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Secondary Sludge Biodegradation and Electricity Generation in Biocathode Microbial Fuel Cells

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Abstract

The looking for sustainable sewage sludge management technology in the wastewater treatment plants, has brought to light the biocathode microbial fuel cells (bMFCs) which allow simultaneous biological stabilization and direct energy generation, avoiding the production of biogas. In the present study, the performance of bMFCs for the treatment of secondary sludge as anodic substrate was evaluated by analyzing the removal of organic matter, destruction of volatile solids and the generation of electrical energy under different operating conditions and applying two types of cathode chambers. The results indicated that VSS and tCOD removals up to 92% and 87% respectively can be achieved in the anodic chamber generating simultaneously energy. Current and power densities of $1.80 \pm 0.09 \text{ A} \cdot \text{m}^{-3}$ and $0.43 \pm 0.02 \text{ W} \cdot \text{m}^{-3}$ respectively were reached, showing that bMFCs are a reliable alternative to generate electricity during the sewage sludge stabilization process. It was revealed that the pH value and the type of cathodic zone are statistically significant factors that influenced the performance of the bMFCs. The obtained results demonstrated that the electrochemical performance of the bMFCs was better at pH value of 6 in the anodic chamber and when aerobic cathode zone was used.

Keywords: Biocathode, electricity, microbial fuel cell, sludge stabilization

1. Introduction

The wastewater treatment plants generate a lot of sludge and numerous approaches have been proposed for their management, such as anaerobic digestion, dewatering, composting, and landfill treatment [1]. The main processes for organic matter removal (accounting for about 55–60% of total BOD₅, COD, or TOC removal) during wastewater treatment are biodegradation, biotransformation, and sorption to activated sludge in the biological steps (like activated sludge and clarification, anoxic/aerobic/aerobic, aerobic/anoxic/oxic, sequencing batch reactors, and membrane bioreactors) [2, 3]. If considering the initial content of volatile solids in sludge of 100%, about 40–60% of BOD₅, COD, or TOC can be degraded during the anaerobic digestion process if mechanical, thermal, chemical, and biological pretreatments are applied [1, 4]. As it is known, the hydrolysis of complex organic matter (particularly the insoluble organic matter) of sludge into dissolved organic matter is the first and the rate-limiting step of anaerobic sludge

digestion [5]. Subsequently, the biodegradable dissolved organic matter fraction can be fermented to volatile fatty acids (VFAs), and they are subsequently converted to biogas by methanogens, while the refractory fraction remains in both, the liquid and solid phase of the anaerobic digestate. The looking for more sustainable sewage sludge management technology in the wastewater treatment plants, has brought to light the biocathode microbial fuel cells (bMFCs) which allow simultaneous biological stabilization and direct energy generation, avoiding the production of biogas. The Microbial Fuel Cell (MFC) is a biochemically catalyzed electrochemical system that converts chemical energy to electrical energy by oxidizing the biodegradable organic matter by means of microorganisms via catalytic reactions [6]. The use of biocathodes can enhance the energy generation, and bMFCs can be applied to convert the organic matter in sewage sludge to electricity under ambient temperature, normal pressure, and neutral pH.

Society is facing an increasing demand for energy and has noticed the urgency of changing the energy structure, which today still relies heavily on fossil fuels. The bioenergy is a renewable resource which provides an efficient way of reducing the global warming impact [7]. MFCs are bioenergy source devices that belong to the field of bio-electrochemical systems, and they are considered a sustainable technology since they allow combining the treatment of low value wastes streams, like the wastewater or the sewage sludge, with a direct conversion of the chemical energy into electrical one through bio-electrochemical reactions using microorganism catalysis [8]. MFCs consist of anode and cathode chambers, which are separated by the proton exchange membranes. The power can be generated through the organic matter anaerobic oxidation, performed by electrogenic bacteria in the anode chamber, and reduction of final electron acceptors in the cathodic one [9]. The electrons are transferred to the anode, and they flow to the cathode via a conductive material having an external resistance; the protons migrate through the membrane, and they are reduced by accepting these electrons through the cathode.

Scaling this technology has been difficult and one of the main limitations has been the cost of the cathode materials incorporating precious metals such as Pt and the unsustainable use of ferricyanide as a catalyst independent of the cathode electrolyte [10]. One of the explorations to eliminate these limitations and improve the cathodic stabilization and power generation, enhancing the economic viability and environmentally sustainability of MFC systems, has been the microbial cathode, which uses electro-trophic bacteria as biocatalysts to accept electrons in the cathode substrate [11]. Moreover, this so-called biocathodes enable the use of alternate electron acceptors that can broaden the utility of MFCs and present potential opportunities for the microbially catalyzed conversion of electrical current into various value-added products [10]. Therefore, bMFCs have attracted a lot of attention and they have been considered as a sustainable way to improve the performance of MFC systems.

For the proper MFC performance, a substrate is required in the anode chamber that provides a source of biodegradable carbon and electrons. Generally, any substrate can be used [12], from simple molecules, such as carbohydrates and proteins, to complex mixtures of organic matter, such as those which can be found in the secondary sludge. For a wastewater treatment plant (WWTP), the main source of energy for the equipment is the electricity and this item represents more than 60% of the plant operating costs [13]. The most widely used wastewater treatment process in Mexico is the conventional activated sludge and their electrical energy consumption is $0.10\text{--}1.18\text{ kWh}\cdot\text{m}^{-3}$ [14]. One of the disadvantages of this process is the generation of large amounts of secondary sludge with high content of organic matter that must be properly treated before their disposal; however, due to the complex sludge composition, their treatment is difficult and expensive [15]. That is

why the developing of alternative technologies that simultaneously degrade organic pollutants and generate energy directly has been one of the main topics in this research. The studies related to the use of sewage sludge as substrates in bMFCs are still very scarce [13, 16]. The main objective of the presented study was to evaluate the performance of a bMFCs for electricity generation using secondary sludge as anodic substrate, applying different operating conditions, and testing two types of cathodic chamber, aerobic and anaerobic. They were measured and analyzed the power generation, current densities, and coulombic efficiencies, as well as the organic matter removals and the volatile solid destructions.

2. Methodology

2.1 Experimental setup

Ten cylindrical dual chamber bMFCs, 12 cm in diameter and 13 cm in height, were made of plexiglass. Each reactor was divided into two compartments by a Nafion® proton exchange membrane (Nafion 117#, Sigma-Aldrich, London, UK) with a cross-sectional area of 156 cm². In order to increase the porosity of the membrane and improve the electrical efficiency of the cell, a pretreatment was performed following the recommendations presented in the reference [17].

The effective volume of each chamber was 0.679 L. All the reactors had anaerobic chambers, 5 of them had aerobic cathodic chambers and 5 had aerobic ones. In the superior part of each chamber there are two holes, one is for the electrode and the other one is for feeding or for reference electrode introduction, or for pH and temperature monitoring. The second hole is sealed in the anaerobic chambers to prevent oxygen diffusion to the anodic chamber, and it is opened in the aerobic ones. To provide homogenization in the anaerobic chambers, recirculation was introduced using peristaltic pumps (Masterflex). For the recirculation two openings were considered on the side of the anaerobic compartments. The mixing in the anaerobic and abiotic cathodic zones were also performed hydraulically using peristaltic pumps. The aeration of the aerobic chambers was performed by air injection and diffusion in the bottom using porous stone diffusers.

Millrose® carbon fiber brushes with twisted titanium wire were used both as anode and cathode, 5.1 cm in diameter and 7.6 cm long, having a projected surface area of 1.46 m².

Electrode and PEM pretreatments were performed according to [17, 18]. Both electrodes were connected using a titanium wire (0.5 mm, purity >99.98%, Alfa Aesar, Heysham, UK).

2.2 Experimental design

The experimental design consisted of a full factorial design (2³), which is a powerful tool that is used to identify the effect of the independent variables on the responses at different levels. The eight experiments were performed twice, and four additional experiments were added with abiotic cathodes, 2 with aerobic cathodic zone and another 2 with aerobic ones.

The independent variables were kind of the cathodic zone (aerobic and anaerobic), VSS concentration of the treated sludge (8 and 16 g/L), and pH in the anodic zone (5 and 6). The experiments were performed twice, in two phases (10 runs in each one). To evaluate the effects caused by the independent variables, the following parameters were determined as response variables: maximum volumetric power density (PD_{vol max}), maximum volumetric current density (CD_{vol max}),

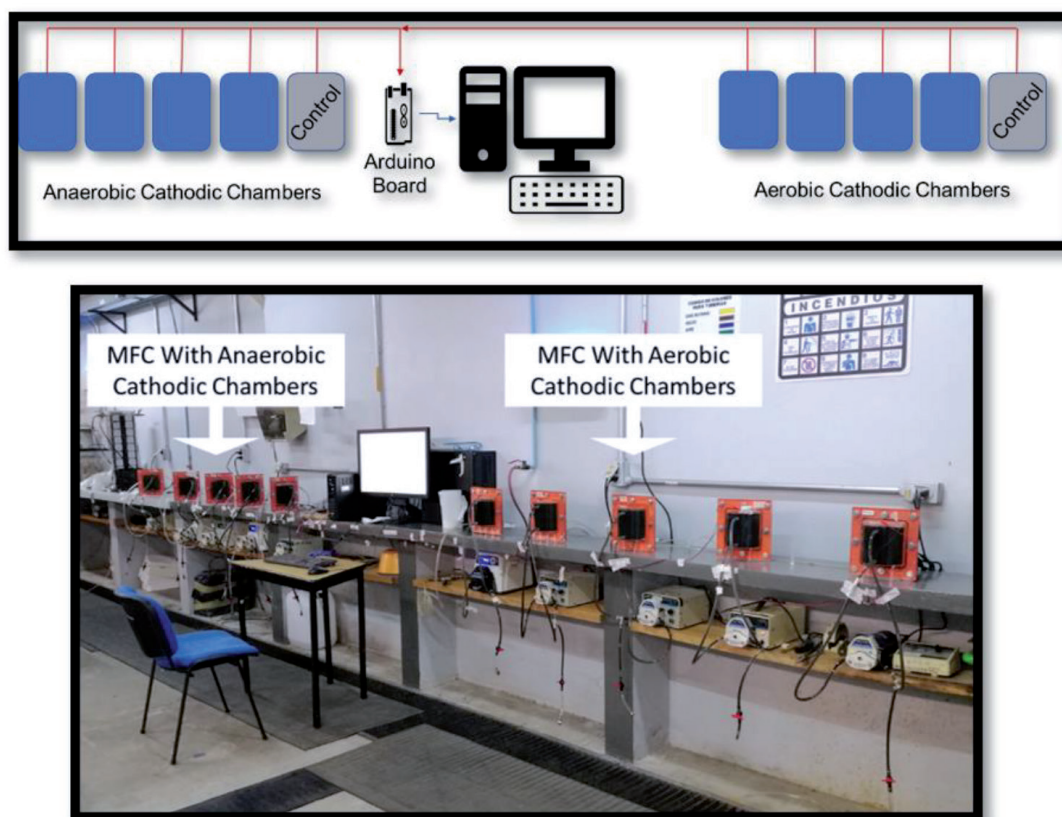


Figure 1.
Schematic diagram of the experimental system.

coulombic efficiency (CE), organic matter removal (R_{COD}), and volatile suspended solids removal (R_{SSV}). The obtained data were analyzed using STHATGRAPHICS Centurion XV ® software. The comparisons of the results were also based on statistical analysis of variance.

The **Figure 1** shows the deployment of the complete experimental system. The left side of the computer shows the anaerobic cathodic zone bMFCs, while the right side of the computer shows the aerobic cathodic zone bMFCs. The purpose of this is to evenly distribute the distance between the computer and the reactors, and to reduce the probability of voltage drops due to the additional resistance that could be caused by the distance of the wiring.

2.3 Inoculation and operating conditions

The experimental bMFCs were operated as sequential batch reactors, allowing the system to adapt to the operating conditions of each cycle (83 days of total operation).

The volume of the catholyte and anolyte were 680 mL each one. The sludge used as substrate for the anode chambers was collected from the secondary settlers of the conventional activated sludge treatment system in one of the wastewater treatment plants located in Mexico City. The sludge was characterized and stored at 4°C until their use as anodic substrate. Two thickened sludge samples were prepared, one with 8 gVSS·L⁻¹ and another one with 16 gVSS·L⁻¹. The pH of the sludge was adjusted to 5 and to 6 before the reactor feeding. Milled granular anaerobic sludge from real scale USBR reactor was used as inoculum in the anodic chambers with TS of 155.67 g·L⁻¹. Almost 5 gTS·L⁻¹ of inoculum was added to each anodic chamber.

Both catholytes, the aerobic and the anaerobic ones, were formed from a combination of two solutions, so that microorganisms can carry out their metabolic

functions: A solution of macronutrients (including the substrate) and a solution of micronutrients (also referred to in this work as a solution of trace elements). The conformations of the first and second solutions are shown in **Tables 1** and **2** [18]. The proportion between both solutions was 8 mL of trace element for each liter of macronutrient solution [19].

The four aerobic cathodic chambers (Aer. C.) were filled with 543 ml of the catholyte and 136 ml of inoculum. Thickened activated sludge from real scale reactor was used as inoculum (SSV of 23231 mg/L, TS of 36875 mg/L). The aerobic cathodic chambers were continuously aerated using porous stone diffusers and aeration system.

A concentration of 733 mg·L⁻¹ of sodium nitrite was added to the anaerobic cathodic chambers as final electron acceptor [20]. The four anaerobic cathodic chambers (An.C.) were filled with 648 ml of the catholyte and 32 ml anaerobic inoculum.

The MFC's were operated for three cycles, where each cycle ended when the energy generation dropped below 50 mV. At each cycle change, both the anolyte and the catholyte were exchanged for fresh, new substances. All experiments were performed in duplicate.

The bMFCs were operated at a temperature of 26.9 ± 2.7°C. To start with the experiments, the bMFC's were left operating at open circuit for 165 hours, this allowed the exoelectrogenic microorganisms to adapt to their environment. Subsequently, the electrical circuit was closed by imposing an electrical resistance

Compound	Quantity
NH ₄ Cl	1.000
K ₂ HPO ₄	1.200
MgSO ₄	0.500
KCl	0.500
KH ₂ PO ₄	0.140
Fe ₂ (SO ₄) ₃ ·H ₂ O	0.010
Yeast extract	0.020

Table 1.
Macronutrientes (in g/L).

Compound	Quantity
FeSO ₄ ·7H ₂ O	1000.0
ZnCl ₂	70.0
MnCl ₂ ·4H ₂ O	100.0
H ₃ BO ₃	6.00
CaCl ₂ ·6H ₂ O	130.0
CuCl ₂ ·2H ₂ O	2.0
NiCl ₂ ·6H ₂ O	24.0
Na ₂ Mo ₄ ·2H ₂ O	36.0
CoCl ₂ ·6H ₂ O	238.0

Table 2.
Trace elements (in mg/L).

of 100 ohms to all the bMFC’s and based on the voltage reading under this condition, we proceeded to calculate the response parameters.

2.4 Analytical methods

The organic matter removals and the volatile solid degradations were calculated based on the obtained results. The sludge stabilization was followed determining the total chemical oxygen demand (TCOD) and volatile suspended solids (VSS). For the determination of TCOD and VSS content, analytical techniques were used according to standard methods [21].

For all the bMFC’s, simultaneously the voltage (V) generation was recorded every hour during the whole operation time of each of the 3 cycles, for this basic data acquisition system was designed, programmed, and implemented. Its assembly consisted of a development board based on the ATmega2560 micro-controller, better known as “Arduino Mega 2560” and electronic accessories such as the prototyping board, 22-gauge parallel cable of two soft copper conductors with individual thermoplastic polyvinyl chloride insulation and joined by a track of the same material (commonly known as duplex cable), alligators, digital temperature sensor and jumper wires with male–male terminals. To avoid data loss in the event of a power outage to the laboratory, the computer was connected to a backup power supply capable of supplying power for two hours without interruption.

The current (I) was calculated using Ohm’s law and the electrical power (P) with the formula $P = V I$. The maximum current density (CDmax) and the maximum power density (PDmax) were normalized with the electrode area.

The CE was calculated according to Eq. (1) where U_i is the recorded voltage in volts (V) of the bMFC at time i , in seconds (s), R is the external resistance, in ohms (Ω), F is the Faraday constant ($96485.3365\text{ C}\cdot\text{mol}^{-1}\text{ e}^{-}$), b is the number of moles of electrons exchanged per mole of oxygen used in the degradation of organic matter ($4\text{ mol e}^{-}\cdot\text{mol}^{-1}\text{ O}_2$), ΔS is the removed concentration of COD ($\text{mg O}_2\cdot\text{L}^{-1}$), V is the volume of the anolyte, in liters (L), and M is the molecular weight of oxygen ($32,000\text{ mg O}_2\cdot\text{mol}^{-1}$) [18, 22, 23].

$$CE(\%) = \frac{\sum_{i=1}^n U_i t_i}{R F b \Delta S V_{anol}} M \times 100 \tag{1}$$

Instrument	Manufacturer	Model
Portable multimeter	HACH	HQ40d
Laboratory Low Maintenance Gel Filled pH Electrode	HACH	IntelliCAL PHC101
Laboratory 4-Poles Graphite Conductivity Cell	HACH	IntelliCAL CDC401
Laboratory Spectrophotometer for water analysis	HACH	VIS DR2800
Peristaltic pump	MASTERFLEX L/S economy drive	HV-77916-10
Potentiostat	GAMRY INSTRUMENTS	Interface 1010E

Table 3.
Instruments used in this study.

Cyclic Voltammetry analysis was done during the last batch cycle of each bMFC in the voltage range of -0.8 V to $+0.8\text{ V}$ at the scan rate of $1\text{ mV}\cdot\text{s}^{-1}$. This technique was conducted using a potentiostat with the cathode as the working electrode, the anode as counter electrode and an Ag/AgCl reference electrode, and it was used to evaluate the oxygen reduction reaction catalytic activity of the bMFC with aerobic and anaerobic cathodic zone. The instruments used for analyses, operation and measurements are presented in **Table 3**.

3. Results and discussion

3.1 Performance of the biocathode microbial fuel cells at open circuit

The startup of all the bMFCs was performed at open circuit conditions, with a cycle duration of 165 h. The voltages increased over the time in the bMFCs with aerobic cathodic chambers (Ae.C.Ch.), while a contrary tendency was observed in the bMFCs with anaerobic cathodic chambers (An.C.Ch.). The maximum voltages obtained at different experimental conditions are presented in **Figure 2**. Higher maximum voltages were obtained with aerobic cathodic chambers. For pH of 5, higher voltages were obtained with the lower VSS concentrations, but at pH of 6, the higher VSS concentration allowed obtaining of higher voltages.

The maximum voltages in the bMFCs were lower than those obtained in the MFCs with abiotic cathodic chamber; higher voltage was obtained only in the bMFCs with aerobic cathodic chamber, operated with a VSS concentration of $15\text{ g}\cdot\text{L}^{-1}$ and pH 5. The analysis of the average voltages indicated that there was not statistically significant difference between the values obtained in the MFCs with biocathodes and in MFCs with abiotic cathodes.

3.2 Performance of the biocathode microbial fuel cells at closed circuit

The next operating cycles were performed at closed circuit with resistances of 100 Ohms and the obtained results are presented at **Figure 3** and the maximum voltages obtained at each operational condition are illustrated in **Figure 4**.

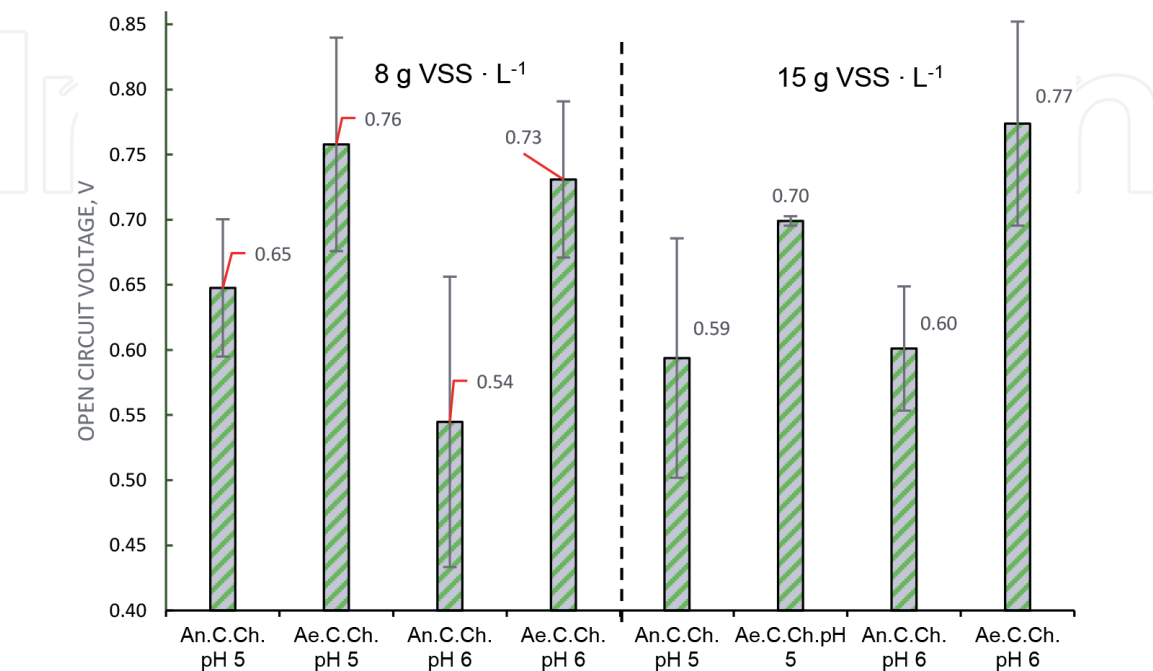


Figure 2.
Maximum voltages reached at open circuit during the first operational cycle.

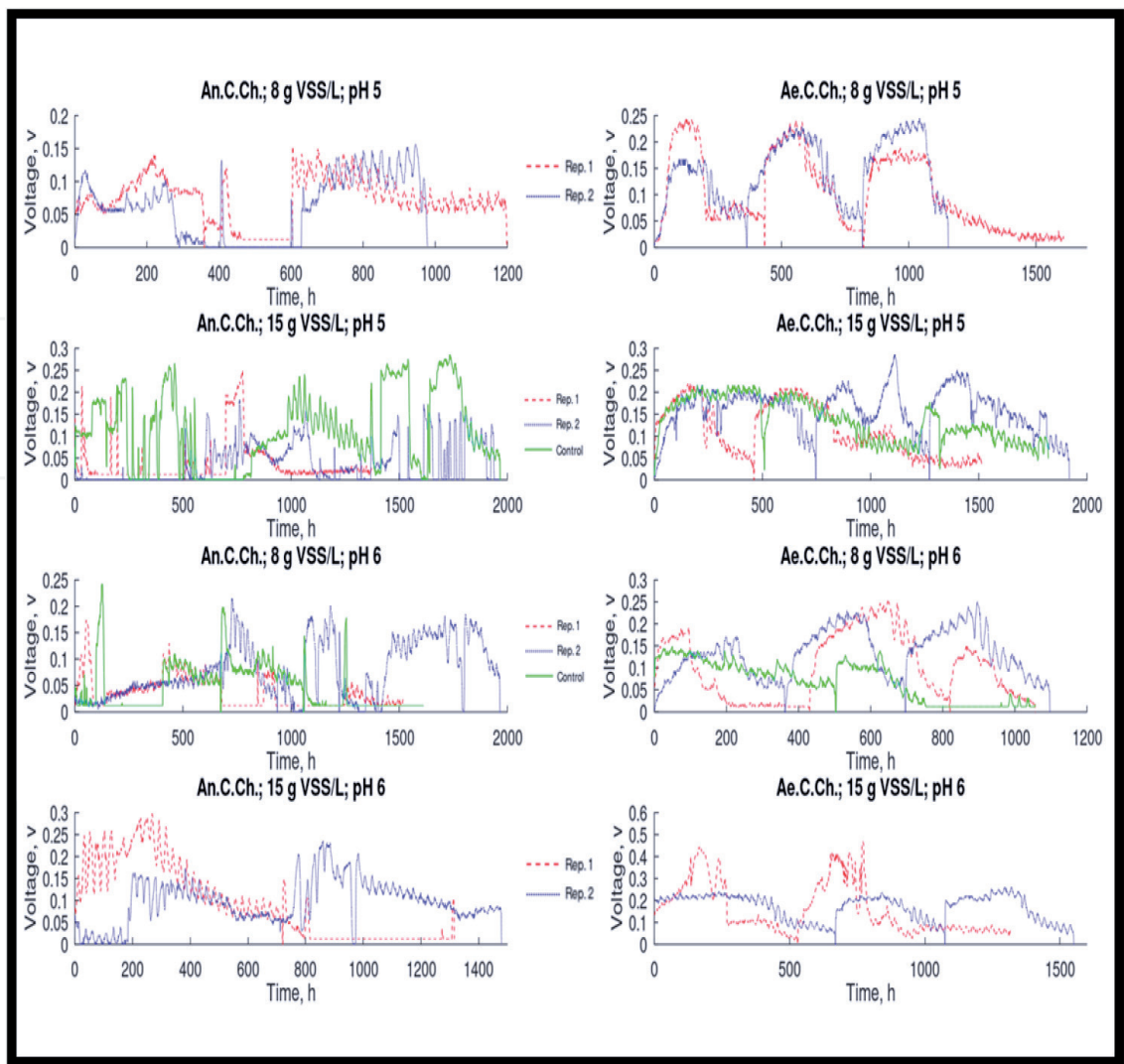


Figure 3.
Obtained voltages in the experimental reactors during the closed-circuit operating cycles.

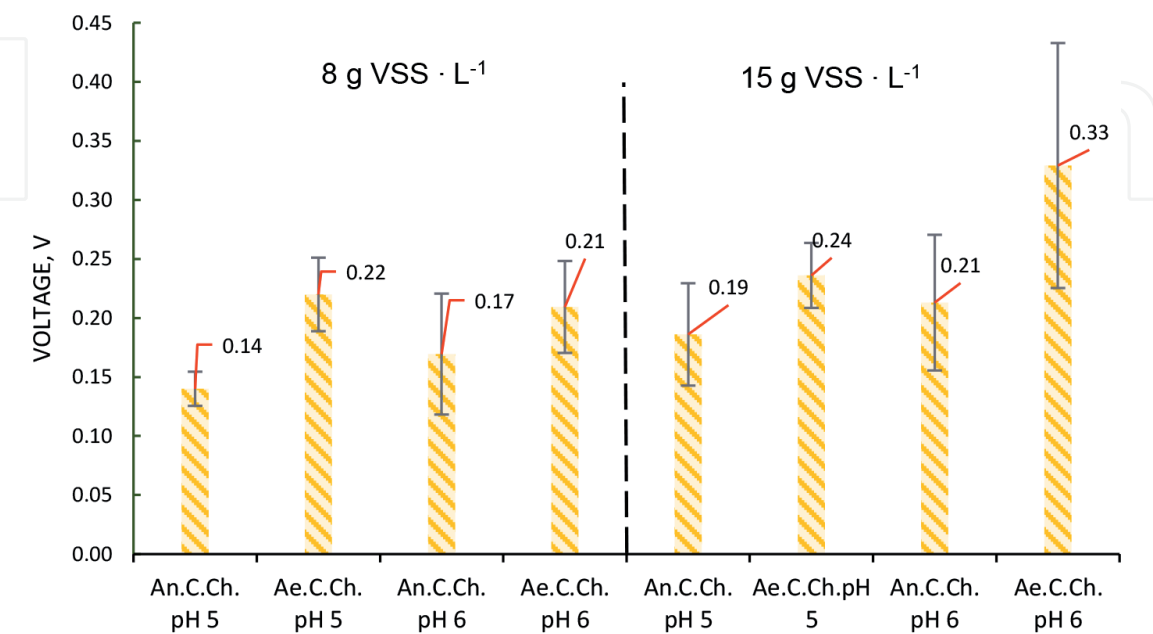


Figure 4.
Maximum voltages obtained during the closed-circuit operating cycles.

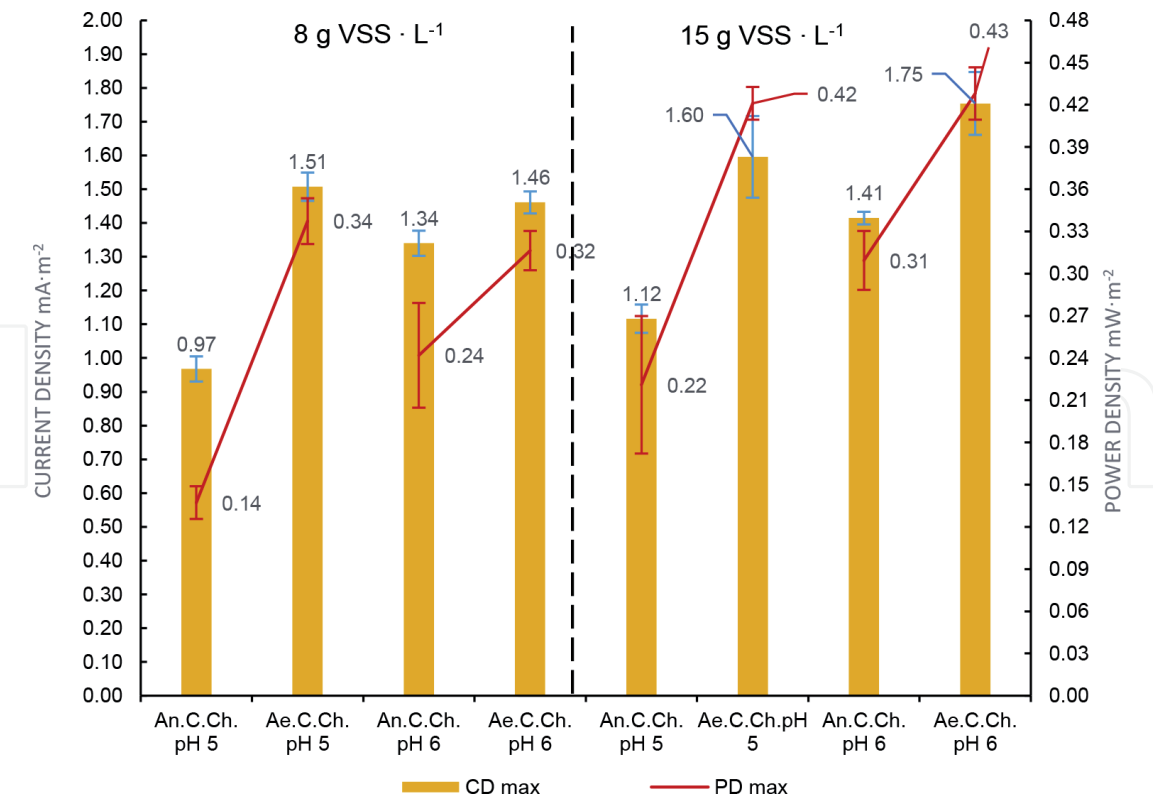


Figure 5.
Maximum volumetric current and power densities achieved during the experiments.

As it can be seen higher voltage were obtained when the oxygen was the final electron acceptor in the cathodic chamber. With respect to the initial concentration of the substrate, the highest VSS concentrations allowed increasing of the obtained voltages. The highest voltages of 0.33 ± 0.03 V were reached with the bMFCs operated with a sludge initial concentration of $15 \text{ g VSS} \cdot \text{L}^{-1}$ and pH of 6.

To corroborate the statistical difference between the effects of each of the factors on the response variables, volumetric power density (PD) and volumetric current density (CD), regression analysis and ANOVA were carried out. The analyzed data regarding volumetric power density and current density are shown in **Figure 5**. Second order polynomic models were used with determination coefficients (R^2) of 0.925 for PD and 0.922 for CD and adjusted determination coefficient ($\text{adj-}R^2$) of 0.876 for DC and 0.87 for DC, which indicated a good capability of the models to predict the responses within the proposed experimental ranges. There is statistically significant difference between the results obtained with different type of cathodic zones, being the aerobic one that allowed obtaining of higher values for both, PDmax and CDmax, compared with the determined in the reactors with anaerobic cathodic zone (**Figure 6**). The effects of the VSS concentrations and pH values were much lower, but statistically significant, greater results were obtained using sludge with higher VSS concentration (of $15 \text{ g} \cdot \text{L}^{-1}$) and higher pH (pH of 6). The lowest effect on PD was the one of pH and on CD was the one of VSS concentration.

A comparison of the electrical power generation in bMFCs and in MFCs with abiotic cathode is presented in **Figure 7**. As it can be observed, higher DCmax and PDmax were obtained in bMFCs with aerobic cathodic chambers operated with $8 \text{ g VSS} \cdot \text{L}^{-1}$ and pH of 6. However, based on the average values, it was obtained that the difference is not statistically significant for PD (p-value = 0.116059), but it is significant (p-value of 0.0874862) for CD, in favor of the system that used biocathode, applying alpha value of 0.1. Statistical t-tests performed for the case of bMFCs

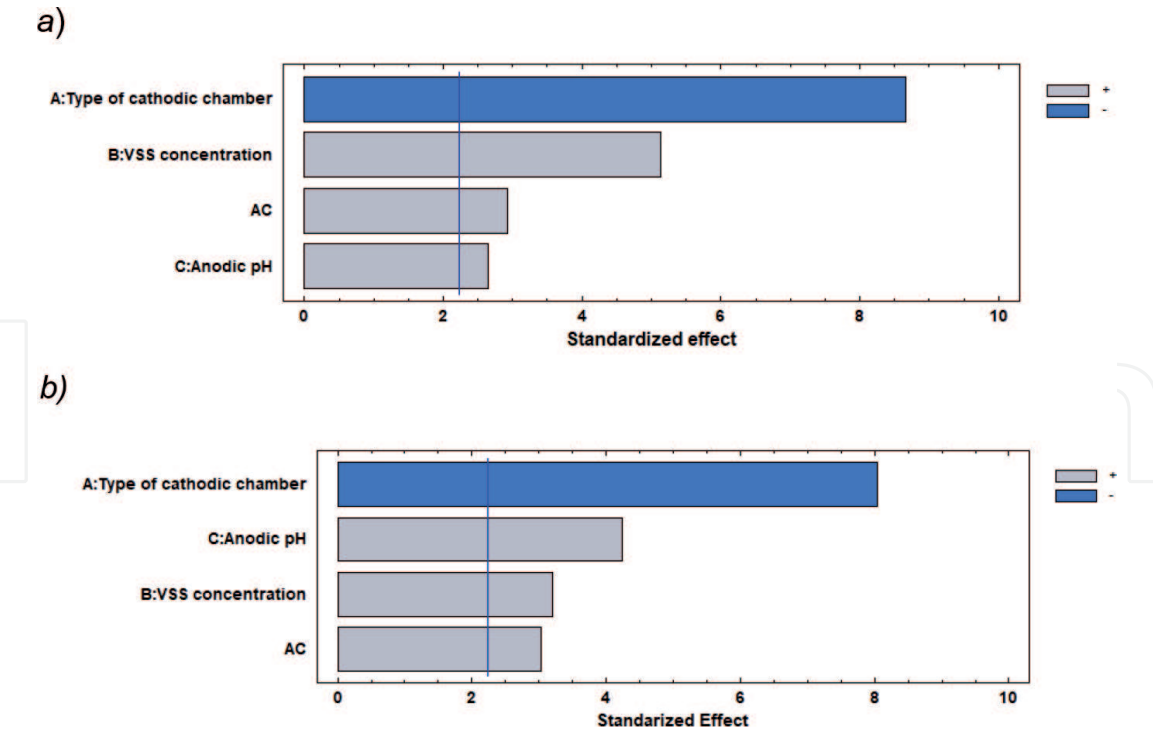


Figure 6. Standardized Pareto diagrams for PD (a) and for CD (b). For the cathodic zone chamber, the blue color represents the effect of Ae.C.Ch.

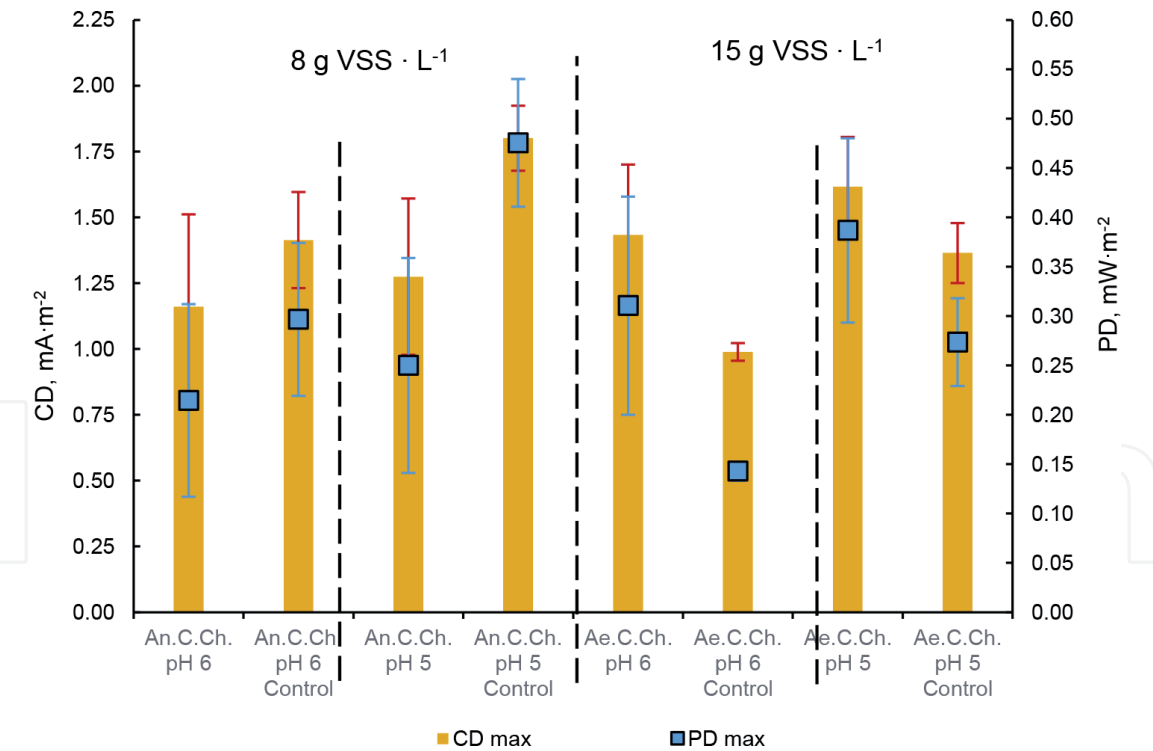


Figure 7. Comparison of power generation with respect to abiotic cathode controls.

with aerobic cathodic chambers and MFCs with abiotic cathode, operated with 16 g VSS · L⁻¹ and pH of 5, showed that there is no statistically significant difference between the results with and without biocathodes for both variables (p-value > 0.1). For bMFCs with anaerobic cathodic chambers operated with 8 g SSV · L⁻¹ and pH of 6, the statistical tests indicated that there was not statistically significant difference between the use of abiotic cathode or biocathode (p-value > 0.1). However, for

bmFCs with anaerobic cathodic chambers operated with $16\text{ g SSV}\cdot\text{L}^{-1}$ and pH of 5, the values of both PD and the CD were lower than the obtained in the MFCs with abiotic cathode (p-value of 0.0302892 and 0.0455172 respectively) with a 90% of confidence.

3.3 Organic matter removal and Coloumbic efficiency

The average TCOD and VSS removals determined in the anodically processed sludge, and the coulombic efficiencies obtained using different initial pH and VSS concentrations, and in bmFCs with aerobic and anaerobic chambers, are illustrated in **Figure 8**. As it can be seen the obtained TCOD and VSS removals were higher than 75%, reaching values up to 92%, which indicates that the sludge stabilization process was successful in all the operational conditions.

Based on the obtained results for TCOD removal, the empirical relationship between the response and variables was expressed by a polynomial equation, with determination coefficient (R^2) of 0.997 and adjusted determination coefficient ($\text{adj-}R^2$) of 0.982, which indicated a good capability of the model to predict the response within the proposed experimental ranges. The calculated effect analysis, with a 96% of confidence and a factor of significance (p) of 0.04, indicated as the most significant factor the interaction of pH with the concentration of VSS, both with positive effects.

For the VSS removal, the model had $R^2 = 0.999$ and $\text{adj-}R^2$ of 0.997, and with a 97% of confidence, the initial VSS concentration had the major effect, followed by the pH. There was not statistically significant effect of the type of the cathodic zone. There was a statistically significant difference between the VSS removals obtained with different initial VSS concentrations ($p = 0.03$) and with different initial pH values in the anode chamber, being p of 0.04 and 0.03 respectively. There was not statistically significant difference between the results obtained in bmFCs with different type of cathodic zone.

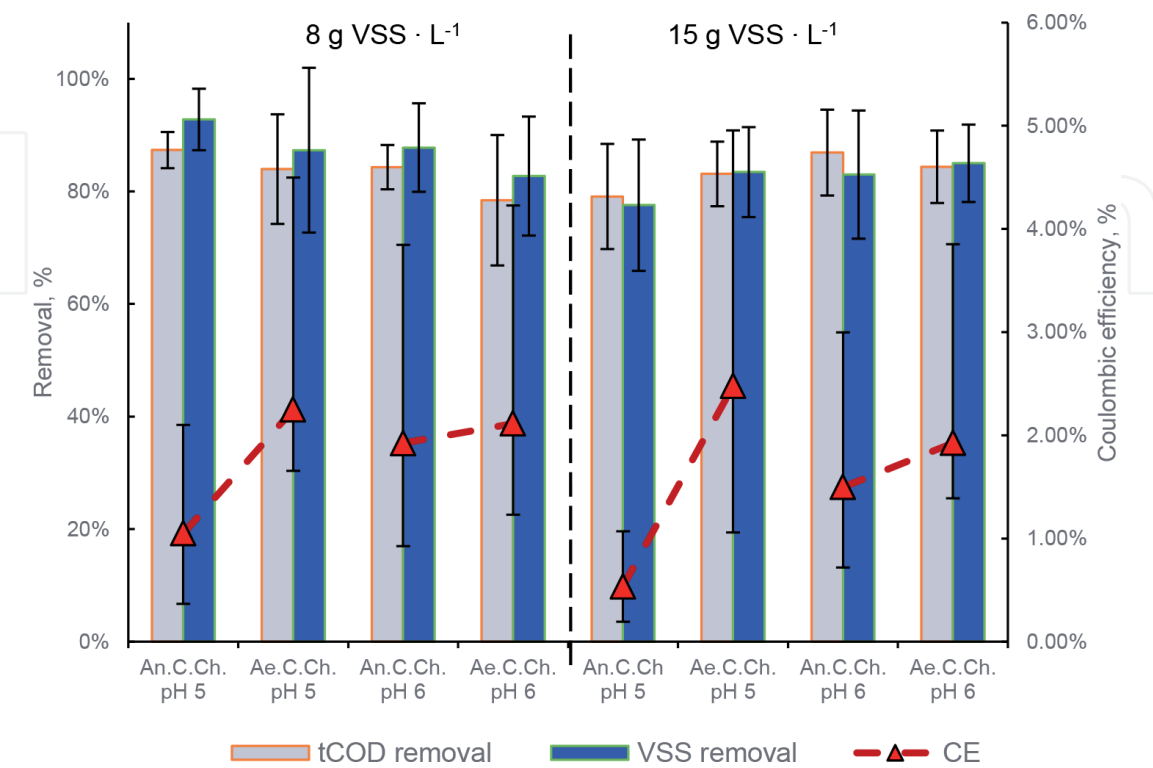


Figure 8.
TCOD and VSS removals, and coulombic efficiencies obtained in the experimental bmFCs.

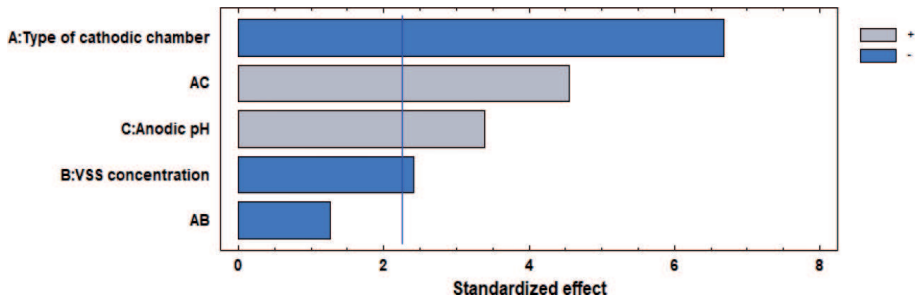


Figure 9.
Standardized Pareto diagrams for CE.

The performed statistical analysis for the Coulombic Efficiency (CE) using a model with R^2 of 0.975 and $\text{adj-}R^2$ of 0.941, indicated that the factors which strongly influenced CE are the type of cathodic zone and the initial pH (**Figure 9**). The use of aerobic cathodic zone and initial pH of 6 allows obtaining of better coulombic efficiencies. The highest coulombic efficiency averages reached in the bMFCs were 2.1–2.3%. These results are lower than those reported by Zhang et al. [18], who reached CE up to 19.4%, although with removals of TCOD up to 40.8%, using a double chamber MFCs with sludge as anodic substrate and biocathodes. On the other hand, the obtaining of small CE values with high COD removals indicates that the electrons released from the organic matter were consumed by processes other than those carried out by electrogenic biofilms, such as fermentative and methanogenic biofilms [24]. This is also consistent with the results obtained by Freguia et al. [25], who indicated that fermentation and methanogenesis are not electrode-dependent reactions, so they could occur with any external resistance as long as the redox potential in the solution is low enough and there are bacteria present that derive more energy from these processes than from electrode-driven oxidation of the substrate. Further research is needed to better understand competitive microbial processes such as exoelectrogenic, biomass growth, fermentative, and methanogenic at the anode to minimize their effects and increase power generation and CE.

3.4 Electrochemical performance of the bMFCs

Polarization curves and power curves generated in the experimental bMFCs are presented in **Figures 10** and **11** respectively. The values of maximum power (P_{max}), internal resistance (IR) and open circuit voltages, obtained from the figures are reported in **Table 3**. The graphs indicated that bMFC with aerobic cathodic chamber, initial sludge VSS concentration of $15 \text{ g} \cdot \text{L}^{-1}$ and pH of 6 was the one who obtained the highest open circuit voltage (553 mV), as well as the highest maximum PD of $0.21 \text{ mW} \cdot \text{m}^{-2}$ at a CD of $0.55 \text{ mA} \cdot \text{m}^{-2}$. The maximum power in the rest of the bMFCs was $0.05\text{--}0.15 \text{ mW} \cdot \text{m}^{-2}$ with current densities of $0.25\text{--}0.60 \text{ mA} \cdot \text{m}^{-2}$. The maximum CD up to $0.67 \text{ mA} \cdot \text{m}^{-2}$ and PD of $0.14 \text{ mW} \cdot \text{m}^{-2}$ was reached with the lowest applied resistance (46 Ohms) in bMFC with anaerobic cathodic chamber, initial sludge VSS concentration of $15 \text{ g} \cdot \text{L}^{-1}$ and pH of 5. These values are lower than with the reported for MFCs with similar structural and biotic characteristics which reached 38 mW m^{-2} [26], 43.6 mW m^{-2} [27].

The results of **Table 4** show that for all reactor configurations, both, the internal resistance, and the open circuit voltages (OCV) were higher when the aerobic cathodic chamber was used. For the case of maximum power density, the results do not show a clear pattern that could help relate the configuration to the observed result.

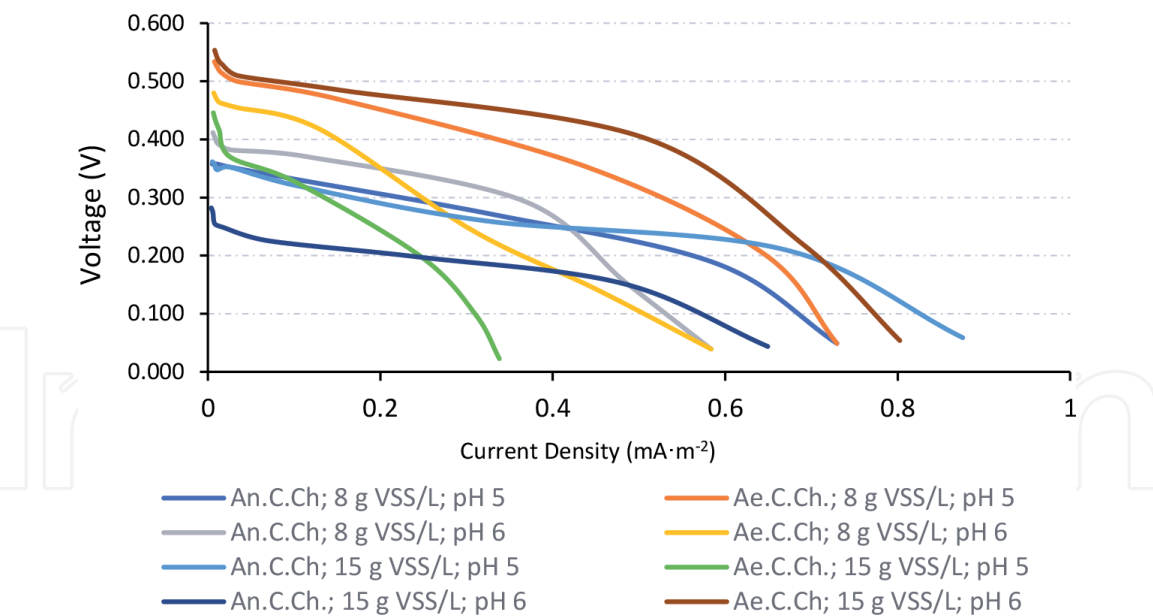


Figure 10.
Polarization curves.

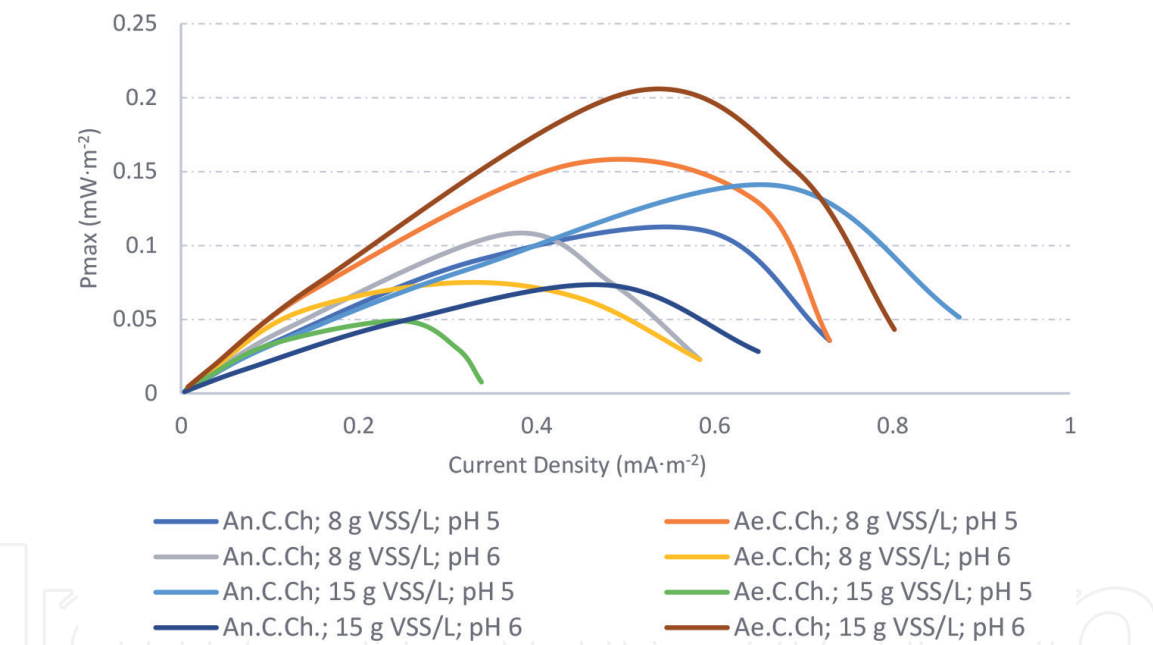


Figure 11.
Power curves.

The voltamperogram generated from all evaluated operating conditions is shown in **Figure 12**. In green, the operating conditions that included Aerobic Cathodic Chamber (Ae.C.Ch.) and in purple those that included Anaerobic Cathodic Chamber (An.C.Ch.). It was also found that at the potentials -800 mV and 800 mV the maximum and maximum current densities of $-21.1\text{ }\mu\text{A}\cdot\text{cm}^{-2}$ and $7.11\text{ }\mu\text{A}\cdot\text{cm}^{-2}$ were achieved (corresponding to -307.9 and 103.8 mA shown in the graph) respectively. These values correspond to the Ae.C.Ch. configuration; $8\text{ g VSS}\cdot\text{L}^{-1}$; pH 6 and agree with the previous analysis for CD_{max} where the type of cathodic zone and the pH have significant effects. The shape of the graph agrees with what is observed in [28] where the reduction of oxygen shows the fall of the curve on left section. Under anaerobic conditions this does not happen as markedly since nitrogen has a lower oxidation capacity than oxygen.

bMFC	R_{int} (Ohms)	PD_{max} ($mW \cdot m^{-2}$)	OCV (mV)
An.C.Ch; 8 g VSS/L; pH 5	223.920	0.110	357.0
Ae.C.Ch; 8 g VSS/L; pH 5	498.200	0.150	534.0
An.C.Ch; 8 g VSS/L; pH 6	207.990	0.110	412.0
Ae.C.Ch; 8 g VSS/L; pH 6	484.430	0.070	480.0
An.C.Ch; 15 g VSS/L; pH 5	97.360	0.140	361.0
Ae.C.Ch; 15 g VSS/L; pH 5	1081.320	0.050	446.0
An.C.Ch; 15 g VSS/L; pH 6	132.410	0.070	282.0
Ae.C.Ch; 15 g VSS/L; pH 6	154.250	0.210	553.0

Table 4.
Internal resistance, OCV and maximum power density.

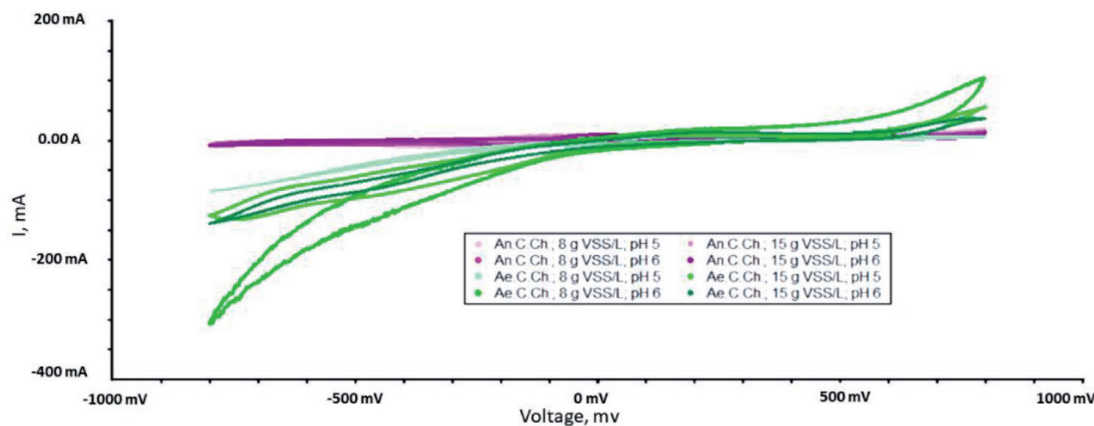


Figure 12.
Cyclic voltammetry obtained in the experimental bMFCs.

4. Conclusions

This study showed that it is possible to stabilize successfully secondary sludge with VSS concentration up to $15 \text{ g} \cdot \text{L}^{-1}$ using microbial fuel cells with biocathodes. The highest organic matter removals reached in the anode chamber, up to 92%, indicates a very good microbial activity in the anodic chambers. The statistical analyses of the obtained results indicated that the kind of the anodic chamber, the variations of VSS concentration in the secondary sludge between 8 and $15 \text{ g} \cdot \text{L}^{-1}$, as well as the variations of pH between 5 and 6 do not influenced significantly the organic matter removal.

The simultaneous generation of electricity is possible together with the degradation of organic matter, which contributes to the sustainability of this method. The bio-cathodic microbial fuel cells with aerobic cathodic chambers allows obtaining of higher voltages, current densities, power densities and coulombic efficiencies compared with the microbial fuel cells with anaerobic cathodic chambers (up to 450 mV, $0.43 \text{ mW} \cdot \text{m}^{-2}$, $1.80 \text{ A} \cdot \text{m}^{-2}$ and 4% respectively).

The effects of the VSS concentrations and pH values were much lower than the type of the cathodic chamber, but statistically significant, greater results were obtained using sludge with higher VSS concentration (of $15 \text{ g} \cdot \text{L}^{-1}$) and higher pH (pH of 6). The lowest effect on the power density was the one of pH and on the current density was the one of VSS concentration. The best configuration for operating MCCs varied according to the parameter of interest that is desired as a response

variable. For the power density, the best configuration is aerobic cathodic chamber, 15 g VSS·L⁻¹ and sludge pH of 5. For the current density the best configuration is aerobic cathodic chamber, 15 g VSS·L⁻¹ and pH of 6. For the case of the coulombic efficiency, the best configuration is aerobic cathodic chamber, 8 g VSS·L⁻¹ and pH of 6,

The performance comparison of the microbial fuel cells with biotic and abiotic cathodes indicated that there was not statistically significant improvement of the response parameters, and there was even a configuration (anaerobic cathodic chambers, 16 g SSV·L⁻¹ and pH of 5) for which better results were obtained with abiotic cathode.

The electrochemical tests confirmed that the configuration with aerobic cathodic chamber, initial sludge VSS concentration of 15 g·L⁻¹ and pH of 6 was the one who obtained the highest open circuit voltage (553 mV), as well as the highest maximum power density of 0.21 mW·m⁻² and current density of 0.55 mA·m⁻². The internal resistance and the open circuit voltages were higher when the aerobic cathodic chambers were used.

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