TREATMENT OF WATER CONTAMINED BY PETROLEUM PRODUCTS THROUGH CONSTRUCTED WETLANDS WITH INTEGRATED PLANT SEDIMENT MICROBIAL FUEL CELLS

Rosen Ivanov, Ani Stefanova, Anatoliy Angelov

University of Mining and Geology "St. Ivan Rilski", 1700 Sofia; rosen_iv@abv.bg

ABSTRACT. Oil exploration and exploitation activities contribute to global economic growth but often lead to pollution of the environment by oil and petroleum products. Constructed wetlands are cheap, environmentally friendly and use biological processes based on photosynthesis process for treatment oil-contaminated waters. Integration of Plant Sediment Microbial Fuel Cells (PSMFC) into them allows the generation of energy in parallel to water treatment. The purpose of this study is to identify the treatment capacity of five variants of PSMFC planted with different vegetation (*Typha latifolia*, *Phragmites, Spartina*, mixed marsh vegetation and cell without vegetation). A solution containing crude oil at a concentration of 100 mg/l is delivered to the PSMFC with a horizontal surface flow and a hydraulic retention time of 14 days. From the chemical analyses performed, the highest treatment level was established in PSMFC 4 planted with *Spartina* and inoculated with mixed culture oil-oxidising bacteria. At the end of the experiment the concentration of pollutant dropped to 0.052 mg/l. The same showed the best electrical parameters during the experiment. The power density reached 11.56 mW/m^2 at a current density of 27.16 mA/m^2 and applied resistance of 300 Ω. The open circuit voltage ranged from 900 to 1100 mV. The results obtained show good prospects for application of plant sediment microbial cells in the passive treatment of waters polluted with crude oil and petroleum products.

Keywords: constructed wetlands, plant sediment microbial fuel cells, passive wastewater treatment, oil and petroleum products pollution

ПРЕЧИСТВАНЕ НА ВОДИ ЗАМЪРСЕНИ С НЕФТОПРОДУКТИ ЧРЕЗ КОСТРУИРАНИ ВЛАЖНИ ЗОНИ С ИНТЕГРИРАНИ РАСТИТЕЛНИ СЕДИМЕНТНИ МИКРОБНИ ГОРИВНИ КЛЕТКИ

Росен Иванов, Ани Стефанова, Анатолий Ангелов

Минно-геоложки университет "Св. Иван Рилски", 1700 София

РЕЗЮМЕ. Дейностите по проучване и експлоатация на нефтени находища допринасят за икономически растеж в световен мащаб, но често това води и до замърсяване на околната среда с нефт и нефтопродукти. Конструираните влажни зони са евтини, екологично чисти и използват биологични процеси, базирани на процеса фотосинтеза за пречистване на замърсени с нефт води. Интегрирането на растителни седиментни микробни клетки (РСМГК) в тях позволява генерирането на енергия при паралелно пречистване на водите. Целта на настоящото изследване е да се установи пречиствателната способност на пет варианта РСМГК, засадени с различна растителност (*Typha latifolia*, *Phragmites, Spartina*, смесена блатна растителност и клетка без растителност) Към РСМГК е подаван разтвор съдържащ нефт в концентрация 100 mg/l, при хоризонтален повърхностен поток и контактно време 14 дни. От направените химични анализи се установи най-висока степен на пречистване при РСМГК 4 засадена с блатна трева и инокулирана със смесена култура нефт-окисляващи бактерии. В края на експеримента концентрацията на замърсителя спадна до 0,052 mg/l. Същата показа и най-добри електрически параметри по време на експеримента. Плътността на мощността достигна до 11,56 mW/m^2 при плътност на тока 27,15 mA/m^2 и приложено съпротивление 300 Ω Напрежението при отворена верига се движеше в границите 900 – 1100 mV. Получените резултати показват добри перспективи за приложение на растителните седиментни микробни клетки при пасивно пречистване на води, замърсени с нефт и нефтопродукти.

Ключови думи: конструирани влажни зони, растителни седиментни микробни горивни клетки, пасивно пречистване на води, замърсяване с нефт

Introduction

Crude oil is the world`s largest non-renewable energy resource, accounting for about 33% of the total consumed energy. Drilling and extraction processes for oil and gas generate huge volumes of oil-contaminated water. The worldwide demand for oil is expected to keep rising in the coming years, which will potentially increase the generation of oil-contaminated water.

Worldwide, water contaminated with crude oil is usually stored in evaporation pits before eventual discharge into the environment without any treatment. The remediation of such oil-contaminated water has become a critical problem in oil-producing countries and requires immediate attention. Moreover, the majority of oil and/or gas wells are not highly productive at the time of their installation and lose their efficiency after some time (Muhammad et al., 2019). Conventional methods of oil-contaminated water treatment based on physical and chemical processes are not feasible to install due to their high capital, operational and maintenance costs (Shubiao et al., 2018).

Using constructed wetlands (CW) with integrated plant sediment microbial fuel cells (PSMFC) is an innovative approach for the remediation of polluted water which requires only aquatic vegetation. They can be applied to any oil-contaminated water stabilisation pit with minimal financial capital (Vymazal, 2014). Recent studies have revealed that the combined use of plants and bacteria in CW with PSMFC can enhance plant growth and pollutant degradation. Plants provide nutrients to rhizospheric microbes through their roots exudates (Felix et al., 2019). These microorganisms have major roles in the degradation of organic compounds, and their efficiency in degrading hydrocarbons increase in the presence of plants. (Rachnarin et al., 2017) Once the pollutant is taken up by plant, endophytes are actively involved in the *in planta* degradation. However, this combination of plants and associated microorganisms has not yet been evaluated at large scales for remediation of oil-contaminated water (Qing et al., 2017).

Generation of energy from plant sediment microbial fuel cells is additional advantage in using this technology for oil-contaminated water treatment (Rasool et al., 2019). Most PSMFC are open systems with anodes embedded in anoxic sediment and cathodes placed in aerobic water layer. The microorganisms in the sediment consume organic substrates and transfer the electrons to the anode. Dissolved oxygen is utilised as an electron acceptor and combines with protons to form water and generate electricity (Panpan et al., 2014; Boyue et al., 2019).

The aim of this study is to evaluate the treatment efficiency of oil-contaminated water and electricity generation by applying CW with PSMFC.

Materials and methods

For the purpose of the study five constructed wetlands with integrated plant sediment microbial fuel cells were made (Figure 1). The cells have a volume of 30 dm^3 and are planted with different aquatic vegetation. (Table 1) 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.

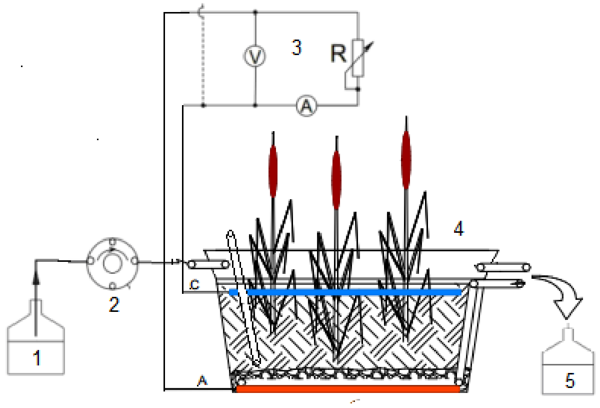

Fig. 1. Scheme of the laboratory installation
1 – Incoming solution; 2 – Peristaltic pump 3 – Digital multimeter, 4 – Constructed wetland with integrated plant sediment microbial fuel cell, 5 – Outgoing solution, A – anode, C – cathode

Before starting the experiment, screening of highly active oil-degrading strains of the laboratory collection, suitable for inoculum in the CW anoxic and aerobic zone, was made.

By peristaltic pump, a solution with a crude oil content of 100 mg/l (total oil content 14 mg/l and COD 39000 mg/l) was delivered to the cells with hydraulic retention time of 14 days. In order to establish the best treatment effect and energy generation, four modes of operation of the cells were studied. In Mode 1, clean water is flowed into the cells with a horizontal surface flow. In Mode 2, synthetic solution with crude oil is flowed into the cells with a horizontal surface flow. In mode 3, synthetic solution with crude oil is flowed into the cells with a horizontal surface flow. The cells are inoculated with a mixed culture of oil-oxidising bacteria (*Pseudomonas veronii, Azoarcus communis, Pseudomonas chlororaphis, Pseudomonas putida, Pseudomonas libanensis).* In mode 4, synthetic solution with crude oil is flowed into the cells with a horizontal subsurface flow. The cells are inoculated with a mixed culture of sulphate-reducing bacteria. After the completion of each of the modes, basic chemical parameters, total oil content and the electrical parameters of the cells were measured.

Table 1. *Scheme of the experiment*

Cell	Vegetation
Cell 1	Without vegetation
Cell 2	*Typha latifolia*
Cell 3	*Phragmites*
Cell 4	*Spartina*
Cell 5	mixed marsh vegetation

Results and discussion

Table 2 shows the basic chemical parameters of the constructed wetlands for the four modes of operation

Table 2. *Basic chemical parameters of the constructed wetlands*

CELL	Mode 1		Mode 2		Mode 3		Mode 4	
№	pH	EC µS/cm	pH	EC µS/cm	pH	EC µS/cm	pH	EC µS/cm
1	7.12	612	6,78	1224	6.83	1105	7.21	1142
2	6.82	825	7.22	1035	7.08	936	7.15	972
3	7.25	890	7.14	997	7.17	952	6.95	1011
4	7.04	734	6.92	894	6.87	789	6.79	846
5	6.97	951	7.31	1012	6.79	960	7.03	999
№	NH_4^+ mg/l	PO_4^{3-} mg/l	NH_4^+ mg/l	PO_4^{3-} mg/l	NH_4^+ mg/l	PO_4^{3-} mg/l	NH_4^+ mg/l	PO_4^{3-} mg/l
1	3.35	3.28	1.89	3.19	1.14	2.16	1.05	1.70
2	2.36	5.24	1.57	0.47	0.86	0.05	0.68	0.05
3	1.4	1.70	1.37	1.51	1.19	0.66	0.89	0.38
4	1.54	3.75	1.46	1.89	1.08	0.01	0.68	0.01
5	1.26	1.69	0.92	1.32	0.67	0.58	0.6	0.28

For all cells, the pH of the water ranges from 6.78 to 7.35, with no significant changes in the individual modes of operation. The same can be said for electrical conductivity. The concentration of nutrients NH_4^+ and PO_4^{3+} is low, with a tendency to decrease over time due to their assimilation from plants.

From the measured concentrations of total oil content, the best results are found under mode 3 (Table 3). Cell 4 is characterised by the highest treatment effect – the concentration of petroleum products is dropping to 0.052 mg/l.

Slightly higher concentrations of petroleum products are measured in Mode 4, but again the lowest values are in Cell 4. In Mode 2 the highest values of petroleum products in the outgoing waters from the cells are measured. In the four modes cell 1 is characterised by the lowest treatment effect. Similar results have also been obtained for COD. The lowest COD in all cells is measured in Mode 3, followed by Mode 4 and Mode 2. The COD values can be linked to the residuals of petroleum products in the effluent from the cells in the individual modes.

Table 3. *Concentration of total oil content and COD in outgoing water*

CELL	Mode 1		Mode 2		Mode 3		Mode 4	
№	COD mg/l	Total oil content mg/l	COD mg/l	Total oil content mg/l	COD mg/l	Total oil content mg/l	COD mg/l	Total oil content mg/l
1	213	-	363	0.21	188	0.067	133	0.12
2	126	-	186	0.13	143	0.067	158	0.098
3	103	-	188	0.1	163	0.055	176	0.077
4	78	-	148	0.071	108	0.052	126	0.06
5	113	-	153	0.15	138	0.089	156	0.11

Data for the measured electrical parameters are presented in Figures 2-5. There are no significant differences in electrical parameters between modes.

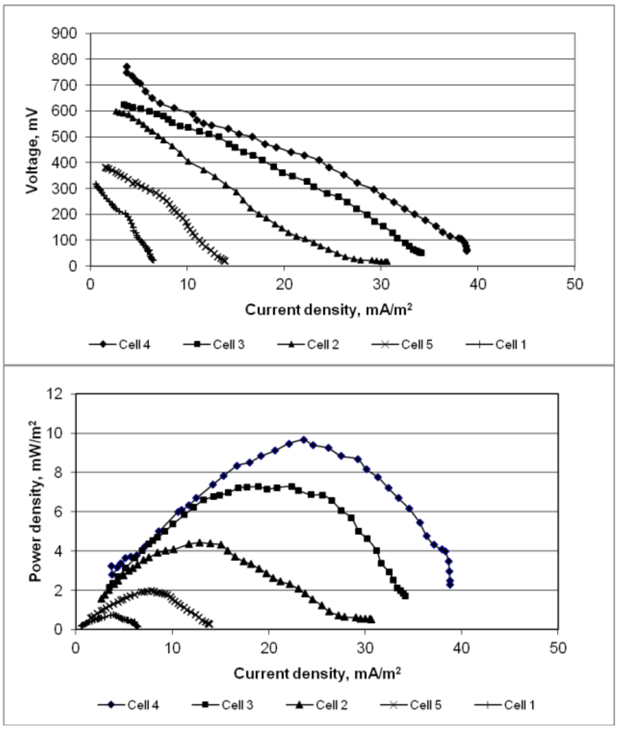

Fig. 2. Polarisation curves in Mode 1

Maximum values of voltage and power density are established in Mode 3. Cell 4 is characterised by the best electrical performance by a power density of 11.56 mW/m² at a current density of 27.15 mA/m² and applied resistance 300 Ω. The open circuit voltage ranged from 900 to 1100 mV. Approximate values of the electrical parameters are measured in cell 3 - power density 9.87 mW/m² at a current density of 25.46 mA/m² and applied resistance of 200 Ω. The lowest values of the electrical parameters are measured in cells 1 and 5.

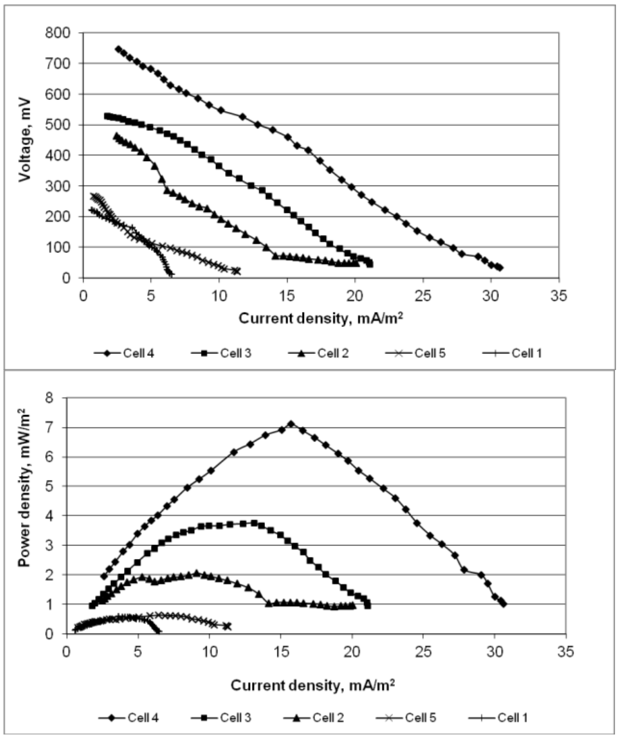

Fig. 3. Polarisation curves in Mode 2

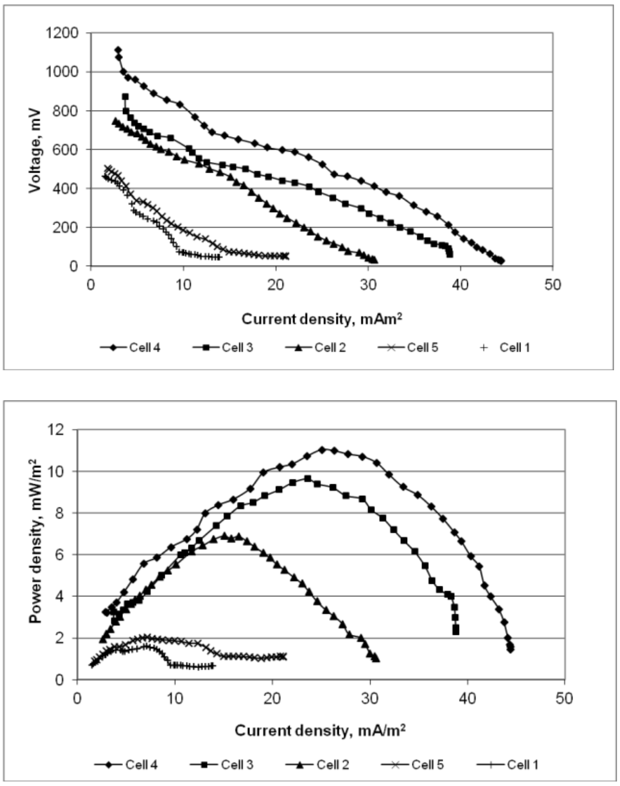

Fig. 4. Polarisation curves in Mode 3

Similar electrical values were measured during Mode 1. Cell 4 again shows the best parameters - a power density of 9.71 mW/m², with a current density of 24.13 mA/m² and an applied resistance of 400 Ω. In cell 1, the lowest values of the electrical parameters were found.

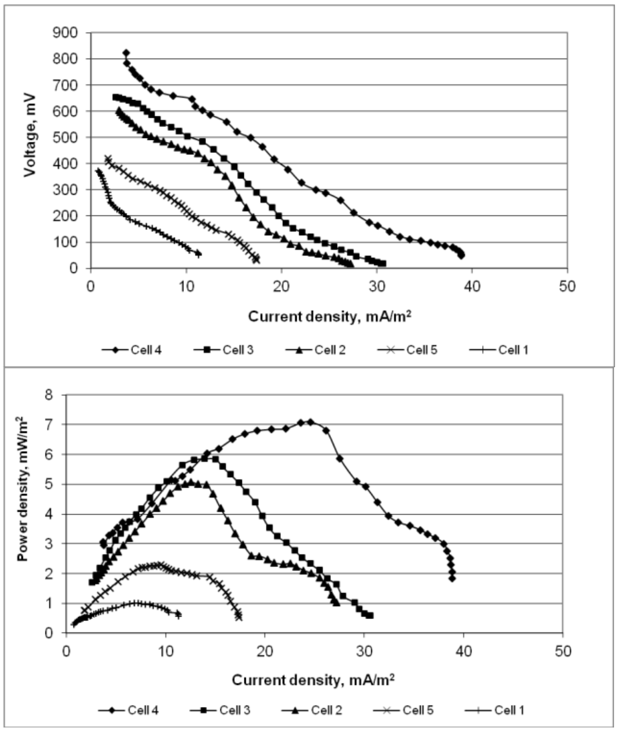

Fig. 5. Polarisation curves in Mode 4

Of the four modes, the lowest electrical characteristics of all cells were measured during mode 2. A maximum power density of 7.16 mW/m^2 at a current density of 17.45 mA/m^2 and a resistance of 200 Ω was measured in cell 4.

Conclusions

In order to study the effect of applied high-activity oil-degrading microflora on the purification of water from petroleum products and energy production from constructed wetlands with integrated plant sediment microbial fuel cells, four technological modes of operation were studied. The best treatment effect is achieved in Mode 3, where the cells are inoculated with a mixed culture of aerobic oil-oxidising bacteria. The lowest value of total petroleum product content – 0.055 mg/l is measured in the outgoing water from cell 4 which is planted with *Spartina*.

From the research and the results obtained, it can be concluded that the added highly active oil-degrading bacteria play a significant role in the water treatment in the constructed wetlands. The vegetation as well as the water flow in the constructed wetlands are also essential.

From the measured electrical parameters of the cells in the individual regimes, it can be seen that the concentration of the petroleum does not significantly affect the energy generated by plant sediment microbial fuel cells. A more important factor is the species of aquatic vegetation. In all modes, the highest energy is generated in the cell planted with *Spartina*.

The results obtained show good prospects for application of constructed wetlands with integrated plant sediment microbial cells in the passive treatment of waters polluted by crude oil and petroleum products.

Acknowledgements. This research was supported by the Bulgarian National Science Fund, Grant No. DM 17/2, 12.12.2017.

References

Boyue L., M. Ji, H. Zhai. 2018. Anodic potentials, electricity generation and bacterial community as affected by plant roots in sediment microbial fuel cell: Effects of anode locations. – *Chemosphere, 209*, 739–747.

Muhammad Afzal, Khadeeja Rehman, Ghulam Shabir, Razia Tahseen, Amna Ijaz, Amer J. Hashmat and Hans Brix. 2019. Large-scale remediation of oil-contaminated water using floating treatment wetlands. – *Clean Water, 2,* 3, 112–119.

Panpan Meng, Haiyan Pei, Wenrong Hu, Yuanyuan Shao, Zheng Li. 2014. How to increase microbial degradation in constructed wetlands: Influencing factors and improvement measures. – *Bioresource Technology, 157*, 316–326.

Qing Zhao, Min Ji, Ruying Li, Zhiyong Jason Ren. 2017. Long-term performance of sediment microbial fuel cells with multiple anodes. – *Bioresource Technology, 237*, 178–185.

Rachnarin Nitisoravut, R. Regmi. 2017. Plant microbial fuel cells: A promising biosystems engineering. – *Renewable and Sustainable Energy Reviews, 76*, 81–89.

Rasool Alipanahi, M. Rahimnenjad, G. Najafpour. 2019. Improvement of sediment microbial fuel cell performances by design and application of power management systems. – *International Journal of Hydrogen Energy*, 125–131.

Shubiao, W., S. Wallace, H. Brix, P. Kuschk, W. Kipkemoi Kirui, F. Masi, R. Dong. 2018. Treatment of industrial effluents in constructed wetlands: Challenges, operational strategies and overall performance. – *Environmental Pollution, 201*, 107–120.

Tetteh, F., Kabutey, Q. Zhao, L. Wei, J. Ding, P. Antwi, F. Koblah, Quashie, W. Wang. 2019. An overview of plant microbial fuel cells (PMFCs): Configurations and applications. – *Renewable and Sustainable Energy Reviews, 110*, 402–414.

Vymazal, J. 2014. Constructed wetlands for treatment of industrial wastewaters: A review. – *Ecological Engineering, 73*, 724–751.