INFLUENCE OF VARIOUS BIOLOGICAL FACTORS ON THE TREATMENT EFFECT OF WATER CONTAMINATED WITH PETROLEUM PRODUCTS AND ELECTRICAL PARAMETERS IN PLANT SEDIMENT MICROBIAL FUEL CELLS

Rosen Ivanov, *University of mining and geology, Sofia, BULGARIA*
Svetlana Bratkova, *University of mining and geology, Sofia, BULGARIA*
Petia Genova, *University of mining and geology, Sofia, BULGARIA*
Katerina Nikolova, *University of mining and geology, Sofia, BULGARIA*

ABSTRACT: A plant sediment microbial fuel cell (PSMFC) is a promising new technology for harvesting energy and remediating a contaminated geo-environment. This study is related to the determation of the influence of various biological factors (different aquatic vegetation and microbial processes) on the degree of water purification contaminated with petroleum products and the generation of energy in PSMFC. For the purpose of the study, five PSMFCs with different vegetation (without vegetation, *Typha latifolia*, *Phragmites*, *Spartina* and mixed marsh vegetation) were constructed and the effect of three microbial processes (denitrification, sulfate-reduction and ferric reduction) were investigated. The best electrochemical parameters and treatment effect are achieved with the process of microbial sulphate-reduction in PSMFC planted with *Phragmites.*

KEY WORDS: Plant sediment microbial fuel cell, Oil degradation

1. INTRODUCTION

Plant sediment microbial fuel cell (PSMFC) is an attractive technology in the field of energy generation and simultaneous contamination remediation. [4] Initially, a PSMFC was studied as an ecological solar cell or a MFC, in which the root-derived organic compounds of a PSMFC were converted into electricity through the syntrophy between plants and electrochemically active bacteria. [3] Theoretically, continuous energy could be generated in PSMFCs through oxidation of plant rhizodeposits and other root-derived organic matter, including sugars, organic acids, amino acids, polymeric carbohydrates, enzymes, and dead plant cell tissue. [5] Both in the PSMFC and in the constructed wetland MFCs, plant roots play an important role in accelerating electricity production and various pollutant degradation. Plants inserted in PMFCs play an important role in converting solar energy into clean energy with no need of plant harvest. [8] The criteria for the selection of plants include hardiness, growth rate, microbial community at the rhizosphere, extensiveness of root system, tolerance and bioaccumulation abilities, local availability, adaptability and rhizodeposition. [6] The rhizosphere is the immediate region around the roots and the root surface extending to about 4 mm where electrodes are inserted during PSMFC operation. It supports a wide range of microbes, microbial activities and provides surfaces for bacterial attachment due to the release of large amounts of rhizodeposits by the plant roots. [2] In PMFCs, the microbial communities in rhizosphere are different, because root exudates differ within and between plant species, and microbial consortia varies with supporting matrix or inoculums and operation conditions. The microbial communities in the rhizosphere are also significantly affected by pollutants in the incoming water. [1] PMFCs have been employed in the generation of bioelectricity from diverse wastewater and they have been proven to be eco-friendly with high organics removal and stable power generation capabilities than other treatment systems. [7] It is important to note that in addition to the species composition of the vegetation, the activity of the bacteria in the anode area and the processes they carry out are essential for the cell's power. [2] To aid in understanding the effects of plants and microbial communities on PSMFC performance and to optimize the construction of PSMFCs, in present work four types of aquatic vegetation (without vegetation, *Typha latifolia*, *Phragmites*, *Spartina* and mixed marsh vegetation) and three anaerobic microbial processes (denitrification, sulfate-reduction and ferric reduction) were studied.

2. MATERIALS AND METHODS

In order to establish the influence of vegetation on the waste water treatment from petroleum products and the generation of energy, five PCMGCs were constructed (Figure 1). The cells have a volume of 30 dm^3 and are planted with different aquatic vegetation (without vegetation, *Typha latifolia*, *Phragmites*, *Spartina* and mixed marsh vegetation). The cells were filled with 20 dm^3 mixture of sediment and peat in a ratio 20:1. Stainless steel electrodes with an area of 400 cm^2 are placed on the bottom and in the surface layer. The cells are designed to provide a different flow of water in the installation under different operating modes. Before starting of the experiment was made screening of highly active oil-degrading strains of the laboratory collection, suitable for inoculum in the PSMFC anoxic and aerobic zone. By peristaltic pump, a solution with an crude oil content of 100 mg/l (total oil content 14 mg/l) and inoculated with highly active oil-degrading bacteria (*Pseudomonas veronii*, *Azoarcus communis*, *Pseudomonas chlororaphis*, *Pseudomonas putida*, *Pseudomonas libanensis)* was delivered to the cells with subsurface flow and hydraulic retention time of 14 days.

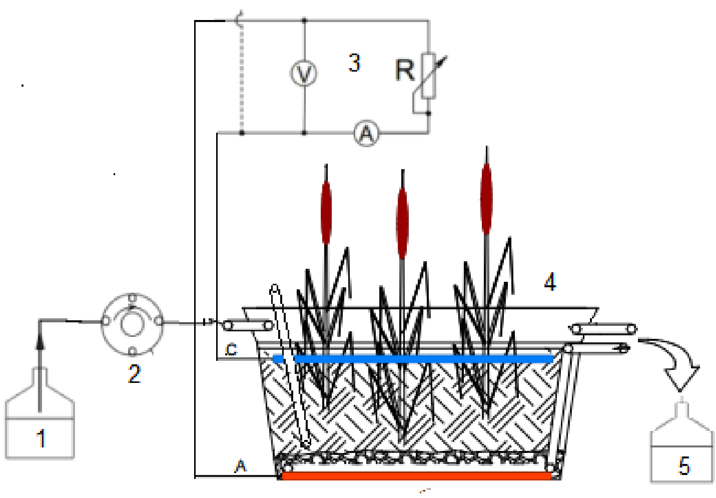

Figure 1. Design of Plant sediment microbial fuel cell
1 – Incoming solution; 2 – Peristaltic pump 3 – Digital multimeter, 4 – Constructed wetland with integrated plant sediment microbial fuel cell, 5 – Outgoing solution, A – anode, C – cathode

After obtaining and analyzing the results, two of the PSMFC were selected to be experimented for the influence of different processes in the anode area on the treatment effect of water contaminated with petroleum products and energy generation. For this purpose.in the anodic area were fed solutions with different chemical composition. Each one of the solutions had a composition that favored one certain microbial process (Table 1). Each one of the processes was ongoing for fourteen days, then were determined the basic electrical parameters of the fuel cell and the changes in physical and chemical indicators of anolyte.

Table 1. Chemical characteristic of initial solution

Process	Initial solution
Denitrification	NO_3^- 1 g/l, 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, Crude oil 100 mg/l
Sulphate-reduction	SO_4^{2-} 1 g/l, Glucose 0.4 g/l, Peptone 0.1 g/l, K_2HPO_4 0.01 g/l, $MgSO_4$ 0.01 g/l, NH_4Cl 0.02 g/l, Crude oil 100 mg/l
Ferric-reduction	Glucose 0.4 g/l, Peptone 0.1 g/l, K_2HPO_4 0.01 g/l, $MgSO_4$ 0.01 g/l, NH_4Cl 0.02 g/l, $Fe(OH)_3$* - 1 g/l, Crude oil 100 mg/l

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

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 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.

2. RESULTS AND DISCUSSION

In table 2 are presented data on various parameters of the anolyte of the PSMFC.

Table 2. Chemical parameters of the anolyte of the PSMFC

Cell №	pH	EC, µS/cm^2	NH_4^+, mg/l	PO_4^{3-}, mg/l	COD, mg/l	Total oil content, mg/l
1	7.21	1142	1.05	1.70	133	0.12
2	7.15	972	0.68	0.05	158	0.098
3	6.95	1011	0.89	0.38	176	0.077
4	6.79	846	0.68	0.01	126	0.06
5	7.03	999	0.6	0.28	156	0.11

The data presented in Table 2 show the minimum concentration of nutrients (N, P) in the anolyte due to the release of nutrients mainly from the peat used as a substrate component in PSMFC. The concentration of these elements is higher in cell 1, where there is no vegetation to further absorb the elements.

Total oil content data show a significant decrease in concentration in all cells after a two-week period. The best purification effect is achieved in PSMFC 3 (*Phragmites*) and 4 (*Spartina*), where the concentration decreases from 14 mg/l to 0.06 - 0.077 mg/l. The highest concentration of petroleum products - 0.12 mg l remains in cell 1 (without vegetation).

The same can be said for COD. All five cells show a significant decrease in the concentration from 4623 mg/l in the initial solution to 126 - 176 mg/l.

The data on measured electrical parameters is presented on Figure 2. The maximum values of voltage, current density and power density were reached in PSMFC 3 planted with *Spartina*. The open circuit voltage in this cell was 825 mV. The maximum power density of 7,12 mW/m^2 was established with an applied voltage of 100 Ω. The reached maximum current density was 25,52 mA/m^2.

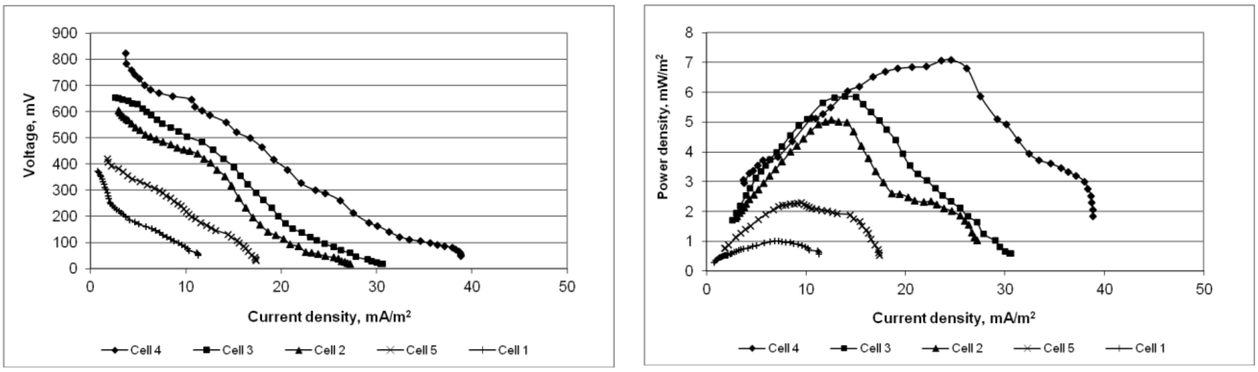

Figure 2. Polarization curves of PSMFCs

A little lower values of the parameters noted above were monitored in the PSMFC 3, plated with *Phragmites*. With a significantly lower voltages and power densities were characterized PSMFC 1, which is without vegetation.
Based on the results obtained for the next stage of the experiment, the cells that showed the best results were selected - PSMFC 3 (*Phragmites*) and PSMFC 4 (*Spartina*).
Table 3 presents the chemical composition of the initial solution before starting the corresponding microbial process. Tables 4 and 5 present data on the different studied parameters in the anolyte of the two PSMFCs at the end of each of the microbial processes.

Table 3. Chemical characteristics of initial solution

Initial solution	pH	Eh, mV	EC, µS/cm^2	Total oil content, mg/l
Denitrification	6,83	-21	2,37	14±0,1
Sulphate-reduction	7,02	-37	2,48	14±0,1
Ferric-reduction	6,66	-140	3,15	14±0,1

Table 4. Chemical parameters of the anolyte of the PSMFC 3

Microbial processes	pH	Eh, mV	EC, µS/cm^2	NH_4^+, mg/l	PO_4^{3-}, mg/l	SO_4^{2-} g/l	NO_3^-, mg/l	Fe^{2+}, mg/l	COD, mg/l	Total oil content, mg/l
Denitrification	7,71	-47	0,963	7,62	13,05	20,36	58,96	2,37	372	0,21
Sulphate-reduction	8,47	-230	0,689	7,98	11,62	90,48	8,32	3,82	221	0,13
Ferric-reduction	7,43	-152	1,025	9,47	19,76	21,18	7,08	86,14	726	0,65

At the occuring of the processes of denitrification, sulphate-reduction and ferric-reduction pH values of the anolytes increased in both cells 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 -146 - -230 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.

Table 5. Chemical parameters of the anolyte of the PSMFC 4

Microbial processes	pH	Eh, mV	EC, $\mu S/cm^2$	NH_4^+, mg/l	PO_4^{3-}, mg/l	SO_4^{2-} g/l	NO_3^-, mg/l	Fe^{2+}, mg/l	COD, mg/l	Total oil content, mg/l
Denitrific ation	7,68	-38	1,235	8,06	12,48	19,61	69,15	3,56	618	0,54
Sulphate-reduction	8,58	-221	0,897	7,56	11,96	101,2	6,78	4,09	495	0,38
Ferric-reduction	7,54	-146	1,452	8,81	17,54	20,40	4,82	84,62	1128	0,90

From the data presented in the tables it can be seen that the concentration of biogenic elements in the anolyte (N, P) is higher than that in the first stage of the experiment. This is due to their presence in the initial solution, as well as to the processes of nitrification and ammonification of the peptone included in all tested solutions.

The significant decrease in the concentration of NO_3^- and SO_4^{2-} and the increased concentration of Fe^{2+}, proves the course of the desired processes.

The COD dynamics data show that in all processes a higher concentration is observed compared to the first stage of the experiment due to the higher concentrations of petroleum products in the water leaving the cells. The highest values of this parameter at 14 days were established during the ferric-reduction process. Lower COD values were measured during the processes in PSMFC 3.

Total petroleum product data indicate that the highest degree of purification is observed during the sulfate-reduction process, with the concentration decreasing to 0,13 mg/l in PSMFC 3. The highest concentration remains in the ferric-reduction process in both cells. PSMFC 3 planted with *Phragmites* shows a greater degree of purification during the three processes.

The data on measured electrical parameters is presented on Figure 3 and 4.

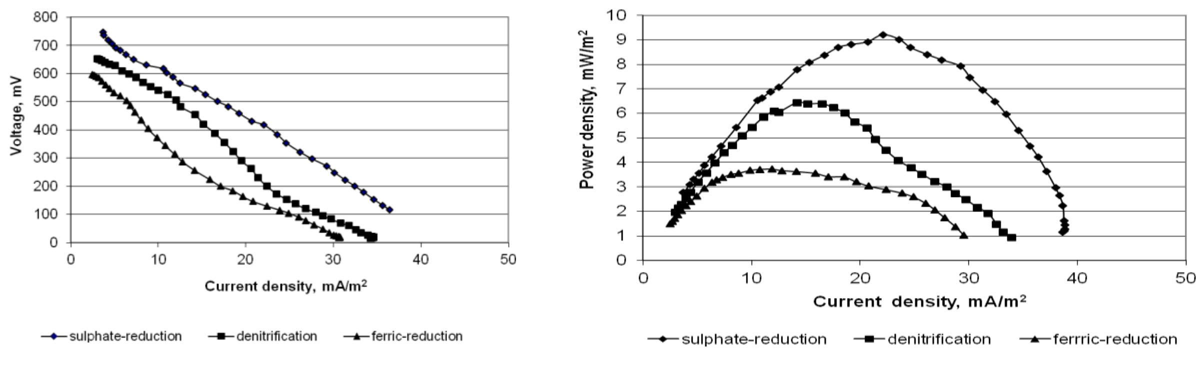

Figure 3. Polarization curves of PSMFC 3

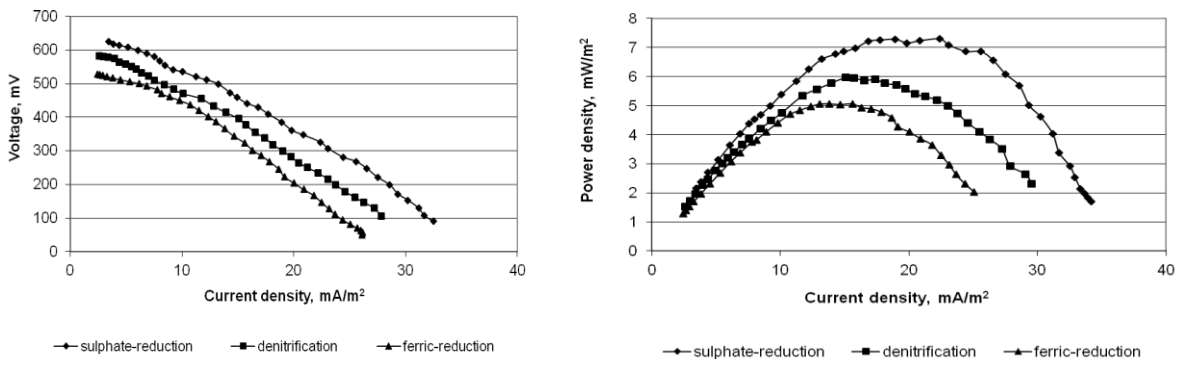

Figure 4. Polarization curves of PSMFC 4

The maximum values of voltage, current density and power density were reached at the process of microbial sulphate-reduction in both cells. Higher values of electrical parameters are measured in PSMFC 3, with the open circuit voltage in this cell was 782 mV. The maximum power density of 9,15 mW/m^2 was established with an applied voltage of 200 Ω. The reached maximum current density was 23.68 mA/m^2. A little lower values of the parameters noted above were monitored for the process of denitrification. With a significantly lower voltages and power densities were characterized the processes of ferric reduction in both cells. All three processes course with greater energy generation in PSMFC 3 planted with *Phragmites*.

3. CONCLUSION

The biological factors in PSMFC have a significant effect on their treatment capacity and the energy generation. From the research and the results obtained, it is established that water contaminated with petroleum products can be successfully purified by PSMFC. For the higher degree of purification, plant species are important, and the best results in this relation were obtained with RSMGC planted with *Spartina*. In this cell were measured the highest electrical parameters. The course of the studied microbial processes impedes the oxidation of petroleum products, but on the other hand, the energy generated by the PSMFC is increased. The highest degree of water purification from petroleum products was found during the sulfate-reduction process. During this process, were also measured maximum values of the electrical parameters of the PSMFC.

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