



HARNESSING BIO-ELECTRICITY FROM WASTE WATER: MICROBIAL FUEL CELL

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ABSTRACT

The microbial fuel cell (MFC) has garnered significant interest in both basic and applied research due to its sustainable and renewable nature in the contemporary energy scenario and is all set to be the trendsetter in the arena of answers to the complex environmental pollution problems and the energy crisis, with a unified approach. The MFC is essentially a hybrid bio-electrochemical system which directly transforms chemical energy stored in the biodegradable substrate to electrical energy via microbial catalysed redox reactions involving microorganisms as biocatalysts under ambient temperature/pressure. The bio catalytic activity of the microorganisms present in the anode chamber generates the reducing equivalents [protons (H^+) and electrons (e^-)] through a series of bio electrochemical redox reactions during substrate degradation in absence of oxygen. These protons and electrons are the source of electricity generation in MFC. The electrochemically active nature of a microorganism supports the effective pumping of redox powers. The MFC has multiple applications based on the utilization of reducing equivalents with different nomenclature. Reducing equivalents facilitate hydrogen production in microbial electrolysis cell (MEC), by-product recovery either from anode or cathode chambers in bio electrochemical system (BES) and enhanced pollutant removal using bio-electrochemical treatment system (BET).

Keywords : Redox Reaction , Catalyst ,Electrolysis etc.

I. INTRODUCTION

PRINCIPLE BEHIND MFC OPERATION

The MFC functions on the basis of anodic oxidation and cathodic reduction reactions. The anode chamber is a bio factory which facilitates the generation of protons and electrons and plays a crucial role between physical and biological components. Protons reach the cathode through the proton exchange membrane (PEM) resulting in a potential difference against which the electrons flow through the circuit (current) towards counter electrode (cathode) and get reduced in presence of oxygen forming water.

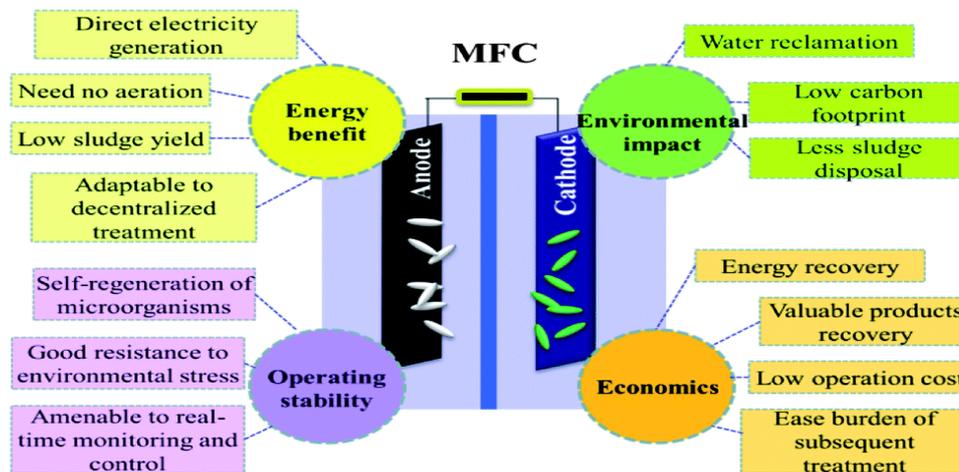
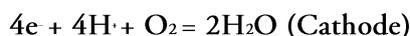


Fig.1 Concept of Microbial Fuel Cell

(Overall) Electrons in the cascade of respiratory chain, transfers between the proteins through redox reactions based on the oxidation reduction potentials of the proteins. The proton flowing across inner and outer membranes based on the redox potentials of cascade, generates a proton motive force and it mobilizes the electrons towards inter membranous space. Since electrons must transfer from a more negative potential to a less negative potential, the extra cellular electron transfer rate is influenced by the potential difference between the final electron carrier and the anode. Activity of anodic bacteria is essential to liberate electrons from the oxidation of organic matter and to transfer them to the electron acceptor. Electrons will be driven to the anode by a potential difference between the terminal intracellular electron acceptor and the anode either by direct electron transfer (DET) or mediated electron transfer (MET). Membrane-bound proteins or conductive bio film (nano wires) facilitate DET while MET occurs through soluble shuttling compounds. Microorganisms use more than one electron transfer mechanism to transfer electrons to the anode. The DET is considered to be a comparatively, more effective mechanism than the MET where the electron losses can be minimized prior to reaching the anode surface. Microorganisms are able to form a bio film on anodes, which plays a crucial role in DET. The nature and group of consortia in the bio film specifically regulates the electron discharge onto anode. Surface positive charge of anode gets increased due to the developed in situ bio-potential which enables the adhesion of negatively charged bacteria. Interaction among the microorganisms also facilitates efficient electron transfer. The MFC systems are designed with dual and single chamber configurations. The double chamber configuration has separate anode and cathode compartment connected through a PEM. The substrate gets oxidized in the anode chamber while reduction occurs in the cathode chamber. Catholytes such as potassium ferricyanide, potassium permanganate, aerated catholytes, etc. were used with variable degree of efficiency. The single chamber MFC configuration consists of the anode chamber only, while cathode is placed in such a way that it is exposed to air (open air cathode). Few other configurations viz., flat plate, tubular, cubical, stack, etc. have also been used for MFC operation. The solid phase microbial fuel cell (SMFC) was designed by Council for Scientific and Industrial Research- Indian Institute of Chemical Technology (CSIR-IICT) to evaluate the

potential canteen based food waste as substrate for bioelectricity generation. A photo-bio electro catalytic/ photo-biological fuel cell (PhFC) was designed by CSIR-IICT to evaluate bioelectricity generation using photosynthetic consortia as the biocatalyst in the mixotrophic mode. Syntrophic association of photosynthetic bacteria and algae showed feasibility of power generation under anoxygenic micro environment by the Ph FC. Benthic/sediment type fuel cell application for bioelectricity generation was evaluated in different types of water bodies. Nature, flow conditions and characteristics of water bodies influence the power generation apart from electrode assemblies, surface area of anode and anodic material. The CSIR-IICT evaluated designed miniaturized floating macrophyte based ecosystem with Eichornia as the major biota for bioelectricity generation from waste water treatment employing three fuel cell assemblies (similar to benthic fuel cell). Based on the observations made from various lab scale optimization studies, the CSIR-IICT developed a semi-pilot scale hybrid bio-electrochemical system with 100 litres capacity using multiple electrode assemblies connected in series (36 chambers) . The semi-pilot scale MFC without membrane was evaluated for one year using domestic sewage operated under anoxic conditions.

II. WASTE WATER V/s BIO-ELECTRICITY

The concept of the MFC is well established in the direction of utilizing wastewater as an anodic fuel making it a sustainable technology for energy generation as well as waste management. Reducing the cost of wastewater treatment and finding ways to produce useful byproducts has been gaining importance in view of environmental sustainability. The organic matter present in wastewater serves as primary substrate for the fermentation process facilitating treatment of wastewater with simultaneous generation of bioelectricity. Theoretically, one kg of chemical oxygen demand (COD)removed can produce 170 W of power. According to an estimate, about 300 million tons of wastewater is generated annually in India by dairy industries which can generate bioelectricity using the MFC method (calculated assuming 40 per cent energy conversion efficiency; 14.7 KJ/g-COD) accounting for a revenue of Rs 12 billion per annum (at a rate of Rs 4 per kWh) along with its treatment. Domestic sewage generated in urban and rural areas of India was estimated to be around 1,42,405 million litre/day (MLD) which could generate about 300 MW/h power accounting for a cost of about Rs 108 billion per annum apart from treatment. This gives a clear estimate about the inherent power present in wastewater that can be harnessed for bio-energy. Wastewater from food waste, electroplating, starch processing, breweries, paper industry, palm oil mill, chocolate industry, domestic sewage, cellulosic waste, vegetable waste, composite chemical wastewater, pharmaceutical wastewater, swine waste, etc. were evaluated at a laboratory scale .

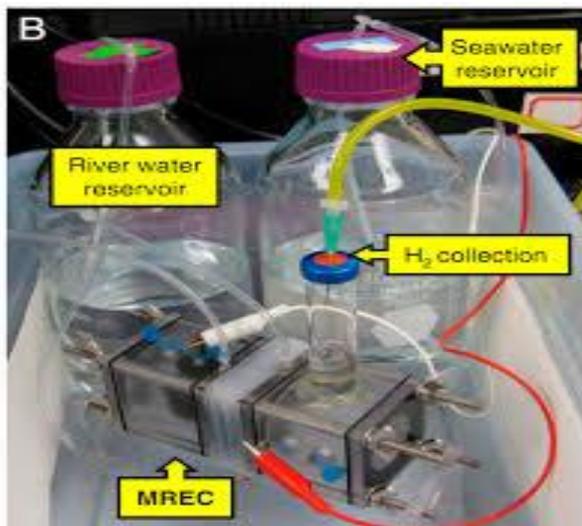


Fig.2 Photo.Showing dual chamber MFC With Ferricyanide cathode (R).

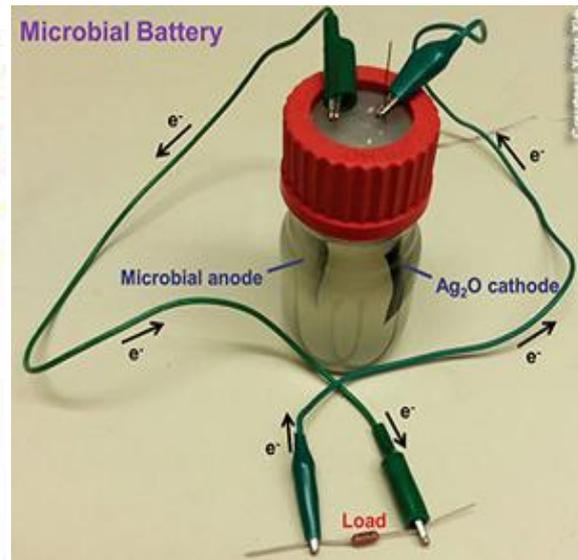


Fig.3 Utilization of Power from Microbial Fuel Cell (L).

III. "MFC" AS TREATMENT UNIT

The MFC can also be termed as a bio-electrochemical treatment (BET) system. The principle of BET relies on the fact that electrochemically active microorganisms can transfer electrons from a reduced electron donor to an electrode and finally to an oxidized electron acceptor generating power. During a BET operation, there exists a possibility to integrate diverse components viz., biological, physical and chemical in the anodic chamber and provides an opportunity to trigger multiple reactions viz., bio-chemical, physical, physicochemical, electrochemical, oxidation, etc., as a result of substrate metabolic activity and subsequent secondary reactions. The anode chamber of the BET resembles the conventional anaerobic bioreactor and mimics the function of a conventional electrochemical cell used for wastewater treatment where the redox reactions help for the degradation of organic matter and toxic/xenobiotic pollutants. Anodic oxidation and cathodic reduction reactions will have a positive influence on the pollutant removal in the BET system. The in situ bio-potential generated during the process helps in the enhanced degradation of different pollutants in both the anode and cathode chambers. Direct anodic oxidation (DAO) and indirect anodic oxidation (IAO) facilitate the effective removal of pollutants. The DAO facilitates the degradation of pollutants absorbed on the anode surface by anodic electron transfer reactions. The oxidants formed electrochemically on the anode surface in turn oxidize the organic matter by IAO. The DAO of the substrate facilitates the formation of primary oxidants which could further react on the anode, yielding secondary oxidants such as chlorine dioxide and ozone, which might have a positive effect on the color removal efficiency through the oxidation process. This process helps to oxidize the organic matter by the liberated oxidation species which might enhance the substrate removal. Reactions between water and radicals near the anode could yield molecular oxygen, free chlorine, hydrogen peroxide, hypochloric acid, etc. which also helps in color/organic oxidation. Pollutants in the anodic chamber also act as



mediators for the electron transfer to anode which can increase the power generation efficiency with simultaneous reduction of pollutants. Various pollutants such as dyes, organic pollutants, solvents, inorganic salts, complex wastewater, colored substances, synthetic estrogens, PAHs, etc. are reported to be treated in these systems. Application of bio cathode also helps in enhancing wastewater treatment efficiency especially in the removal of specific pollutants. Bio cathodes reportedly reduced pollutants such as nitrates or sulfates or chloro-organics in the cathode compartment.

IV. FACTORS INFLUENCING BIOELECTRICITY GENERATION

Electrical energy can be obtained from fuel cell operation only when a reasonable current is drawn, but the actual cell potential is decreased from its equilibrium potential because of irreversible losses present in the fuel cell. Electron transfer from the biocatalyst to the anode and then to the cathode is generally hampered by different losses which lower the conversion efficiency. There exists a close similarity between bio-electrochemical and biochemical reactions wherein both encounter an activation barrier that must be overcome by the reacting species or biocatalyst. The power generation capacity of the MFC depends on the catabolic activity of the anodic biocatalyst and its electron transfer efficacy to the anode. However, the transfer of electrons between the biocatalyst and the anode is low because of the sluggish kinetics which subsequently results in a low power yield. The electron transfer resistances in the MFC arise due to factors such as the reactor configuration, materials used, nature of anolyte and metabolic activities of the biocatalyst, which tend to decrease the MFC performance pertaining to power generation as well as substrate degradation. The power output of the MFC can be improved by enhancing the electron transfer efficiency between the biocatalyst and the anode. Most of the earlier studies with the MFC were reported with pure culture as biocatalyst with simple defined substrates. However, usage of mixed culture instead of single strains is always a better option in the MFC operation because of ease in maintenance and their survivability even in wastewater. Selective enrichment of the mixed culture with an electrochemically active bacterial population will have more benefits. Poising mild potentials during reactor start up, growth under restricted electron mediating conditions, bio-augmentation of electrochemically active strains, etc., are few strategies developed for the selective enrichment of biocatalysts. The nature of the anode will also have significant influence on the substrate conversion efficiency and the synergistic interaction between anode and biocatalyst is crucial for efficient extracellular electron transfer. High electrical conductivity (low electrical resistance), inert nature (non-oxidation/non self-destructive nature), sustainability of properties with time, etc. are some of the important properties of the anode which can influence the performance of the MFC. More often, graphite is used as a bio anode material for fuel cell applications in both catalyzed and non-catalyzed forms. Few other materials viz., platinum, stainless steel, nickel, etc., were also used as anode apart from carbon based materials. Extracellular electron transfer will be high under acidophilic pH compared to neutral and basic pH due to the higher activity of intracellular electron carriers which helps in translocation of electrons from bacteria to the extracellular environment. On the contrary, wastewater treatment was reported to be higher under neutral pH. Ion exchange membrane between anode and cathode for the development of a gradient is also an important factor that influences the MFC performance.

Usually, the anode chamber of MFC will be operational in an anaerobic microenvironment. However, very few studies have reported that, aerobic microenvironment under low DO – dissolved oxygen (anoxic) conditions and high substrate concentration will have a potential to generate power. Cathodic reduction of reducing equivalents is crucial along with the anodic oxidation for power output in the MFC system. Reduction reaction at the cathode indirectly influences the substrate oxidation in the anode as well as it can help to overcome the electron losses. Microorganisms can also be used as a catalyst in the cathode chamber for improved cathodic reduction reaction where biocatalysts retrieve electrons directly from the cathode which are then transferred to a final electron acceptor such as oxygen, nitrogen, sulfur, etc. The electron transfer in the MFC can also be increased by using different types of artificial and natural mediators. Genetic modification of specific genes in the biocatalyst related to the proteins that function for the exocellular electron transfer, was also reported by a few researchers. The operation of the MFC under the optimized conditions with selectively enriched mixed culture as catalyst and wastewater as substrate will have a commercial viability in the near future.



Fig.4 Semi-pilot scale MFC (without membrane) with 100 litres capacity was designed with 36 chambers and evaluated for more than one year using domestic sewage (R).

V. FUTURE SCOPE

The MFC is poised to change the visage of the energy scenario and wastewater treatment processes in the near future. However this requires extensive research with respect to appropriate design of fuel cell, effective reactor configuration, low cost components of fuel cell, reduction in electron loss, etc. Interaction between the anode and the biocatalyst needs to be understood and optimized to fully exploit the capacities of these systems. At present, apart from power generation, the MFC application has been extended towards waste remediation, specific pollutants removal and recovery of value added products. Bio-electrochemical treatment is gaining prominence which will facilitate enhanced treatment efficiency with simultaneous energy generation. Based on the oxidation reduction reactions occurring in the MFC, various complex pollutants can be removed by increasing the power generation potential, especially in the cathode chamber. The other face of the MFC is recovering value added products from the carbon source present in waste through bio-electrochemical process and the conversion of wastewater components or CO₂ into valuable products under mild applied potential. This is based on the reduction mechanism at cathode and by reducing the activation energy required for the



conversion of waste carbon to valuable product through applied potential associated with the in situ bio potential. Bio catalyzed electrolysis is a novel H₂ production process with a potential of converting dissolved organic substances in wastewater, in the absence of electron acceptor under small external voltage (>0.2 V in practice). Other value added products viz., ethanol, butane 1, etc., can also be recovered at cathode of bio electrochemical systems but these studies are at an early stage and needs optimization of process parameters. The applications of the MFC are at present in the developing stage, but it will make every effort to meet the energy needs of society by utilizing waste carbon resources in the near future.

VI. CONCLUSION

The achievable power output from MFCs has increased remarkably over the last decade, which was obtained by altering their designs, such as optimization of the MFC configurations, their physical and chemical operating conditions, and their choice of biocatalyst. MFCs are capable of converting biomass at temperatures below 20 °C and with low substrate concentrations, both of which are problematic for methanogenic digesters. A major disadvantage of MFCs is their reliance on bio films for mediator-less electron transport, while anaerobic digesters such as up-flow anaerobic sludge blanket reactors eliminate this need by efficiently reusing the microbial consortium without cell immobilization. Another limitation is the inherent naturally low catalytic rate of the microbes. Although some basic knowledge has been gained in MFC research, there is still a lot to be learned in the scale up of MFC for large-scale applications. However, the recent advances might shorten the time required for their large-scale applications for both energy harvests.

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