AMMONIUM-BASED POLYMER IONIC LIQUID MEMBRANE FOR WASTEWATER TREATMENT AND BIOENERGY PRODUCTION

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Abstract.

Air-breathing cathode microbial fuel cells (MFCs) fed with citrus juice processing wastewater were employed for bioenergy production and simultaneously for wastewater treatment. Polymer inclusion membranes based on the ionic liquid methyltrioctylammonium chloride were tested as separator in this microbial fuel cell assembly. Regarding the wastewater treatment capacity, the evolution of the chemical oxygen demand (COD) removal over time reaches a maximum value of45 %. In addition to COD removal, an electrochemical characterization of the wastewater before and after being treated was also performed. Despite this type of feedstock not being ideal for bioenergy production in air-breathing cathode MFCs due to the acidity of the substrate, enough amount of bioenergy is produced to consider this technology a suitable alternative for reusing citrus juice processing wastewater.

Keywords: Bioenergy, ionic liquid, microbial fuel cell, polymer inclusion membrane, wastewater treatment

1. Introduction

Society and scientific community are deeply aware of dealing with two of the most important global challenges: water scarcity in many countries and depletion of fossil fuels. Shortage of water supplies and water scarcity are two issues which are affecting more and more people around the world. In the coming years, it is expected an increase of the water scarcity and fresh water sources due to the increment of the world population. The lack of safe drinking water has devastating consequences for human beings such as the emergence of new diseases as well as a large impact on economy. For these reasons, big efforts have been made to develop effective and low-cost methods for water treatment [1–3].

On the other hand, both the depletion of fossil fuels and their contribution of carbon dioxide to the atmosphere have promoted the development of more efficient bioenergy sources [4]. In this context, microbial fuel cells (MFCs) have demonstrated to be a promising technology for addressing the current energy crisis and the water scarcity in underdeveloped countries. MFCs use bacterial microorganisms to oxidize the organic matter contained in a substrate for dual function, namely, bioelectricity production and wastewater treatment. Their main advantage versus other technologies for bioenergy production is the direct production of electricity from the oxidation of the substrate, low operation temperatures, and they do not require any energy input. Regarding the conventional wastewater treatments such as anaerobic digestion, MFCs produce less amount of sludge [5, 6]. The current applications of this technology are still at laboratory scale, however, MFCs proved to be suitable for industrial applications. Big efforts have been made in recent years to improve this technology. A better understanding of the mechanisms of electron transfer, the use of low-cost materials, and the design of novel MFC assemblies have promoted their large-scale applications [7]. Although simple substrates such as glucose or acetate have been widely employed to optimize this technology, the most interesting application of MFCs is their application for wastewater treatment. The use of complex substrates such as domestic or industrial wastewater allows MFCs to produce bioenergy from low-cost and abundant substrates [8]. Until now, different complex substrates employed so far as fuel in MFCs are: domestic wastewater and brewery [9], swine wastewater [10], lignocellulosic biomass industry output [11], brewery wastewater [12], synthetic wastewater [13], starch processing wastewater [14], dye wastewater [15], landfill leachates [16], and slaughterhouse wastewater [23].Ionic liquids (ILs) are organic salts which melt at temperatures below 100 C. They usually consist on an inorganic anion and an organic cation. In recent years, these compounds have gained much attention in a wide variety of research fields due to their special properties. Their near-zero vapour pressure, long-term stability, high conductivity, and the possibility of modifying their properties by varying the anode and cathode structure have made possible their application in several types of research works. ILs are considered as a green alternative to conventional organic solvents [17, 18].In this work, polymer inclusion membranes based on ILs have been employed as separator in aircathode single-chamber MFCs fueled by citrus juice processing wastewater. This type of membranes has showed good results in MFCs fed with domestic wastewater and oil industry wastewater [19, 20]. The performance of MFCs has been evaluated in terms of power output and wastewater treatment capacity, analyzing the evolution of chemical oxygen demand (COD), total suspended solid (TSS), nitrite, orthophosphate, and ammonium sulfate in the substrate during the process.

2 Materials and Methods

2.1 Reagents

The casting method was employed to prepare polymer inclusion membranes based on methyltrioctylammonium chloride, [MTOA+][Cl–]. Polyvinylchloride (PVC) was used as polymeric network to retain the IL in the membrane. Both reagents were provided by Sigma Aldrich S.L. Each membrane contains 70 wt% IL [19].

2.2 Experimental Setup

The air-breathing cathode MFC assembly used consists of a single-chamber glass reactor. The anode is a combination of graphite granules where the biofilm grows, and a graphite rod which collects the electrons produced during the organic matter oxidation. The cathode is made of carbon cloth coated with a platinum spray, which catalyzes the oxygen reduction reaction (ORR). The system was loaded with an external resistance of 1 kΩ, which closes the circuit (Fig.1).

The temperature was set at 25 °C and the tests were performed during 217 h. Additional reactors to the MFCs were used simultaneously. Reactors named as baseline contain both carbon granules for biofilm support and wastewater, without any external load. Otherwise, control reactors only contain wastewater. In this case, the conditions were the same than in traditional anaerobic digestion. They served to compare the wastewater treatment capacity of MFCs with that obtained in conventional anaerobic digestion with and without any biofilm support.

2.3 Wastewater Characterization

Wastewater from industrial lemon juice processing with an initial content of chemical oxygen demand (COD) of 2440 mg L^{-1} was used as substrate for bioenergy production. A chemical characterization of the wastewater employed was performed before and after its use as fuel in the MFCs. COD removal was determined at 24, 48, 72, and 217 h of operation following the AFNOR method T90-101. A spectrophotometer Spectroquant Nova 30 (Merck) was used for determining this parameter.

Soluble COD removal (CODR) is defined as the ratiobetween the total COD consumed during the process and theinitial COD (COD0). The consumed COD is the differencebetween the value at the beginning of the process and the valueat a given time (t) (CODt) according to Eq. (1):

$$COD_R(\%) = \frac{([COD]_0 - [COD]_f}{[COD]_0} \times 100$$

Total suspended solids, hardness, alkalinity, and ion analysis were determined by AFNOR standard methods [20, 21].

2.4 Polarization and Power Curves

Once MFCs reach the steady state in terms of voltage response, polarization and power curves were determined by varying the external loading between 11MO and 1O by using a variable resistor box [22]. The current (I) and power densities (P) were calculated according to the equations I = V(cell voltage)/R (externalresistor) and P =V2/R, and then normalized to anode capacity.

2.5 Coulombic Efficiency

Coulombic efficiency is defined as the electricity produced from the organic matter oxidation versus the maximum possible recovery [22]. This parameter can be determined as the ratio between the coulombs transferred to the anode from the substrate and the maximum coulombs transferred if the whole substrate was able to produce current electricity.

$$Y_Q = \frac{coulombs\ produced}{total\ theoretical\ coulombs} \times 100$$

The integral of the current over time allows determining the total coulombs obtained. Therefore, the coulombic efficiency (Y_Q) for an MFC working during a period of time (t) in fed batch mode is calculated by:

$$Y_Q = \frac{M_m \int_0^t i(t)dt}{F \cdot \Delta COD \cdot b \cdot V} \times 100$$

where M_m is the molecular mass of oxygen (32 g mol^{-1}), i(t) is the rated current (Cs^{-1}), F is the Faraday constant (96 485 C mol $electrons^{-1}$), ΔCOD is the variation of COD during time t ($COD_{initial}$–COD_t), b denotes the moles of electrons produced per mole of oxygen (b = 4), and V is the volume of liquid in the anodic chamber (0.25 L).

2.6 SEM-EDX Characterization

In order to study the morphology, chemical composition, and distribution of the most important chemical elements contained in the membranes, a scanning electron microscope Hitachi S-3500Ncoupled to an analyzer Brucker AXS X-ray were employed. Scanning electron microscopy (SEM)and energy dispersive X-ray (EDX) analysis of the IL-based membranes prepared were performed before and after being used as separator in MFCs.

3 Results and Discussion

3.1 Citrus Juice Processing Wastewater

Treatment Capacity of [MTOA+][Cl–]-Based MFCs

The evolution of the COD removal by[MTOA+][Cl–]-based MFCs fed with citrus juice processing wastewater is illustrated in Fig. 2. After 24 h of operation, MFCs remove 12.5% of COD, increasing over time. The maximum value of COD removal (44 %) is reached after 217 h. Due to the specific properties of the feedstock employed, e.g., very low pH, the maximum COD removal is about half of that obtained in MFCs fed with other types of wastewater [19, 23].Regarding the COD removal by conventional anaerobic digestion (control and baseline tests), the values follow the same trend as those obtained by MFCs, increasing over time. From the beginning of the process until 72 h of treatment, the COD removal by control and baseline tests is similar in both cases, being more different at 217 h of treatment. This difference could be due to the fact that graphic granules (controls)improve the growth of the microorganisms and consequently the water depuration. Both control and baseline tests reach lower values of this parameter than MFCs during the whole process. These results demonstrate that the MFC reactor[MTOA+][Cl–]-based membrane enhances the wastewater treatment capacity of the devices in comparison with conventional anaerobic digestion. Polymer inclusion membranes based on ILs favour the proton exchange between the anode and the cathode which improve the performance of MFCs in terms of wastewater treatment. Moreover, operating the reactors as MFCs enhances the biofilm growth, which also promotes the COD removal.

Additionally to the COD evolution, other physicochemical parameters were also monitored. Tab. 1 summarizes these parameters in the substrate before and after the treatment in MFCs, control reactors, and baseline reactors. The pH of the feedstock increases after its treatment in MFCs. This is the normal behaviour of this type of fuel cells. The increase of the pH demonstrates that the protons produced during the organic matter oxidation are not accumulated in the anode, meaning that the [MTOA+][Cl–]-based membrane facilitated the proton transfer from the anode to the cathode. The high pH of the anodic chamber may affect the metabolic activity and, therefore, the mechanism of proton and electron production from electroactive bacteria.

Regarding the speciation of the main ions contained in thefeedstock, 20.5% and 28.16% of ammonium and sulfates, respectively, are reduced. By contrast, the reduction of nitrites and ortophosphates reaches higher values, i.e., up to 55.3%and 85.7 %, respectively. The significant decrease in orthophosphate content may be due to the conversion into organic phosphates by the biofilm. In the case of nitrites and sulfates, they can be used by bacteria to grow and they can also act as oxygen donor in the absence of oxygen. The reduction of these parameters is more evident when the reactors are working as MFCs because oxidation of organic matter and biofilm growth are quicker than in control and baseline reactors.The same trend is observed in the evolution of Kjeldahl nitrogen. MFCs allow this parameter to be reduced up to28.57 %, i.e., a higher percentage compared to the control and baseline reactors. Furthermore, changes in baseline values are more pronounced than in the control because the graphic granules in baseline experiments improved the growth of the microorganisms in the reactor. Higher values of TSS are found in MFCs. This carbonaceous material favours the biofilm growth around it, which can also be detached from the granules, increasing the amount of TSS. In the case of chloride, this parameter varies slightly. Considering MFCs, this variation is probably caused by the release of a small amount of ILs to the media.

3.2 SEM-EDX Characterization of the [MTOA+][Cl–]-Based Membrane Used as Separator in MFCs Fed with Citrus Juice Processing Wastewater

In this work, polymer inclusion membranes based on[MTOA+][Cl–] are used for the first time as separator in aircathode single-chamber MFCs fueled with citrus juice processing wastewater. IL-based membranes were characterized before and after being employed as separator by SEM-EDX. The purpose was providing information about the morphology and chemical composition of the membrane. ig. 3 a displays the surface of [MTOA+][Cl–]-based membranes before being used in MFCs. The image depicts a smooth and uniform surface. Once the IL-based membrane is applied as separator in MFCs, its surface becomes mottled (Fig. 3 b).

The grain observed may be due to the deposition of some compounds belonging to the wastewater. Thus, traces of new chemical elements (P, S, Ca, Fe, Zn) were found absorbed in the membranes. In the case of oxygen, a higher concentration was detected in the membrane surface after usage which may be due to the absorption of citric acid or others carboxylic compounds in the membrane. Fig. 4 describes the evolution of the characteristic compounds of the membrane before and after being employed as separator. The peak related to chloride decreases after usage as separator. This might be due to the fact that a small amount of IL is released to the medium because the polymeric matrix which also contains chloride is not water-soluble. These results are in line with those presented in Tab. 1 which point to a little increase of chloride in the MFC medium.

3.3 Bioenergy Production

The evolution of the voltage over time is depicted in Fig. 5. During the first 24 h, the voltage decreases to 80mV due to the rupture of the long-chain molecules of the substrate. Furthermore, the low pH of the feedstock could slow down the bacteria metabolism and, therefore, the oxidation of organic matter. After that period, an exponential increase of the voltage followed by a plateau is detected where this parameter is maintained around 100mV. Despite obtaining stable values, these are lower than those reached by using domestic wastewater, probably due to specific characteristics of the feedstock [23].The voltage achieved indicates lower bacterial activity than using wastewater with higher values of pH. The polarization and power curves of the MFCs after the system reached the steady state are illustrated in Fig. 6. The maximum power output by MFCs fed with citrus juice processing wastewater was 31 mW m^{-3} anode at a current density of 400 mA m^{-3} anode. The internal resistance of the system corresponding to this point is 4.12 kW. Khan and Obaid [24] compared the electricity production by different devices fed with waste citrus fruit, namely, by galvanic cell, fuel cell, and microbial fuel cell. They reported that among the waste from lemon, orange, grapefruit, and mixed fruit juice, the substrate which allows double-chamber MFCs to reach the highest power output was lemon fruit, i.e., 0.8mW with E. coli inoculum. In the case of other types of food industry wastes such as fermented apple juice, an inoculum of either anaerobic sludge or compost leachate are required to power an MFC. Cercado-Quezada et al. [25] reported that compost leachate MFCs fed with fermented apple juice reach a maximum power output of 78mWm–2. Fig. 7 shows the coulombic efficiency of the MFCs tested during the process. This parameter increases over time, reaching a maximum around 175 h of operation time. This behavior might be due to the biofilm growth since it is responsible for the organic matter oxidation and therefore, the electricity production. 4

Conclusions

The composition of wastewater from the juice industry necessitates an expensive treatment. In this work, an air-cathode single-chamber MFC based on an IL membrane is applied to treat lemon juice processing wastewater and to produce simultaneously bioenergy. Regarding the wastewater treatment capacity, the setup tested allows for reaching a maximum COD removal of 44% at 217 h of operation time. Other parameters such as Kjeldahl nitrogen, nitrites, ammonium, orthophosphates, sulfates, and hardness were also reduced during the process. In terms of bioenergy production, MFCs working with [MTOA+][Cl–]-based membranes and fed with lemon juice processing wastewater produced a maximum power output of 32 mW m^{-3} anode.

Acknowledgment

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Abbreviations

COD = chemical oxygen demand
IL = ionic liquid
MFC = microbial fuel cell

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Table 1. Comparison of physicochemical parameter pf the citrus processing wastewater before and after treatment.

Water parameter	Method	Initial	Final Values		
			MFC	Baseline	Control
pH	[-]	5.25	6.92	6.59	7.49
TSS, mg L^{-1}	AFNOR 90-105	0.09	0.38	0.16	0.14
COD, mg L^{-1}	AFNOR 90-101	2440	1366	1843	1693
Total phosphate, mg L^{-1}	AFNOR 90-022	1.27	5.08	2.27	5.12
Ortophosphates, mg L^{-1}	AFNOR 90-110	2.17	0.31	2.39	1.42
Kjeldhal nitrogen, mg L^{-1}	AFNOR 90-110	39.20	28.0	36.4	30.8
Nitrites, mg L^{-1}	AFNOR 90-013	0.38	0.17	0.48	0.41
Ammonium, mg L^{-1}	AFNOR 90-015	14.63	11.63	13.89	13.61
Sulfates, mg L^{-1}	Rodier	71.00	51.83	66.83	62.67
Chlorides, mg L^{-1}	AFNOR 90-014	340.8	411.8	340.8	369.2
Hardness, mg L^{-1} $CaCO_3$	Rodier	476	396	476	476
Alkalinity, meq L^{-1}	Rodier	43.6	67.6	71.6	71.6

Figure 1. Single-chamber air breathing cathode MFC assembly.

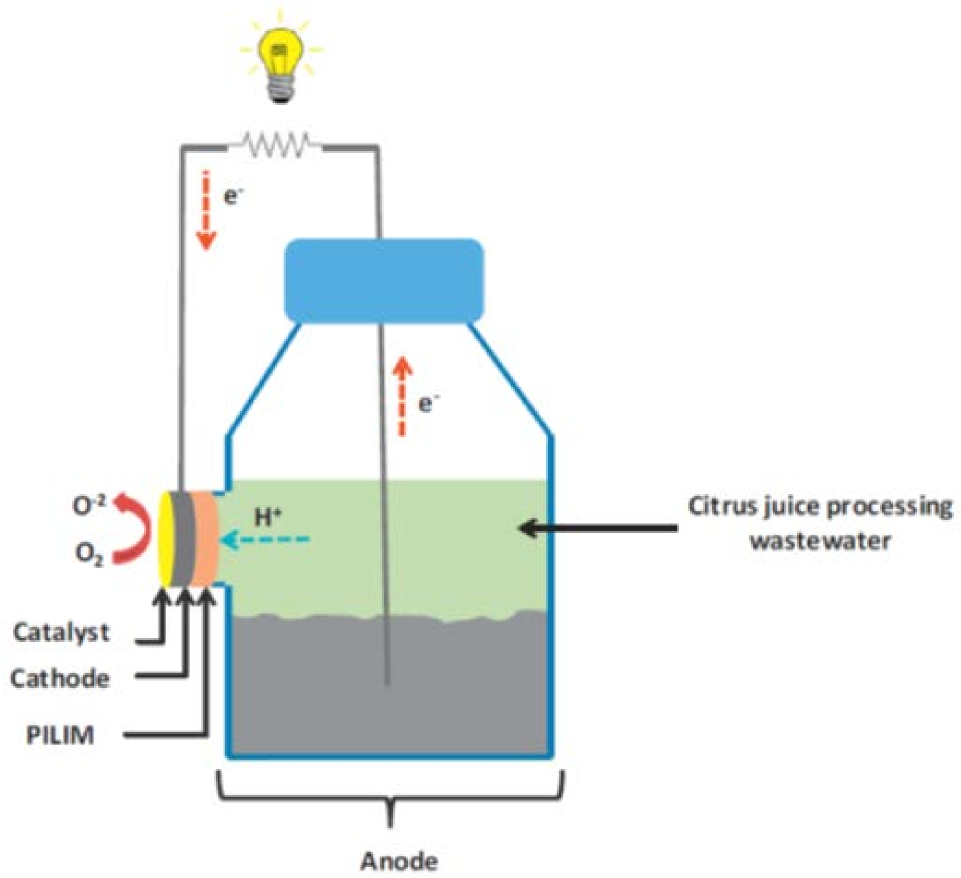

Figure 2. COD removal evolution of the citrus processing wastewater.

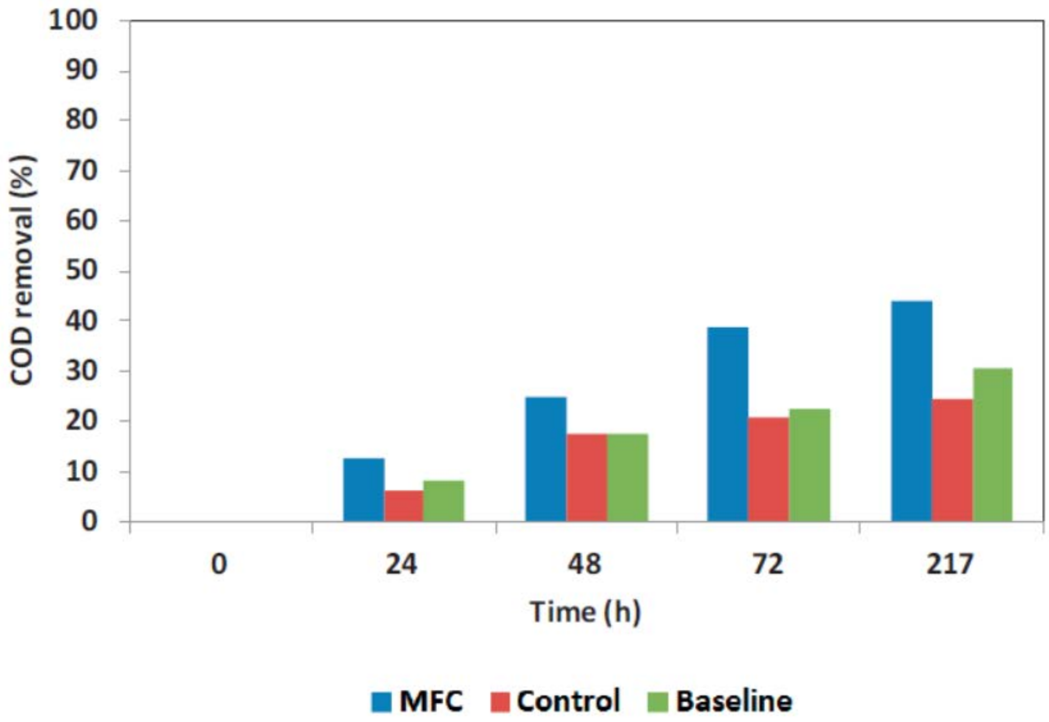

Figure 3. Scanning electron microscopy of [MTOA+][Cl-] based membranes before a) and after b) being used in MFCs.

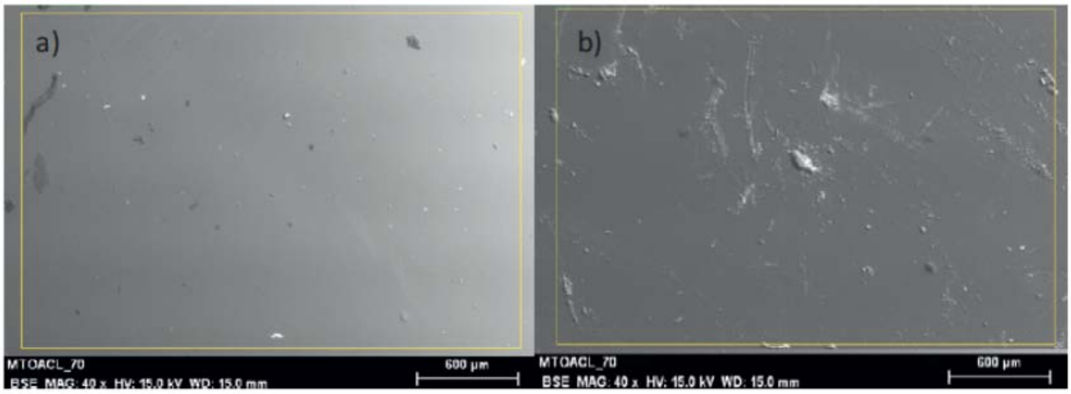

Figure 4. EDX spectrum of the fresh [MTOA+][Cl-] based membrane and the membrane used as separator in MFC.

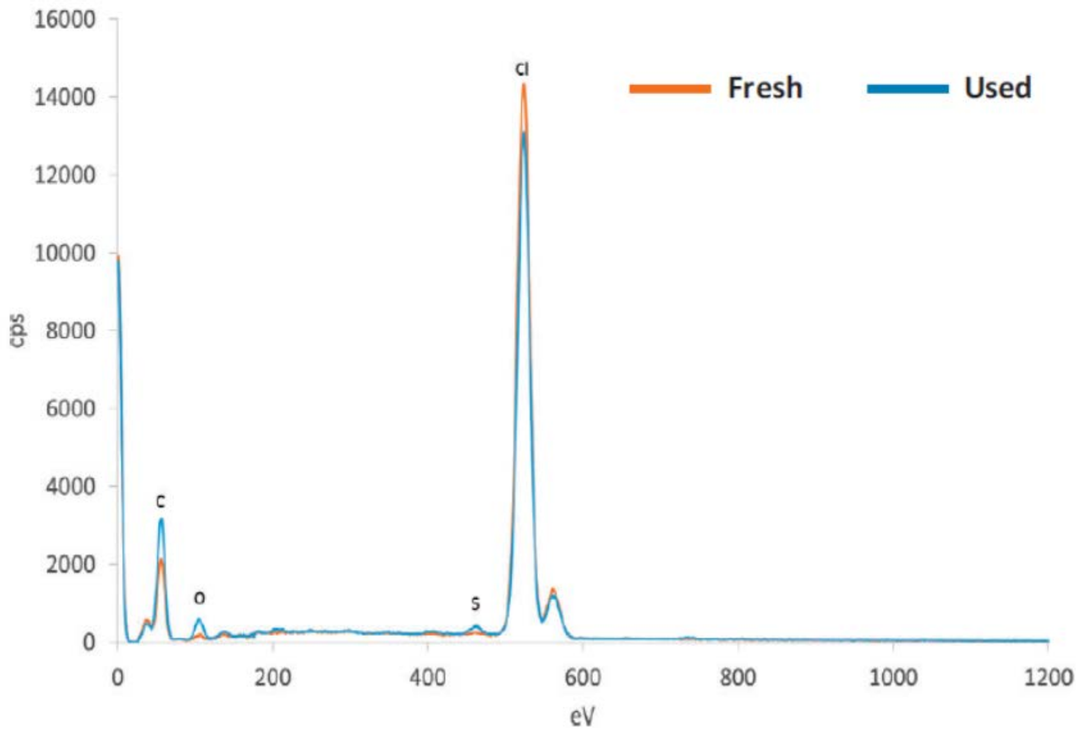

Figure 5. Evolution of the voltage of MFCs working with [MTOA+][Cl-] based membranes and fed with citrus juice processing wastewater.

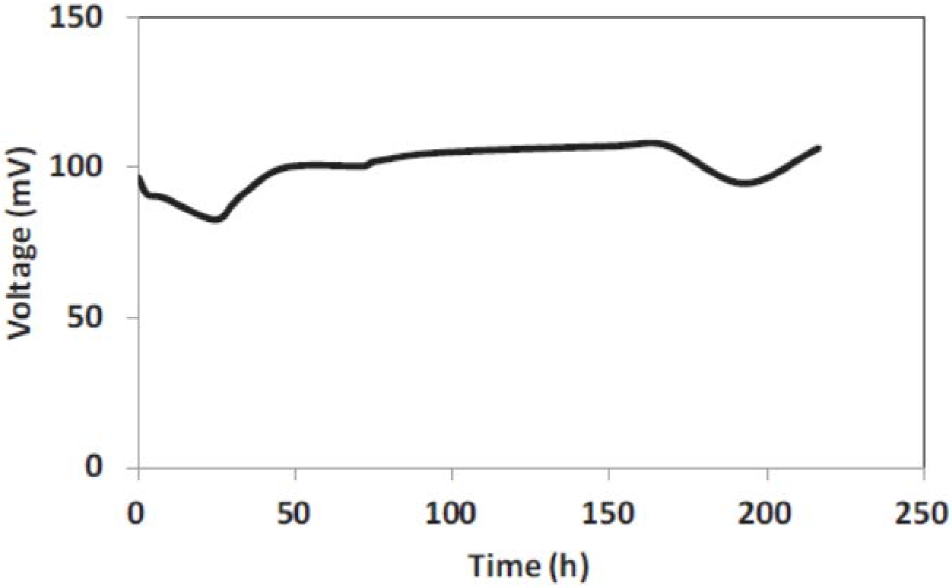

Figure 6. Polarization and power curves of MFCs working with [MTOA+][Cl-] based membranes and fed with citrus juice processing wastewater.

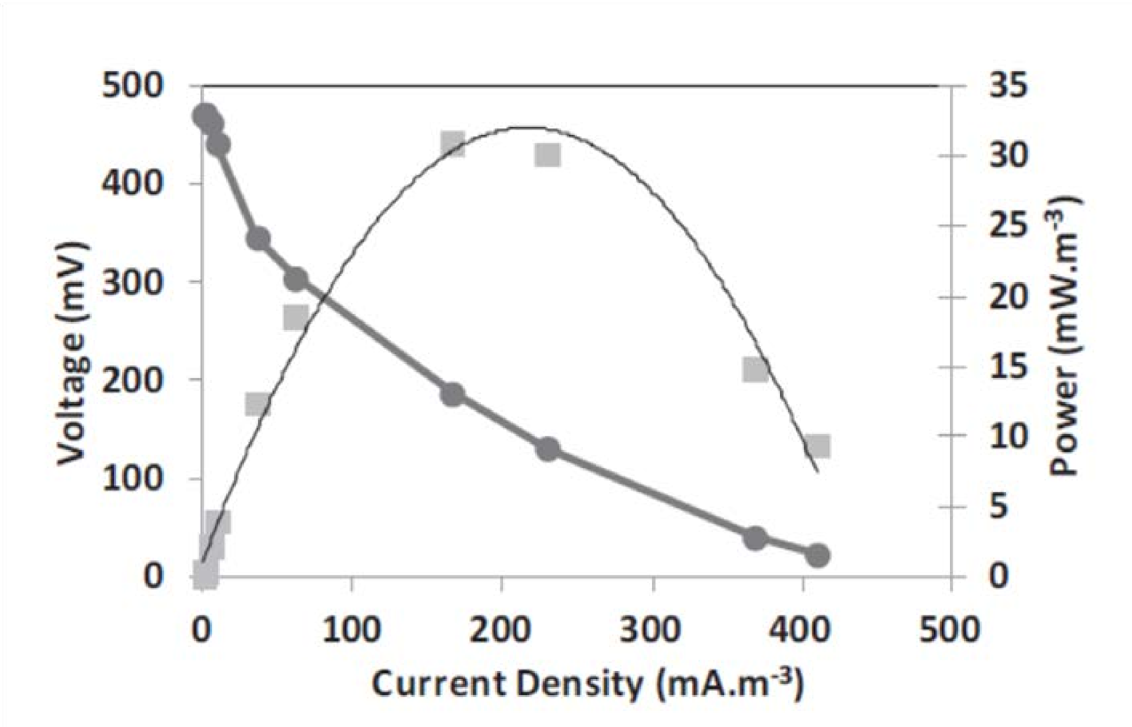

Figure 7. Profile of the coulombic efficiency (Y_Q) of MFCs working with [MTOA+][Cl] based membranes and fed with citrus juice processing wastewater.