Alternatives such as nylon fibers, ceramics, glass fibers, and degradable shopping bags are been used [69][70][71][72][73][74]. Ceramics are being seen as one of the key material to be further used in MFC because of porosity, high strength, and chemical inertness. The first study which used ceramic as PEM was conducted in 2003 which utilized porcelain membrane between graphite electrodes. The research showed that protons were able to pass through the porous membrane and was the starting steps in the usage of ceramic material in MFC [75]. After that much research has been conducted using various materials like earthenware, terracotta and clayware [76].

3.4 Microbes Used

Microorganisms are the heart of MFC as they are the ones responsible for treatment and electricity generation. The first study was conducted by M.C Potter [13] in 1911 showed that microbes like yeast saccharomyces cerevisae and bacteria like E.Coli (Bacillus Coli) provided a voltage which was important in electricity generation. Till now much research has been conducted on MFC but still, there are many limitations which hinder the use of MFC in a commercial way are because of low power density and high initial cost. Thus for maximizing the power output of MFC, much understanding of microorganisms used is to be developed. The crucial breakthrough in the MFC community came when extracellular electron transfer was possible without a mediator. The basic function of bacteria is to colonize on the anode electrode and bio-catalyze the substrates in order to generate electricity [77] [78]. Table 1 shows different microorganisms that were used in MFC by various studies.

3.5 Substrate

Substrate is one of the most crucial members of the MFC, being an electron donor it plays a vital role in establishing electricity generation [79]. A variety of substrates has been used till now in MFC ranging from pure compounds to complex mixtures of organic matter present in wastewater. Most common substrates are acetate [80] & Glucose [81]. Apart from this various substrate used are cellulose particles [82], corn stover biomass [83], ethanol [84], Lactate [85], Landfill leachate [86], phenol [87], Starch [88], Sucrose [89]. Wastewater from different industries was used as a substrate which consisted of complex mixtures. Brewery wastewater [90], Paper recycling wastewater [91], Swine wastewater [92], chocolate industry wastewater [93] and many more were used.

TABLE 1

Different Microorganism used in MFC

Sr. No	Microorganisms	References
1	Geobacter SPP	[114]
2	G. Sulfurreducens	[114][115][116][117]
3	Shewanella oneidensis	[118]
4	Shewanella putrefaciens	[119] [120]
5	Escherichia coli	[121][122][123]
6	Clostridium butyricum	[124]
7	Pseudomonas aeruginosa	[125]

8	Gluconobacter oxydans	[126]
9	Geothrix fermentas	[127]
10	Chlorella vugaris	[128]
11	Dunaliealla tertiolecta	[129]
12	Scenedesmus obliquus	[130]
13	Chlorella pyrenoidosa	[131]
14	Corilous versicolor	[132]
15	Agaricus meleagris	[133]
16	Streptococcus lactis	[134]
17	Erwinia dissolven	[134]
18	Lactobacillus plantarum	[134]
19	Paracoccus denitrificans	[135]
20	Paracoccus pantotrophus	[135]
21	Proteus vulgaris	[136]
22	Proteus mirabilis	[136]

4 DESIGN OF MFC

Keeping in mind the advantages offered by MFC by treating wastewater and generating electricity have attracted many researchers all over the world. But due to complex mechanism and high material cost has been one of the major factors inhibiting its application in real life and not only in the laboratory. Researchers are still trying to develop and optimize the design of MFC in to make MFC an acceptable technology. A typical MFC can be a single or dual chamber consisting of anode and cathode in chambers made of a different material having a membrane or being membrane-less for proton transfer. In this study single chamber, dual chamber, stacked MFC, and Up-flow MFC has been investigated.

4.1 Single Chamber MFC

Single chamber MFC (SC-MFC) is easier in design and cost-effective compared to dual Chamber MFC (DC-MFC). Membrane-less SC-MFC was built by Carlo Santoro et al [94] which studied the effect of Pt-based and Pt-free cathode performance of the current generation having human urine as a source. Batch mode SC-MFC was developed having anode chamber capacity of 130 mL and air cathodes. Carbon brush was used as anode and carbon cloth as a cathode which was coated with microporous layer for better transfer of oxygen. They tested the setup for about 1000 hours and concluded that Pt-free cathode performed almost as Pt-based cathode which makes the system further cost-effective [94]. Figure 2 shows the schematic diagram of single-chamber MFC.

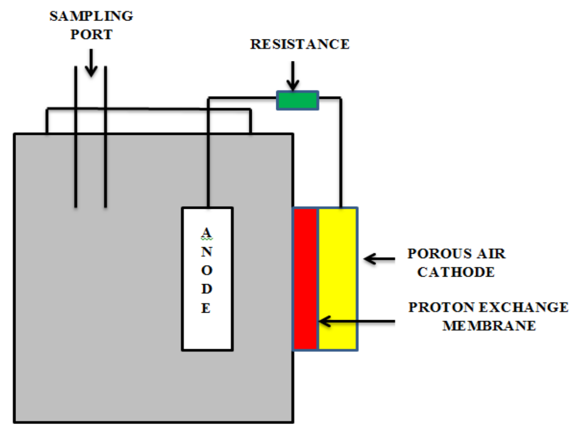

Fig. 2 *Schematic of Single Chamber MFC*

Mohanakrishna et al [95] studied the treatment of petroleum refinery wastewater in SC-MFC. The petroleum refinery waste was collected from the refinery in Doha, Qatar having 2150 mg L^{-1} of COD. Membrane-less SC-MFC made of plexiglass having a working volume of 350 mL were developed. A carbon fiber brush was used as anode and carbon cloth with platinum coating was used as the cathode. Electroactive biofilm generation on the anode was done by inoculation of domestic wastewater (COD: 780 mg L^{-1}) and acetate (3g L^{-1}). The external supply of 500 mV was supplied after 3 cycles of operation. The substrate removal efficiency of 58% was achieved at 500 mV. Similarly, efficiency of 37% and 32% were achieved at 300 mV and 100 mV [95]. Sawasdee et al [96] studied electricity generation and wastewater treatment of tannery waste in SC-MFC. Wastewater was collected from the primary sediment tank in Thailand. The pollution estimated was about 1100 mg L^{-1} of COD and pH was 8.17. Initially, the SC-MFC was injected with 1mL of inoculum with synthetic wastewater (COD: 500 mg L^{-1}) as electron donor at pH 7. The SC-MFC was kept with an open circuit till the power output, % of COD removal and Nitrogen removal were a steady state. After that system was brought to a closed circuit with 1000 and 10 ohm resistors and was fed with tannery wastewater. Pollution decrease up to 88% was observed under optimum conditions [96].

4.2 Dual Chamber MFC

Zhao yu et.al [97] studied electricity generation and simultaneously treatment of sewage wastewater. A DC-MFC was constructed for the operation made out of carbon felt as anode and Platinum net as cathode separated by a Nafion membrane. External resistance of 1000 ohms was provided. Glucose was used as the source simulated like domestic wastewater. Maximum power density of 320.2 mW m^{-2} was observed. They concluded that maximum COD removal was achieved after 6 hours of working of MFC which was 49.2% [97]. Figure 3 shows the schematic diagram of the dual-chamber MFC.

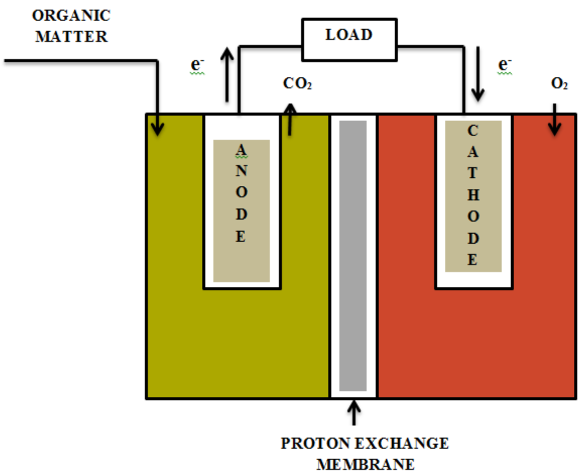

Fig. 3 *Schematic of Dual Chamber MFC*

Chi-Wen Lin et al [98] constructed DC-MFC with both chambers made from serum bottles having a working volume of 0.8 L, separated by Nafion as PEM membrane. External resistance of 1000 ohms was provided. Carbon cloth was used as both anode and cathode. Sludge samples were collected from wastewater treatment plants. Maximum voltage of 110.4 mV was in the absence of the mediators. Whereas the power output grew when the mediators were added but the time taken for degradation was increased to 1.56-2.15 times the former [98]. Sedky H.A Hassan et al [99] constructed DC-MFC for electricity generation from rice straw. The two chambers were constructed by two media bottles separated by Nafion as PEM. Carbon paper was used both as anode and cathode having the cross-section area of 10cm^2. A mixed culture of Cellulose-degrading bacteria was used as inocula in the experiment. Nutrient mineral buffer was used as the medium whereas rice straw (1g/L) was used as a carbon source. Both the chambers were filled with 200 mL of nutrient mineral buffer. Anode chamber was flushed with N_2 gas for 5 min and then sealed. The power density of 145 mW m^{-2} was achieved with a rice straw concentration of 1 g L^{-1} [99].

4.3 Stacked MFC

MFC cannot generate sufficient power output to even run small scale equipment. This is the major reason due to which it has not been implemented yet in use. To eradicate this problem, MFC is stacked together in series or parallel connection for more power output based on the requirement which was studied by Aelterman et al [18]. They also concluded that parallel connection gave better output compared to series connection. S. Mateo et al [100] constructed a module of 112 MFC's which were arranged in 7 stacks, each stack had 16 MFC units. The MFC was constructed from polymeric material of 4mm thickness. The MFC was the type of air-breathing cathode, in which cathode was made of carbon paper of 0.866 cm^2 area, contained 10% Teflon and was modified by 0.5 mg Pt cm^2. The anode was made out of carbon felt having the same cross-section area and both the electrodes were separated by Nafion as PEM [100]. A stack of 7 MFC units was prepared by Li Zhuang et al [101] out of the PVC pipe by separating with clapboards inside the tube. Air cathode made of carbon felt was used and was prepared of the same size as the Cation exchange membrane (CEM) and were placed enveloping around the tube. Graphite felt was used as an anode. Each MFC unit had a working volume of 295 mL. Both parallel and series connection was tested out having an external resistance of 1000 ohms. 83.8% of COD removal was achieved by parallel stack connection whereas series stack connection COD removal rate stood at 77.1% [101].

5 APPLICATION OF MFC

5.1 Treatment of Wastewater and Electricity Production simultaneously

Treatment of Wastewater and having electricity production simultaneously has been the biggest and most researched application of MFC. Ramya Nair et al [102] studied dual-chambered MFC which were constructed by using plastic containers and Carbon rod as anode and cathode. The salt bridge was built for proton transfer by a different percentage of agarose (7-12%) and 4% Potassium chloride. The Anode was inoculated with wastewater collected from the primary clarifier from SRM, University. After taking results for thirty-two consecutive days the found that Salt-Bridge with 10% agarose provided the best result. They achieved a current production of 0.97 mA at 0.95 V after 22 days of operation. They achieved a maximum power of 78.21 W m^{-2}. In terms of Wastewater treatment, they achieved a great reduction in Chemical oxygen demand (COD) of 75.5% by closed reflux titrimetric method and 91.7% in Biological oxygen demand (BOD) by dilution method [102]. J.S. Sudarsan et al [103] also experimented with electricity production of different wastewater at different agarose concentrations (7-12%). They compared results of different wastewater which comprised of Dairy waste, Hostel Sewage Waste and, Sugar waste. They constructed dual-chambered MFC which were constructed by using food plastic containers. Carbon rods of height 9 cm and diameter 0.5 cm were used as anode and cathode. They concluded by the experiment that Hostel Sewage wastewater has the highest production of electricity with 10% agarose concentration over a period of 32 days. They achieved about 0.97mA current at a voltage of 0.95 V after 528 hours of operation. They achieved a reduction of 75.5% in COD and 92% in BOD when compared to the initial waste before inoculation [103]. Surbhajan Sevda et al [104] performed the experiment on High strength wastewater (9978 mg L^{-1} of COD), Half Diluted wastewater (4984 mg L^{-1} of COD) and Centrifuged wastewater (410 mg L^{-1}). They also studied electricity production from the constructed MFC and their feasibility. They constructed three sets of Air-cathode MFCs, which comprised carbon cloth treated with Phosphate Buffer Solution as anode and non-plantnized, Gas diffusion electrodes as a cathode. Both electrodes had an area of 10 cm^2. The MFCs were constructed by plexiglass having a working volume of 25 ml each. Zirfon was used as PEM. They achieved a maximum voltage output of 762 mV and a maximum power density of 382.5 W m^{-2} by High strength wastewater at the 14th day of MFC operation. 59% of the reduction of total COD in high strength wastewater was achieved during the whole experiment. The centrifuged wastewater showed the least power output of 0.12 mW m^{-2}. MFC running on diluted wastewater showed the best reduction in terms of COD at 70% [104]. Much research has been done on electrodes which result in concluding that cathode has a major role to enhance the power output of MFC. M. Radha et al [105] studied the performance of cathode catalysts for electricity generation from wastewater and waste paper. They constructed three dual-chambered MFC having cathode catalyst as Iron phthalocyanine (FePc) with Multi-walled carbon nanotube (MWCNT), FePc with Ketjan Black. The chambers were made of borosilicate having a volume of 250 ml. Carbon cloth was used as anode whereas Graphite was used as cathode having the same cross-sectional area of 3cm*3cm. The two chambers were connected by Nafion as PEM. An external resistor of 66 ohms was connected externally. Anolyte were paper sludge and wastewater, whereas catholyte was phosphate buffer solution with potassium permanganate. The raw paper recycling waste was collected from the paper recycling industry in Tamil Nadu. The experiment showed that cathode catalyst FePc with MWCNT resulted in a maximum power density of 9.34 W m^{-2}. They also concluded that FePc with MWCNT can be an appropriate and more feasible change compared to the Pt metal catalyst used before in MFCs [105].

5.2 Hydrogen Production

Hydrogen has been seen as the future in terms of fuel as it is the most abundant element in the universe comprising 75% of the matter. Though hydrogen is only about 0.07% in the atmosphere and 0.14% in an earth surface, it can be easily produced from other compounds available to us. Hydrogen is produced by many methods but, R. Nandi et al [106] studied various methods of production of hydrogen from microbial activity. They studied in detail about the production from anaerobes (Clostridia, Methylotrophs, Methanogenic Bacteria, Rumen Bacteria & Archaea), Facultative Anaerobes (Escherichia coli & Enterobacter), Aerobes (Alcaligenes & Bacillius), Photosynthetic Bacteria. They concluded that anaerobic bacteria produced optimum H_2 with having a stoichiometric ratio of 1:4 with glucose being substrate, while facultative Anaerobes produced at a ratio of 1:2. The former process being productive is complex than the latter, thus not being feasible at present. Photosynthetic process by cyanobacterium has the potential of being the most productive in terms of all but involves complex mechanism which is yet to be fully developed for making it feasible enough to generate h_2 at big volumes. This study was done in 1998 after which much research has been done in the area of production of h_2 from MFC [106]. Yaseen Nalakath et al [107] studied the hydrogen production from dairy waste at a different iron concentrations as iron effects on the production of hydrogen. They constructed the setup with a 250 ml Erlenmeyer flask. The flask was tightly sealed by two rubber corks, one for the sample collection and other for Hydrogen gas. The gas was collected in an inverted jar and the produced amount was measured. The sample was collected from nearby dairy unit excluding grease or any other material which would hinder the growth of bacteria. The sample was heated for 2 hours at 110 degrees centigrade for removing methanogens and enhancing bacteria for hydrogen production. They mixed wastewater, sludge, and iron in different proportions. They concluded after three days of observation that hydrogen production at 2 g L^{-1} of iron is optimum at 90% sludge and 10% wastewater composition [107]. Jhansi L Varanasi et al [108] studied energy extraction from the cellulosic substrate by thermophilic dark fermentation method for optimum hydrogen production followed by Microbial fuel cell. Two dual-chambered MFC were made out of polyacrylic having a working volume of 110 ml. The chambers were separated by anion exchange membrane having a cross-section of 16 cm^2. Carbon felt was anode and Graphite block as cathode with 50mM potassium ferricyanide as catholyte. An external resistor of 1000 ohm was used to close the circuit. An enriched thermophilic mixed culture was produced in the laboratory for high h_2 production. One of the MFC's anode was inoculated with electroactive consortia (10%) with fresh leachate collected from a thermal power plant. The mixture was enriched in acetate medium. The mixture in MFC 1 was initially operated for 30 days prior to the experiment. Both the MFCs were evaluated in terms of COD, Hydrogen production and power produced. The maximum hydrogen produced was found at 4-5 hours after initial fermentation which was around 22.5 ml h^{-1}. Maximum power density of MFC 1 was found 85.8 mW m^{-2} and 76 mW m^{-2} for MFC 2. Reduction of 75% in COD was observed while overall energy recovery stood at 30.49% [108].

5.3 Desalination

One of the major problems in the present time is the lack of freshwater due to population rise, Industrialization and climate change. The biggest source of water which is seawater (97%) cannot be used for drinking due to the high concentration of salt. Microbial Desalination Cell (MDC) can be a major breakthrough in this field by converting this seawater into drinkable water by lowering the salt concentration. MFC can be modified to make MDC. MDC can be made by adding one more chamber between anodic and cathodic by pair of membranes, Anion exchange membrane (AEM) and cation exchange membrane (CEM) [109]. A Schematic diagram of MDC is shown in figure 4. Sevda et al [110] experiment with petroleum refinery waste to generate electricity and used that electricity for the desalination of saltwater. One dual-chamber Osmotic Microbial fuel cell was built and one dual chamber Up Flow Microbial Desalination cell (UMDC) was built. The chamber was built of plexiglass a having working volume of 1000ml in Osmotic MFC the cathodic and anodic chamber was separated by a forward osmosis membrane. In UMDC the middle chamber was separated by AEM and CEM respectively. Carbon cloth was used as a cathode whereas carbon brush with titanium wire was used as an anode. Both the cells were coupled to form a single system. Both the cell was connected to an external resistor of 100 ohms. By the experiment, they observed that there is 93% reduction in COD from petroleum refinery wastewater whereas 48% of the salt was removed from the saltwater [110]. VRV Ashwaniy et al [111] also studied the reduction of petrochemical industry and desalination by MDC. Three chamber MDC were built with acrylic sheets. Working volumes of the cathodic and anodic chamber was 500 ml whereas desalination chamber had 250ml. Graphite rods of surface area 127 cm^2 was used as anode and cathode. The chambers were separated by AEM and CEM. External resistor of 1000 Ohms was attached to the circuit. Three setups were prepared with different cathodes. One consisted of the chemical cathode with a saline concentration of 35 g NaCl L^{-1} and the other two with microalagae biocathode on the different saline concentration of 35 g NaCl L^{-1} and 20 g NaCl L^{-1}. The anodic chamber was filled with Petroleum wastewater collected from the industry in Chennai. The test was conducted for 32 days. They concluded that microagale biocathode MDC (35 g NaCl L^{-1}) performed better in terms of COD removal efficiency 55.3% and the maximum voltage produced 654 mV [111].

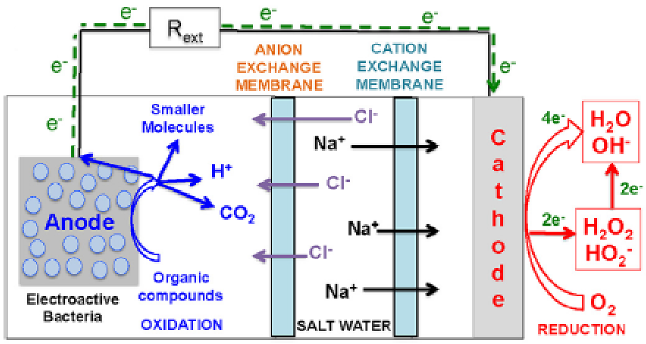

__Fig. 4__ Microbial Desalination Cell [26]

5.4 Biosensors

MFC has one more major application as biosensor as it can do on-line monitoring of BOD in organic content and control of biological wastewater treatment process as present methods lack that quality. Coulombic yield of MFC gives very much idea of BOD of the liquid stream of wastewater which can be utilized as biosensor [112]. Sumaraj et al [113] studied the performance of MFC as biosensors by studying the detection of organic matter of wastewater. They created two MFC comprising of two different Proton exchange membrane, MFC1 comprised of Nafion and MFC2 comprised of low-cost clayware and studied the effect of them on the performance of MFC as a biosensor. The evaluated that MFC1 has low response time and better performance to detect low COD concentration from 22 mg L^{-1} to 51 mg L^{-1}. Whereas MFC2 can only sense concentration as high has 67 mg L^{-1} to 212 mg L^{-1}. The response time was also varied in both the MFC's. MFC 1 responded quickly with sensing time of 210 min and 120 min, While MFC2 sensed the concentration at 310 min and 120 min. They proposed that variation in results by both MFC is because of the PEM used. The variation is caused by proton conductivity (PC) and thickness of the membranes. Nafion has PC 40 times more than Clayware (CWPEM), while CWPEM is 17 times thicker than NPEM. They concluded that low cost clayware PEM can be used in MFC for monitoring the BOD keeping in mind the economics of the device. Nafion has better performance but the cost is about 400 cm^{-2} compared to 0.4 cm^{-2} of clayware [113].

6 CONCLUSION AND FUTURE ASPECTS

The world facing problems like global warming and climate change, using of carbon-based fuels has to go down and we have to make way for the usage of more and more renewable sources for energy generation. Thus MFC has great potential in the future for not only energy generation but has many different applications. MFC not only generates electricity but the source for energy generation is waste, which makes it more special compared to the traditional energy sources. This paper shows that MFC has many applications apart from electricity generation and wastewater treatment like desalination and hydrogen production. The complexities of MFC and high-cost of electrodes and PEM make it tough and not feasible enough to utilize it on a commercial basis. The major area of research in MFC which would make it feasible is the cost aspect of the electrodes and the PEM. The usage of ceramic material has shown great hope being used as electrode and PEM. Another area is the use of biofilms on electrodes which are used over electrodes has to be eradicated by using microbes like anodophilic for better output. The intensive ongoing research has turned the tide and has led to better power outputs and different applications like desalination and hydrogen production. Furthermore research is required in understanding the concepts better and optimize them to the fullest as MFC has many disciplines that work together. Seeing the potential of MFC, It can have a major impact on a country like India for providing green and clean energy.

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