Waste treatment and Sustainable Bioelectricity Generation using Microbial fuel cell

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DOI: https://doi.org/10.34024/jsse.2023.v1.15460

***Abstract*—In the last decade, great attentions have been paid to microbial fuel cells (MFC) due to the possibility to be the solution for the three bigger world project – energy security, climate changes and waste management. Different from all the conventional wastewater treatment which are energy intensive, MFC can use waste as substrate/fuel to directly generate electricity through microbial reactions in anode and microbial/enzymatic/abiotic electrochemical reactions in cathode. In this sense, the MFC is an emerging technology for treat waste and produce wealth products (energy and some added value substance – organic acids, nutrients). Although, there are a large number of research in new materials and operational conditional to improve the MFC performance, as yet there are practical barriers, such as low power generation, expensive electrode materials and the inability to scale up MFC. Therefore, this work summarizes information about the recent advances in MFC research, focused on MFC configurations, material electrodes, and performances. Limitations and challenges in applying MFC to treat waste are also discussed, moreover future perspective pointed the new hot topics to solve these problems.**

***Keywords*— Microbial fuel cells; Bioelectrochemistry, Microbial electron transfer, Wastewater treatment, renewable energy.**

I. Introduction

In 1911, Michael C. Potter firstly reported the idea of energy from molecules' catabolism could be used to produce electricity, however it was a few decades later that microbial fuel cells (MFC) have been intensively studied [1]. A lot of progress has been made since then, in terms of microbial, biochemical and electrochemical reactions, in relation to the operating factors conditions. Among other potential technologies being intensively studied for bioenergy production, MFC have been proposed for many applications, ranging from wastewater simultaneous carbon and nitrogen treatment, synthesis of aggregated value products, as well to energy generation to remote low power charging devices, such as environmental and monitoring sensors and robots [2], [3].

The actual major challenge, in terms of sustainability, is to unify new renewable alternatives for power generation and to maintain environmental quality. In that way, scaling up MFC for simultaneous sanitation and energy generation are indispensable, in order that wastewater treatment facilities can no longer only be designed for environmental standard attendance. The wastewater treatment requires about 0.5 to 2 kWh / m^3 containing about 3 to 10 times the energy required to treat it [4].

This paper intends to present an overview about microbial fuel cells as a potential energy source and waste treatment technology. In the following sections, it is presented the mechanism involved in the MFC functioning, affecting factors, potential and current applications, and future perspectives.

II. Microbial Fuel Cells

Microbial fuel cells (MFC) are commonly defined as a device using microorganisms as biocatalysts to convert stocked energy, in organic and inorganic compounds, into electrical current, i.e., MFC is a bioelectrochemical system that converts chemical energy to electricity, from an inactive substrate, through catalytic reactions of microorganisms [5]–[7]. Considering this common definition, the term biocatalyst has been used mistakenly. Microorganisms in MFC cannot be considered catalyst, because they retain part of the free Gibbs energy in the reaction for its metabolic success, as well they determine the reaction balance [8].

There are several MFC configurations that dependent on field applications. The dual chamber MFC is the most common one. The biocatalyst facilitates the organic fuel oxidation in the anodic compartment, as can be seen in (1), where the released electrons are transferred to anode through different mechanisms. An external circuit conducts the absorbed electrons in the anode to the cathode. Also, a selective membrane allows protons to be transferred to the cathode, in order to reduce the oxidizing agent. Generally, oxygen is the oxidizing agent that reacts with electrons and protons where, in the cathode, water is produced on the electrode surface, as can seen in (2) [7], [9].

Glucose oxidation (Anode reaction):

$$C_6H_{12}O_6 + 6\ H_2O \rightarrow 6\ CO_2 + 24\ H^+ + 24\ e^- \quad (1)$$

Oxygen reduction (Cathode reaction):

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

Global reaction of MFC:

$C_6H_{12}O_6 + 6\ H_2O + 6\ O_2 \rightarrow 6\ CO_2 + 12\ H_2O$ (3)

In that way, MFC can be compared to the functioning of galvanic cells, in which the electrons flows occur, from the lowest oxidizing potential electrode (anode) to the highest one (cathode). In addition, they are respectively referred as the negative and positive pole [5].

III. CONVERSION OF ORGANIC WASTE TO BIOENERGY

A. METABOLIC PATHWAYS FOR ORGANIC MATTER CONVERSION INTO ELECTRICAL ENERGY

There are several factors affecting the anodic performance, where the most expressive ones are: (i) the nature and the rate of the anaerobic metabolism, as well (ii) the nature and the rate of electron transfer, from the microbial cell to the anode. In the anode, three major pathways may occur to catabolize the substrate: respiratory chain, anaerobic respiration and fermentation. They depend on the type and availability of exogenous oxidants, i.g., oxygen, nitrate, sulphate, and organic compounds, respectively. Comparing aerobic respiration and anaerobic digestion, in terms of free Gibbs energy, respiratory chain is the path with the highest energy gain, and, therefore, high electricity production, as can be seen in (4). On the other hand, fermentation is the path with the lowest energy gain for the organisms, example in (5) and (6), but its fermentation products have high aggregated value [8], [10]. Despite the highest energy gain, aerobic respiration is limited to oxygen availability and microbial organisms capable of complex organic catabolism [8]. Taking into account anaerobic digestion, the electrons from the oxidized substrate may be used to reduce other molecules, producing methane and hydrogen. When this process is performed, the total energy production for electricity is reduced [5], [9].

$C_6H_{12}O_6 + 6\ O_2 \rightarrow 6\ H_2O + 6\ CO_2\ \Delta G°=-2895\ kj/mol$ (4)

$C_6H_{12}O_6 \rightarrow C_4H_8O_2 + 2\ CO_2 + 2\ H_2\ \Delta G°=-225\ kj/mol$ (5)

$C_6H_{12}O_6 + 2\ H_2O \rightarrow 2\ C_2H_4O_2 + 2CO_2 + 4\ H_2\ \Delta G°=-206\ kj/mol$ (6)

The main metabolic pathways in MFC are the complete and incomplete oxidation for organic substrate and the hydrogen oxidation. As polymers undergo to hydrolysis, simple compounds such as sugars, amino acids, peptides and organic acids start to be formed. When complete oxidation occurs, these compounds are converted to carbon dioxide and the electrons are used to reduce the anode. Recent findings stated that the genre Rhodoferax can perform the complete oxidation [5].

Other organisms can perform the incomplete oxidation producing organic acids such acetylic, butyric, lactic, propionic acids and ethanol. The known classes for performing this metabolic pathway, in mesophilic condition, are Gammaproteobacteria, Betaproteobacteria, Alphaproteobacteria and Clostridia [6], [11]. Similarly, but in thermophilic condition, the genres Bacillus and Therminocola perform this metabolic route to reduce the anode [12], [13].

After hydrolysis converting the complex organic matter into simple one, fermentation may occur and produce high aggregated valued products as acetate and butyrate. Moreover, short-chain organic acids and hydrogen may also be formed. The microorganisms responsible for this metabolic pathway belong to genre Clostridium, Alcaligenes and Enterococcus. Also, bacteria of Geobacteraceae class can remove the electrons from acetate and reduce the anode [5]. In relation to hydrogenotrophic bacteria, they oxide hydrogen completely in the hydrolysis and fermentation step, then electrons are used to reduce the final electron acceptor in MFC, the anode electrode [5], [11].

The anode potential determines the final electron acceptor potential, and therefore, the microbial metabolism. In this context, changes in redox potentials define microbial metabolism. In MFC, methanogenic arches and sulphate ion reducing-bacteria will compete against anode-reducing bacteria for electrons' donors. For high redox potential in the anode, when oxygen is present, respiratory chain can be used by bacteria to complete oxidation of organic matter. On the other hand, if the redox potential is decreased, fermentation and anaerobic digestion will take place in the process. Also, whether alternative electrons acceptors are available, such as sulphate and nitrate, microorganisms will perform the incomplete oxidation of organic matter. The released electrons will reduce the mediators, such as, sulphate and nitrate, and the organic compounds present in the media will be the electrons acceptors competing with anode's electrode. Therefore, it results in low efficiency for electrical current production [5]. In the sulphidogenic, hydrogen and innumerable amount of organic compounds as formate, ethanol, methanol, acetate, pyruvate, propionate, butyrate, aromatic compounds, and branched and long-chain organic acids can be oxidized by sulphate ion reducing- bacteria to reduce sulphate (SO_4^{2-}) to sulphide (S^{2-}) [9], [10].

B. MECHANISMS OF MICROBIAL FUEL CELLS FUNCTIONING: ELECTRONS TRANSFER TO ELECTRODE

In order to occur electron transfer to a solid electrode, it has been discussed in the literature different approaches in which involve linking species to facilitate the electron transfer from the microbial cell to the anode's electrode. In this sense, the electron transfer outside of the cell must lead to a redox active species that is capable of electronically linking the bacterial cell to the electrode. These redox active linking species may be referred as diffusional redox shuttles, outer membrane redox protein or a primary metabolite. Reference [8] gives a complete discussion about the mechanism of MFC functioning, and also, states some requirements for an efficient linking specie, i.g., (i) ability to physical interaction between the inner of cell (cytoplasm) to the outer of cellular membrane (electrode), (ii) it must possess a low oxidation overpotential at given electrode surfaces, and (iii) it should be as close to the redox potential of the primary substrate as possible.

According to References [8], [10] the mechanisms of electrons transfer to anode's electrode can be categorized into two groups: the one in which the electrons transfer is direct (DET), and the other one in which redox mediators are dissolved in the media or adhered in the anode's electrode (MET).

In the first category, physical contact between microbial cellular or organelles membrane and the electrode are needed in order electrons transfer to occur. In this context, macromolecules as cytochrome c - type present in the cellular membrane can mediate the electron transfer to a solid final electrons' acceptor. In MFC, anode's electrode is the final one. The microorganisms associated to this direct process belong to the Geobacter, Rhodoferax and Shewanellagenres [8], [10].

Although the direct contact between macromolecules and electrode does not need mediators, the contact zone becomes limited to the firsts 50 μm of electrodes' biofilm, thus it is limited to certain bacterial density. In this case, lower efficiency may be expected for such configuration. Countering this limitation, a recent finding of an electronically conductor named as microbial nanowires (pili) produced by the Geobacter and Shewanella strains, allow contact to the anode's electrode to be more distant, and therefore, more numerous and effective [8].

MET systems come exactly to overcome the problematic of non-homogenous oxygen gradient in the biofilm layer, and also cells struggling to directly contact the solid acceptor. In the MET mechanism, the connection between microbial metabolism and anode's electrode must be mediated by pairs of redox species added externally or produced by microorganism's metabolism. The adding of exogenous mediators is not a promissory alternative for macroscale dimension, however the endogenous redox mediators are of great interest for excluding the needing of the exogenous ones. They differ in relation to their origin and relevance to the metabolism they came from. In this case, they can be referred as primary or secondary metabolites. The first ones are essentially connected to microbial metabolism such as fermentation and catabolic substrate degradation products. In contrast, the second ones are not essentially connected to microbial main metabolic pathway; in fact, other organisms produce these secondaries metabolites in which aim to specific purpose such intercellular communication or antibiotics, e.g., bacterial phenazines (pyocyanine) and 2-amino-3-carboxy-1,4-naphthoquinone, ACNQ [9], [10], [14].

In order to use primary metabolites as electrons transfer or oxidizing agent for anode's reduction, it is necessary that the redox potential of primary metabolite to be more negative as possible, but not more negative than substrate redox potential, e.g., sulphate reduction and sulfide oxidation in anode's electrode, iron (II) oxidation to iron (III) in presence of humic substances and formate, ethanol and hydrogen oxidation in anode as well. Some precautions must be aware when working with anaerobic respiration in relation to Fe^{3+} / Fe^{2+} as the linking species. Because the redox potential of Fe^{3+} / Fe^{2+} is too positive they must be complexed with humic acids in order to make it more negative [8], [10].

On the other hand, MET via secondary metabolites are referred as such effective via because endogenous redox mediators work as a reversible shuttle cycle. As it takes electrons from the cell, it reduces itself; then, the reduced mediator will carry those electrons to anode's electrode surface reducing it. After this step, the mediator will become oxidized and available for new cycles increasing the electron rate transfer. Operating in discontinuous mode (batch) is more interesting because mediators can be dragged by the flow in the continuous one [8], [10], [14].

IV. MICROBIAL FUEL CELLS CONFIGURATIONS

Different microbial fuel cells (MFC) configurations are possible and have been studied for many applications, e.g., air–cathode MFCs, aqueous cathodes using dissolved oxygen, single, double or triple-chamber reactors, tubular packed bed reactors and biocathodes.

In MFC of dual chamber with ions selective membrane, there are two chambers, each one for anodic and cathodic electrodes, a selective membrane of ions that allows only protons to flow to the cathode, blocking oxygen diffusion to the anode [9], [14]. However, the configuration is only viable for laboratory studies due to the operational cost of membrane and of aeration in the cathode. The bottlenecks when using selective membranes are the operational cost with manutention due to clogging of suspended solids as well expensive material [15]–[17]. Another adverse effect of using selective membrane is the increasing in resistance of electrode in which decreases the electrical energy generated [6], [16].

In MFC of single chamber with ion selective membrane, the operational costs are reduced and its configuration is simpler compared to the previous one. There is only a single compartment for anodic electrode while the cathodic one is exposed directly to the atmosphere. The oxygen will be the final acceptor reducing itself to water. The protons will be transferred through cathode's pores and there is no water loss because of hydrophobic material utilized [9], [14].

Recently, it has been discussed the advantages and disadvantages of also using biocathode compared to the most of the previous works performed in biofilm- free cathode. In this context, several researches have been argued the enhancement of MFC performance for power generation, and also simultaneous treatment of organic carbon and nitrogen can be reached using biofilm- covered cathode [2], [5], [10], [14]. Pointing this ambit out, inorganic acids as electrons acceptor has taken place. Under anaerobic or low oxygen concentration, denitrifying bacteria are capable of utilizing electrons from cathode's electrode to reduce nitrate or nitrite to nitrogen gas [18]. In regard to microbial community, Alphaproteobacteria, Betaproteobacteria, Gammaproteobacteria and Flavobacteria were observed in biological electrode [19]–[21]

The major advantaged of biocathode are the lower construction and operation cost because it does not require a metal catalyst such precious metal Platinum-types or artificial electron mediator. Compared to the abiotic ones, the metallic catalysts need to be replaced continuously. On the other hand, biological ones function as catalysts and as they age, the microbial metabolism is lowered and replaced naturally by the newer ones. This excludes the necessity of replenishment [18].

Despite of the benefits presented above, there are some bottlenecks to overcome when referring to biofilm-covered cathode. The first one is the operating parameters. The pH fluctuation is continuously reported in literature due to protons consumption of reduction reactions in the cathode and proton production in anode. When talking about simultaneous nitrification and denitrification in the same compartment, one process produces protons and the another consumes it which could give some stability depending on the configuration. According to Reference [20] operating an electroactive biofilm single reactor concluded that alkalinity produced in the nitrite reduction neutralized the acidity in the anode by 19 % what could favor anodic and cathodic reactions. Another operational parameter regards to carbon and nitrogen ratio, it is strictly related to nitrification, denitrification efficiency [22], thus stablishing an agreement and controlling such ratio in wastewater substrate is important. The same for establishing an optimal dissolved oxygen (DO) parameter because a low DO value drives ammonia accumulation, while a high DO one inhibits denitrification, resulting in nitrate accumulation [22].

The second bottleneck of biocathode relates to material. Despite in the literature bringing a list of potentials biofilm- free cathode materials, there is no agreement in establishing a suitable one for biocathode that requires high surface area and low resistance. And the last one is to increase power output for pilot-scale due to the poor efficiency of electron transfer [10], [18].

V. OPERATING CONDITIONS

The performance of the Microbial Fuel Cells can be influenced by the improvement of certain operating conditions such as: temperature, hydraulic retention time and electrode material.

A. TEMPERATURE

Regarding temperature, it can be said that changes in temperature can change kinetics, mass transfer (activation energy, mass transfer coefficients, solution conductivity), thermodynamics (Gibbs free energy and electrode potential) and the nature and distribution of the microbial community (different species have different optimal growth temperatures) of the microbial fuel cell (MFC) [23]

Temperature is also a crucial operational factor as both organic matter removal and direct power generation increase when the temperature rises, usually to the optimum growth temperature of the microbial community that can be between 30 - 37 ° C. for mesophilic communities and between 50 and 60 ° C for thermophilic communities. This increase may be related to the increase in microbial metabolism, or the reduction in ohmic resistance due to the increase in conductivity of the liquid medium [23].

Reference [23] studied the effect of temperature on the cell voltage and the electrochemical behavior of the MFC with experiments that were carried out at different temperatures during a period of 5 h. Meanwhile, the rest of the variables were kept constant in both the anodic and cathodic compartments of the MFC. The authors observed that the modification in the operation temperature of the anodic compartment of an MFC modifies the response, causing an increase in the power intensity while increase the temperature. This response can be explained due to the higher microbial activity, but the higher conductivity of the membrane also had an effect. The study also stated that the temperature modifications did not modify the system in the long term[23].

It is also possible to observe that the MFC biofilm is active at temperatures between 5 and 45 ° C and it can be concluded that lower or higher operating temperatures resulted in reduced biofilm and MFC performance due, respectively, to lower metabolism velocities and irreversible denaturation of enzymes leading to biofilm decomposition and inactivation of metabolic activity of microorganisms.

B. HYDRAULIC RETENTION TIME (HRT)

Hydraulic retention time, which is the ratio between the treatment system's useful volume and the affluent flow, and consequently the shear force, are important parameters in wastewater treatment, and directly affect the design and operation of the process, operating and installation costs and the energy demand of the treatment systems. Therefore, HRT and shear force need to be investigated before MFC is used as a technology for wastewater treatment and direct power generation. Higher HRTs will lead greater investment costs. Therefore, changes in HRT also have a significant effect on the power generation and wastewater treatment characteristics of the MFC [24].

Reference [25] observed that in high HRT could lead to a lower energy generation due to the lower substrate concentrations that reduced cell metabolism at the anode chamber.

The reduction in HRT also has an adverse effect on organic matter removal and Coulombic efficiency, which is the ratio between the amount of substrate energy directed to the generation of direct electricity. Reference [26] observed that high HRT (small applied organic loads) allowed higher energy recoveries and removal efficiencies of organic matter. With the reduction in HRT, the contact time between the microorganisms and the substrate decreases, reducing the average efficiency of

MFC to remove organic matter because of the kinetic limitation.

HRT is a factor that influences microbial adhesion and biofilm formation due to affluent flow, upward velocity and shear force. According to Reference [27], increasing the shear force, it results in strong attachment of microbes and dense biofilms and consequently there is an improvement in MFC performance with increase of the generated current. These same authors observed that gradients higher than 120 s^{-1} have an adverse effect on the generation of direct electric energy, since the shear force was higher than the tensile force, reducing the electric current and the biofilm thickness due to the breakdown of microorganisms. Their results showed that applying high shear rates in an MFC can result in a specific electrochemically active biofilm that is thicker and denser and attaches better, and hence has a better performance.

C. ELECTRODE'S MATERIALS

The electrode determines the performance and installation cost of the MFC, being a key component. Developing a good electrode design is the biggest challenge in making MFC an economically attractive technology that can be applied on a large scale. These electrodes can be classified into two main groups, bio-electrodes (including anode and biocathode) and chemical-electrodes (more specifically, air–cathode and aqueous air–cathode), according to the presence or absence of biological catalysts. Bio-electrodes, which function not only as an electrical conductor but also as a support material for the adhesion of microorganisms and, therefore, require high surface roughness, good biocompatibility and efficient electron transfer between the microorganisms and the electrode surface [28], [29].

The other group includes chemical electrodes, the electrode material for air–cathodes with a catalyst is composed of a base material, a catalyst, a binder, and a waterproof coating. The base material usually serves as a support material and current collector, so high conductivity and mechanical strength are crucial. Catalysts are important to cells with air-cathodes because they facilitate oxygen reduction of air but they are not essential. If necessary, the catalyst is immobilized on the substrate surface with a binder, and a hydrophobic coating is regularly added onto the cathode to avoid water loss. There is also ways to reduce the cost of air–cathodes with several highly specific materials, such as activated carbon, that do not require a catalyst. For aqueous air–cathode, only base material, catalyst and binder are needed[28], [29].

Electrode configuration is another factor that influences MFC performance and application as a viable technology for wastewater treatment and direct power generation. Commonly, electrodes can be classified according to their configurations: the plane electrode and the three-dimensional electrode. Plane electrode is more common for air–electrode. This is important because, when the air–electrode contains a chemical catalyst, it needs an effective configuration to ensure the oxygen reduction into a three-phase reaction involving the catalyst, the air, and water [28]–[30].

The electrode material must have some general and proper characteristics for it to be used in MFC. For all types of electrodes, the base material should generally have good electrical conduction, good chemical stability (not being degraded during MFC processes), high mechanical strength and low cost. Non-corroding carbonaceous and metal materials such as graphite plates, bars, granules, carbon fibrous material (felt, cloth and paper), reticulated vitrified carbon, stainless steel, titanium can basically meet these general requirements, and therefore are the most commonly used base materials [28], [30].

The materials used as anode electrodes also have several specific characteristics for improving interactions between the electroactive biofilm and the material surface. The most important characteristics are: electrical conductivity; resistance to corrosion; high mechanical strength; developed surface area; biocompatibility; non-toxic to microorganisms and economic [11], [28], [30], [31].

Carbonaceous materials are widely used as MFC electrode, mainly in anodes because they meet the requirements mentioned above. On a laboratory scale, carbon paper, graphite plates and carbon fabric are the most commonly used flat carbonaceous materials [11], [28], [31].

Carbon paper is very thin and relatively stiff but slightly brittle. Graphite plates or sheets have higher strength than carbon paper. These materials have a compact structure and a relatively smooth surface, which facilitate the quantitative measurement of biomass per unit of surface area. But, their low specific area and high cost inhibit the application of these electrodes in large-scale MFCs [29].

In comparison with carbon sheets, carbon cloth is more flexible and much more porous, allowing more surface area for bacterial growth. However, it is very expensive to use for MFC, which hinders its application in large-scale [28], [29].

Graphite or carbon felt is a fiber fabric, but it is much thicker than the materials previously described. It has a loose texture that confers more space for bacterial growth than carbon cloth and graphite sheets. But, the main disadvantage is related to the growth of bacteria, which is more likely to be restricted by the mass transfer of substrate and products on its inner surface. In order to increase the available surface area for bacteria, the felt is cut into cubes and placed into an anode chamber[28], [29].

There are also many studies about the reticulated vitrified carbon (RVC). It is a significantly porous (>97%), conductive, and rigid but brittle material. RVC has a high specific surface area (51 – 6,070 m^2 / m^3), and similar to graphite felt, RVC can be used as packing material to fill the anode chamber. However, its fragility makes it difficult to use on a large scale [29], [30].

The graphite brush anode is an ideal electrode because it achieves high surface area (7,170 – 18,200 m^2 / m^3), high porosities (> 95%), and efficient current collection. The graphite brush has a larger surface area than carbon paper, which facilitates microbial adhesion and energy generation [6].

One option for increasing the surface area of carbonaceous materials and improving electron transfer to the electrode is to perform electrode pretreatment incorporating layers of carbon nanogranules and other materials such as manganese (IV), iron

(III), platinum and polyamines [6], [29].

VI. APPLICATIONS

Microbial fuel cells (MFC) is a sustainable platform for bioenergy generation, biosensors and remote power source. In regard to bioenergy production, the current applications are: phototrophic MFC (PMFC), benthic MFC (BMFC), biohydrogen and methane productions. For biosensors systems, it has been reported meteorological and contaminant sensors based on low power devices, implantable power sources and robots[2].

Phototrophic MFC involves photoautotrophic microorganisms or living plants inoculated in the fuel cell. In that way microorganism or plants are capable of convert solar energy directly in electricity. The main advantage of such applications is the independence of organic substrates making PMFC self-sustained. The range of power density reported in this system with different inoculum varied from 67 mW/ m^2 to 790 mW/ m^2 [32]. Benthic microbial fuel cells exploit the benthic potential in sediments to energy production. According to Reference [2] benthic sediments are used in the anode where microorganisms take advantage of nutrient rich sources, while the cathode is exposed to aerobic surface waters. Then biofilm will attach in cathode surface when exposed to seawater and catalyze oxygen reduction increasing cells' voltage from 1,2 to 1,6 V [2]. The main application of this device is to provide power for environmental sensors and telemetry devices, especially in remote locations. Moreover, despite low power generations, this device also can remotely be used to charge capacitors that need high power densities.

In respect to environmental monitoring devices, MFC can be used as power sources in remote locations because the cost to replace a battery or other components in sensing devices can overcome new deployments. In addition, MFC have been applies as biosensors for environmental surrounding changes. Their functioning is based on the sensing part - the biological one - and the use of a transducer capable of converting any change such organic substrate concentration, pH and temperature into a signal. The liability of microorganism for such changes affects directly power density. Measuring it through a signal and quantify it are the key for their functioning [2]. Nowadays, biosensors already are being developed for contaminants monitoring and more studies are being performed to increase their accuracies. Similarly, biological oxygen demand sensors (BOD) are been tested for the real time determination for surface water qualities. This type of sensor is based on calculating coulombic yield in which is closely related to BOD and the presence of organic contaminants in the water. Other devices are discussed as well in terms of heavy metal and toxic compounds.

MFC are been used as power sources for medical devices that can deliver drug doses in regular intervals to organs without the need of surgery for battery replacement [2].

Robots have been built using MFC. The first produced one is the Gastrobot (aka Chew-Chew train) in which an artificial stomach colonized by E.Coli and HNQ as mediator of sugar's metabolism were not a self-sustained approach because human interference was needed to introduce reduce chemicals and substrate into the stack of abiotic/chemical fuel cells. Then, electrical generation could be used to charge the bank of Ni-Cd batteries for robots functioning. The second one came up with EcoBot- I in which MFC were used to charge capacitors that once full charged it would occasionally actuate in robot's movement. Similarly, the EcoBot-II arrived with innovative way to reach remote areas and to report temperature wirelessly independent on chemical mediators but still needing some human intervention. Only in the third version of the Ecobot's series, a self-sustainable idea could be reached through MFC stacks [2], [31].

MFC have successfully been used for several types of wastewater, including synthetic wastewater based on pure compounds, and complex wastewater, such as beer brewery, domestic, starch processing, paper recycling plants, cassava mill, winery and olive oil wastewater [33]. However, one of the bottlenecks to development of this interesting application of MFC technology is the nutrients ratio (nitrogen, phosphorous) which may affect the performance of the bio-electrochemical system [33] Therefore the unbalanced COD/nutrients ratio for biological processes makes it important to look for a co-substrate waste for actual full-scale treatments, which is a major challenge for the application of the technology [33].

VII. FUTURE PERSPECTIVES

Microbial Fuel Cells have gained interest over the past few years because it is a promising sustainable technology for simultaneous energy generation and wastewater treatment, with the advantage over conventional technologies of having higher conversion efficiency and also a low generation of solid waste.

The potential of MFC is enormous and the performance of MFC has improved almost exponentially at laboratory-scale, where the current densities of MFC already has approached values that would be suitable for practical implementation, but the application of the MFC in the industry or in large scale still requires more research, there is an urgent need of studies performed in the field especially to minimize costs and create architectures that are inherently scalable [11], [34], [35]. This technology still faces some bottlenecks that needs to be studied so it can be applied in different situations.

The low power generation is one of the main bottlenecks for MFC technology, which greatly limits its development and industrial application such as, charge transfer, concentration overpotential or the cathodic reaction, which usually requires costly catalysts. In this sense, inexpensive materials need to be researched in order to make this technology efficient [28], [35].

There is a lot of research needed for biological optimization, that indicates the adaptation of bacterial community to the optimized reactor conditions and screening, identification of microbes and their ability to generate electric current are crucial subjects for future research [11].

New materials for MFC are being developed to improve their economic feasibility and performance and designing new configurations are examples of changes that are being made in order to make the scaling-up of MFC viable [35]. Latest studies on MFC cover a broad range of research subjects, including electrode materials, MFC designs, biocathodes, exoelectrogenic microorganisms and substrates [35]. Another way to improve the operating conditions of MFC is the combination of different materials, such as the inclusion of conductive polymers [35]. However, research questions of implementation are inherently more complicated when it comes to working in more complex conditions such as real industrial effluents or natural environments (sediments, marine environments, lagoons, etc.) [31].

The cathode reaction is still one of the major limiting factors of the MFC technology in terms of reaction rates. Therefore, the modification of electrode materials is an effective way to improve the performance of MFC. And regarding these materials, some researchers have proposed the use of noble metals such as phthalocyanine (FePc), pyrolyzed iron (II) and cobalt tetramethoxy-phenyl-porphyrin (CoTMPP) to prepare new catalyst-free cathodes for MFC to minimize the limitation of the high price of the materials that are currently used. Another alternative are new nanocomposite materials that are much less expensive and have improved the performance of these devices in recent years, or to use nanoparticles on a metal-coated cathode [11], [35]. There are also studies about an attractive and economic alternative, the biocathodes, where the oxygen reduction reactions are facilitated by bacterial metabolism within the biofilm formed on the cathode [35].

About the membranes used in microbial fuel cell, the design of the ion exchange membrane directly affects the final cost of the process and the performance. Internal resistance, oxygen diffusion, substrate loss or biofouling are some important considerations that must be taken into account when selecting a membrane [11], [35].

The high cost of the materials is also a limiting factor for the application in large scale. The absence of the membrane, however, have been put forward as possible solutions. In addition, other options have been suggested, including the use of other types of membrane: cation-exchange membranes (CEM), anion-exchange membranes (AEM), bipolar membranes (BPM) and ultracentrifugation membranes (UCM) [11], [35]. Other works have focused on reducing the cost of MFC by using ceramic materials as support to prepare different types of membranes or on using of membranes based on ionic liquids (ILs) that could open up new possibilities in the MFC field.

There are also different types of MFC configurations that have been proposed for lab-scale studies. The distance between electrodes, and the specific surface of the anode, cathode or separator are key factors that influence the internal resistance of the system and the power density.

A further challenge is related with the low energy produced by MFCs, which is currently orders of magnitude lower compared to that of chemical fuel cells. The harvesting and management of the low power generated by MFC has given rise to new hybrid systems that partially address this problem by coupling MFC with external off-the-shelf harvesting systems based mainly on supercapacitors [31].

Moreover, it is known that there is a strong influence of the operating conditions of microbial fuel cells in the removal of organic matter and the generation of direct electric energy in the treatment of wastewater. Temperature is one of the most important limiting factors because it affects the growth of microorganisms which leads to influence the electricity generation in MFC. Conductivity (ionic strength) and pH of anolyte also have a significant effect on the MFC efficiency. Meanwhile low pH helps to transfer protons to the cathode and minimizes proton concentration gradients across the membrane, high pH suppresses the growth of methanogens which indirectly increases the MFC performance [11], [28]. Therefore, all of these studies suggest that MFC will be of practical use in the future and will become a preferred option among sustainable bioenergy processes. There is a lot of scientific works that have demonstrated that this technology offers potentially promising prospects for wastewater treatment and power generation. New low-cost materials are being developed and applied in MFC in order to improve their efficiency, so it can be suitable for wastewater treatment in large scale. The implementation of microbial fuel cells also requires an increase in efficiency and the use of new low-cost materials and, to date, pilot-scale attempts have proved to be unsatisfactory. Moreover, the choice of MFC operating conditions can be decisive regarding bioenergy generation and the MFC performance [35].

VIII. CONCLUSION

In this work, the recent advances in MFC research, focused on MFC configurations, material electrodes, and performances were studied.

MFC can be classified in two-chambered, single-chambered, membrane-less and biocathodes. Enven thoug the membrane-less and biocathode were found to be the least expensive, futher development is necessary to solve the problems related to low energy generation.

Moreover, the direct and indirect electron transference were discussed and several operational conditions affect these processes, such as, temperature, electrode material and hydraulic retention time. Several researches have been doing to expand the current knowledge base and explore new domains in order to improve MFC designs and minimise costs.

IX. REFERENCES

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