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ORIGINAL RESEARCH

On the Effects of Ferricyanide as Cathodic Mediator on the Performance of Microbial Fuel Cells

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Abstract
This study provides an insight into the long-term influence of the use of ferricyanide in the cathode chamber of a microbial fuel cell (MFC) on the power generated and the COD removal attained. Two MFCs were operated in semicontinuous mode, using winery wastewater as fuel, activated sludge as the anodic inoculum, and concentrations of 0.05 and 0.25 M of ferrocyanide added in the cathode chamber as redox mediators. The MFC used had two chambers separated by a proton exchange membrane Sterion®. The results show that permeability of the membrane to mediators is a factor of the major significance. Under no crossover, the mediator produced a positive effect on the electricity generation and COD removal. However, as the experiments progressed, a significant concentration of mediator was detected in the anode chamber and the performance of the MFC gets worse. This work reports results that help to understand the main processes happening in the MFC.

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Highlights

- Crossover of ferrocyanide and ferricyanide to the anodic chamber reduces efficiency in the production of electricity
- The couple ferrocyanide/ferricyanide in the cathode chamber of an MFC can improve the performance in terms of COD removal and energy efficiency
- At low mediator concentration, a maximum in the power generation and COD removal can be attained
- At high mediator concentration, there was inhibition of biodegradation of winery wastewater

Keywords Wastewater treatment · Energy recovery · Winery wastewater · Microbial fuel cell · Ferrocyanide

Introduction

Nowadays, there is a tremendous need to develop cost-effective and less energy-intensive technologies for the treatment of wastewater. In this context, novel systems for the simultaneous recovery of energy and treatment of wastewater have gained interested and among them, microbial fuel cells (MFCs) seem to be promising and worth of study, in spite of being still far away from practical applications. MFC consist of an anode, where the microorganisms oxidize the organic matter of wastewater to generate electrons and protons, and a cathode where the electrons and protons reduce an electron acceptor. The protons in anode chamber can travel through the membrane or through the liquid, while the electrons pass by an external circuit. Both react with an electron acceptor in cathode chamber resulting in power generation [1, 2].

Many previous studies have demonstrated that MFC is greatly influenced by many factors, such as the microorganism, the material of electrodes, and the operational parameters [1, 2]. Among these factors, the cathodic electron acceptor has been found to be crucial to MFC performance. Most studies used oxygen as the electron acceptor in MFC, because of its high oxidation potential and availability, and it is economically attractive and environmentally friendly because water is formed as the only end product. However, the performance of MFC is low using oxygen due to the slow kinetics of oxygen reduction (Ter Heijne et al. 2006;).

Recently, a number of studies have shown that ferrocyanide/ferricyanide is excellent cathodic electron acceptor, due to its good performance in the MFC. Several researches obtained very high power densities using ferricyanide in the cathodic chamber of MFC such as 4310 and 3600 mW m^{-2} [3, 4] while the power generation is typically less than 1000 mW m^{-2} using dissolved oxygen [5]. The rapid oxidation of ferrocyanide by oxygen to form ferricyanide and the reversibility of this reaction, which favors the easier cathodic reduction of the ferricyanide (as compared to the oxygen reduction), are the main characteristics looked for in this mediator [6]. However, toxicity for microorganisms of the couple ferrocyanide/ferricyanide is well known and it becomes a major challenge in MFC, making necessary a good isolation of the anodic chamber to prevent the inhibition of the biological processes, in particular those carried out by bioelectrogenic microorganisms.

Obviously, the best way to prevent the transport of ferrocyanide and ferricyanide to the anodic chamber is a proton exchange membrane, in particular taking into account that both species are anions. This is not a perfect solution because of the permeability of the membrane, which may prevent the perfect isolation of the anodic chamber with respect to the cathode mediator.

Winery wastewater is a promising feedstock for MFC technology [7, 8], due to its rich composition in sugars, vitamins, minerals, and redox-active mediators such as tannic acid, and in a recent study, a power density as high as 465 mW m^{-2} was obtained with a two-compartment MFC directly fed with this type of wastes [9]. The aim of this work is to assess how the use of ferrocyanide can help to improve the performance of this type of MFC by enhancing the efficiency of the cathodic reduction in such devices. Therefore, in the present study, potassium ferricyanide is studied as the electron acceptor in the cathode chamber of a two-chamber MFC, in order to evaluate the removal of winery wastewater in the power generation. A Sterion® proton exchange membrane has been used to separate the compartments of the cell. This membrane shows low permeability as compared to other commercial membranes [10]. However, as the permeability of membranes is always a factor to be considered, concentration of the mediator couple ferrocyanide/ferricyanide was decided to be monitored in the anodic chamber. Likewise, it was decided in the design of the tests not to modify it during the test, in order to have a clear view of the performance of this type of MFC, pointing out their advantages and disadvantages. On the other hand, taking into account the typical low reproducibility of the MFC devices (clearly justified in terms of the great deal of parameters that influence on their performance), it was decided to run simultaneously (and under the same operation conditions except for the ferrocyanide/ferricyanide concentration) two MFCs during approximately 40 days, and then to reverse the ferrocyanide/ferricyanide concentration in their respective cathode chambers, without changing the electrodes or other components of the electrochemical cell.

Material and Methods

MFC Configurations and Operation

Two MFCs (so-called MFC_1 and MFC_2) were used in this study. The MFCs were made of acrylic tubes (inner diameter 40 mm; length 180 mm) and divided by a Sterion® membrane into two chambers, with 70 mL (anode) and 100 mL (cathode), respectively. The Sterion® membrane was pretreated with 3 % (*v*/*v*) hydrogen peroxide solution, 0.5 mol L^{-1} sulfuric acid, and ultrapure water. Carbon felt (KFA10, SGL Carbon Group®) were used as electrode in both chambers without being copped with Platinum. A stainless steel wire and an external resistance of 120 Ω connected the anode and the cathode.

The MFCs were operated in parallel in semicontinuous mode and at room temperature. Every day, 50 mL of liquid was removed from the anode chamber and replaced by fresh winery wastewater. A peristaltic pump was used to recirculate catholyte from the reservoir (500 mL) through the cathode chamber of the MFC at 1.66 mL s^{-1}. Oxygen was supplied in cathode reservoir using an aquarium aerator and porous stone diffuser in all experiments. When ferricyanide is used in the catholyte of MFC, the ferricyanide is reduced to ferrocyanide. Then, the ferricyanide can be recovered by the oxygen supplied in the reservoir, oxidizing the ferrocyanide formed in the cathode.

Firstly, the MFCs were started-up using HCl (pH 3.0) in the cathode compartment for 6 days. Then, to evaluate the influence of ferricyanide concentration (in the cathode) on MFC performance, two concentrations were chosen: 0.05 and 0.25 M. The MFC_1 was started up with 0.05 M of ferricyanide in the cathode and was operated for 46 days. Then, the MFC_1 was run using the solution of 0.25 M of ferricyanide between the 47th and 80th day of operation. The MFC_2 was operated just in the reverse conditions of MFC_1, firstly with 0.25 M and then with 0.05 M of ferricyanide, in order to evaluate the potential hysteresis of the system.

Inoculum and Wastewater

The inoculum was collected from the activated sludge reactor at the municipal wastewater treatment plant of Ciudad Real (Spain) and concentrated by sedimentation. The concentration of total solids and total volatile solids were 15.8 and 11.1 g L^{-1} respectively. To inoculate the MFCs, a solution of 90 % of seed sludge and 10 % winery wastewater was added into the anode chamber and kept for 24 h before the start of the operation. The winery wastewater used in this work was taken from the collecting tank of the wastewater treatment facility of the winery Bodegas Crisve (Socuellamos, Spain), and stored at 4 °C before being used. Table 1 shows the composition of this winery wastewater. $NaHCO_3$ (6000 mg L^{-1}) was used to adjust and buffer the pH to 6.5. Dibasic sodium phosphate ($Na_2HPO_4{\cdot}2H_2O$) and ammonium sulfate ($(NH_4)_2SO_4$) were added to increase the phosphorous and nitrogen concentrations to 10 mg P-PO_4^{3-} L^{-1} and 100 mg N-NT L^{-1}, because in a previous study, it was determined that the unbalanced chemical oxygen demand (COD)/N/P ratio is one of the biggest problems in treating this type of wastewater in biological system [9].

Analytical Methods

A GLP22 Crison® pH meter, a GLP 31 Crison® conductivity meter, and an Oxi538 WTW® oximeter were used to measure pH, conductivity, and dissolved oxygen, respectively. The total suspended (TSS) and volatile suspended (VSS) solids were measured gravimetrically [11]. The COD and concentration of phosphorous were measured using a spectrophotometric method (DR2000, HACH®). The total nitrogen was monitored using a Multi N/C 3100 Analytik Jena analyzer. The ferrocyanide concentrations were analyzed by the spectrophotometer method (KODAK, 1999).

Electrochemical Measurements

A digital multimeter (Keithley® 2000) was connected to the system to continuously monitor the value of the cell potential, and the data were recorded in a personal computer. The polarization curves from the MFC were obtained by varying the resistance in the circuit and measuring the voltage. Power density (mW m^{-2}) and current density (mA m^{-2}) were based on the surface area of the anode (7.0 cm^{-2}). The current (I) was calculated using Ohm's Law (I = E/R), and the output power of the cell using P = I × E, where I (A) is the current, E (V) is the voltage, R (Ω) is the external resistance, and P (W) is the power. Coulombic efficiency (CE) was based on total current generation and the maximum current that can be produced from COD oxidation and was calculated according to a procedure described in a previous work [11].

Table 1 Characteristics of winery wastewater used

Parameter	Value
pH	4.11
Conductivity (mS cm^{-2})	2030
COD (mg L^{-1})	6850
TOC (mg L^{-1})	1030
Total nitrogen (mg L^{-1})	18.3
Total phosphorous (mg L^{-1})	0.95

Results and Discussion

Electricity Production

Figure 1. shows the changes in the cell potential (resistance of 120 Ω) and the polarization curves of a mediatorless double chamber microbial fuel cell operated in the same conditions than the two MFCs tested in this work and used as a reference.

As it can be observed, the system rapidly met a steady-state cell voltage of 150 mV and the maximum power density was around 750 mW m^{-2}. These values were going to be used in this work as reference for comparison purposes because the MFC_0 was operated under the same conditions of the two MFCs with mediators. At this point, Fig. 2 shows the changes in the voltage (resistance of 120 Ω) and the concentration of ferrocyanide/ferricyanide measured at the anodic chambers during the four tests carried out. During the first period (which lasted 46 days), the cathodic chamber of MFC_1 contained 0.05 M of mediator (ferrocyanide/ferricyanide) while the cathodic chamber of the MFC_2 five times more (0.25 M). From day 46 onward, the concentrations of the mediators in both cells were changed in order to evaluate the differences and the robustness of the microbiological processes.

It can be clearly observed that low concentration of mediator in the cathode have a very positive effect on the production of electricity. Thus, when an MFC was operated with acid chloride solution (pH of 3.0) in the cathode, without ferrocyanide/ferricyanide redox couple, the average voltage was around 150 mV. As a consequence of using 0.05 M of ferrocyanide/ferricyanide redox mediator in the cathode, the average voltage increased to 275 mV, as it shows in the first period of operation of the MFC_1, and to the 188 mV reached by MFC_2 during its second operation period. According to previous works [5, 12, 13], this was an expected behavior because of the lower mass transfer limitations of the transport of reduction agents to the cathode surface and the improved electrochemical reduction of the mediator. A very important aspect to be pointed out is that in both cases, the concentration of the mediator in the anode is not negligible and it increases with time up to values of around 150 mg dm^{-3} at the end of the 45-day-long period. This high concentration could be the reason for the decrease in the production of electricity of MFC_1 during the last 10 days of the first testing period.

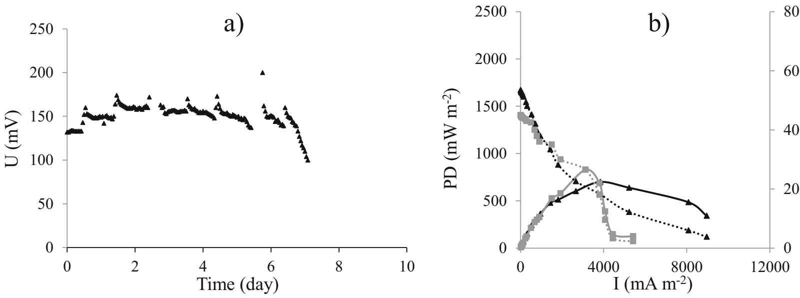

Fig. 1 **a** Electricity produced in MFC_0 treating winery wastewater without ferricyanide mediator in cathode chamber (*black triangle*). **b** Polarization curves obtained at days 4 (gray) and 6 (black).

Regarding the use of a higher concentration of mediator in the cathode chamber, the first period of MFC_2 showed a significantly lower value of the electricity produced, even if comparing this production with the production of the mediatorless MFC. In fact, the exponential growth phase was not observed, at least as clearly as in the mediatorless cell and in MFC_1. In this case, it can be observed that the concentration of the mediator in the anodic chamber was significantly higher and a possible explanation for these worse results is that this concentration may have been affecting bioelectrogenic microorganism growth during the very sensible first acclimation period. Thus, at the end of the first testing period, the final concentration of the mediator in MFC_2 was five times higher than in MFC_1. On the contrary, the increase of the mediator concentration in the cathode chamber of MFC_1 by five times up to 0.25 M during the second period of the operation showed a significant improvement in the electricity production reaching a considerable voltage peak of 500 mV. However, after reaching this value, it was observed a continuous drop down to almost 280 mV at the end of the 35 days length of the second period. In turn, the concentration of the mediator in the anode chamber increases, with almost the same rate as that in the MFC_2 operated with the same concentration of the mediator, suggesting that these high concentrations of mediator in the anode chamber may have been inhibiting the performance of the cell [14]. Even though the permeability of membrane with ferricyanide was expected to be too low, the diffusion coefficient of the ferricyanide ion

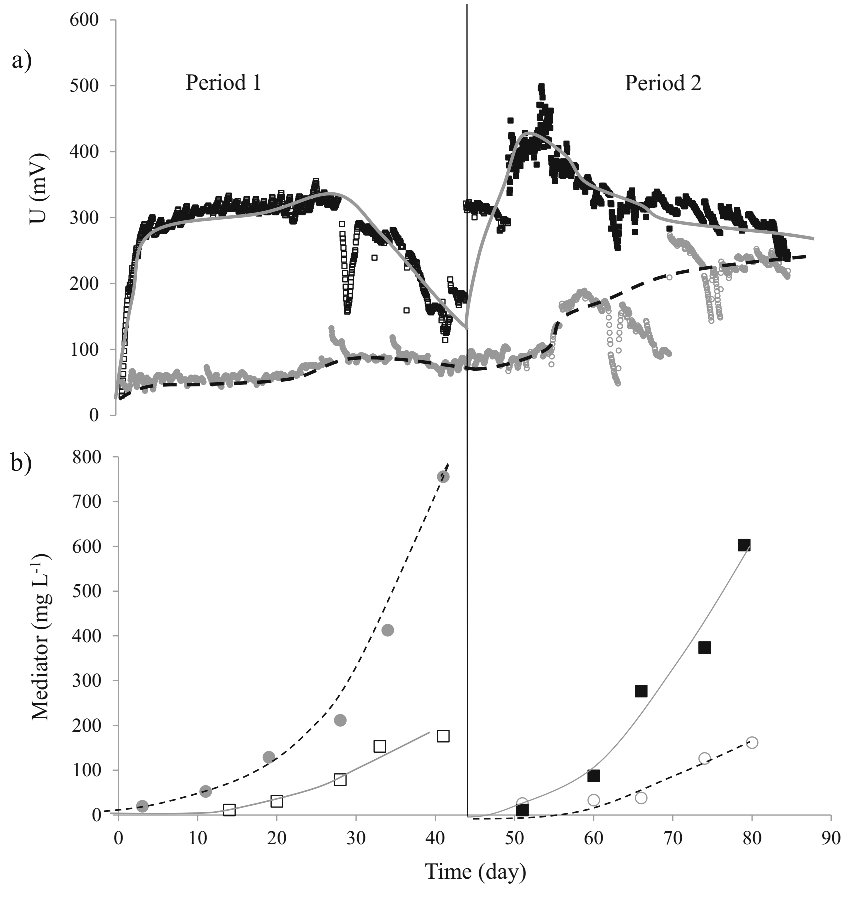

Fig. 2 **a** Electricity produced during the experimental period of the MFC treating with winery wastewater in different ferricyanide concentrations in cathode: 0.05 in MFC_1 (*white square*), 0.25 in MFC_2 (*black circle*), 0.25 in MFC_1 (*black square*) and 0.05 in MFC_2 (*white circle*). **b** Temporal variation of ferricyanide in anolyte when 0.05 M of ferricyanide was used in MFC_1 (*white square*) and MFC_2 (*white circle*) and when 0.25 M of ferricyanide in MFC_1 (*black square*) and MFC_2 (*black circle*)

across the PEM membrane is 2 10^{-8} cm^2 s^{-1} [15, 16]. As can be observed in high concentration of ferricyanide in the cathode, significant amount of the ion can diffuse across the membrane decreasing the MFC performance in terms of electricity generation, because the microbial activity is reduced and the membrane was clogged making more difficult the transport of protons through the cathode chamber [17, 18].

Figure 3 shows polarization curves recorded at different times during all experimental periods to determine the maximum power output and the main electrochemical features of the MFC. It is worth to mention that the polarization curves had the same behavior than the cell voltage. Thus, when the MFC was run without a mediator in the cathode chamber (Fig. 2), the MFC showed a maximum of power density of 828 mW m^{-2} (265 mV). Using a 0.05 M ferricyanide concentration in the cathode chamber resulted in a substantial increase in power density, with values of 1783 and 906 mW m^{-2} for MFC_1 and MFC_2, respectively. By increasing the mediator concentration up to 0.25 M, the maximum power densities obtained were 1420 and 279 mW m^{-2} in MFC_1 and MFC_2, respectively, values that were under those observed when 0.05 M mediator was used and are in agreement with the discussion made before for the cell potential.

COD Removal

Electricity production in MFC is carried out by bioelectrogenic microorganisms, and according to the results shown, the effect of the use of a mediator in the cathodic chamber of an MFC can be initially good, but its transport to the anodic chamber may turn down the production of electricity.

The COD consumption is a very interesting parameter because it does not only inform about the activity of bioelectrogenic microorganisms but also gives information about the performance of the complete community of microorganisms contained in the microbial fuel cell. Figure 4 shows the changes in this parameter during the performance of the two MFCs in the two periods studied.

As it can be observed, the COD consuming rate in MFC_1 when 0.05 M of mediator solution was used increased continuously until reaching a value around 1400 mg L^{-1} day^{-1}. During this period, the maximum COD removal efficiency occurred in the 45th day with 41 % of the influent COD biodegraded. By increasing the mediator concentration in the cathodic chamber of this cell up to 0.25 M, the COD consuming rate in MFC_1 decreased to 1000 mg L^{-1} day^{-1} and the COD removal efficiency was reduced to 15 %. This result clearly indicates that the increase in the ferricyanide concentration in the anode chamber influenced negatively the microbial activity, not only in bioelectrogenic microorganisms but also in the complete COD degrading community.

Regarding MFC_2, when it was operated with 0.25 M ferricyanide, the COD consuming rate and the COD efficiency removal increased during the experimental period up to values of 1000 mg L^{-1} day^{-1} and 20 %, respectively. Comparing with MFC_1, these lower values were a consequence of the

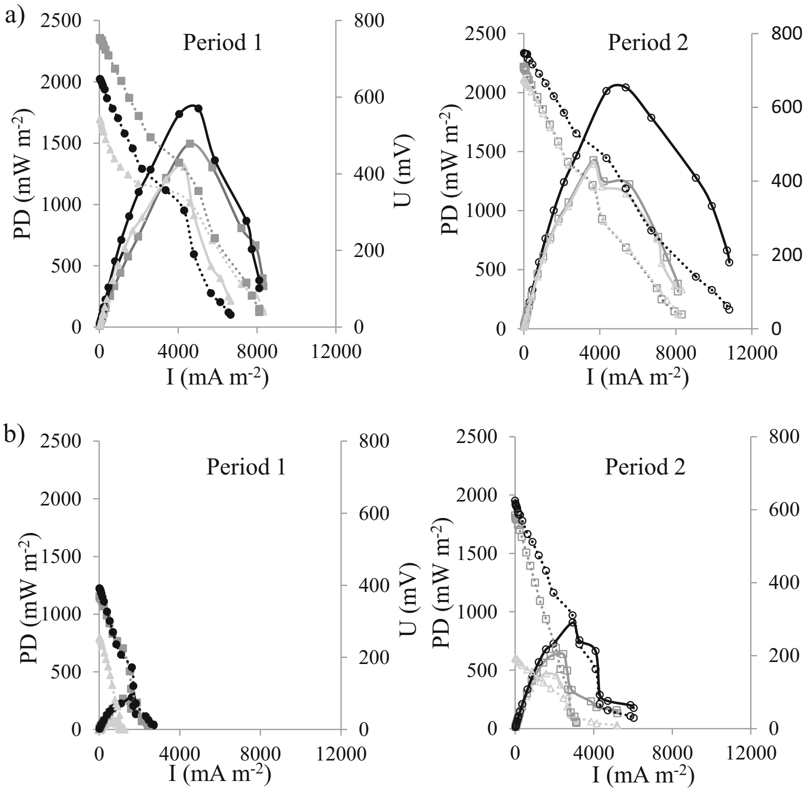

Fig. 3 **a** Polarization curves obtained in the MFC_1 fed with winery wastewater: *period 1* 0.05 M of mediator; *period 2* 0.25 M of mediator. **b** Polarization curves obtained in the MFC_2 fed with winery wastewater: *period 1* 0.25 M of mediator; *period 2* 0.05 M of mediator

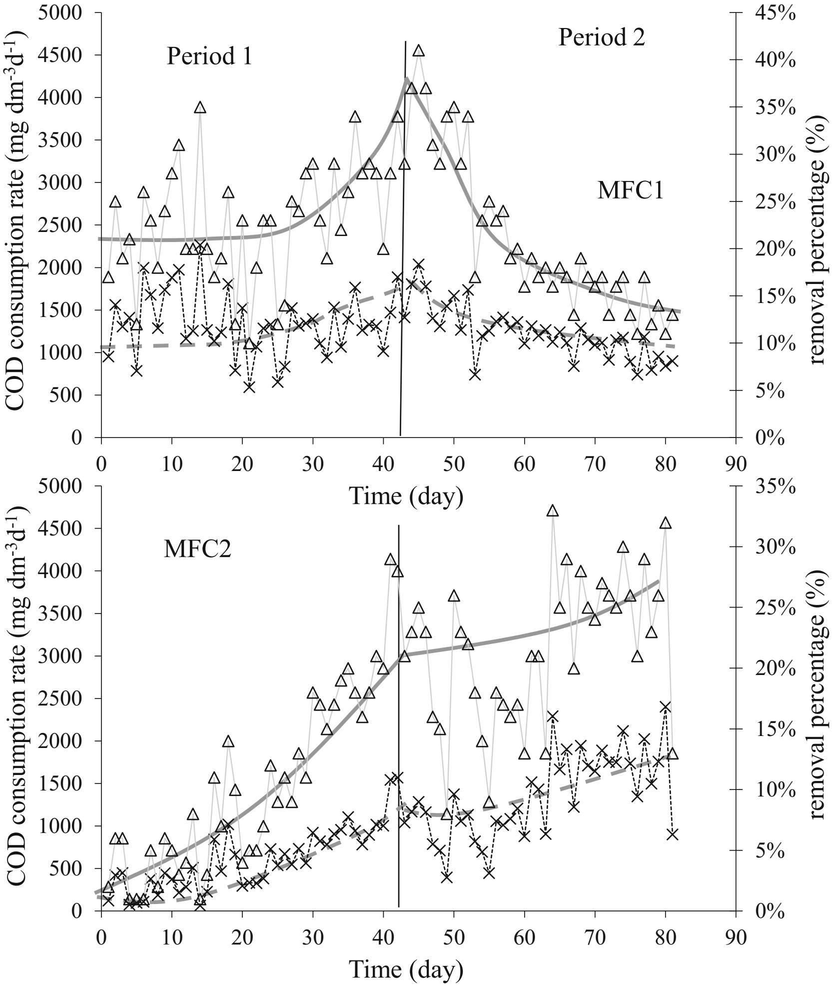

Fig. 4 Changes in the anodic chamber the COD consuming rate (*cross*), the COD removal efficiency (*white triangle*) and trend (*dash line*) during the performance of the two MFCs operated with mediator in the cathode chamber. The MFC_1 was operated with 0.05 M of mediator in period 1 and with 0.25 M of mediator in period 2. The MFC_2 was operated with 0.25 M of mediator in period 1 and with 0.05 M of mediator in period 2

ferricyanide passed through PEM, affecting the performance of the microbial community but also indicating that microorganisms could get over in the presence of important concentrations of mediator in the anode chamber. However, when the mediator concentration fell by five times (during the second operation period), it can be observed that the COD consuming rate almost doubled and the COD removal efficiency was increased up to 30 %. These results clearly shows that the decrease in the mediator concentration in the anode compartment enhanced the organic matter removal by microorganisms. In relation with the literature, these values of COD removal efficiency were lower than those observed by [7] and similar to the reported by [19], who reported yields of about 67 and 27 %, respectively, for the same type of wastewater.

Figure 5. shows the time course of nitrogen concentration consuming rates and the resulting nitrogen removal efficiency during the complete period studied

As it can be seen, the changes were consistent with those observed in the COD removal. When 0.05 M of ferrocyanide/ferricyanide mediator solution was used in MFC_1 and MFC_2, it can be seen an increase in the consumption of nitrogen during the performance of both cells and the nitrogen-consuming rate was around 100 mg NT L^{-1} day^{-1} at the end of the tests. On the contrary, when MFC_1 was operated with 0.25 M ferrocyanide/ferricyanide mediator in the cathode chamber, the NT-consuming rates were slightly smaller than in other operational conditions and they settled down in a value of around 50 mg NT L^{-1} day^{-1}, indicating the negative effect of the transport of mediator to the anode chamber. In the case of MFC_2 (that initially was operated with this mediator concentration), the increase in the nitrogen consumption was much slower although there was a significant increase, pointing out the capacity of adaptation of microorganisms to this mediator.

It is worth pointing out that although significant changes in the COD consuming rate were observed for the different concentrations of mediators applied in the cathode chamber, the activity of electrogenic microorganisms in terms of coulombic (or electric) efficiency was kept almost constant as it can be clearly seen in Fig. 6. When the MFC_1 was run using 0.05 of mediator, the coulomb efficiency was 16 %. Because of the lower COD removal and the similar production of electricity, the coulomb efficiency increased up to 34 % in

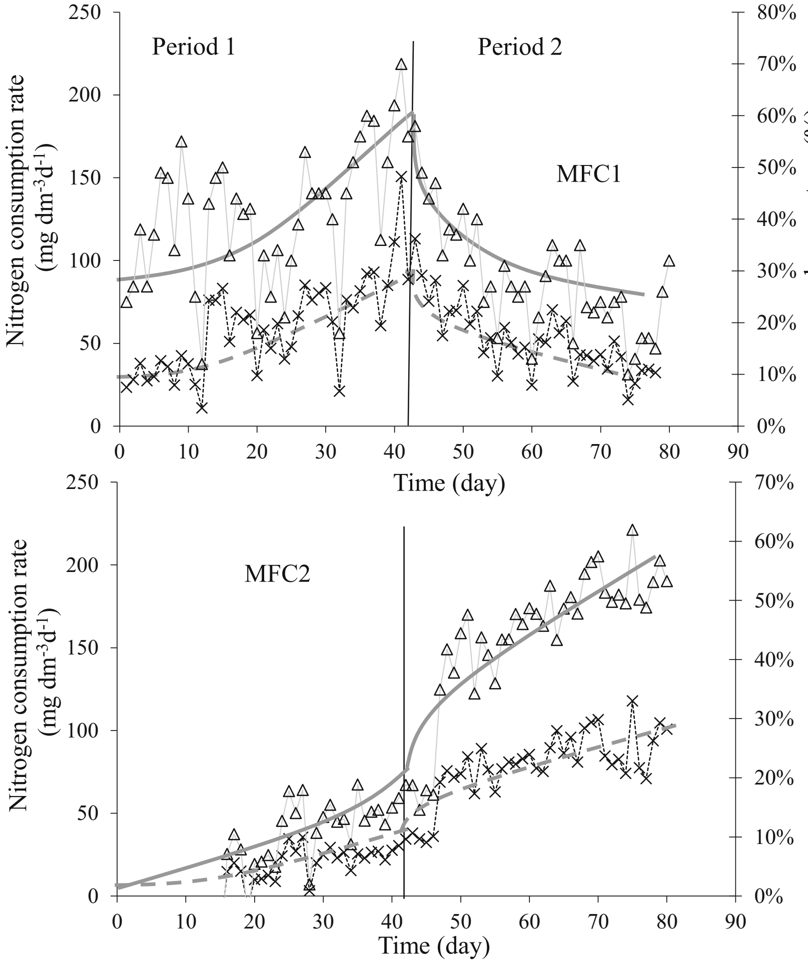

Fig. 5 Changes in the anodic chamber the nitrogen consuming rate (*cross*), the nitrogen removal efficiency (*white triangle*) and trend (*dash line*) during the performance of the two MFCs operated with mediator in the cathode chamber. The MFC$_1$ was operated with 0.05 M of mediator in period 1 and with 0.25 M of mediator in period 2. The MFC$_2$ was operated with 0.25 M of mediator in period 1 and with 0.05 M of mediator in period 2

MFC$_1$ when it was operated with 0.25 M of ferrocyanide. Regarding the MFC$_2$, operated during the first period with 0.25 M of mediator, the electric efficiency increased in the first moment as a consequence of low COD removal. Then, the electric efficiency decreased to around 7 %. In changing the concentration of the mediator in this cell dropping down to 0.05 M, an increase was observed up to a value of around 12 %. Values obtained were within the typical range and suggested that other microorganisms such as methanogens and sulfatogens were competing for the COD and the transport of mediator affected significantly not only to bioelectrogenic microorganisms but to the whole community of microorganisms contained in the anodic chamber. The important crossover of the mediator through the PEM membrane advice against the use of this technology for the improvement of the performance of MFC.

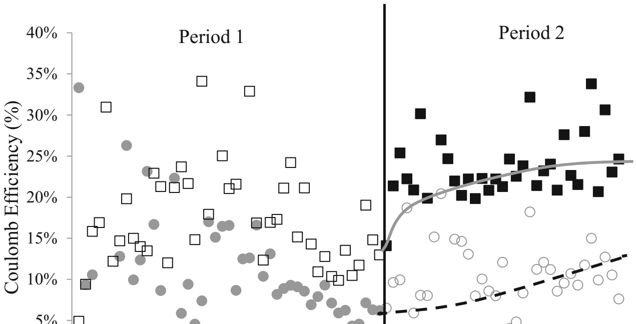

Fig. 6 Electrical efficiencies during the life test of the MFC fed with winery wastewater in different concentrations of mediator in the cathode chamber. The MFC$_1$ was operated with 0.05 M of mediator in period 1 (*white square*) and with 0.25 M of mediator in period 2 (*black square*). The MFC$_2$ was operated with 0.25 M of mediator in period 1 (*black circle*) and with 0.05 M of mediator in period 2 (*white circle*)

Conclusions

There is an important influence of ferricyanide concentration on the performance of dual chamber MFC operated in semicontinuous mode, both in terms of energy recovery and COD removal. Under no crossover of mediator to the anodic chamber, performance of the MFC is improved. However, permeability through PEM led to significant increases in the concentration of mediator in the anodic chamber, which affects both the electricity production and the COD consumption rate. Taking into account the low robustness of the membrane technology, it can be advisable not to use this type of mediator in MFC for the treatment of winery wastewater.

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