INFLUENCE OF ELECTRICAL CONDUCTIVITY AND TEMPERATURE IN A MICROBIAL FUEL CELL FOR TREATMENT OF MINING WASTE WATER

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ABSTRACT:*The influence of electrical conductivity and temperature on the efficiency of MFC with a basic microbial process in the anode zone - microbial sulphate reduction has been determined. A technological scheme of a laboratory installation has been synthesized allowing permanent control and management of basic process parameters - pH, electrical conductivity, temperature and OCV.*

The studies have been carried out at the optimal values of OCV, power density and current density for four different conductivity values and temperature under abiotic conditions in the anode zone of the fuel element and a comparison has been made with the biological process of the microbial sulphate reduction. On the basis of LabView^R has been offered a possibility of measuring different electrochemical parameters of the MFC that determine its efficiency. The results obtained will be used to optimize the work of MFC based on the microbial sulphate reduction process to treat wastewaters with high content of sulphates.

KEYWORDS: Microbial fuel cell, microbial sulphate reduction, acid mine drainage treatment.

1. INTRODUCTION

The role of renewable energy sources in the development of modern civilization is becoming more and more significant, not only because of the depletion of conventional energy resources, but also because of the environmental problems associated with the use of carbon-based fossil fuels. In the last 10-15 years, there is a significant interest among a scientific community for microbial fuel cells (MFCs) due to the possibility of simultaneously generating electricity and the removal of different pollutants from waters.

To date, various organic compounds have been used for the operation of microbial fuel cells, as well as some inorganic ones, which are typical pollutants in industrial and domestic wastewater [4]. To optimize the performance of this type of fuel elements, a significant set of constructive solutions has been developed to scale MFC for industrial realization [5, 6]. Some of the studies in recent years have been focused on the application of the microbial sulphate reduction process in the anode zone of MFCs for the treatment of sulphate-rich wastewater [1, 3]. On the other hand, the high content of sulphates in mining wastewater in concentrations above 3 g/l is a significant environmental problem [2]. Microbial fuel cells based on the microbial sulphate reduction (MSR) in the anode zone provide the opportunity to remove the sulphates from incoming water simultaneously with the generation of electricity. At this process the hydrogen sulphide is oxidized on the anodic surface to elemental sulfur [1]. Other final products are also possible in this process depending on the composition of the anolyte and the conditions of the medium - thiosulphates, polysulphides or dithionates.

The control and management of the ongoing chemical, electrochemical and biological processes in microbial fuel cells are essential to optimize their performance and to prove of the applicability of this type of fuel elements in practice.

The main objective of the present study is to demonstrate a technological scheme for monitoring and control of basic key parameters (pH, temperature, electrical conductivity and open circuit voltage), for the operation of the microbial fuel cell based on process of microbial sulphate reduction. A major focus of the research is - to determine the effect of temperature and electrical conductivity of the anolyte in the anode zone in MFC, on its effectiveness.

2. MATERIALS AND METHODS

A scheme of the laboratory installation of the microbial fuel cell is shown in Fig. 1. The microbial fuel cell was constructed in two equal sized anode and cathode sections, arranged in a U-shaped structure, separated by a cation-exchange membrane.

The volume of the anode and cathode sections was 0.48 dm^3, each. For the separation of the anode from the cathode space, a CMI-7000S membrane (Membrane International Inc.) was used with an area of 0.0012 m^2. As electrodes was used graphite rod, with a diameter of 8 mm and a length of 11 cm. The area of one electrode was 0.0028 m^2.

Approximately half of the volume of the 0.7 dm^3 buffer tank (4) was filled with 0.3 kg of modified zeolite, as the same played the role of a sulphidogenic bioreactor coupled sequentially to the anode section of the fuel element. The modified zeolite playes the role of a biofilm carrier from SRB and other metabolically related groups of microorganisms. The natural zeolite used was clinoptilolite from the Beli Plast deposit, Eastern Rhodopes, Bulgaria, with fraction of 2.5 - 5.0 mm. The elemental composition of the zeolite used was as follows: SiO_2 - 67.96, Al_2O_3 - 11.23, Fe_2O_3 - 0.83, K_2O - 2.85, Na_2O - 0.74, CaO - 3.01, MgO - 0.06, TiO_2 - 0.90. The cation exchange capacity and exchange ions in meq /100g were: CEC - 112.75, K + - 33.88, Na + - 21.01, Ca_2 $^+$ - 63.48, Mg_2 $^+$ - 2.68. Thus, in the proposed U-shaped microbial fuel cell (4) and sulphidogenic bioreactor, two zones were clearly formed - an area of active microbial sulfate reduction (where zeolite was located) and anode zone in which the microbial produced H_2S was oxidized.

A modified Postgate medium with a volume of 1.1 dm^3 was added to fill the anode and the sulphidogenic bioreactor (3). An inoculation of the microbial cell was performed with 50 ml of a mixed culture of sulphate reducing bacteria. After the formation of an active biofilm of SRB, a feeding with the culture medium started at a continuous cultivation mode. The medium from the tank (1) was feeded into the fuel cell with a regulated flow-rate through the peristaltic pump (2). The homogenization in the microbial fuel cell was accomplished by a recirculating pump (11).

The outflows from the settler were collected in a collecting tank (12) with a volume of 3 dm^3. A thermo-adjustable water bath was used to achieve the required temperature in MFC (10). The nutrient medium had the following composition in g/l: K_2HPO_4 - 0.25, NH_4Cl - 0.5, wt. Na_2SO_4 - 2.0, $CaCl_2$ - 0.1, $MgSO_4.7H_2O$ - 4.0, Na - lactate - 6.0, Yeast extract - 0.25 and had a pH of 6.5. The concentration of sulphates in the culture medium was 3 g/l, as the ratio between organic carbon and the final acceptor of electrons was 0.67.

Concerning the composition of the catholyte in the cathode semi-element of the microbial fuel cell, 100 mM $K_3[Fe (CN)_6]$ solution was used in 67 mM phosphate buffer solution at pH 7.0. A final electron acceptor, in this case, was the oxygen of the air, which in its reduction, together with the protons presented in the cathode space, formed water. For this purpose,

it was possible to aerate the cathodic zone with air, as the experiments were conducted in an open air mode.
The pH was measured using pH electrode (VWR) and pH meter HANNA HI 9021. The Eh was measured using Electrode Sen Tix ORP (WTW). The electrical conductivity was measured using Conductivity Electrode WTW LF90.
At certain points of the laboratory installation the values of pH, TDS and Eh parameters were measured. At the same sampling points were determined spectrophotometrically the concentrations of sulphates by $BaCl_2$ reagent at 420 nm and the concentration of hydrogen sulphide - using the Nanocolor 1-88/05.09 test at a wavelength of 620 nm.

The electric parameters of the fuel cell were measured with a Keithley-175 digital multimeter, as for a load resistance was used a precise potentiometer with a maximum value of 11,5 kΩ. To take the cyclic VA characteristics of the fuel element, the Potentiometer "ACM-Gill AC" was used, and the data was visualized and recorded in real time on the PC. Using the NI USB-6009 controller (DAQ Board) and software based on LabVIEW virtual instruments [8], the parameters pH, T, TDS and OCV were monitored. According to the chosen scheme (Figure 1) the ability to control the TDS parameter was demonstrated (by the value of electrical conductivity) in the anode zone of MFC.

3. RESULTS AND DISCUSSION

To study the influence of anodic conductivity on MFC performance, four variants of solutions were tested. Nutrient medium for SRB, as described above, was used as a basic composition of the anolyte, wherein the concentration of SO_4 was 3 g/l.

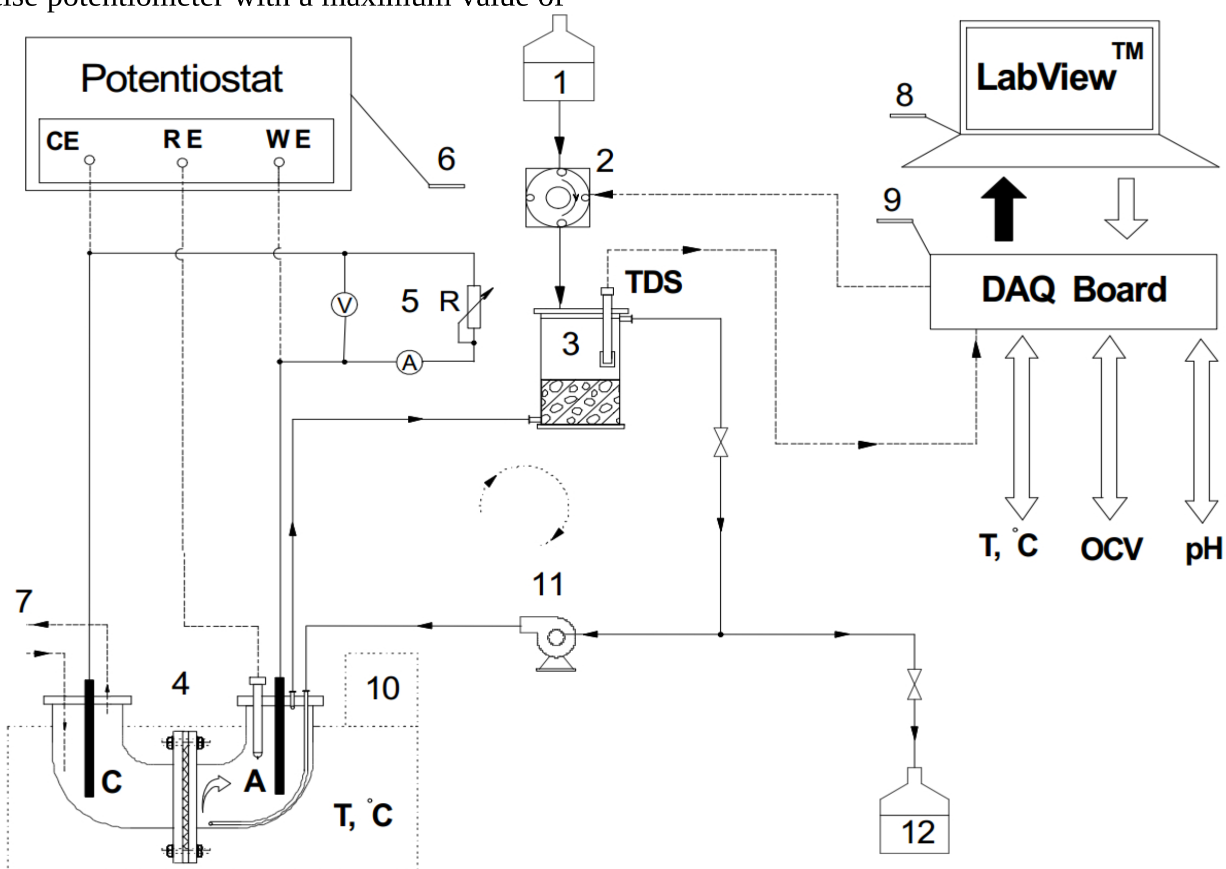

Figure 1. Laboratory-scale scheme of Microbial Fuel Cell (MFC)

1- feeding solution, 2- dosing peristaltic pump, 3- Bioreactor, 4- Microbial fuel cell, 5- electricity chain with a consumer, 6 - Potentiostat, 7- air , 8- PC, 9- DAQ Board (NI USB-6009), 10- tempered water bath, 11- recirculation pump , 12- collector tank, RE- reference electrode, WE- working electrode, CE- counter electrode, OCV- open circuit voltage, TDS- total dissolved solids.

To conduct the laboratory experiments under abiotic conditions, the anolyte solutions were prepared with equal H_2S concentrations of 500 mg/l (achieved by the addition of Na_2S in each anolyte). In order to provide different conductivity values, the concentration of sulphate ions was varied in each one of the variants as follows: variant 1 - 4.5 g/l, variant 2 - 3 g/l, variant 3 - 1.5 g /l, variant 4 - 0.5 g/l. Before the start of the experiments, the pH of all variants was adjusted to 7.5.

The measured values of Eh, SO_4^{2-}, electric conductivity (EC) and open circuit voltage (OCV) in the anolyte are presented in Table 1.

Table 1. Different variants on anolyte in MFC.

	Variants of Anolyte			
	1	**2**	**3**	**4**
T, ^oC	21 - 24			
pH	7.50 - 7.55			
Eh, mV	-414	-376	-373	-342
SO_4^{2-}, g/l	4.5	3.0	1.5	0.5
EC,mS/cm	10.13	7.82	5.20	3.67
OCV, mV	752	708	710	712
H_2S, mg/l	485 - 505			

These experiments showed a significant dependence of increasing the maximum value of the power density (with about 36.5%) and the current density at the increase of electrical conductivity (Figure 2). The obtained result was probably due to a reduction in the internal resistance of the fuel element. Similar results have been obtained in other studies [9], where it has been clearly demonstrated that the MFC electrochemical parameters could be improved by the addition of inorganic salts to the composition of anolyte.

It should be kept in mind that there was a significant difference in the behavior of the fuel element under abiotic and biotic conditions in the anode area, regarding the values of electrical conductivity. Under abiotic conditions, typical of the so-called "Sulphide" fuel cells, the relation of EC was clear (Figure 2). On the other hand, in the MSR process in the MFC anode zone, complex biochemical transformations of the organic substrate and reduction of sulphates to hydrogen sulphide were occuring. Therefore, the EC value was dynamic and difficult to predict. However, it is likely that the EC change was due to a decrease in sulphate concentration in the anolyte because of the MSR process and H_2S oxidation on the anode surface of MFC. In a series of other studies, the influence of temperature on the operation of the fuel element was determined. For this purpose, polarization and power density curves were taken at 4 different temperatures, using variant 2 of the anolyte (Table 1), respectively - 40 ^oC, 32 ^oC, 24 ^oC and 10 ^oC.

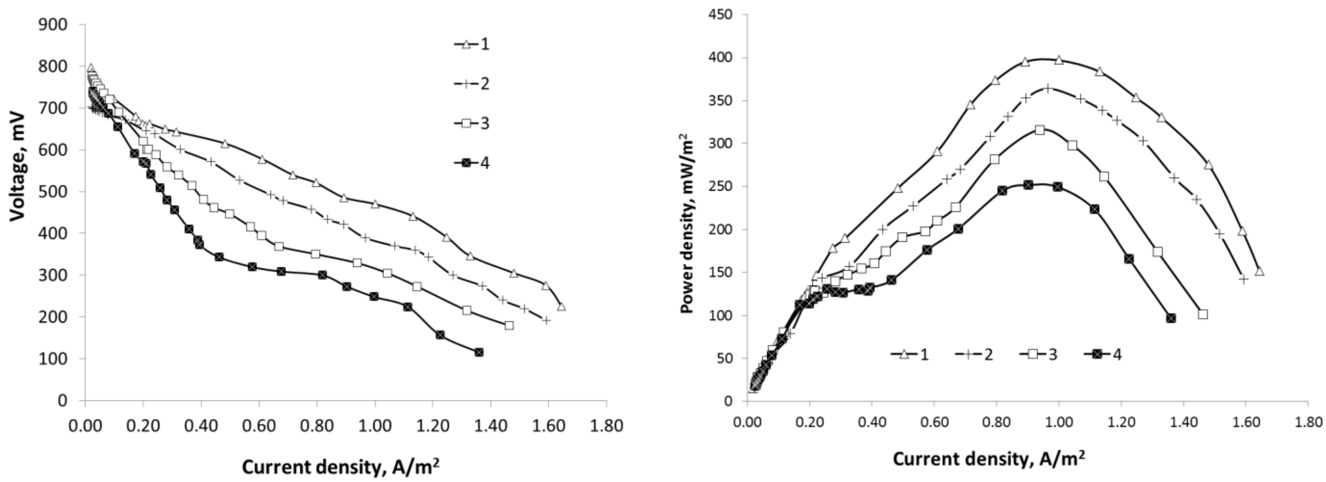

Figure 2. Polarization curves and power curves at different electrical conductivity values in the anode camera in MFC.

The results obtained are presented in Figure 3. There was an obvious tendency to increase the maximum power density from 341 mW/m^2 to 511 mW/m^2, changing the temperature from 10 ^oC to 40 ^oC (Figure 4). The latter was also confirmed by the cyclic VA characteristics, where the amplitude of the current increased with the highering of the temperature.

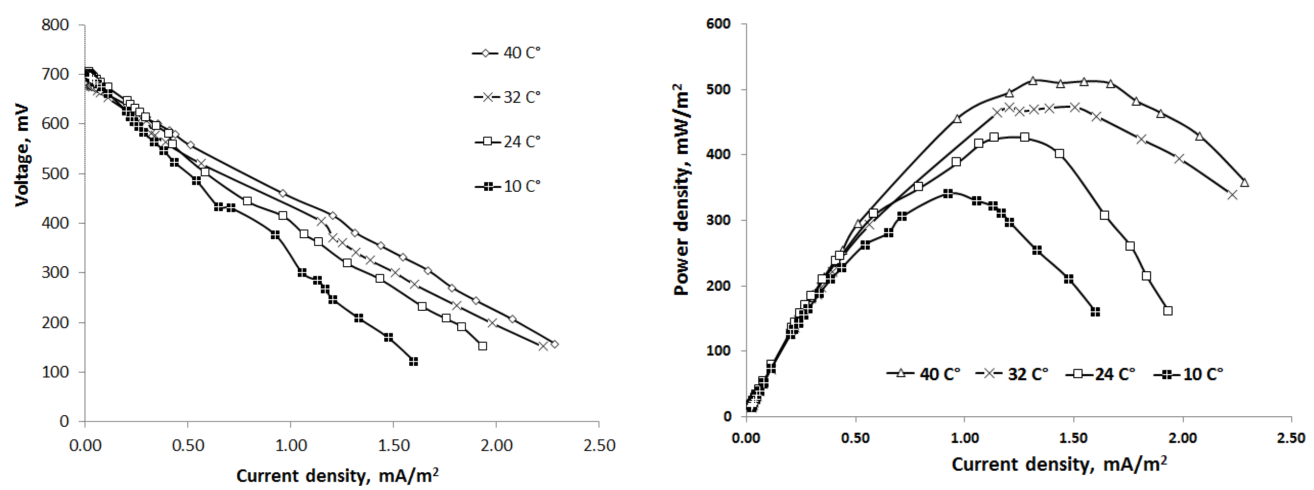

Figure 3. Polarization curves and power curves at different values of temperature in MFC.

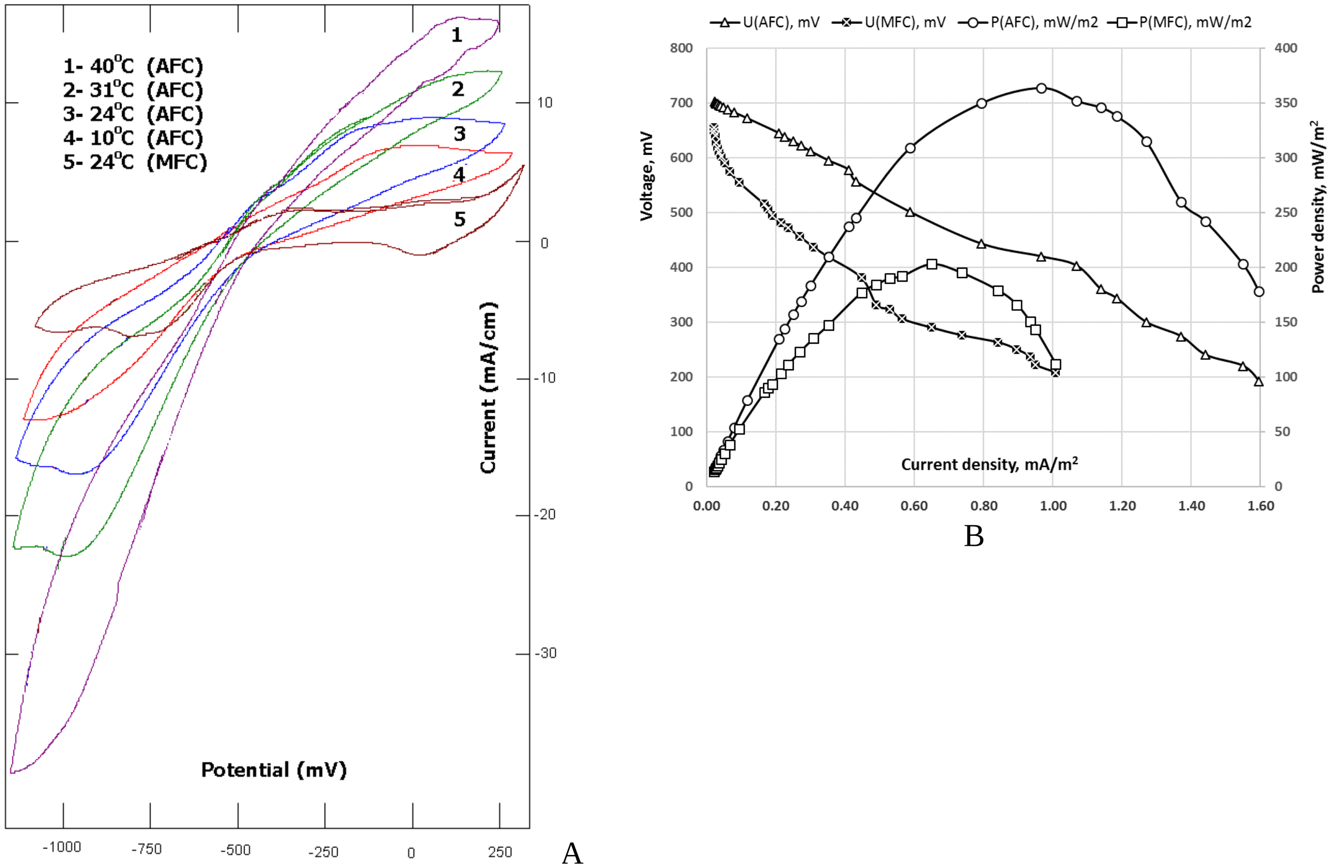

Figure 4. Cyclic VA characteristic (A) in AFC at different temperatures and comparison between polarization curves and power curves (B) on AFC and MFC.

A comparison was made between a biotic (MFC with an MSR process in anodic area) and an abiotic variant (abiotic fuel cell - AFC) of the fuel element at a temperature of 24 °C (Figure 4). It was found that values of electrochemical parameters were significantly reduced in the presence of a biological process in the anolyte.

The decrease was established in both the maximum power density values and the current amplitude values in the cyclic VA characteristic of MFC with an MSR biological process in the anode zone (Figure 4). This was probably due to lower concentrations of the biologically produced H_2S (approximately in the range of 245- 266 mg/l), compared to the abiotic variant (485 – 505 mg/l). In previous studies [1], it has been demonstrated the direct relationship between the H_2S concentration in the anodic zone and the electrochemical parameters of the fuel element.

4. CONCLUSIONS

In these investigations it was established the influence of EC and temperature on different electrochemical parameters of fuel cell, for 4 different conductivity values and temperatures in abiotic conditions (in sulphide AFC). These results were compared with such of MFC based on the MSR process.

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