

## Research Article

# Set up of a Microbial Fuel Cell for the Treatment of a Garden Compost Leachate: Impact of the External Polarizing Electric Resistance Upon the Chemical Oxygen Demand Removal

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## Abstract

Microbial fuel cells (MFCs) are new and growing renewable energy devices. They transform chemical products into electricity with the help of microorganisms (enzymes, bacteria, microbes, etc.) acting as biocatalysts. They are nowadays displaying technological development since they concomitant simultaneously the wastewater treatment and the electric power generation. These two novelties incite researchers in the field, the utilization of this promising technology. As a matter of fact, a bioelectrochemical fuel cell has been elaborated and set up for garden compost leachate treatment. Following a previous study on the microbial anode formed from wastewater under the application of an electric potential either positive or negative by using chronoamperometry. In this work, we propose the simple method of connecting the two electrodes (anode and cathode) by electrical resistance, to flow a current. The impact of the polarizing electric load on the achievement of the MFC has therefore been studied. Moreover, the chemical oxygen demand (COD) removal for the MFC running for 7 days has been also investigated. It decreased and showed simultaneously an increase in the cell voltage. Thus, the effects of the external load on the current and power generation, as well as on pollutant removal, have been studied by modifying each time the external load. The external polarizing resistance (EPR) was increased from 1 to 10 k $\Omega$ , to assess the pollutant decay of the organic matter contained in the wastes. As a result of this, the voltage was increased, whilst the current was decreased, with increasing values of the EPR. The results have been discussed with respect to the type and the predominant microorganisms (electrogenic/fermentative) being involved during the generation of the electric current. This new technology is very promising for converting waste into electricity by offering a way to clean up the polluted environment.

**Keywords:** Microbial fuel cell, Waste treatment, External polarizing resistance, COD removal, Electrocatalytic microorganisms

## 1 Introduction

It is well known that the planet's energy needs are constantly increasing. They require a lot of resources to meet the daily needs of the population. Indeed, human beings use different forms of energy (fossil, renewable, etc.) for various reasons,

mainly in form of lightning, heat and transport. Amongst these energies, the rapid development of technologies related to the production of energy from renewable sources should be reconsidered. However, renewable energies are developing more slowly than fossil fuels, which continue to grow up strongly [1].

Nowadays, conventional energy is produced from a fossil fuel composed of organic matter, carbon-rich chemical compounds, such as hydrocarbon. These fuels can be found in the soils of the earth; they were formed by the accumulation and degradation of organic matter over millions of years. Amongst these fossil resources, we cite the most commonly used three hydrocarbons which are namely coal, oil and natural gas. The environmental impact of the combustion of fossil fuels makes it necessary to find other methods of energy production. Nowadays, more attention has been devoted to other energy sources that are plentiful and environmentally acceptable [2].

Among these new and renewable technologies, clean electrochemical devices (fuel cells) are in particular encouraging alternatives to fossil fuel energies that could lead to reduced CO<sub>2</sub> emissions and consequently to a cleaner environment [3]. From the ecological point of view, this new technology can follow the electric energy crisis and the pollution of wastewater from various industries that contain significant amounts of organic substances that cause the pollution of the environment if it is not well treated [4]. Currently, managers of industrial units are choosing the MFC promising technology for the treatment of their sewage and outflow liquid wastes, in order to preserve the environment [5]. Among others, the nutrient salt removal by steel-making slag in sediment MFCs, has been reviewed by Touch *et al.* [6]. The MFC, also called bio-battery, is therefore a bio-electrochemical device that recovers chemical energy from organic matter using the metabolism of certain bacteria to produce electrical energy. The power generated by these MFCs can reach up to 1 W/m<sup>2</sup> projected to the anodic surface. The bioelectricity production using shade macrophytes in constructed wetlands-MFCs has been recently achieved successfully by Guadarrama-Pérez *et al.* [7], which ascertained this promising technology.

A MFC is composed of two half-cells acting as anodic and cathodic compartments which are separated by a cation exchange membrane, in general, the perfluorinated Nafion. As it has been already reported by Santoro *et al.* [8], in the anodic compartment (often a carbon used as an anode), the microorganisms form the biofilm called biocatalyst that oxidizes the organic matter and produces protons and CO<sub>2</sub>. Whilst the cathode half-cell utilizes metal catalysts or nanoparticles (i.e.

platinum, nickel, manganese dioxide, etc.), for oxygen reduction. This finding has been approved by a recent investigation undertaken by Zerrouki *et al.* [9], by synthesis of low cost organometallic-type catalysts for application in MFC technology. Besides, a critical review of recent proton exchange membranes applied in MFCs for renewable energy recovery has been carried out by Shabani *et al.* [10], to study the crucial role of polymer ionic membranes role in this technology. Certain microorganisms called electroactive bacteria (EAB) are able to transfer the electrons resulting from this oxidation to an electrode (the anode). These electrons then flow in the external electrical circuit through a resistor to the cathode which catalyzes the reduction of oxygen to water [11]. However, an air exposed single-compartment MFC utilizing micro-algal biocathodes was already designed, for the simultaneous biodegradation of real dye textile wastewater and the generation of bioelectricity [12]. MFCs can continuously generate clean power at room temperature, atmospheric pressure and neutral pH without additional maintenance. The only by-products are CO<sub>2</sub> and H<sub>2</sub>O, which do not require any additional handling, since the CO<sub>2</sub> produced is biogenic, which is included in the biogeochemical carbon cycle, avoiding the net emission of carbon to the atmosphere.

This article aims to better understand the formation of an EAB on the anodic surface, and the mechanisms involved in the competition between EAB and other bacterial communities, in order to improve the selection of the EAB anodic surface. Particular attention will be paid to the EPR being utilized to allow the delivery of electrical current. It seems that they are the most relevant variable to be able to increase the power density of the MFC, to control the current and the voltage during the functioning of the MFC [13]. It is commonly known that a low current and high voltage result in an MFC connected in series with a higher resistance. In contrast, a higher current and a lower voltage can be produced if the MFC is discharged to a low resistance. Besides, in an MFC, if the external resistance is equal to the internal resistance (i.e. the slope of the ohmic linear part of the polarization curve), the maximum power will be obtained [14], [15]. Moreover, considering the fact that increasing the output power is one of the main drawbacks of the MFC technology, the EPR effect, is thus very pertinent for harnessing the power output for real applications [16], [17]. It has been also

reported the external load effect on MFCs operating in the batch mode [18]. It is necessary to carry out a study on the influence of the external load on MFCs working in continuous mode, for process automation as well as for large-scale implementation.

In this article, we focus on the influence of the electric resistance on the achievement of the MFC elaborated with leachate of a garden soil compost. The electrical current generated as well as the abatement of COD will be discussed with respect to the variation of the external resistance. The results will be interpreted in connection with the type and predominant microorganism population during the functioning of the MFC.

A biofilm of garden soil compost leachate was formed onto the Carbon Felt (CF) bio-anode in an MFC that functioned during a certain period. The MFC was then connected to a series of electric polarizing resistances, to enhance the electroactivity of the biofilm. The EAB obtained in this way, was sufficiently effective in decomposing successfully the organic matter and therefore increasing the abatement of the COD removal of the leachate. The MFC technology is thus advantageous in generating the bio-electricity regarded as a promising renewable energy in the future with the concomitant preservation of the environment.

## 2 Theoretical Background

In the MFC technology, two issues are important to consider which are as follows:

### 2.1 Metabolic bacterial mechanisms

Within a bacterium, the electron transfer whether direct or indirect occurs at the beginning or end of a cascade of reactions of oxidation and reduction. These are keys to catabolic processes necessary for the survival of the bacterium. These processes are the natural cellular respiration and fermentation mechanisms. They are used by the bacterium to degrade matter (by oxidation) and extract energy which will be stored in the form of ATP considered a universal energy source.

### 2.2 Selection of EAB

As far as we know, the selection of an EAB can be carried out via two processes: An anode inoculated

by a biofilm underwent electric potential to form a microbial anode from a source of inoculum. The microbial anode formed at a high polarization potential produces a higher current than that formed at a lower potential. The high potential would result in larger biodiversity of the microbial communities growing on the anode surface, giving the best chances to catch and grow suitable anode-respiring bacteria [19].

Moreover, after being cultured and enough matured, the EAB is readily formed on the surface of the receiving material (in generally supported carbon material). However, it can also be transported via the transplantation biological sonication using ultrasound. In a previous study, the ultrasonic scratching and transplantation of an EAB in an MFC were achieved successfully by using fruit peeling leachate. In effect, an MFC connected to an EPR allowed the formation of the EAB, after functioning for a long time. After having been well formed, the EAB was then scratched by ultrasound and re-inoculated in new leachate to be transplanted onto the bio-anode. This procedure permitted the microbial electron charge transfer and therefore the enhancement of the bio-energy production of the MFC [20].

## 3 Experimental

### 3.1 Materials and methods

The garden soil was purchased from Neuhaus (France). It is made from a mixture of sphagnum peat moss and peat alternatives. A quantity of this soil was diluted in KCl solution (60 mM) at 33% (V/V). The mixture was then placed in an Erlenmeyer flask and stirred carefully with a magnetic stirrer for 72 h. It was filtered through filter paper to give the final leachate compost. De-ionized water (18.2 MΩ.cm) was used to prepare aqueous solutions. The garden compost was used as a source of inoculum for the formation and growth of the EAB. The materials used for the electrodes have been chosen for their high conductive powers, biocompatibility and non-toxicity toward the microorganisms. The carbon felt (CF) 99.9% purchased from Thermo Scientific Alfa Aesar, was used as the bio-anode material during the experiments. Its dimensions were 4 cm in height, 1 cm in width and 1 cm in thickness. Before the use, the CF underwent a cleaning step, by immersing it in a dilute solution of

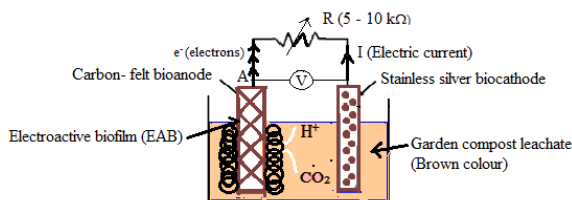
HCl acid 37% for 2 h. It was then carefully washed with ultrapure water and dried in an oven at 40 °C overnight. A stainless silver wire 0.5 mm in diameter and 5 cm in height, was utilized as the bio-cathode material.

### 3.2 MFC design

The MFC was composed of a glass chamber of 80 mL in volume (i.e. with a single compartment). The compartment was filled with the filtered garden compost solution in which both the bio-anode and bio-cathode electrodes were immersed (Figure 1). The cell was then connected in series to EPR to allow the flow of the electrical current prior to utilization in the COD removal of the garden compost leachate. A digital voltmeter was also connected in parallel for monitoring the voltage delivered by the MFC. This latter was left functioning for 90 days, to permit the formation and the growth of the EAB. In order to observe the impact of the EPR on its achievement, the MFC was left functioning permanently, with the aim perhaps to improve the performance of the involved electrodes [21], [22]. It was thus connected successively to different EPR values ranging between 5 and 10 k. For each resistance, on the first day, the values of the voltage were recorded for 4 h, every 10 min, to yield the evolution curve. The day after, the curve of polarization (i.e. voltage vs current density) was obtained when the cell was discharged to an electrical resistance that varied from 1  $\Omega$  to 1 M $\Omega$ . The curve of power (i.e. power vs current density) was therefore deduced. Then, it was left functioning for 7 days. At the end of each experiment, a sample of the leachate was taken for the COD analysis.

### 3.3 Chemical oxygen demand (COD)

At the end of each experiment, the COD analysis was performed. It was an important technique with which one can characterize the presence of all oxidizable substances in the leachate whether they were biodegradable or not (organic compounds) [23]. The COD analysis allows the determination of the organic matter concentration contained in the leachate through the necessary quantity of oxygen for their total chemical oxidation. It was quantified according to the ISO 15705 standard (ISO 15705, 2002) that is based on the method



**Figure 1:** Schematic representation of MFCs connected to several EPRs ranging from 5–10 k $\Omega$ .

of closed-tube small-scale. The Pyrex tubes contained a mixture of 3 mL of the sample, 2 mL of digestion solution ( $K_2Cr_2O_7 + HgSO_4$ ) and 4 mL of catalyst solution ( $Ag_2SO_4 + H_2SO_4$ ). The tubes were sealed tightly and heated at 148° C for 2 hrs in a CR 2200 WTW heating block. After cooling down, the solutions were titrated with Mohr's salt solution ( $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ ), in the presence of ferroin indicator. Then, the COD values in mg ( $O_2$ )/L were obtained. They were calculated by introducing the experimental data in Equation (1).

$$COD \text{ (mg/L)} = 8000 \times \frac{(a-b) \times N}{V} \quad (1)$$

where:

*a*: volume (mL) of Mohr salt used for the blank test (distilled water).

*b*: volume (mL) of Mohr salt solution used for sample assay.

*V*: volume (mL) of the sample solution

*N*: normality of Mohr salt solution (0.1 N)

Subsequently, the COD abatement was calculated to assess the efficiency of effluent treatment, as follows [24]:

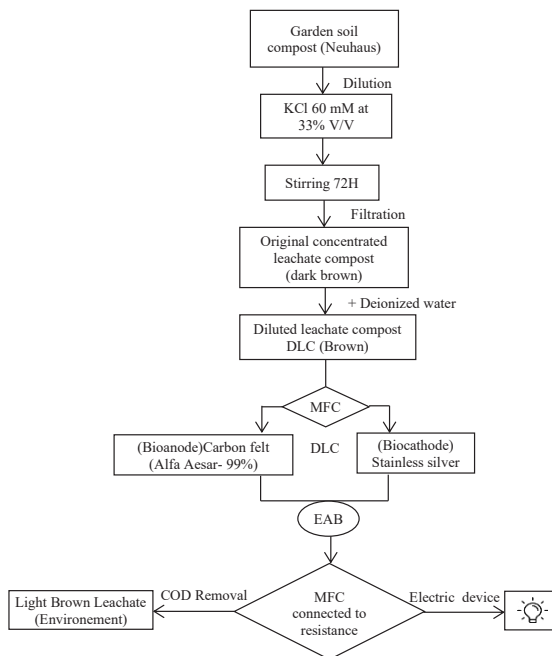
$$COD \text{ (%) } = 100 \times \frac{(COD_{Initial} - COD_{Final})}{COD_{Initial}} \quad (2)$$

The flow diagram of the experimental set up used throughout this investigation, is illustrated by Figure 2.

## 4 Results and Discussion

### 4.1 Impact of external resistance on the growth of anodic biofilm

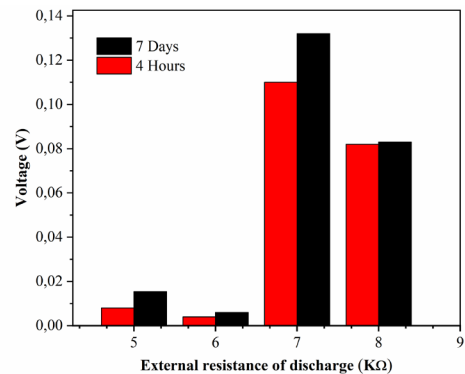
The purpose of connecting several different external resistors and highlighting the effectiveness of these discharge resistors for the polarization of the bioanode,



**Figure 2:** Flow diagram describing the steps of the experiment.

in order to have a good electroactivity of the bacterial biofilm. The EAB is naturally polarized by connecting the battery in series with the various EPRs. Indeed, when the MFC battery begins to operate correctly, an electric current is delivered in the circuit; the biofuel cell polarizes, attracts the EAB and therefore becomes favorable to the formation of the EAB if the latter has not yet formed. However, it makes advantageously more electroactive if it has already been formed. The electric current was generated thanks to the anodic oxidation of the substrates contained in the leachate.

In order to follow up the growth of the EAB at the anode, the variation of the voltage vs time for a set of MFCs discharging into the EPRs 5, 7 and 8 k $\Omega$ , in the 1st day for 4 h and at the end of the experiment (7th day), was studied. The results obtained are represented in Figure 3 and indicate that the higher voltages were recorded with the EPRs 7 and 8 k $\Omega$ . Whilst, the resistances 5 and 6 k $\Omega$  displayed lower values. This finding seems to be in quite good agreement with those published previously since it has been reported that a higher polarizing electric load leads to lower currents and in consequence higher voltages [25]. Nevertheless, when using 8 k $\Omega$ , the voltage decreases



**Figure 3:** Evolution curves of MFCs discharging into the polarizing electric resistances 5, 6, 7 and 8 k $\Omega$ , successively during the 1st day (during 4 h) and at the end of the experiment (7th day).

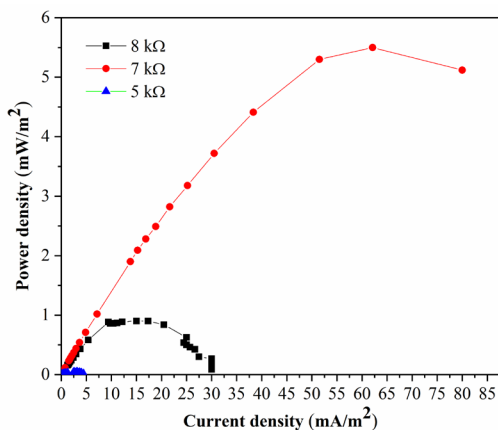
a little bit. Moreover, with 7 k $\Omega$ , the values of the 1st and 7th day are remarkably relatively different from each other; but not quite for 8 k $\Omega$ . The optimum value of 7 k $\Omega$  is obtained probably due to the modification of the bacteria population according to the electron transfer managed by the EPR. Table 1 summarizes the values of voltages and electric currents yielded in the 7th day for MFCs with resistances 5, 7 and 8 k $\Omega$ .

**Table 1:** Values of voltages and electric currents yielded in the 7th day for MFCs with EPR 5, 7 and 8 k $\Omega$

EPR (k $\Omega$ )	Voltage (mV)	Current ( $\mu$ A)
5	15.4	3.08
7	132	18.85
8	83	10.375

In the literature, it has been suggested that population growth and distribution in MFC biotic compartments are influenced by external load changes [16], [26]. These results obtained showed that the decrease in the resistance delayed the start-up phase of the MFC stack. This was consistent with the results shown by Zhang *et al.* [27]. In addition, as it was already pointed out by Jung *et al.* [28], the external resistance of a MFC regulates both the anode availability as an electron acceptor and the electron flux through the circuit. It was thus found that its effects on the MFC using an organic substrate, yielded average current densities ranging from 40.5 mA/m<sup>2</sup> (9,800  $\Omega$ ) to 284.5 mA/m<sup>2</sup> (150  $\Omega$ ) for MFC supplied with acetate (i.e. A substantial increase of current





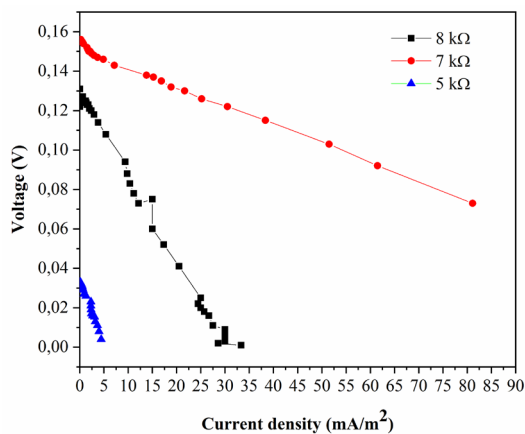
**Figure 4:** Power density curves of the MFCs with EPRs 5, 7, and 8 kΩ.

density). Their results show that the external resistance impacts all the potential, the current, the anode biofilm community and the methanogenesis.

#### 4.2 Electrochemical characteristics of the MFC

The characteristic curves of power density vs current density are presented in Figure 4 and those of polarization in Figure 5 of the MFCs of the polarizing external resistances 5, 7 and 8 kΩ. These curves were obtained using different resistance values between 10 Ω and 10 MΩ. These curves were utilized to assess the electrical properties of our cell, namely the open circuit potential, the short-circuit current and the external resistance corresponding to the maximum power density. According to Figure 4, we notice peaks in the curves which correspond to the maximum power and current densities that can be produced by the MFC for 7 days of operation. It is thus obvious to get the lowest value of the maximum power density and current density for the EPR 5 kΩ the value was 0.047 mW/m<sup>2</sup> and 3.08 mA/m<sup>2</sup> respectively. In contrast, the highest values were obtained with 7 kΩ (i.e. 5.5 mW/m<sup>2</sup> and 62.1 mA/m<sup>2</sup>). Nevertheless, with 8 kΩ, the values 0.9 mW/m<sup>2</sup> and 15 mA/m<sup>2</sup> were recorded. So we can conclude that the energy of the MFC increases by increasing the EPR and a low efficiency from a lower one. The same behavior was observed by Ouis *et al.* and Zerrouki *et al.* successively [29], [30].

Figure 5 represents the curves of polarization, that present the tension according to the density of the

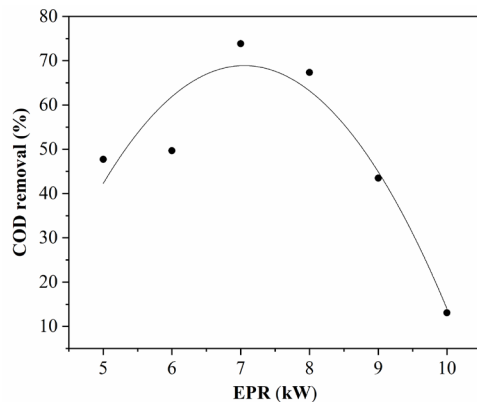


**Figure 5:** Polarization curves of the MFCs using EPRs 5, 7 and 8 kΩ.

current, of MFCs with EPRs 5, 7, and 8 kΩ. One notices three regions in these curves: the first region illustrates the overvoltage of activation that is due to the loss of energy during the initiation of Ox/Red reactions and the electron transfer between the bacterial cell and the surface of the anode. In the beginning, a zero current density was created by the MFC yielding the highest voltage known as open circuit voltage (i.e. without prior electric connection between the two electrodes). Regarding the second region, a linear ohmic overvoltage is caused by the electrolyte. Whilst, the third region shows a second overvoltage which generates the higher short-circuit current density resulting from the loss of concentration appearing during diffusion.

#### 4.3 Effect of the various polarizing external resistances on the COD removal

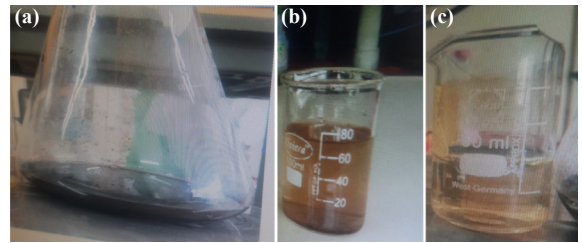
From the previous results, it was deduced that the change in the EPR, impacted the performance during the operation of the MFC, and we therefore assessed its impact on the amount of oxygen necessary to oxidize any organic matter contained in our garden soil. The COD analysis has been carried out before and after the operation of the working MFCs. The quantities of COD removal were determined by using Equation (2) and the initial COD of the leachate without undergoing any prior treatment by the MFC (i.e. 306 mg/L). As shown in Figure 6, the obtained values could be approximated to within the accuracy of the readings



**Figure 6:** Variation of COD removal versus EPR.

by a parabolic line shape. This means that the COD removal increases by increasing the EPR reaches a maximum and then falls again to attain the minimum value using higher values of EPRs. Besides, it is clear that the highest COD removal value (i.e. 73.85%) was obtained with 7 k $\Omega$ , and then it decreased subsequently to reach the lowest value (i.e. 13.07%) with 10 k $\Omega$ . These results are quite consistent with those reported by Potrykus *et al.* [31]. Contrary to the abatement, which increases by the reduction of the resistance, and decreases by its increase.

From these results, it can be concluded that the wastewater treatment capacity with MFCs operating with EPR, is very important. As shown in Figure 6, the leachate decreased (i.e. COD removal efficiency increased) when increasing the EPR. In effect, the raw substrate COD in the leachate decreased in the resistance range (5–7 k $\Omega$ ). This finding results perhaps, from the contribution of the fermentative non-electrogenic metabolisms, as it was already pointed out by Potrykus *et al.* [31]. This particular interval resistance does not unfortunately permit this bioelectrochemical device to attain a higher generation of electricity. Conversely, in the resistance range (7–10 k $\Omega$ ), the COD removal efficiency follows its usual behavior, i.e. the greater the EPR, the lesser the COD removal and consequently the less electricity production. It has been reported previously that at higher external resistances, there exists a lower potential at anode, which may alter the metabolic activities of the microbial consortium. In effect, its presence can provide suitable mechanisms for efficient utilization of organic matter [32]. These results are also in agreement with those reported by



**Figure 7:** Photograph showing (a) the original garden soil leachate (dark brown), (b) After 90 days (brown), and (c) Light brown (after using in MFC).

G.S. Jadhav *et al.* [33].

On the other hand, in the case of MFC operated with 100  $\Omega$ , Katuri *et al.* [25] observed relatively higher COD removal, yielding a higher current. The abatement of COD lowered by fewer percentage with external resistance 10 k $\Omega$ . It has also been confirmed that MFCs operated with even higher resistances and at open circuit (i.e. infinite resistance) had much lower COD removal. Two explanations were possible: an anode with lower potential at a higher resistance, which may alter the metabolic activities of the anodic microbial community, in agreement with Picioreanu *et al.* [34], and also the presence of different microbial species (including fermentative species) which provided different mechanisms for efficient utilization of organic matter. All these findings support amply our results.

Finally, Figure 7 displays a real photo taken for the garden soil before and after the operation in the MFC functioning for 7 days. As it is illustrated in this figure, the difference between the color of the pure leachate without undergoing any treatment, which is brown compared to that obtained from the MFC working during 7 days for the treatment of the waste, which is light brown; it is almost transparent making in evidence the removal of waste from the leachate and its conversion into green sustainable renewable energy. However, the original garden soil leachate is dark brown.

## 5 Conclusions

The results obtained in this investigation make evidence that the external charge has a considerable effect on the distribution of the bacterial consortium in the MFC, as no resistance proves less efficiency in

the degradation of matter contained in wastes. So, the present investigation shows that high load external resistor leads to high voltages and low currents. In effect, the EPR 7 k $\Omega$  gives the equilibrium voltage value of 132 mV and the current of 18.85  $\mu$ A, and simultaneously makes evidence of the conversion of the wastes (i.e. organic matter) contained in the soil compost, into low electric energy. Whilst, the lower resistance of 5 k $\Omega$  yields a lower equilibrium voltage of 15.4 mV and a current of 3.08  $\mu$ A. Regarding the power, we obtained the lowest value with 5 k $\Omega$  i.e. 0.047 mW/m<sup>2</sup> with a maximum current of 3.08 mA/m<sup>2</sup>. However, 7 k $\Omega$  allowed the values 5.5 mW/m<sup>2</sup> and 62.1 mA/m<sup>2</sup>. Thus, we may conclude that we can improve the energy of the MFC by utilizing the appropriate resistance. This study also focused on the COD analysis, which demonstrated that the lower resistance in the MFC promotes high COD removal efficiency. A maximum COD removal abatement of 73.85% was achieved using 7 k $\Omega$ . Finally, it may be concluded that the application of the external resistance to polarizing the MFC prior to its operation, is very important for the treatment of wastewater. MFC technology overcomes the difficulties encountered in the conventional treatment of waste. It thus enables the recovery of the eco-friendly bioenergy from the organic wastes, without recalling to the costly anaerobic digestion process and subsequently the inevitable production of excess sludge.

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### Author Contributions

I.L.: conceptualization, research design, experimental measurement and investigation, writing up original draft; M.K.: methodology, data analysis, editing; C.I.: discussions, reviewing. All authors have read and agreed to publish this manuscript.

### Conflicts of Interest

The authors declare no conflict of interest.

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