Célula combustível microbial: Uma revisão narrativa sobre a geração de energia e produção de biopolímeros

Microbial Fuel cell: A narrative review about Power generation and production of biopolymers

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RESUMO
Os altos níveis de poluição e escassez de combustíveis fósseis têm acelerado a demanda pela consolidação de tecnologias de energia limpa. Especificamente, os Sistemas Bioeletroquímicos (BES) têm se mostrado uma alternativa como biorrefinaria para produção de energia. A existência de mais de um mecanismo de ação microbiológica permite a ocorrência de múltiplas linhas de pesquisa inerentes à BES, dentre essas diferentes possibilidades, as células a combustível microbiológicas (MFC) serão o mecanismo adotado nesta revisão narrativa por serem as BES mais estudadas. O funcionamento do MFC é baseado na degradação da matéria orgânica no compartimento anódico por um biofilme fixado ao eletrodo. O biofilme, além de se apresentar como vital para a transferência eletrônica entre o microrganismo e o eletrodo, ainda é responsável pela produção de biopolímeros. Os fatores limitantes dessa tecnologia são a baixa produção de energia por unidade de área do ânodo e os custos do material, mas uma vez superada, tem potencial para ser aplicada como uma solução amigável para tratamento de efluentes, usina de energia sustentável e biorrefinaria de biopolímeros. A matéria orgânica residual gera simultaneamente energia e um bioproduto com possível valor agregado de mercado, tanto financeiro quanto ambiental, pelos benefícios trazidos pela substituição do polímero petroquímico pelo biopolímero. Isso torna o MFC um destaque global em pesquisas para habilitar, otimizar e esclarecer os caminhos para uma nova era de energia mais sustentável.

Palavras-chave: Biorrefinaria, Energia sustentável, Sistemas eletroquímicos.

ABSTRACT

The high levels of pollution and scarcity related to fossil fuels has accelerated the demand for the consolidation of clean energy technology. Specifically, the Bioelectrochemical Systems (BES) have been shown to be an alternative as biorefinery to produce energy. The existence of more than one mechanism of microbiological action allows the occurrence of multiple lines of research inherent to BES, among these different possibilities, microbiological fuel cells (MFC) will be the mechanism adopted in this narrative review because they are the most studied BES. MFC functioning is based on the degradation of organic matter in the anode compartment by a biofilm attached to the electrode. The biofilm, in addition to presenting itself as vital for the electronic transfer between microorganism and electrode, is still responsible to produce biopolymers. The limiting factors of this technology are low power output per unit area of the anode and material costs, but once overcome, has the potential to be applied as a solution friendly for effluent treatment, sustainable power plant and biopolymers biorefinery. Residual organic material simultaneously generate energy and a bioproduct with possible aggregated market value, both financial and environmental due to the benefits brought about by the replacement of petrochemical polymer by biopolymer. This makes MFC a global highlight on research to enable, optimize and clarify the paths for a new energy era more sustainable.

Keywords: Biorefinery, Electrochemical systems, Sustainable energy.

1 INTRODUCTION

The increased demand for the consolidation of clean energy technology, due to high levels of pollution and scarcity related to fossil fuels, has gained the attention of several research groups in the world (COSTA et al., 2019; JAYASHREE et al., 2014; ZHANG, AHN & LOGAN, 2014).

An area that comes standing out under the eyes of the researchers is the biorefinery. Biorefinery are unities capable of transforming organic material on to distinguished sources of energy, such as heat or electricity (MORGAN-SAGASTUME et al., 2014). The biorefinery wastes, solid or liquid, organic and inorganic are raw material for the biological conversions that can produce renewable resources like energy, minerals, among others (MORGAN-SAGASTUME et al., 2014).

Bioelectrochemical Systems (BES) have been shown to be an extremely promising process fulfilling its biorefinery function in the production of energy, due to the fact that traditional waste treatment systems are processes that require high energy consumption (PANT, 2012; MOHAN, et al., 2010). BESs allow the recovery of important chemicals, production of fuels and even direct generation of electricity, this still combined with waste treatment (ROY & PANDIT, 2019).

The intrinsic ability of some microorganisms to oxidize organic material through metabolic activity makes BESs attractive and allows the formation of products and bioproducts (BANU, et al., 2019). There are several mechanisms through which microorganisms are capable of exercising this natural ability, such as (a) reactions of oxidoreduction occurring at the anode, (b) oxidoreduction reactions occurring at the cathode, (c) adsorption and absorption in the electrodes and (d) combinations of the mechanisms mentioned, depending on the type of BES (BANU, et al., 2019).

Knowledge of the existence of more than one mechanism of microbiological action allows the occurrence of multiple lines of research inherent to BES. In general, BESs are functioning like each other, where commonly an active biofilm is adhered to the anode, oxidation reactions occur and, consequently to the release of electrons from this reaction, generating energy. However, the difference is found in the cathode where different products are formed depending on the type of BES used (ROY & PANDIT, 2019).

Among these different possibilities, microbiological fuel cells (MFC) will be the mechanism adopted in this approach because they are the most studied BES (BANU, et al., 2019; ROY & PANDIT, 2019). As for the operating mechanism, MCCs fit more precisely in variant (a) redox reactions occurring at the anode. This is because electricity comes from reactions of degradation of organic matter in the anode compartment (BAJRACHARYA, 2016). The generation of energy is only possible due to the biofilm, which it must be presented in the form of a thin layer, since the increase in its thickness can cause a decrease in the power produced (BEHERA et al., 2010).

Biofilm, in addition to presenting itself as vital for the electronic transfer between microorganism and electrode, is still responsible to produce biopolymers (PANT et al., 2010). This biopolymer production is related to an alternative metabolic route for reoxidation of NADH (KALATHIL et al., 2013), the fixation of the biofilm itself by polymeric network means (BANU, et al., 2019), among other factors not yet well elucidated (BANU, et al., 2019; ROY & PANDIT, 2019).

Therefore, it will be approached in this narrative review the functioning and mechanisms of generating electricity, as well as the production of biopolymers in a MFC. Seeking to emphasize the need for and importance of studying the consolidation of integration between these technologies for greater feasibility of implementing these techniques.

2 METHODOLOGY

The method applied on the development of this review was the narrative survey to describe and discuss the topic "Power generation and production of biopolymers" on a theoretical and contextual point of view. This means that this survey did not followed a linear path throughout its evolution. The initial topics were result of the "*microbial fuel cell*" and "*biopolymer*" search and then based on the most important results given by Science direct platform the reading of those articles allowed the discovery of secondary papers linked to the theme with important and well-structured information.

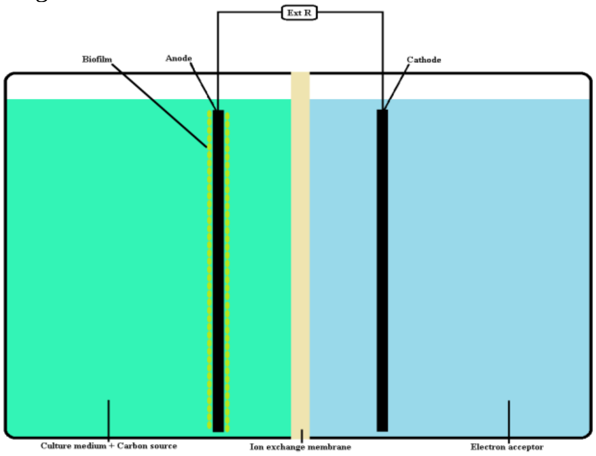
Thus, this method allows a freer approach to the theme but introduces a critical analysis of the theme based on the information gathered during the review phase.

3 POWER GENERATION AND ITS CHALLENGES

BESs can be classified according to their mode of operation as MFC, microbial electrolysis cell (MEC), microbiological desalination cell (MDC), microbiological electrosynthesis, among others (BANU, et al., 2019; ROY & PANDIT, 2019; BAJRACHARYA, 2016). Even though there are differences in mode of operation most BESs consist of an electroactive biofilm present in the anode, which can promote the oxidation of organic material and generate energy (BANU et al. 2019).

Like all BESs, MFC has as its main components a cathodic compartment and an anodic compartment, where oxidation reactions occur and reduction, causing an electron flow in the cell that due to the potential difference results in an electrical signal (ROY & PANDIT, 2019). Figure 1 shows the structure of a MFC.

Figure 1- Basic conformation of a microbial fuel cell.



Source: Autor

ANODIC COMPARTMENT

The anode material has a considerable influence on the formation of the biofilm and electron transfer between microorganisms and electrode (BAJRACHARYA, 2016). The composition of the material used must comply with some basic requirements for the proper functioning of the MFC, such as being a good driver of electricity, not be corrosive and allow the biofilm to form and adhere to its surface by microorganisms (ROY & PANDIT, 2019).

According to Bajracharya (2016) the electrical performance of MFC is also directly linked to the contact area between the microorganisms and the anode, where Higher performances were achieved in materials with a larger surface area, such as for example, corrugated graphite plates. The greater the surface area of the electrode, the greater the area available for microorganisms to adhere and perform electron transfer. Thus, the increase in surface area of the anode implies a notable increase in current density generated at MFC (BANU, et al., 2019; SIMENG LI & GANG CHEN, 2018; BAJRACHARYA, 2016).

Since the anode has an influence on the biofilm formation, it is important to observe what causes this response on the interaction between anode and biofilm. Banu et al. (2019) clarifies that the generation of current in the MFC depends directly on the metabolic reactions of the microorganisms that occur in the biofilm adhered to the anode.

Exoelectrogenic microorganisms, which are the microorganism's responsible oxidation of organic matter and generation of electrical energy, transfer by mediators produced by themselves, and by nanowires/direct contact. The genera of microorganism known for direct electronic transfer (without the need to produce a mediator) are

Geobacter and *Shewanella*, while species, such as *Pseudomonas aeruginosa*, need to produce mediators for the transfer of electrons released by oxidation of organic material (LOGAN, 2008).

The oxidation of organic matter present in the anode compartment, by any one of the electronic transfer mechanisms, is described by Equation 1 when using acetate as a carbon source.

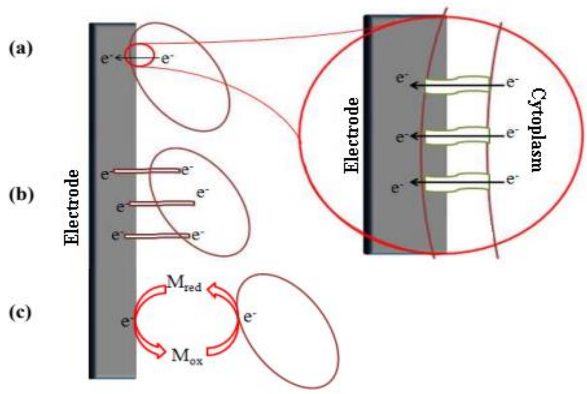
$$CH_3COO + 4H_2O \rightarrow 2HCO_3^- + 9H^+ + 8e^- \qquad \text{Equation 1}$$

Figure 2 illustrates in a simplified way the electronic transport mechanism of different species of microorganisms in a biofilm adhered to the anode. Where the direct electron transfer is demonstrated in the part marked by the letter (a), the electron transfer by nanowires is marked in the figure by the letter (b) and the letter (c) shows the electron transfer mechanism that needs the help of a mediator chemical external to the cell.

Teleken et al. (2017) evaluated through mathematical modeling the kinetics of electric current generation in a CCM inoculated with marine sediment, taking as parameters the data obtained through cyclic voltammetry, and found that the microorganisms present in this sediment preferably used the direct mechanism by nanowires to establish electrochemical contact with the anode.

Even with different specific electronic transfer mechanisms, we know MFCs do not perform all their electron transfer by means of a unique mechanism. This is because for the oxidation of organic matter a varied population of exoelectrogenic microorganisms is necessary (BANU, et al., 2019).

Figure 2- Mechanism of electronic transfer of exoelectrogenic microorganisms. (a) Transfer by direct contact; (b) Transfer by nanowires; (c) Transfer by external mediator.



Source: Gomes, A. S. O. (2011) adapted.

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When compared to MFCs that have pure cultures, those from pure cultures mixed stand out in relation to greater and more stable power generation (ROY & PANDIT, 2019; BANU, et al., 2019), and this superiority in efficiency can be linked to the fact that different microbial strains use different mechanisms transfer and different fractions of the available substrate. So, a mixed culture makes better use of the reactor resources and the space available for electronic transfer (BANU, et al., 2019).

This difference between microbial strains chosen to act as an agent oxidant on organic matter also depends on the conformation of the MFC that can be single-chamber or double-chamber (BANU, et al., 2019). Dual-chamber MFCs have electron acceptor compounds in the cathode compartment (TAMBOLI & ESWARI, 2019). Single-chamber MFCs present only to the compartment anode and the cathode electrode is usually exposed directly to the environment (WANG & LI, 2019). Simeng Li and Gang Chen (2018) studied, among other parameters, the influence of the conformation of the MFC on the generated power and demonstrated that the MFC of double chamber as the one that generates a greater electrical power output.

CATHODIC COMPARTMENT

The study and knowledge of the characteristics of the electron acceptor chosen for completing the electrochemical circuit is of great importance for the generation of MFC's power and energy (ROY & PANDIT, 2019). The cathodic limitations, as poor reduction kinetics and slow rate of electron acceptor reduction reactions at the cathode are the major limiting factors which restrict the product output from BES (ROY & PANDIT, 2019).

Logan (2008) showed that there are several materials that can be used as electron acceptors. Among these, the most studied is oxygen due to its high potential E 0 (E 0 - theoretical voltage), although this acceptor is not as efficient large as calculated. In addition, for the use of oxygen as an acceptor of electrons it is necessary to incorporate catalysts such as platinum, activated carbon and manganese oxides in the cathode composition material to assist in the reactions of reduction (FENG et al., 2019).

Alternatively, ferricyanide ($Fe(CN)6^{3-}$) is used, with potential, E 0, practical achieving better results without the need for investment in more advanced materials high quality to obtain them. MFCs that use ferricyanide as electron acceptor has the anode reduction reactions described by Equation 2:

$$[Fe^{+3}(CN_6)^{-3}] + e^- \rightarrow [Fe^{+2}(CN_6)^{-4}] \qquad \text{Equation 2}$$

The importance of the electron acceptor is restricted to its electrical potential, a since it has zero interference on the biofilm present in the anode (LOGAN, 2008).

4 MONITORING OF ENERGY GENERATION

To measure the amount of energy generated by a MFC and to control the flow of electrons it is necessary to add a resistance to the external circuit between the anode and the cathode which influences the performance of the MFC (SIMENG LI & GANG CHEN, 2018). External resistance is crucial for experiments involving MFC and higher efficiency range, however, both high (> 10 kΩ) and low resistances (<10 Ω) end up with an extremely low power output (SIMENG LI & GANG CHEN, 2018; ROY & PANDIT, 2019). At higher external resistance, the decrease in anode potential and electron discharge to the cathode is limited by external circuit load; however, it is restricted by kinetic or mass transfer limitations at low external resistance (ROY & PANDIT, 2019).

The electrical generation of MFC, promoted by the interaction of microorganisms in the anode, and the electron acceptor at the cathode, can be described and calculated using well-consolidated equations. The first example is the theoretical voltage of the MFC, based on the potential difference between the anode and the cathode. Roy & Pandit (2019) show that the theoretical voltage of the MCC can be described by Equation 3:

$$E_{MFC} = E_{Cathode} - E_{Anode} \qquad \text{Equation 3}$$

Where: E_{MFC} represents the total cell voltage, $E_{Cathode}$ the cathode potential and E_{Anode} the anode potential.

A deeper analysis of this Equation 1 is performed by Logan (2008), where presents it as a specific solution to a more complex equation of electromotive force from thermodynamic relationships, stating that MFCs respect Ohm's Law, which is presented in Equation 4:

$$V = I \,.\, R_{ext} \qquad \text{Equation 4}$$

Where: V represents the practical voltage of the MFC, I the practical current of the MFC and R_{ext} a resistance applied to the circuit.

This relationship of current, voltage and external resistance allows us to build of a polarization curve (BRANCO et al., 2020; ROY & PANDIT, 2019). The curves polarization are comparative graphs that show relationships between density of current power and density or voltage and current density. Roy & Pandit (2019) showed that the polarization curves present important information about electrode, substrate and about the electrochemical reactions that are taking place inside the MFC. To build the polarization curve, it is necessary to know the power generated by MFC, then Logan (2008) shows that among several physical relationships you can present the MFC power in an alternative way according to Equation 5:

$$P = I^2 \,.\, R_{ext} \qquad \text{Equation 5}$$

Where: P is the power obtained in the MFC, I is the measured current and R_{ext} is the external resistance applied to the circuit.

However, only the power information does not convey the real efficiency of a MFC. Therefore, a term that represents the area of the anode electrode, which allows us to compare powers between different MCCs with more precision resulting in Equation 6:

$$P = \frac{I^2 \,.\, R_{ext}}{A_{Anode}} \qquad \text{Equation 6}$$

Where: A_{Anode} is the area of the anode available for biofilm formation.

These are the most common and simple information to obtain from a MFC. Other analyzes such as cyclic voltammetry, Coulomb efficiency and spectroscopy of electrochemical impedance are determinations for checking internal resistance and measurement of biocatalytic activity (LOGAN, 2008; ROY & PANDIT, 2019).

Thus, Table 1 presents a compilation of the results obtained by some authors regarding the different conformations of MFCs, electron acceptors allied the substrate used and different materials present in the electrodes and their influence on power density generated.

The MFC with the highest observed power density (1470 mW/m^2) used to compose the anodic chamber, acetate as substrate and graphite fiber electrode, and for cathodic chamber, activated carbon and manganese oxides, with oxygen as an acceptor of electrons (YANG et al., 2014). MFC with lower power density (21.97 mW/m^2) had anodic and cathodic carbon felt electrodes, used acetate as a substrate and nitrate as an electron acceptor (OON et al., 2017). So, with based on the theoretical framework and data collection regarding the different conformations of MFCs, the influence of these parameters on the generation of energy.

Table 1 - Materials used in anodic and cathode compartments and their respective performance in a MFC.

Authors	Anode material	Substrate	Cathode material	Catalyst	Electrons acceptor	Ionic membrane	P max (mW/m^2)
YANG et al., 2014a	Graphite fiber	Acetate	Activated charcoal and carbon black	Activated charcoal	Oxygen	-	1430
YANG et al., 2014b	Graphite fiber	Acetate	Activated charcoal and carbon black	Activated charcoal	Oxygen	-	1470
TATINCLAUX et al., 2018	Graphite plate	Effluent	Carbon fabric	MnO_2	Oxygen	-	48,4
TATINCLAUX et al., 2018	Graphite plate	Effluent	Carbon fabric	Pt	Oxygen	-	65,4
DAI et al., 2017	Carbon felt	Ethanol	Carbon felt	-	Potassium ferricyanide	CMI 7000	437
TELEKEN et al., 2017	Graphite plate	Acetate	Graphite plate	-	Potassium ferricyanide	CMI 7000S	28,18
DE SÁ et al., 2017	Graphite plate	Acetate	Graphite plate	-	Potassium ferricyanide	CMI 7000S	27,53
MORAES, 2016	Graphite granules	Acetate	-	-	Potassium ferricyanide	CMI 7000S	238,5
BRANCO et al. 2020	Graphite plate	Acetate	Graphite plate	-	Potassium ferricyanide	CMI 7000S	335,32
FARAHANI et al., 2018	Graphite brush	Acetate	Graphite brush	Activated charcoal + MnOx	Oxygen	Nafion 117	467
MIROLIAEI et al., 2015	Carbon fabric	Glycose	Carbon fabric	-	Oxygen	Nafion 117	26,97
MAJIDI et al., 2019	Graphite brush	Acetate	Carbon fabric	MnO_2	Oxygen	Nafion	180
OON et al., 2017	Carbon felt	Acetato	Carbon felt	-	Nitrate	Nafion 117	21,97

(-) not used or described.

5 PRODUCTION OF BIOPOLYMERS

BESs have been studied to simultaneously generate electrical energy and produce bioproducts (COSTA et al, 2019; KUMAR et al, 2018; MOHAN et al, 2018). These bioproducts are generated by microorganisms that produce biopolymers during the degradation of organic compounds (BANU et al, 2019). Depending on the conditions that the MFC is submitted and the microorganism responsible for the production of the biopolymer, it can be produced and excreted by the cell in the form of exopolysaccharides or stored intracellularly (BANU et al, 2019; SRIKANTH, REDDY & MOHAN, 2012).

Some MFC operating parameters such as temperature, pH, period between feeds, substrate characteristics and external resistance applied to the system may undergo changes during the cell operation (ROY & PANDIT, 2019; SIMENG LI & GANG CHEN, 2018). These changes can lead to route deviations metabolic effects of microorganisms causing variations in energy production (BANU et al., 2019). As a result of this imbalance, metabolites such as proteins, enzymes, polymers, oligomers, among others (GURAV et al., 2019; MORGAN-SAGASTUME et al., 2014; SALEHIZADEH & VAN LOOSDRECHT, 2004). COSTA et al. (2019) highlight the possibility of biopolymer being excreted and not stored by microorganisms.

According to Banu (2019), normally the biochemical pathways linked to production of biopolymers are the central and important pathways, such as the Krebs cycle, the beta oxidation, the Calvin cycle, and glycolysis. He further states that Acetyl-CoA is the most common intermediate between the common metabolic pathways and the pathways that biopolymers.

In addition, different strains of microorganisms can produce and store these biopolymers, depending on the environmental conditions in which found and the available substrate (GURAV et al., 2019). That is, the microorganisms exposed to adverse conditions tend to prevent a possible scarcity of resources, thus, they promote the retention of essential nutrients for cell maintenance. These nutrients are stored in the form of compounds that are precursors for both cell maintenance pathways when compared to biopolymer production pathways. Thus, since there is still no shortage of resources, the metabolic route of microorganisms is diverted to the production of biopolymer which can later be degraded by even for the reuse of resources.

Banu (2019) suggests that the production of biopolymers, such as polyhydroxyalkanoate (PHA) and polyhydroxybutyrate (PHB), is related to phosphate retention in anodic compartment. The synthesis of these biopolymers and the intracellular accumulation, usually occurs due to excess carbon available in the culture medium, associated with the presence of growth limiting components, such as sulfur, phosphate, nitrogen, oxygen, or magnesium (SRIKANTH, REDDY & MOHAN, 2012; SALEHIZADEH & VAN LOOSDRECHT, 2004).

The study by Srikanth et al. (2012) shows that the metabolic pathway of re-oxidation of cofactors, such as NADH, $FADH_2$, and others, occur with the aid of oxygen, when it is present. In the absence of oxygen, or when there are not enough amounts of oxygen, microorganisms seek alternative ways to reoxidate cofactors. This causes the accumulation of Acetyl-CoA and NADH, facilitating the microorganism to start of the biopolymer production route (WU et al., 2019; SRIKANTH, REDDY & MOHAN, 2012).

The presence of oxygen at extremely low levels that allows the microorganisms to partially reoxidate cofactors, reduced availability of ATP, suppressing cell growth. Then the ATP available is used to activate the transport mechanism of the carbon source, acetate, which allows the accumulation of biopolymer by the microorganism (WU et al., 2019; SRIKANTH, REDDY & MOHAN, 2012).

Due to the thermal and physical properties of biopolymers they are assimilated to respective polymers from fossil sources, they can be used in several areas, such as health (scaffolds), various effluent treatments (flocculant), nanomaterials, among others (BANU et al, 2019). Biocompatibility, recyclability, and the fact that it does not generate any type of waste to obtain it, make the biopolymers more attractive than conventional polymers, on the other hand processing bioplastic is more difficult and cost expensive stopping their common usage (BANU et al, 2019).

However, even with all the knowledge about the functioning of the mechanism of anaerobic re-oxidation of microorganisms, it is still difficult to pinpoint clarity on the medium used by exoelectrogenic microorganisms, or by the mix of cultures in MFC so that it is possible to simultaneously generate electricity and an accumulation / generation of biopolymer (WU et al., 2019). therefore, more research directed at the metabolic pathway that these microorganisms adopt to produce biopolymers.

6 FINAL CONSIDERATIONS AND FUTURE PERSPECTIVES

With the advancement of studies related to the generation of electricity by MFCs, initial limitations have been overcome and other barriers to their development are being found. Limitations on its efficiency, such as low output power per unit area of the anode and the material costs for building the cells are currently the limiting factors for scaling up to be advantageous and economically viable.

As mixed culture inoculants are related to the greater potency of exit, the mechanisms of synthesis of biopolymers still need to be better elucidated to understand the metabolic pathways, making it possible to control the characteristics of the culture medium and external physical factors to obtain the best results, both in terms of output power and in the content of biopolymer produced.

Once these limiting factors that we find in BES in general and more specifically to MFC are overcome, it has the potential to be applied as a solution friendly for effluent treatment, sustainable power plant and biopolymers plant. Fulfilling its function initially proposed as a biorefinery where it can of residual organic material simultaneously generate energy and a bioproduct with possible aggregated market value, both financial and environmental due to the benefits brought about by the replacement of petrochemical polymer by biopolymer. This makes MFC a global highlight on research to enable, optimize and clarify the paths for a new energy era more sustainable.

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