REGRESSION ANALYSIS OF FACTORS AFFECTING MICROBIAL FUEL CELL EFFICIENCY

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ABSTRACT. In a laboratory installation of a Microbial Fuel Cell (MFC), based on the process of microbial sulphate reduction in the anodic chamber of the cell, the factors influencing the efficiency of the fuel element have been investigated. Under the conditions of a planned laboratory experiment, the temperature, pH, H_2S and sulphate concentration in the anodic chamber, and the dissolved oxygen content in the cathodic chamber of MFC have been varied. Meanwhile, the Open Circuit Voltage (OCV) and the maximum values of power in MFC are measured as possible target functions. A multifactorial regression analysis has been performed with respect to the selected independent parameters and the target function. A mathematical model of the target function has been obtained from the selected independent variables that can be used to optimise the operation of a microbial fuel cell based on the microbial sulphate reduction process.

Keywords: Microbial Fuel Cells, microbial sulphate reduction and multifactorial regression analysis

РЕГРЕСИОНЕН АНАЛИЗ НА ФАКТОРИТЕ ОКАЗВАЩИ ВЛИЯНИЕ ВЪРХУ ЕФЕКТИВНОСТТА НА МИКРОБНА ГОРИВНА КЛЕТКА

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РЕЗЮМЕ. В лабораторна инсталация на микробна горивна клетка (МГК), базирана в анодната зона на процеса на МСР, са изследвани факторите оказващи влияние върху ефективността на горивния елемент. При условията на планиран лабораторен експеримент са варирани стойностите на температурата, pH, концентрация на H_2S и сулфати в анодната зона и съдържанието на разтворен кислород в катодната зона на МГК.Паралелно са измервани като възможни целеви функции - напрежението на отворена верига (OCV) и максималната стойност на мощността на микробната горивна клетка. Направен е многофакторен регресионен анализ по отношение на избраните независими параметри и целевата функция. Получен е математически модел на целевата функция от подбраните независими променливи, който може да се използва за оптимизация на работата на микробна горивна клетка, базирана на процеса на микробна сулфатредукция.

Ключови думи: микробни горивни клетки, микробна сулфатредукция и многофакторен регресионен анализ

Introduction

The environmental issues associated with the use of carbon-based fossil fuels and the increasing role of renewable energy sources are becoming more urgent in the development of modern civilization. It has been proven that microbial fuel cells (MFCs) are a promising innovative technology for energy generation and wastewater treatment due to their low costs and sustainability (Chouler et al., 2016). These are systems where electroactive microorganisms using different energy sources (mainly organic compounds, but also some inorganic substrates such as hydrogen, sulphide, iron or ammonium) convert this energy directly into electricity. The efficiency of this type of system for energy generation shows a continuous trend to improvement, but it is still low compared to conventional energy sources.

It has been found that a significant set of factors influences the efficiency of MFCs, such as these related to the constructive features and the choice of suitable materials, as well as those determined by the environmental conditions in the anodic and cathodic chambers of the biological fuel elements (Stefanova et al., 2018).

Some of the studies in recent years have been focused on the application of the microbial sulphate-reduction process in the anodic chamber of MFCs, used for the treatment of sulphate-rich wastewaters (Angelov, et al., 2013). Wastewaters with high sulphate contents (of over 3 g/l) are typical of the mining and the ore processing industries and form a major environmental problem (Johnson and Hallberg, 2005). The microbial fuel cells based on the process of microbial sulphate reduction (MSR) in the anodic zone provide the opportunity to remove sulphates from the incoming water together with the generation of electricity. In this process an oxidation of the hydrogen sulphide on the anode to an elemental sulphur and other final products is performed.

The analysis of the factors affecting the chemical, the electrochemical and the biological processes occurring in MFCs is essential in order to optimise their performance and to demonstrate the applicability of this type of fuel elements in practice.

The main objective of the present study is to perform an analysis of a selected set of technological factors, affecting the operation of a microbial fuel cell, based on the process of microbial sulphate reduction in the anodic chamber of the fuel element. For this purpose, under the conditions of a planned experiment, the influences of temperature, pH, sulphate and H_2S concentrations in the anodic zone and oxygen content in the cathodic one, on the open circuit voltage (OCV) and the maximum power values (P_{max}) of the MFC are studied.

Materials and methods

For the conduction of the experiments a laboratory-scaled installation of the microbial fuel cell is used and the scheme is presented in Fig. 1. The microbial fuel cell is constructed in 2 equal in sizes sections, anode and cathode, located in a U-shaped construction, separated by a cation-exchange membrane. The volume of the anodic and cathodic chambers is of 0.48 dm^3 each. For the separation of the anode from the cathode, a cation-exchange membrane type CMI-7000S (Membrane International Inc.) with an area of 0.0012 m^2 is used. Graphite rods with a diameter of 8 mm and a length of 9 cm are used as electrodes. The surface geometric area of one electrode is 0.0028 m^2. Approximately half of the volume of the buffer tank (the vessel is with a volume of 0.7 dm^3) is filled with 0.3 kg of modified zeolite(4). The same is a sulphidogenic bioreactor sequentially connected to the anodic chamber of the fuel element. The modified zeolite plays the role of a biofilm carrier from the SRB bacteria and other metabolically related groups of microorganisms.

A modified Postgate nutrient medium with a volume of 1.1 dm^3 is added to fill the anodic chamber volume and the sulphidogenic bioreactor. The inoculation of the microbial cell was performed with 50 ml of a mixed culture of sulphate-reducing bacteria (SRB). After the formation of an active biofilm of SRB, it begins a feeding of the nutrient medium for the continuous cultivation of the bacteria. The medium from the tank (1) feeds into the fuel cell with a regulated flow through the peristaltic pump (2). The homogenisation in the microbial fuel cell is accomplished by means of a recirculating pump (5).

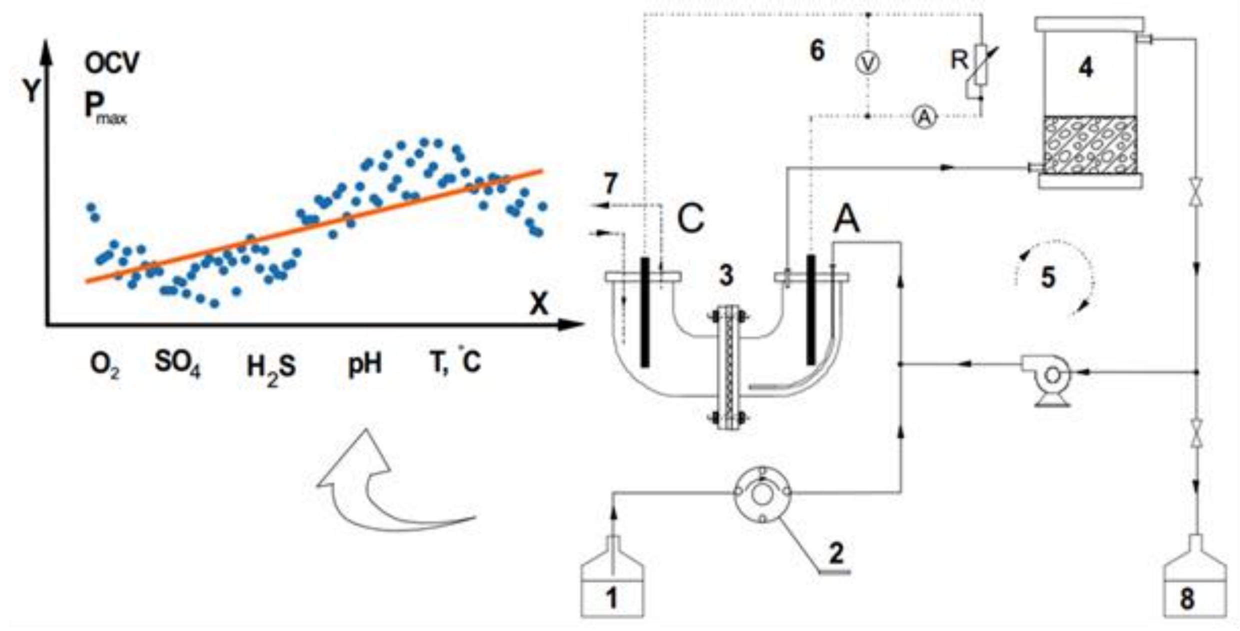

Fig. 1. A scheme of the laboratory-scaled installation of MFC, where experiments are conducted to determine the impact of T, pH, dissolved oxygen, SO_4 and H_2S contents through the method of the linear regression analysis.
1 - feeding solution in anodic area, 2 - dosing peristaltic pump, 3 - microbial fuel cell, 4 - bioreactor, 5 - recirculation pump, 6 - electricity chain with a consumer, 7 - air flow in cathodic area, 8 - collector tank.

The solutions outgoing from the settler are collected in a collecting tank (8) with a volume of 3 dm^3. For the achievement of the required temperature in MFC, a thermo-regulated water bath is used. The used nutrient medium has the following composition, in g l: K_2HPO_4 - 0.25, NH_4Cl - 0.5, wt. Na_2SO_4 - 2.0, CaCl2 - 0.1, $MgSO_4.7H_2O$ - 4.0, Na - lactate - 6.0, yeast extract - 0.25 and has a pH of 6.5.

For the purpose of the linear regression analysis, experiments with the MFC under abiotic conditions are conducted, thus it is possible to maintain the values of the independent parameters (T, pH of the anolyte, dissolved oxygen in the catholyte, SO_4^{2-} and H_2S in the anolyte) constant for the time of the tests. The obtained values of the dependent parameters (OCV and P_{max}) under abiotic conditions are compared with those, obtained under biotic MFC operational conditions.

For the purpose of the linear regression analysis with the change in the values of each of the independent parameters, the values of the rest were kept constant. The selected constant values of the independent parameters are T - 24°C, pH 7.5, SO_4^{2-} - 3g/l, H_2S-360 mg/l and dissolved oxygen content in the catholyte - 6.8 mg/l in an open air mode. For the appropriate temperature variation range, the experiments are carried out under thermostated conditions.

The concentration of sulphates in the medium is changed to 4 variants - 0.5, 1.5, 3.0 and 4.5 g/l. Respectively, in order to determine the influence of the H_2S in the anolyte 4 concentrations are maintained - 150, 250, 350 and 450 mg/l by the addition of an appropriate amount of Na_2S in the anolyte. The pH value is also changed in 4 variants - 5.5, 6.5, 7.5 and 8.5 by adding 0.1 N HCl solution and/or 0.1 N NaOH solution. A 100 mM solution of K_3 [Fe (CN) $_6$] in a 67 mM phosphate buffer solution at pH 7.0is used as a catholyte in the cathodic semi-element of the microbial fuel cell. In this case, a final electron acceptor is the oxygen in the air, which in its reduction, together with the protons present in the cathodic space, form water. For this purpose, it is possible to aerate the cathodic chamber, so the experiments are carried out in 4 aeration modes - 0.5, 1.0, 1.5 l/s air and without aeration - in open air mode.

The pH is measured using a pH electrodes (VWR) and a pH meter HANNA HI 9021. The Eh is measured using a WTW Electrode Sen Tix ORP. The electrical conductivity is measured using the Conductivity Electrode WTW LF90.

In some certain points in the laboratory-scaled installation the parameters pH, TDS and Eh are measured. Corresponding to the same sampling points, the concentrations of sulphates by $BaCl_2$ reagent at 420 nm and hydrogen sulphide using Nanocolor 1-88 / 05.09 at 620 nm are determined spectrophotometrically.The electric parameters of the fuel cell are measured with a Keithley 175 digital multimeter, with a precision potentiometer with a maximum value of 11 k, used for a load resistor (consumer). The maximum power value P_{max} is measured by the plotting of polarisation curves for each of the tested variants. Using a NI Sensor DAQ controller (DAQ Board) and a software based on the Virtual Instrumentation LabView^R (Mironescu et al., 2007), the parameters pH, T, Electrical conductivity, OCV and P_{max} are monitored.

Result and discussion

The purpose of the planned experiment is to achieve an analytical dependence by the appropriate processing of the experimental data, through a multifactor regression analysis- a mathematical model that would allow an assessment of the weight of each of the independent factors on the process. To obtain a correct model in the regression analysis, each one of the independent parameters must be varied, while the remaining ones are kept constant (He et al., 2016).

For the purpose of the regression analysis an experiment is planned, whereas the values of the independent parameters - T - 24°C, pH 7.5, SO_4^{2-} - 3g/l, H_2S - 360 mg/l and dissolved oxygen content in the catholyte - 6.8 mg/l are kept constant at the independent variation of each one of them. At the same time, the values of the dependent parameters - OCV and P_{max}, the target functions of this multifactorial linear regression analysis, are monitored. The selected ranges for the variation of the independent parameters correspond to their possible real values, in the MFC operation based on the MSR process in the anodic chamber. The results obtained for the two target functions, OCV and P_{max}, and the selected ranges of variation of the independent parameters are presented in Table 1. The measured values of OCV and P_{max} are averaged, as from 3 to 5 reiterations are made.

The regression analysis is performed with both programmes - *StatPlus^R and XLStat^R* (Zar et al., 2007) and similar results are obtained. From the various possible variants for the type of resultant regression equation, a multifactorial linear regression of the following type is chosen:

$$Y_{1,2} = a + b.X_1 + c.X_2 + d.X_3 + e.X_4 + f.X_5 \quad (1)$$

Table 1. *Data for the target functions OCV and P_{max} in the laboratory-scaled installation of MFC for the purpose of the regression analysis*

pH- 7.5, SO_4 - 3g/l, H_2S- 360 mg/l, O_2- 6.8 mg/l				
T, °C (X_1)	10	24	32	41
OCV, mV (Y_1)	650	708	778	820
P_{max}, mW (Y_2)	0.457	0.556	0.613	0.724
T- 24°C, SO_4 - 3g/l, H_2S- 360 mg/l, O_2- 6.8 mg/l				
pH, (X_2)	5.5	6.5	7.5	8.5
OCV, mV (Y_1)	654	690	749	782
P_{max}, mW (Y_2)	0.385	0.419	0.490	0.529
T- 24°C, pH- 7.5, H_2S- 360 mg/l, O_2- 6.8 mg/l				
SO_4, g/l (X_3)	0.5	1.5	3.0	4.5
OCV, mV (Y_1)	516	620	708	781
P_{max}, mW (Y_2)	0.393	0.432	0.568	0.643
T- 24°C, pH- 7.5, SO_4 - 3g/l, O_2- 6.8 mg/l				
H_2S, mg/l (X_4)	113	237	360	561
OCV, mV (Y_1)	614	661	720	779
P_{max}, mW (Y_2)	0.330	0.418	0.546	0.577
T- 24°C, pH- 7.5, SO_4 - 3g/l, H_2S- 360 mg/l				
O_2, mg/l (X_5)	6,8	7,9	8,8	9,6
OCV, mV (Y_1)	655	682	736	775
P_{max}, mW (Y_2)	0.452	0.555	0.627	0.762

Accordingly, the accepted indications are as follows: Y_1- OCV (mV), Y_2- P_{max} (mW), X_1 - temperature (°C), X_2- pH the anolyte, X_3–sulphates concentration in the anolyte (g/1), X_4- H_2S concentration in the anolyte (mg/1), X_5–dissolved oxygen content in the catholyte (mg/l).The values of the obtained main regression indicators are presented in Table. 2.

Table 2. *Main regression indicators*

	Y_1 (OCV)	**Y_2 (P_{max})**
Correlation coefficient - R	0.9432	0.9304
Determination coefficient - R^2	0.89	0.87
Uncertainty coefficient	0.15	0.19
Standard error - S, %	28.9162	0.0492
Number of observations	20	20

The final variant of the obtained regression equations is as follows:

$$\begin{aligned} Y_1 &= -127,59 + 5,9114.X_1 + 34,17.X_2 \\ &+68,07.X_3 + 0,38.X_4 + 14,89.X_5 \end{aligned} \quad (2)$$

$$\begin{aligned} Y_2 &= -1,063 + 0,0094.X_1 + 0,062.X_2 \\ &+0,058.X_3 + 0,0006.X_4 + 0,073.X_5 \end{aligned} \quad (3)$$

The results obtained from the regression analysis confirm the adequacy of the choice of the independent variables and their expected significance for the selected target functions (OCV and P_{max}). The value of the correlation coefficients (R_{Y1} = 0.94, R_{Y2} = 0.93 - Table 2) is in the range 0.9-1, which gives reason to believe that the obtained regression equations give functional dependencies between the dependent and the independent variables.

On the basis of the calculated values of the regression coefficients, it can be said that the factors with the greatest influence on the value of the OCV are the pH of the anolyte and the sulphate content therein, followed by the concentration of dissolved oxygen (in the cathodicchamber), the temperature and the concentration of H_2S in the anode. Regarding the influence on the value of P_{max}, it is found that the influence of the dissolved oxygen in the cathodicchamber is the most serious factor, the other independent parameters are arranged in the order mentioned above. This is also confirmed by other studies, in which the influence of oxygen in the catholyte, the conductivity of the anolyte, the influence of pH and temperature are established (Nikolova et al., 2013). It should be kept in mind that for the accurate maintaining of the independent factors values, the OCV and P_{max} are measured under abiotic conditions and therefore the influence of the biomass on the electrically active SRBs and other metabolically related microorganisms is not taken into account. The valuesof the determination coefficients R^2 (89% for OCV and 87% for P_{max}), indicating the percentage of changes in target function values due to the selected independent factors, again leads to a strong dependence between the selected independent and dependent parameters. The resulting regression equations are valid only in the selected ranges of variations of the independent factors.

Conclusion

The obtained results from the study confirm that a great number of factors influence the efficiency of MFC based on the process MSR in the anodic chamber. In the multifactorial linear regression analysis, are driven models to determine the influence of the temperature, pH, the concentrations of sulphates and H_2S in the anode and the oxygen content in the cathodic zone, on the values of OCV and P_{max}.

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