

INFLUENCE OF VARIOUS FACTORS ON THE EFFICIENCY OF MFC BASED ON THE PROCESS OF MICROBIAL DISSIMILATORY SULFATE-REDUCTION

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ABSTRACT: Microbial Fuel Cell (MFC) based on the process of microbial dissimilatory sulfate-reduction, provides the possibility of generating electricity while removing sulfates from the electrolytic solution. A MFC was constructed using Cation Exchange Membrane type CMI-7000S and graphite electrodes without addition of any toxic mediators as electron acceptors in the anode chamber, partially filled with natural zeolite.

In a series of investigations the influence of basic technological parameters on the generated voltage was established in open circuit (OCV) - temperature, pH, ratio COD/SO₄ and aeration intensity in the cathodic zone. A multifactorial regression analysis based on the experimentally obtained data was made as the importance of each of the investigated factors was established.

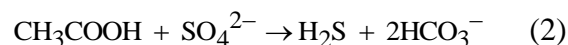
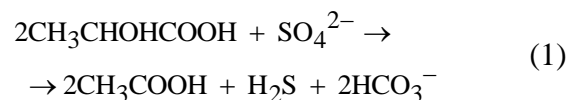
KEYWORDS: Sulfide, Microbial Fuel cell, Wastewater, Electricity, Sulfate removal.

1. INTRODUCTION

The global energy crisis and climate change need a carbon-neutral, sustainable energy sources as alternatives to fossil fuels. The technology using MFCs in which microorganisms mediate the direct conversion of chemical energy stored in organic matter or bulk biomass into electrical energy has gained considerable interests in recent years. Beside electrical power production, more emphasis is recently devoted to alternative applications such as hydrogen production, bioremediation, seawater desalination, and biosensors. Various organic compounds and sources of wastes have been successfully utilized for power generation in MFCs.

The electrochemically active bacteria responsible for substrate oxidation and electron transfer are the key component of MFC.

Sulfate-rich wastewaters (in orders of grams per liter, [4]) are generated by many industries that use sulfuric acid, sulfate feedstock or reduced sulfur compounds and by mining activities. In this process, dissimilatory microbial sulfate-reduction (DMSR), hydrogen and dissolved organic compounds or even crude oil components are used as electron donor for microbial reduction of sulfate leading to the production of sulfide. In absence of oxygen the dissimilatory sulfate-reducing bacteria (SRB) use organic carbon and sulfate in the process of anaerobic respiration (eq. 1 and 2).



The by-products of the reaction, hydrogen sulfide and bicarbonate, can be used to

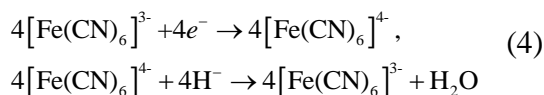
precipitate many metals (eq. 3) and raise the pH of the water, respectively [5].



M - metal such as Fe, Cu, Zn and others

DMSR based MFCs simultaneously remove the sulfates in wastewaters and produce green energy. For that purpose, sulfate-reducing bacteria oxidize organic compounds and reduce sulfate anions. As a result hydrogen sulfide and bicarbonates are formed. For this type of MFCs there is not a necessity of additional mediators as the biologically produced sulfide plays the role of the mediator. In this process H₂S oxidation to elemental sulfur occurs on the anode surface [6]. An elemental sulfur is formed in the anode chamber as by-product. Various parameters such as temperature, pH and ratio of TOC to SO₄²⁻ in the solution will affect the growth and activity of sulphate-reducing bacteria.

As an electron acceptors in the cathode chamber can be used (KMnO₄), (K₃[Fe(CN)₆]) and (K₂Cr₂O₇). The released protons in the anodic chamber migrate through a proton selective membrane into the cathode chamber. The protons may be consumed by ferricyanide in one cathode configuration, or by oxygen in another. Both ferricyanide and oxygen in the presence of electrons donated from the cathode surface react with protons and are reduced to ferrocyanide and water [2], (eq. 2)



The main aims of this study are to evaluate the influence of basic technological parameters on the generated voltage in open circuit (OCV) - temperature, pH, ratio COD/SO₄ and aeration intensity in

the cathodic zone and to establish the importance of each of the investigated factors through a multifactorial regression analysis based on the experimentally obtained data.

2. MATERIALS AND METHODS

A two-chambered tubular MFC was used, chambers set into one another and separated with a proton exchange membrane of type CMI-7000S (Membrane International Inc.). The anodic chamber was with volume of 0.65 dm³, the cathodic tube - 0.06 dm³. The membrane area was 0.0007 m². The electrodes were two 9 cm in length carbon rods with diameter of 8mm and a calomel electrode. One of the graphite electrodes and the calomel one were placed in the anodic section and the other carbon - in the cathodic one (Figure 1). The surface area of each carbon electrode was 0,0024 m².

The laboratory installation of microbial fuel cell is shown in Figure 1.

About half of the anode chamber was filled up with 0.5 kg modified zeolite, a carrier element for the sulfate-reducing bacteria biofilm and other metabolic related microorganisms. The used natural zeolite was of clinoptylolite type with fraction size in the range of 2.5 – 5.0 mm from Beli plast deposit, Eastern Rodopes, Bulgaria. Its elemental composition was as follows in percentage: SiO₂ - 67.96, Al₂O₃ - 11.23, Fe₂O₃ - 0.83, K₂O - 2.85, Na₂O - 0.74, CaO - 3.01, MgO - 0.06, TiO₂ - 0.90. Cation exchange capacity and the exchanged ions in meq/100 g were respectively: CEC – 112,75, K⁺ - 33.88, Na⁺ - 21.01, Ca²⁺ - 63.48, Mg²⁺ - 2.68. Two zones were formed in the so designed MFC – first zone of active sulfate reduction (filled with zeolite) and the second one, where the microbial produced H₂S was oxidized.

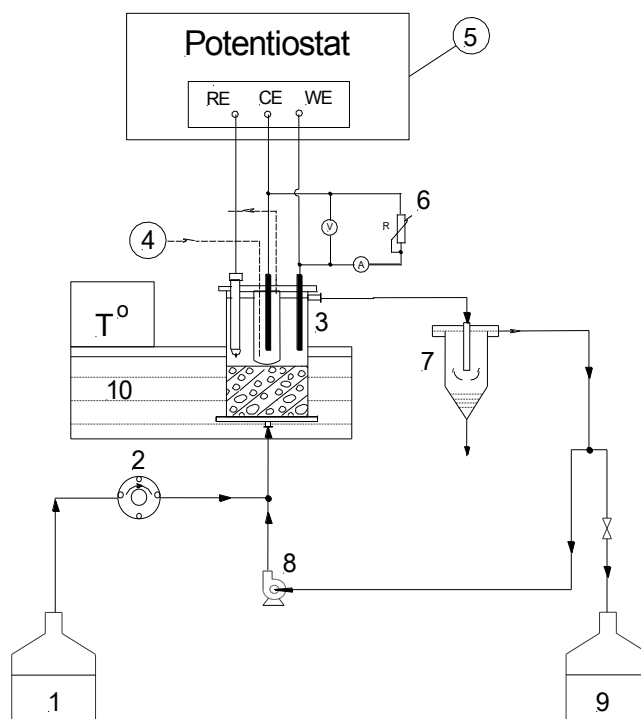


Figure 1. Laboratory installation

1 - Stock solution tank, 2 - peristaltic pump, 3 - Microbial fuel cell, 4 – air, 5 – potentiostat, 6 – electrical circuit with external consumer, 7 - settler, 8- recirculation pump, 9- collector tank, 10 - heating bath, RE- reference electrode , WE- working electrode, CE- counter electrode

0.48 dm³ of modified culture medium of Postgate was poured in the volume of MFC. The anodic chamber was inoculated with 40 ml mixed culture of sulfate-reducing bacteria. After the biofilm has formed, MFC was fed continuously with culture medium. The medium from stock solution tank (1) was feeding the microbial fuel cell with regulated debit by peristaltic pump (2). In the end of that period started a continuous feeding of the bioreactor with the Postgate medium at different residence times.

The homogenization in MFC was performed by recirculation pump (8) at ascending flux run. The settler (7) with a volume of 2 dm³ gathered the produced elemental sulfur. The solutions from this settler outflowed in a collector tank (9) with a volume of 9 cm³. The experiment was carried out in a temperature range of 21 to 22^oC. The culture medium of Postgate contained 0.25 g/l K₂HPO₄, 0.5 g/l NH₄Cl, 2.0 g/l Na₂SO₄, 0.1 g/l CaCl₂,

4.0 g/l MgSO₄·7H₂O, 6.0 g/l Na-lactate, 0.25 g/l yeast extract, pH 6.5.

Regarding the composition of the catholyte in the cathodic semi-element of the MFC was used 100 mM solution of K₃ [Fe (CN)₆] in 67 mM phosphate buffer pH 7.0. During the reduction of terminal electron acceptor - air oxygen, together with the protons from the cathodic area, was forming water. For this purpose, there was an opportunity of cathodic chamber aeration by a pump with a flow rate of 0,5 dm³/60s.

In some defined points of laboratory installation pH and Eh, mV, were measured. The same places were sampled for spectrophotometric determination of sulfates by BaCl₂ ($\lambda_{\text{fixed}}= 420 \text{ nm}$) and hydrogen sulfide (1-88/05.09 Nanocolor test, $\lambda_{\text{fixed}}= 620 \text{ nm}$). Electric parameters of MFC were measured with a portable digital multimeter Keithley Model-175, as an external resistances was used a potentiometer with maximum value of 13.5 k Ω . For the establishing of the system

electrochemical behavior was used a potentiostat - ACM 3 connected to PC for reporting and analysis of the accumulated data.

3. RESULTS AND DISCUSSION

The previous studies [1] have established the optimal operational modes of MFC to the process of microbial sulfate reduction in the anodic area in terms of various parameters. To establish the efficiency of the MFC it is necessary to select a series of independent parameters affecting the various electrochemical properties of the cell - a cathode and an anode electrode

potentials, open circuit voltage (OCV), polarization curves, cyclic voltammogram and others.

The presented polarization curve (Fig. 2) and a cyclic voltammogram (Fig. 3) are taken at a temperature of 21°C, a residence time of 72h to the refresh rate of the stock solution in the anodic chamber of fuel cell, and in an open air mode for cathodic chamber, without forced aeration.

Maximum value of power density (power density) is 0,68 W/m², at a current density of 3,2 A/m², obtained at 150 Ω of the consumer.

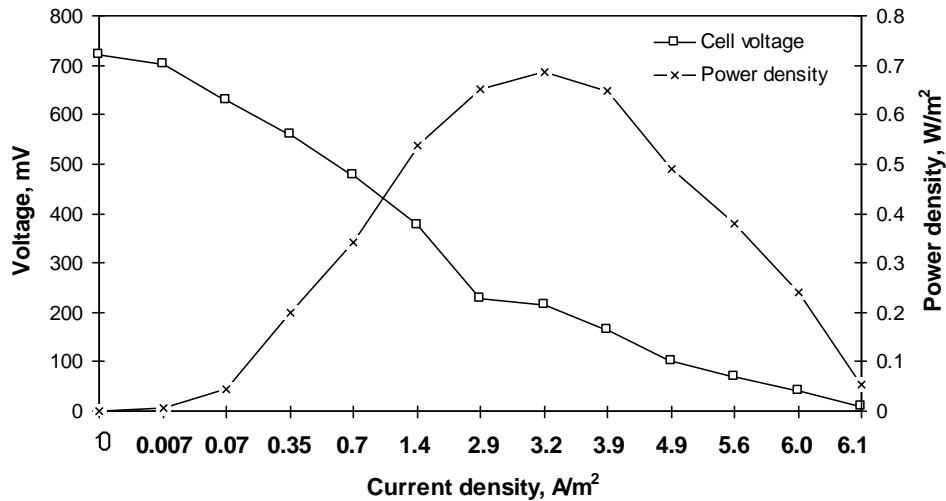


Figure 2. Polarization curve of MFC, based on the DMSR process at a residence time of 72 h

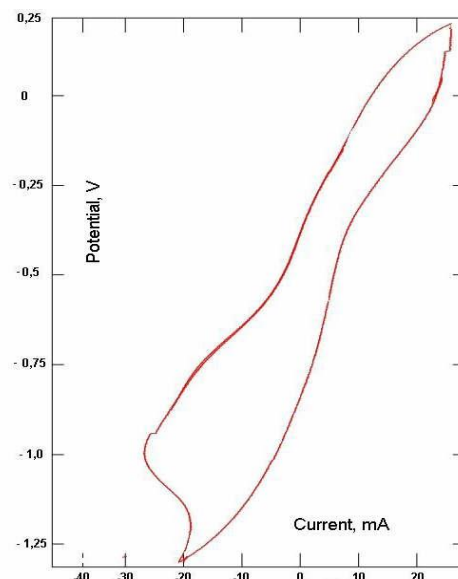


Figure 3. Cyclic voltammogram of MFC, based on the DMSR process (residence time - 72h)

This study was carried out at a flow rate of feed solution providing a residence time of 72 h in the anodic chamber [1]. Optimal for the operation of the process DMSR are: temperature - 36°C, COD/SO₄ ratio in the anodic chamber - 2.7, pH of the solution ≈ 8.0 and cathodic chamber aeration rate - 0.15 dm³/60s.

For the purpose of regression analysis a planned experiment was carried out and the following independent parameters were selected - temperature (T, °C), pH of the medium in the anodic area, COD/SO₄²⁻ ratio in the solution feeding the anodic area and aeration intensity in cathodic chamber. As a dependent on these parameters factor (target function) was selected the rate of reduction of voltage in OCV - K_{OCV} (%), determined according to eq. 5:

$$K_{OCV} = \frac{OCV_{max} - OCV}{OCV_{max}} \cdot 100 \quad , \% \quad (5)$$

wherein: OCV_{max} (mV) - the maximum value obtained under optimal conditions, OCV (mV) - current value of the voltage of the open circuit.

The study purpose was to obtain an analytical relation by a multi-regression analysis through the suitable processing of the obtained experimental data - a mathematical model for assessment the importance of each of the independent factors of the process [3]. For a correct model of the regression analysis is necessary each one of the independent parameters of the process to vary while the others remain stable.

The selected ranges of variation of independent parameters correspond to the possible values in real operating conditions of the MFC. The selected appropriate ranges of variation of the independent parameters are represented in Table 1. To provide a suitable temperature ranging, the experiments were conducted in thermostated conditions. Another examined independent parameter was the ratio between COD and the concentration of sulfates in the MFC anodic zone (COD/SO₄²⁻). Different rates of COD/SO₄²⁻ were ensured by manipulating the chemical composition of the feed solution.

Table 1. Experimentally obtained data under the terms of the planned study

pH=8,0; COD/SO ₄ =2,7; Aeration rate=0,15 dm ³ /60s				
X ₁ - T, °C	21	26	31	36
Y - K _{OCV} , %	3,33	2,67	2,00	0,67
T=36 ⁰ C; COD/SO ₄ =2,7; Aeration rate=0.15 dm ³ /60s				
X ₂ - pH ()	6,5	7,0	7,5	8,0
Y - K _{OCV} , %	18,67	8,67	4,00	0,67
pH=8,0 ; T=36 ⁰ C; Aeration rate=0.15 dm ³ /60s				
X ₃ - COD/SO ₄	2,1	2,3	2,5	2,7
Y - K _{OCV} , %	7,20	5,33	4,00	0,67
pH=8,0; COD/SO ₄ =2,7 ;T=36 ⁰ C				
X ₄ - Aer. Rate, dm ³ /60s	0	0.05	0.10	0.15
Y - K _{OCV} , %	10,67	2,67	2,00	0,67

pH ranged from 8.5 to 6.5 by fine dosing of 0.1N HCl. The aeration rate was varied by an external compressor flow range 0 - 0.15 dm³/60s. As fixed values of the independent factors were selected the averages: temperature - 36⁰C, COD/SO₄²⁻- 2.7, pH - 8.0 and aeration rate in the cathodic zone 0.15 dm³/60s.

The measured values of the OCV at the different variants of the experiment are the averages (3-5 reps). In Table. 1 are shown the calculated values of K_{OCV}.

The regression analysis was made in parallel with the programs XLSTAT and StatPlus 2007. The resultant regression equation was selected as multifactor linear regression of the form:

$$Y = a + b.X_1 + c.X_2 + d.X_3 + e.X_4 \quad (6)$$

Respectively the accepted designations are as follows: Y - reduction rate of the voltage in OCV, KC (%); X₁ - temperature (T, °C), X₂ - pH of the feed solution, X₃ - ratio COD/SO₄, X₄ - the degree of aeration (O₂, mg / l). The values of the received basic regression coefficients are presented in Table 3.

Table 2. Goodness of fit coefficients

R	0,95
R Square – R ²	0,91
Standard Error – S, %	1,69
Total Number Of Cases	16
Coefficient of uncertainty	0,05

Table 3. The values of the regression coefficients in the model

Coefficient	Mean	Standard deviation
a	34,125	4,425
b	7,813	0,443
c	2,625	0,177
d	0,131	0,044

The final form of the resulting regression equation is as follows:

$$Y = 138,16 - 0,23.X_1 - 10,91.X_2 - 12,61.X_3 - 54,85.X_4 \quad (7)$$

4. CONCLUSIONS

Results of the regression analysis confirm the adequacy of the choice of independent parameters and their expected relevance to the chosen target function (the reduction rate of the voltage in OCV). The value of the correlation coefficient R=0.95 ranges from 0.9 to 1, that means the resulting regression equation gives the functional relationship between dependent and independent factors.

Based on the calculated values of the regression coefficients (Table 3), it can be said that the factor with the greatest influence is the aeration rate, then the COD/SO₄²⁻ ratio and pH and with the least impact on the target function is the temperature. The resulting regression equation is valid only in selected ranges of variation of the independent factors.

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