INVESTIGATION OF THE DESIGN OF PLANT SEDIMENT MICROBIAL FUEL CELL ON THE ELECTRICAL PARAMETERS AND THE WATER TREATMENT EFFECT FROM PETROLEUM PRODUCTS

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Abstract: *Most applications of constructed wetlands (CW) have been designed to treat municipal or domestic wastewater but at present, constructed wetlands are successfully applied to many types of wastewater. The criteria for CW design and operation include site selection, plant selection, substrate selection, wastewater type, plant material selection, hydraulic loading rate, hydraulic retention time, water depth, operation mode and maintenance procedures. Integration of plant sediment microbial fuel cells (PSMFC) into them allows water treatment and parallel energy production. The purpose of this study is to investigate the influence of design of PSMFCs and various operation modes on electrical parameters and water treatment effect from petroleum products. The best results were achieved with downstream water flow, substrate - mixture of sediment and peat in a ratio of 3:1, use of stainless steel electrodes and the absence of a separator between aerobic and anaerobic areas. With this design and operating mode was achieved maximum power density of 10,40 mW/m^2 and water purification of petroleum products of over 99% in CW with integrated PSMFC*

Keywords: PLANT SEDIMENT MICROBIAL FUEL CELLS, OIL DEGRADATION, CONSTRUCTED WETLANDS

1. Introduction

Most applications of constructed wetlands (CW) have been designed to treat municipal or domestic wastewater but at present, CW are successfully applied to many types of wastewater. The criteria for CW design and operation include site selection, plant selection, substrate selection, wastewater type, plant material selection, hydraulic loading rate (HLR), hydraulic retention time (HRT), water depth, operation mood and maintenance procedures. [7] Particularly, the factors such as plant selection, substrate selection, water depth, HLR, HRT, and feeding mood may be crucial to establish a viable CW system and achieve the sustainable treatment performance. Wetland plants which have several properties related to the treatment process could play a strategic role in CWs, and are considered to be the essential component of the design of CW treatments. For the selection of plants, tolerance of waterlogged-anoxic and hyper-eutrophic conditions and capacity of pollutant absorption are recommended besides adaption to extreme climates. [5] The substrate is the critical design parameter in CWs in particular, because it can provide a suitable growing medium for plant and also allow successful movement of wastewater. Moreover, substrate sorption may play the most important role in absorbing various pollutants such as phosphorus. Selection of suitable substrates to use in CWs for industrial wastewater treatment is an important issue. The selection of substrates is determined in terms of the hydraulic permeability and the capacity of absorbing pollutants. Poor hydraulic conductivity would result in clogging of systems, severely decreasing the effectiveness of the system, and low adsorption by substrates could also affect the long-term removal performance of CWs. Substrates can remove pollutants from wastewater by exchange, adsorption, precipitation and complexation. The adsorption capacities of substrates vary each other and their capacity of sorption may depend primarily on the contents of the substrate, moreover, it could be influenced by the hydraulic and pollutant loading. [3]

Water depth is a crucial factor in determining which plant types will become established, and it also influences the biochemical reactions responsible for removing contaminants by affecting the redox status and dissolved oxygen level in CWs. [1]

Hydrology is one of the primary factors in controlling wetland functions, and flow rate should also be regulated to achieve a satisfactory treatment performance. The optimal design of hydraulic loading rate and hydraulic retention time plays an important role in the removal efficiency of CWs. Greater HLR promotes quicker passage of wastewater through the media, thus reducing the optimum contact time. On the contrary, an appropriate microbial community may be established in CWs and have adequate contact time to remove contaminants at a longer HRT.[8]

The feeding mode of influent has been shown to be another important design parameter. The difference of feeding mode (such as continuous, batch and intermittent) may influence the oxidation–reduction conditions and oxygen transfer and diffusion in wetland systems and, hence, modify the treatment efficiency. Various studies were conducted to evaluate the effect of influent feeding modes on the removal efficiency of CW treatments. In general, batch feeding mode can obtain the better performance than continuous operation by promoting more oxidized conditions. [6]

Plant Sediment Microbial Fuel Cells (PSMFCs) are a particular type of Microbial Fuel Cells that utilizes organic materials. PSMFCs are capable of converting a wide range of organic materials in aquatic ecosystems, like CWs, to electricity. The fuel cell consists of anode and cathode electrodes, which can be produced from conductive materials such as graphite, carbon paper, carbon felt, carbon fabric, and carbon brush. [4] The anode is placed in an anaerobic part and buried under sediments while the cathode is placed in the aerobic part (the upper section of the sediment) floating in the catholyte liquid. [2] However, recent researches on PSMFCs have demonstrated that they can generate only a small amount of energy continuously at mW level. Researchers have focused on creating bigger electrodes, improving electrode materials and adding different fuels to sediments to increase the energy supplied. [8] The purpose of this study is to investigate the influence of the design of the PSMFC integrated in CW on the electrical parameters and the water treatment effect from petroleum products.

2. Materials and Methods

In order to determine the effect of the substrate on the efficiency of plant sediment microbial cells (PSMFC), three variants of sediment microbial fuel cells (SMFC) with different sediment to peat ratio (3: 1, 1: 1 and 1: 3) in the substrate were constructed. The sediment microbial fuel cell consists of a 1000 cm^3 plastic container. They are filled with a substrate of 800 cm^3 volume. After insertion of the substrate, the cells were filled with water. AISI 304 stainless steel electrodes with a surface area of 40cm^2 were placed at the bottom of the cell and the surface in the water layer.

The same sediment microbial fuel cells were used to determine the effect of the separator type on efficiency. A layer of bentonite 1 cm thick was placed in the first cell between the anode and cathode zones. A layer of 1 cm thick perlite was placed in the second cell and no separator was placed in the third cell.

In order to determine the influence of the electrode material on the energy generated, two of the sediment microbial fuel cells were used. The first uses stainless steel electrodes and the second uses graphite electrodes. The surface area of the electrodes is 40cm^2.

After determining the influence of the substrate, the type of separator and the electrode material, two plant sediment microbial fuel cells were constructed in which experiments were carried out to determine the influence of the design and the course of the water flow on the degree of purification of water contaminated with petroleum products and the energy generation.

PSMFC 1 (Figure 1) have a volume of 30 dm^3 and are planted with *Spartina*. The cells were filled with 20 dm^3 mixture of sediment and peat in a ratio 3:1. 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, COD 4690 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 hydraulic retention time of 14 days.

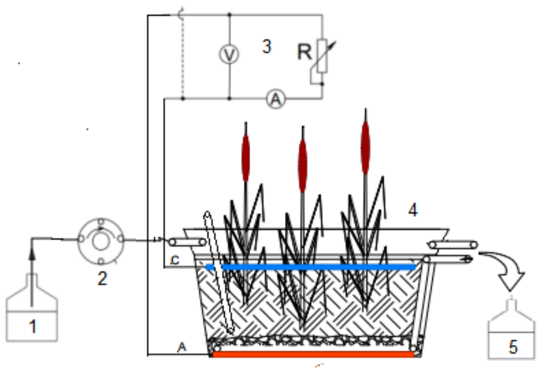

Fig. 1 *Design of Plant sediment microbial fuel cell 1*
1 – Incoming solution, 2 – Peristaltic pump, 3 – Digital multimeter, 4 – Plant sediment microbial fuel cell, 5 – Outgoing solution, A – Anode C – Cathode

On Figure 2 is shown a scheme of the laboratory model of the PSMFC 2.

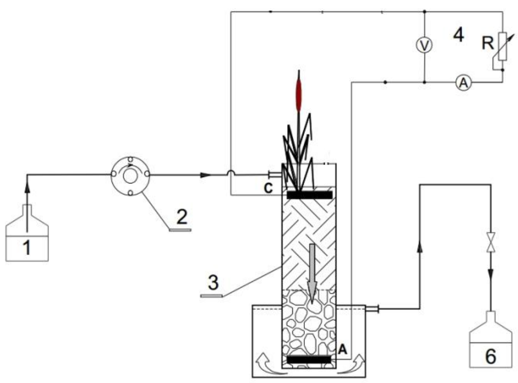

Fig. 2 *Design of Plant sediment microbial fuel cell 2*
1 – Incoming solution, 2 – Peristaltic pump, 3 – Plant sediment microbial fuel cell, 4 – Digital multimeter, 6 – Outgoing solution, A – Anode C – Cathode

PSMFC 2 consisted of a cylindrical base with a volume of 3650 cm^3.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 formed as a spiral whose surface is 400 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. The PSMFC was planted with *Spartina*. The device was filled with water and in the surface layer of water was placed a second electrode - the cathode. The cathode was also a spiral and had a surface of 400 cm^2. By peristaltic pump, a solution with an crude oil content of 100 mg/l (total oil content 14 mg/l, COD 4690 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 hydraulic retention time of 14 days.

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.

3. Results and Discussion

After stabilization of the electrochemical parameters, the electrical parameters of the three SMFCs with different sediment to peat ratio in the substrate were measured and compared. The data from the made polarization curves are presented in Figure 3. From the graphs it can be seen that with the best electrical parameters are characterized SMFC with a sediment peat ratio of 3:1. It achieves a maximum power density of 2,07 mW/m^2. The lowest power density was found in SMFC with a sediment peat ratio of 1:3. This result is due to the fact that as the amount of peat in the substrate increases, the concentration of biogenic elements in the water increases. This leads to an increase in the ionic strength of the solution and to a higher electrical conductivity between the cathode and anode area.

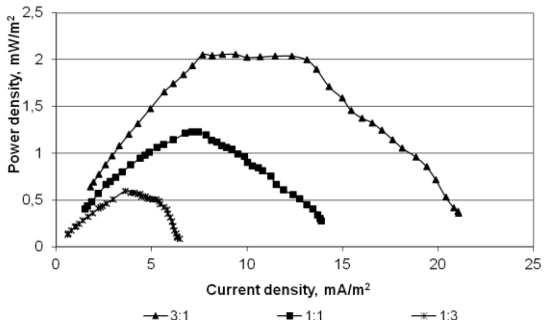

Fig. 3 *Polarization curves of SMFC-s with different ratio of sediment and peat in substrate*

The data from the measured electrical parameters at different separators between the anode and cathode area in the SMFCs are presented in Figure 4.

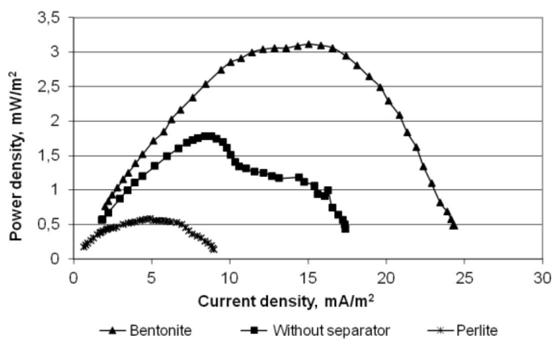

Fig. 4 *Polarization curves of SMFC-s with different substrate*

The graphs show that the best electrical parameters are achieved using bentonite as a separator. In this variant, a maximum power density of 3,12 mW/m^2 is reached. The lower power density is characterized SMFC without separator – 1,75 mW/m2. The lowest electrical parameters were measured using a perlite separator.

Figure 5 shows the polarization curves measured during the experiment with different electrode material.

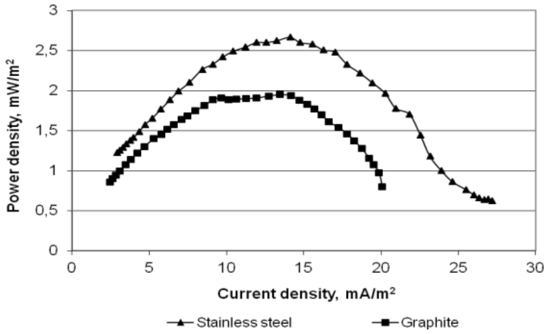

Fig. 5 *Polarization curves of PSMFC-s with different electrode materials*

From the presented data it can be seen that higher values of electrical parameters are achieved when using stainless steel electrodes. The measured power density in this variant is 2,64 mW/m^2. Using graphite electrodes, a power density of 1,96 mW/m^2 was measured.

Following the experiments carried out and analysis of the results, two plant sediment microbial fuel cells were constructed to conduct experiments related to determining the influence of the design and the course of the water flow on the degree of purification of water polluted with petroleum products and energy generation. PSMFCs are constructed with a substrate containing sediment and peat in a 3: 1 ratio. Despite the best results achieved with the use of bentonite as a separator in SMGC, no separator was installed in the PSMFCs. Studies have shown that the use of bentonite significantly impedes the penetration of water into the anode area, which would disrupt the normal operation of the PSMFC and effectivennes of water treatment from petroleum products. Stainless steel electrodes are placed in the PSMFC.

14 days after the start of the downstream flow experiment, the electrical parameters in the PSMFCs, the total oil content and the COD of the effluent were measured. Figure 6 shows the graphs of the polarization curves of the two PSMFCs.

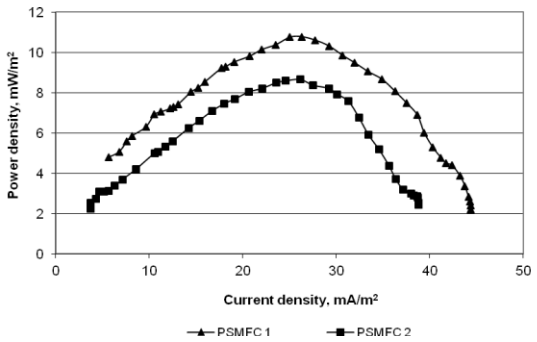

Fig. 6 *Polarization curves of PSMFC-s in downstream flow mode*

The graphs show that better electrical parameters are measured in PSMFC 1, where the power density reaches 10,40 mW/m^2. A power density of 8,78 mW/m^2 was measured in PSMFC 2.

Table 1 presents data of the total oil content and COD in the outgoing water cells. The data show a higher degree of purification of the oil products in PSMFC 1. The same applies to COD. The total oil content measured at the outlgoing waters of the cell was 0,075 mg/l with a COD of 185 m /l.

Table 1: *Chemical parameters of the outgoing waters of the PSMFC-s in downstream flow mode*

	Total oil content, mg/l	COD, mg/l
PSMFC 1	0,075	183
PSMFC 2	0,095	204

Figure 7 presents the data from the polarization curves of the PSMFC in upstream flow mode.

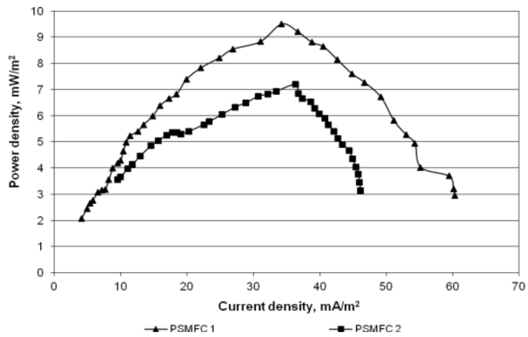

Fig. 7 *Polarization curves of PSMFC-s in upstream flow mode*

The graphs again show better electrical parameters in PSMFC 1. The power density achieved is 9,52 mW/m^2, while in PSMFC 2 it is 7,22 mW/m^2. The graphs also show that in upstream flow mode, lower energy is generated in both cells.

Table 2 presents data for the total oil content and COD in effluent fromPSMFC in upstream flow mode..

Table 2: *Chemical parameters of the outgoing waters of the PSMFC-s in upstream flow mode*

	Total oil content, mg/l	COD, mg/l
PSMFC 1	0,088	195
PSMFC 2	0,104	213

The data again show a higher degree of water purification from petroleum products in PSMFC 1. From the data, it is found that in upstream flow mode, a lower degree of water purification from petroleum products is observed in both RSMGCs compared to a downstream flow mode.

4. Conclusion

From the performed studies and the results obtained, it can be concluded that the design of the PSMFCs and the water flow through the cell have a significant impact on both the purification capacity and the energy generation. The highest electrical parameters was measured at a sediment:peat ratio of 3:1. Placing a bentonite separator between the anode and cathode area significantly increases the energy generation due to an increase in the redox gradient between the two zones. On the other hand, the use of a separator has proven to be inappropriate for the upstream and downstream water flow in the PSMFC because of the difficulty of passing water through the cell and reducing the efficiency of the treatment process. The use of a separator in PSMFC is appropriate for substrate or surface flow of purified water in which it does not pass between the aerobic and anaerobic area of the cell. The material from which the electrodes are made also affects the energy generation. When using stainless steel electrodes, higher electrical parameters were measured in both PCMGCs. Also, during prolonged work on graphite electrodes, passivation of mobilized biomass and metabolic products was observed. In this way, the active contact surface of the electrodes is significantly reduced.

With the downstream water flow through the PSMFCs, higher efficiency of water purification from petroleum products is found. In both tested runs, lower concentrations of petroleum products in outgoing water were measured in PSMFC 1.

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5. References

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