

Recent developments and perspectives of development of microbial fuel cells in Ukraine

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Microbial fuel cells (MFCs) are devices able to transform chemical energy of organic compound (carbohydrates, fats, proteins, etc.) into electricity (or hydrogen) via electrochemical reactions involving biochemical pathways. MFCs are bioelectrochemical systems that generate electrical current using bacteria. This process is based on the catabolism of organic substances such as glucose, acetate, butyrate or other organic compounds contained in wastewaters. Due to oxidation of the organic compounds, electrons are released, transferred to the anode and delivered to the cathode through an external electrical circuit. MFCs could be defined as devices able to transform chemical energy of organic compounds into electricity via electrochemical reactions involving biochemical pathways [1].

Despite the fact that the idea of using microbial cells for electricity production was put forward by Potter in 1911, the current concept of MFCs design was proposed only in 1977 by the research team of Suzuki Toyu. The idea was picked up and studied later in more detail by Bennetto. They foresaw the possibility of microbial fuel cells using to generate electricity in third world countries. Beginning in the 1980s, Bennetto's research helped to understand the process of fuel cell operation. Many scientists still admit his unquestionable authority in resolving this issue [2, 3].

More recently, Dr. Logan's research team of the University of Pennsylvania, which is working on the introduction of MFC in the industry, found that electricity generation is not the only result of MFC work. It turned out that with the addition of electricity to the system, hydrogen is produced on the cathode. In this case, the whole system becomes a microbial electrolysis cell (MECs). As research concepts, MFCs

and MECs are parts of the group of bioelectrochemical systems (BESs) [1, 3]. A significant number of scientific publications appeared in the last two decades shows that the interest in the use of microbial fuel cells is constantly growing. The scientific teams of the laboratories in the USA, China, Australia and other countries have been engaged in research in the field of optimization of the MFCs during recent years. The objective of this work is to review the current state of research in the field of MFCs in Ukraine as well as to determine the prospects for their further development.

1. Recent developments in MFCs in Ukraine

In recent years, the theme of the MFCs has received a new powerful impetus. This is primarily due to growing interest in the production of so-called "green" electricity. Microorganisms are capable to use a wide range of organic substances as a fuel, including a variety of waste; this makes the MFCs very promising for research. Thus, according to the authors of the review article [2], the number of publications about MFCs has rapidly increased over the last decade from 100 publications in 2006 to 1020 in 2016, quoting from 2000 to 32,000, respectively; for MECs: publications from 15 to 280 publications for the same 10 years, quoting from 200 to 5500, respectively. Unfortunately, although this review has about 500 references, non-English publications of Ukrainian scholars are not provided.

Researches in the field of MFCs are conducted at the Department of Environmental Biotechnology and Bioenergy in the National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute" led by Professor Kuzminskiy. Researches are conducted in three main directions.

The first one refers to research of hydrogen producing in MECs for wastewater treatment. The rational hydrogen production process parameters were determined. The new three-stage method of anode biofilm formation with high exoelectrogenic ability was developed and constructively executed. Possibility of various organic wastes using as a nutrient medium for hydrogen production was substantiated: the efficiency of organic brewery wastewater compounds that had been pre-treated under anaerobic conditions with hydrogen producing bacteria was 0.02 g H₂/g COD (chemical oxygen demand); the efficiency of glycerol conversion to hydrogen was 39

%; the efficiency of hydrogen production from malting plant wastewaters was 0.01 g H₂/g COD [4, 5].

The second direction of the research is devoted to the development of biotechnological method for electricity generation by the association of chemoorganotrophic microorganisms on the substrates of different origin. It was substantiated the rational technological parameters of the exoelectrogenic biofilm formation process and electrical energy generation, in particular, COD is 0.6÷0.8 gO/dm³, the temperature is 30÷35°C, pH is 7÷8 units, cultivation modes are periodic (duration is 6÷8 days) or continuous (MFC-bioreactor hydraulic load is 1.1÷1.3 m³/(m³·day), with specific current density (12÷15)·10⁻³ A/m² at R_{ex}=0,5Ω). The work shows the new technical and technological solutions for the flow microbial fuel cell with mobile electrode blocks for the implementation of the modified selection procedure for exoelectrogens biofilm. Power density of microbial fuel cell is 3.6÷7.5·10⁻³ W/m², and wastewater treatment efficacy was 35÷40% (in values of COD) [6 – 8].

The third direction of the research is devoted to hydrogen production in the photobioelectrochemical system. The process is investigated in the two-chamber system with protone-exchange membrane and polycrystalline silicon solar cell, as the source of additional energy. The silicon solar fuel cell is chosen due to the structure of its energy levels. While using the sodium acetate as a model substrate for photobioelectrochemical system the maximum process Columbic efficiency reaches 45 % with hydrogen yield – 0.01÷0.015 gH₂/gCOD. For the model mixture that simulates dairy wastewater maximum hydrogen yield is 0.007÷0.01 gH₂/gCOD. The Columbic efficiency fluctuates within 32÷48% and depends on the mixture composition and the method of the biofilm formation [9, 10].

The process of electric current generating is studied by a group of scientists from the Department of Microbiology at Lviv National Ivan Franko University (Bilyy O., Vasiliev O., Hnatush S., Katernyak S., Maslovska O., Ferensovich Y.P. etc.). They study pure culture of *Desulfuromonas Acetoxidans* IMV B-7384, which are typical representatives of exoelectrogens. The purpose of their work is to study the

metabolism of *Desulfuromonas acetoxidans* in the presence of various compounds in the nutrient medium (like ferrum (III) citrate, fuchsin, methylene blue, etc.). *Desulfuromonas acetoxidans* IMV B-7384 are highly perspective microorganisms for construction and development of microbial fuel cell technologies aimed for wastewater remediation from transition metal ions. Metal ions catalyze formation of reactive oxygen species that could harmfully affect bacterial cells. Activity of glutathione peroxidase, glutathione-S-transferase and glutathione reductase of *D. acetoxidans* IMV B-7384 bacteria was investigated under the influence of different concentrations of ferric (III) citrate. Enhancement of activity of enzymes of glutathione system confirms their necessary role in antioxidant protection of *D. acetoxidans* IMV B-7384 cells [11].

Unfortunately, there are no other studies in this area in Ukraine. In the country that is energy dependent and has problems with wastewater treatment, there is no research on energy production in the MFCs. Such low interest can be explained by insufficient financing of scientific research in this area, since the study of electricity generation processes in bioelectrochemical systems at this stage involves the use of expensive materials and equipment.

2. Perspectives of microbial fuel cells development in Ukraine

Recent studies of aerobic biocathodes, in which oxygen is used as an electron acceptor, have attracted increased interest because of their stable high power output compared to the chemical cathode. It is known that the presence of oxygen suppresses the denitrification. Therefore denitrifying biocathodes are usually considered to be anaerobic. However, a number of microorganisms have recently been isolated from an anaerobic reactor based on its ability to use nitrates as an electron acceptor in air-saturated conditions.

The proposed development of aerobic denitrifying biocathodes for sustainable wastewater treatment and power generation will include the development of the following issues:

- establishment of sufficient electrical contact between the bacteria and electrodes surface;

- achievement of the appropriate voltage for useful energy obtaining in MFCs;
- avoidance of expensive abiotic catalysts to ensure widespread use;
- increase of the cathodic potential for rising denitrification degree.

Despite all the significant obstacles microbial fuel cell technology has a great future. Firstly, the "fuel" for MFCs is very simple to find, especially now since the problem of wastewater treatment and organic waste utilization is very acute. MFCs technology solves both problems. Secondly, the efficiency of MFCs using can be very high (although so far only theoretically) [2, 3, 12].

3. Conclusion

MFCs can be used for fuel production and in bioremediation of different organic wastes. However, this technology is only at the research stage but urgent need for recycling organic wastes, as well as the intensive search for alternative sources of energy, is an important stimulus for large-scale research in the field of MFCs.

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