INFLUENCE OF VARIOUS MICROBIAL PROCESSES IN THE ANODIC AREA ON THE EFFECTIVENESS OF PLANT SEDIMENT MICROBIAL FUEL CELL

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ABSTRACT: The plant sediment microbial fuel cells (PSMFCs) ecofriendly and efficiently transform solar radiation in electricity through the integration of live plant roots in the anodic area of sediment MFC. The bacteria in the anodic area, as the processes they perform, significantly affect the generated power of the cell. This study is related to the determation of the influence of various microbial processes in the anodic area of PSMFCs. For the purposes of this investigation are used PSMFCs, planted with Carex acuta. Four process are studied (fermentation, denitrification, sulphate-reduction and ferric-reduction) and for each experiment are monitored basic electrical parameters, changes in the physical and chemical indicators of anolyte and the number of basic physiological groups of microorganisms. The best electrochemical parameters are achieved with the process of microbial sulphate-reduction.

KEY WORDS: Plant sediment microbial fuel cells, Sediment microbial fuel cells, Microbial fuel cells

1. INTRODUCTION

In different natural marine and freshwater sediments are often observed redox gradients. These gradients are as a result of a spatial separation of the microbially-mediated redox reactions related to the biological degradation of organic compounds of the sediment. [2] In surface water of the water basins there is a high oxygen content ant the process of aerobic respiration is the dominant one. In depth, wherein the oxygen is depleted, various microorganisms carry out processes of reduction of iron, manganese, nitrates and etc., using them as final electron acceptors at the degradation of organic compounds. [4] In anaerobic sediments dominate the processes of microbial sulphate-reduction, fermentation and methanogenesis as they are the most thermodynamically favored in these environments.

Sediment microbial fuel cells (SMFCs) are a relatively new technology, at which the anode is placed in the sediment and the cathode is in the surface layer of water. The microorganisms in the anodic space decompose the organic matter and thus the produce electrons and protons. [3] Plant SMFCs are technologies that have recently appeared, in which an electric current can be generated by microorganisms, using organic compounds excreted from the roots of the aquatic plants. [1] It is important to be noted, that besides the species composition of the vegetation, the activity of bacteria in the anodic area, as well as the processes carried out, are essential for the performance of the cell. [5] In the present work, the influence of the four microbial process (fermentation, denitrification, sulfate-reduction and ferric reduction) occurring in the anodic area, on the efficiency of a plant sediment microbial fuel cell.

2. MATERIALS AND METHODS

2.1 Materials

For the purpose of the experiment it was used a plant sediment microbial fuel cell. The cell (Figure 1) consisted of a cylindrical base with a volume of 3650 cm3.The bottom of the vessel was covered with a layer of gravel with a thickness of 7 cm (≈ 3 kg). The particle fraction was in the range 10-20 mm. In the center of the container was placed a perforated in the base PVC tube with a diameter of 110 mm and a height of 440 mm. At the base of the tube was placed

an electrode of stainless steel with 112 cm length of and a 4 cm width. The electrode was formed as a spiral whose surface is 364 cm^2 and was covered with a 7 cm layer of gravel. The top the tube was filled with a mixture of sediment and peat in a ratio of 3:1 (Table 1). The SMFC was planted with Carex acuta. The device was filled with water and in the surface layer of water was placed a second electrode - the cathode. The cathode is made of stainless steels with a carbon coating for better conductivity. The dimensions of the cathode were: length - 400 mm and width - 20 mm. The cathode was also a spiral and had a surface of 160 cm^2

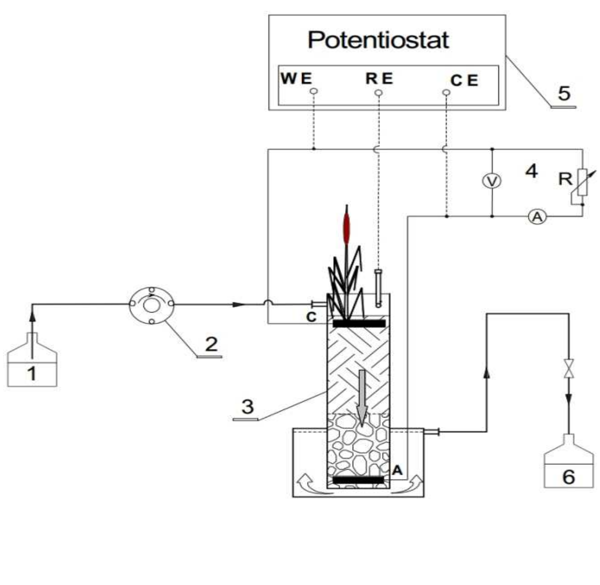

Figure 1. Design of Plant sediment microbial fuel cell
1 – Incoming solution, 2 – Peristaltic pump, 3 – Plant sediment microbial fuel cell, 4 – Digital multimeter, 5 – Potentiostat, 6 – Outgoing solution

Table 1. Chemical composition of the peat.

N (NH_4 and NO_3)	100 – 250 mg/l
P (P_2O_5)	120 – 300 mg/l
Fe	up to 65 g/m^3
Microelements	50 g/m^3
pH	5.5 – 6.5
Electroconductivity	1 – 2 mS/cm

Table 2. Composition of anolytes in order ofmicrobial processes investigation

Process	Initial solution
1 - Fermentation	Glucose 0.4 g/l, Peptone 0.1 g/l, K_2HPO_4 0.01 g/l, Mg/SO_4 0.01 g/l, NH_4Cl 0.02 g/l
2 - Denitrification	NO_3^- 1 g/l, Glucose 0.4 g/l, Peptone0.1 g/l, K_2HPO_4 0.01 g/l, Mg/SO_4 0.01 g/l, NH_4Cl 0.02 g/l
3 – Sulphate-reduction	SO_4^{2-} 1 g/l, Глюкоза 0.4 g/l, Пептон 0.1 g/l, K_2HPO_4 0.01 g/l, Mg/SO_4 0.01 g/l, NH_4Cl 0.02 g/l
4 – Ferric reduction	Глюкоза 0.4 g/l, Пептон 0.1 g/l, K_2HPO_4 0.01 g/l, Mg/SO_4 0.01 g/l, NH_4Cl 0.02 g/l, $Fe(OH)_3^*$ - 1 g/l

*$Fe(OH)_3$ was obtained by reacting ferric chloride with sodium hydroxide and the precipitate was washed with distilled water.

In order to establish the influence of various microbial processes on the efficiency of PSMFC in the anodic area were fed solutions with different chemical composition (Table 2). Each one of the solutions had a composition that favored one certain microbial process.

Each one of the processes was ongoing for seven days, then were determined the basic electrical parameters of the fuel cell, the changes in physical and chemical indicators of anolyte and the number of basic physiological groups of microorganisms. As a control for comparing the electrical parameters of the PSMFC was used a variant in which the anodic zone was filled with water.

2.2. Analytical methods

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 electroconductivity was measured using Conductivity meter WTW LF90. The concentration of organic compounds was determined by measuring its oxidation (by $KMnO_4$). The ammonium concentration was measured by the Nessler method. The nitrate concentration was measured by sodium salicylate method. The phosphate concentration was determined by the molybdenum-blue ascorbic acid method. The concentration of Fe(II) was measured by sulfosalicylic acid method.

The electrical parameters of PSMFC was measured using portable digital multimeter UNI-T UT33C. A precise potentiometer with maximum value of 13.5 kΩ used for measuring of external resistance.

The count of viable microbial cells was made by the plate or liquid media count methods. The aerobic heterotrophic bacteria were counted by plating on agar, as three replicates were made for each dilution. A two-tube most-probable number technique was applied for estimation of the number of anaerobic heterotrophic bacteria, bacteria fermenting sugars with gas production, denitrifying bacteria, Fe^{3+}-reducing bacteria and sulphate-reducing bacteria.

3. RESULTS AND DISCUSSION

In Tables 3 and 4 are presented data on various parameters of the anolyte of the PSMFC at the beginning and end of each microbial process.

Table 3. Dynamics of pH, RedOx potential and electroconductivity of the anolyte at the tested microbial processes

Process	pH initial	pH final	Eh, mV initial	Eh, mV final	EC, mS/cm initial	EC, mS/cm final
1 - Fermentation	6.83	6.69	-47	-58	1.21	0.69
2 - Denitrification	6.57	6.71	-62	-68	2.34	1.97
3 – Sulphate-reduction	6.49	6.62	-70	-225	3.12	2.70
4 – Ferric reduction	6.66	6.77	-140	-136	2.86	2.27

A reduction in the values of pH of the solution in the anodic area of PSMFC was established only for the fermentation of glucose due to the production of various organic acids. At the occuring of the processes of denitrification, sulphate-reduction and ferric reduction pH values of the anolytes increased due to the consumption of protons or the generation of bicarbonate ions in the tested microbial processes with different final electron acceptors. More reducing conditions (Eh in the range -136 - -225 mV) after seven days were established under conditions, favorable for the processes of sulphate and ferric reduction, which was associated with the oxidation-reduction status of the various redox couples. The electroconductivity at all processes decreased in time due to transformation and/or assimilation of the dissolved ions.

Table 4. Dynamics of permanganate oxidation and concentration of phosphates, nitrates, ammonium, sulfates and ferrous ions in the anolyte.

Process	PO, mg/l initial	PO, mg/l final	PO_4^{3-} mg/l initial	PO_4^{3-} mg/l final	NO_3^-, mg/l initial	NO_3^-, mg/l final	NH_4^+, mg/l initial	NH_4^+, mg/l final	SO_4^{2-}, mg/l initial	SO_4^{2-} mg/l final	Fe^{2+}, mg/l initial	Fe^{2+}, mg/l final
1 - Fermentation	295.3	194.4	17.33	9.47	78.6	59.59	28.4	22.86	14.6	8.6	3.6	2.4
2 - Denitrification	264.7	124.2	20.64	13.95	1012.6	90.22	32.33	19.13	15.9	7.3	4.1	3.3
3 – Sulphate-reduction	233.6	115.2	24.13	14.70	75.29	67.06	24.61	11.61	1014.5	46.1	3.9	2.7
4 – Ferric reduction	247.8	120.6	25.72	19.7	75.68	66.86	39.17	13.09	23.4	9.1	2.8	84.5

The data presented in Table 4 shows that the concentration of biogenic elements in the anolyte (N, P and S) was higher than that in the initial solution. This was due to the release of nutrients mainly from the peat, used as a component of the substrate in the

PSMFC. A part of the ammonium ions was transferиed into anolyte and due to the ammonification of peptone, that was incorporated in the composition of all tested solutions… The concentration of all biogenic elements decreased in time, due to their use as a final electron acceptor at the anaerobic microbial processes and their assimilation by the microflora inhabiting the anodic area. Under the created conditions with the highest average rate was the process of microbial sulphate-reduction - 138.3 mg/l.d. The average rate of denitrification was 131.8 mg/l.d, and of ferric reduction - 12.1 mg/l.d.

The data on the dynamics of permanganate oxidation shows that after a period of one week, for all the processes were monitored reducing concentrations of organic substances. The highest values of this parameter on the seventh day were detected for the processes of fermentation of glucose and formation of various organic acids in high concentrations.

The data from the microbiological analysis (Table 5) confirms the occurring of the desired microbial processes. The addition of easily degradable sources of carbon and energy led to an increase in the number of all investigated groups of microorganisms with 1 to 2 orders. In the absence of final electron acceptors were implemented various fermentations of glucose, as dominant populations in the biocoenoses were the bacteria fermenting sugars with gas production. The denitrifying bacteria were characterized by the highest number (7.0×10^6 cells/ml) when adding nitrate concentrations, favorable for the denitrification. With the usage of sulphates as final electron acceptors was reported a rapid increase in the number of sulfate-reducing bacteria, which reached to 6.0×10^7 cells/ml at the end of the experiment. The number of ferric reducing bacteria was highest in variants with imported ferric ions in the form of $Fe(OH)_3$.

Table 5. Dynamics of the number of different groups of microorganisms

Groups of microorganisms	Cells/ml				
	Before adding of solutions	Fermentation	Denitrification	Sulfate-reduction	Fe^{3+}-reduction
Aerobic heterotrophic bacteria	3.8×10^5	9.1×10^7	2.5×10^7	5.6×10^6	3.8×10^7
Anaerobic heterotrophic bacteria	7.0×10^5	2.5×10^7	7.0×10^6	2.5×10^6	6.5×10^6
Bacteria fermenting sugars with gas production	2.0×10^3	2.5×10^6	1.3×10^4	5.0×10^4	6.0×10^4
Denitrifying bacteria	2.5×10^5	1.1×10^4	7.0×10^6	2.5×10^5	7.0×10^4
Fe^{3+}-reducing bacteria	6.0×10^4	7.0×10^5	1.3×10^5	5.0×10^4	2.5×10^6
Sulphate-reducing bacteria	5.0×10^2	2.5×10^3	5.0×10^3	6.0×10^7	5.0×10^3

The data on measured electrical parameters is presented in Figure 2 .The maximum values of voltage, current density and power density were reached at the process of microbial sulphate-reduction. The open circuit voltage at this process was 1120 mV. The maximum power density of 11.75 mW/m^2 was established with an applied voltage of 200 Ω. Trhe eached maximum current density was 42.52 mA/m^2.

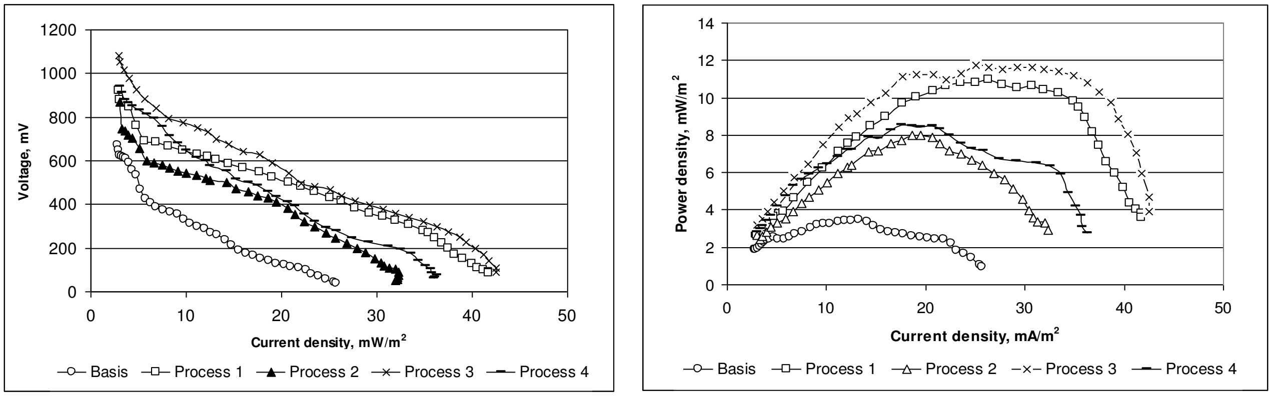

Figure. 2. Polarization curves of PSMFC`s

A little lower values of the parameters noted above were monitored for the process of fermentation. With a significantly lower voltages and power densities were characterized the processes of ferric reduction and denitrification, but from the figure it is obvious that in the course of these processes the efficiency of the cell increased significantly in comparison with initial electrical parameters of the system, taken in the variant with filled with water anodic zone.

For the studied microbial processes in the anodic area the lowest maximum power density of 7.97 mW/m^2 was established at the process of denitrification.

4. CONCLUSIONS

For all tested microbial processes best electrical parameters were achieved for the microbial sulfate-reduction. The value of open circuit voltage at this process was 1120 mV, and the maximum power density – 11.75 mW/m^2. The process of denitrification was characterized with the worst electrical parameters, as the maximum power density was only 7,97 mW/m^2. The occuring microbial processes led to substantially improvement of the PSMFC efficiency in comparison with the initial electrical parameters.

5. REFFERENCES

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