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MICROBIAL FUEL CELLS – MINIREVIEW OF TECHNOLOGY AND APPLICATION

Abstract
Nowadays it can be seen that interest in renewable energy is growing up significantly. Among others we can observe huge development of fuel cells. These devices are used mostly for power production but it is not their only application. There are lots of different types of fuel cells. One of the lasts inventions are microbial fuel cells (MFC), which are based on use of microorganisms. There are lots of research focusing on constructions and application of MFC in different ways.

Keywords
Microbial fuel cell, microorganisms, wastewater, membranes, electrodes

Introduction

Fuel cells are electrochemical devices that produce useful energy in the form of electricity as a result of a chemical reaction of hydrogen with oxygen. By-product of this process is water. In microbial fuel cells transformation of organic matter to electricity occurs with the participation of isolated and purified enzymes (most commonly used dehydrogenase and oxidase) or microorganisms cultures. Direct application of microorganisms in the microbial fuel cells eliminates the need for isolation and purification of enzymes, which is often difficult and expensive. Additionally it provides the natural environment for biological processes - the cell. But also leads to the necessity for ensuring adequate living conditions for microorganisms [1]. It also should be mentioned that there are two main types of microbial electrochemical technologies (MET) - microbial fuel cells (MFC) and microbial electrolysis cells (MEC). Microbial electrolysis cells partially reverse the process to generate chemical products like hydrogen or methane from organic material by applying an electric current while microbial fuel cells produce electric current from the bio-decomposition of organic compounds.

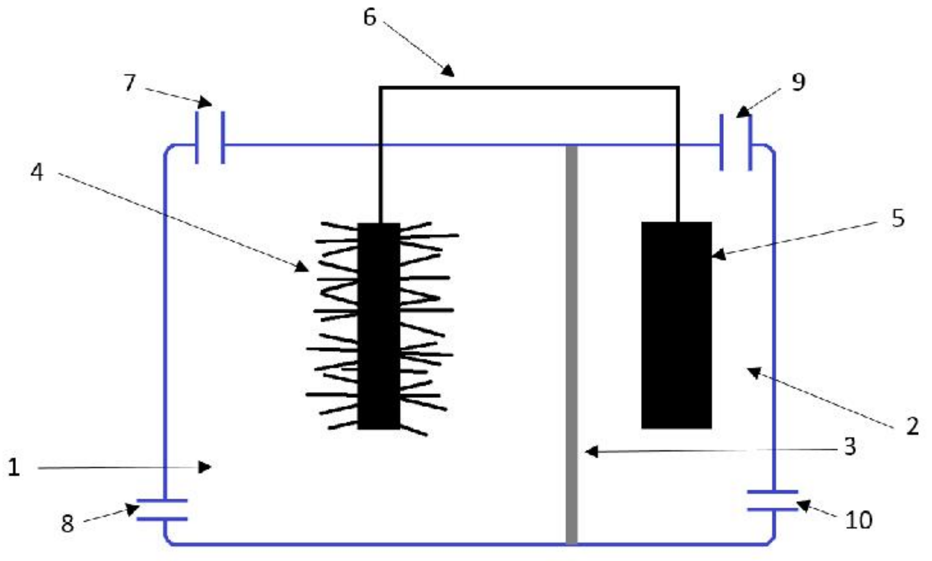

Fig 1. Scheme of typical two-chambered MFC. 1 – anodic chamber, 2 – cathodic chamber, 3 – membrane (PEM), 4 – anode, 5 – cathode, 6 –electric current , 7 – feed input, 8 – feed output, 9 – oxygen input, 10 – cathodic chamber output
Source: Author's

Typical microbial fuel cell consists of anode and cathode chambers separated by an ion-selective membrane permeable for ions. Usually membrane is permeable for protons. Then it is called as proton exchange membrane (PEM). Another popular type of MFC is one-chambered MFC, where cathode come into directly contact with surrounding atmosphere.

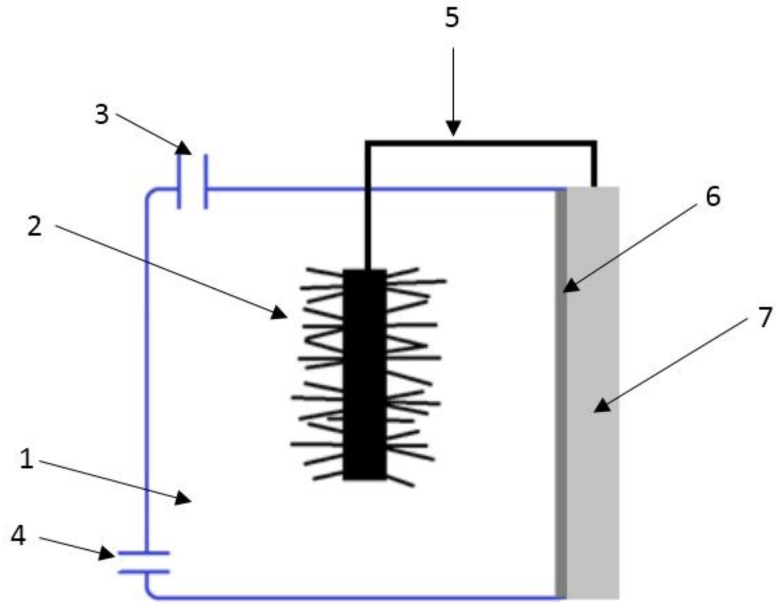

Fig 2. Scheme of one-chambered MFC. 1 – anodic chamber, 2 – anode, 3 – feed input, 4 – feed output, 5 -electric current, 6 -membrane (PEM), 7 – cathode
Source: Author's

Operating principle of the simplest MFC is based on the conversion of chemical energy contained in organic compounds directly into electricity. It is possible because of oxidation of organic matter by microorganisms (which act as specific biocatalysts) contained in the anode chamber and transfer of electrons to the nearby electrode. Simultaneously the release of protons into solution takes place. This process is performed under anaerobic conditions. Then released electrons move toward the cathode through an external electrical circuit which in presence of the potential difference between the anode and the cathode produces electricity. At the same time protons generated on the anode migrate through the semi permeable membrane to the aerobic cathode chamber. At the cathode chemical or microbial reduction occurs in which protons in conjunction with electrons and oxygen are forming water [2].

Performance of MFC and parameters affecting on its efficiency

Efficiency of microbial fuel cells is a key issue in the context of their use as competitive technology to produce renewable energy. Therefore, the main challenge to researchers is to create such cell which would generate a large amount of power when fed by industrial or domestic waste. In most cases electricity produced by the MFC is given in the mV or mA (sometimes per square meter of fuel cell anode surface area). While productivity of cells is characterized by various parameters such as: *Coulombic efficiency (CE)* specified by number of transported electrons in relation to the number of electrons theoretically generated by the substrate or of substrate bioconversion rate. Specified biological parameters are also frequently used which is for example chemical oxygen demand (COD) which depends both on the amount of bacterial cells and the kinetics of the processes performed by bacteria or organic biomass availability in provided feed. *Coulombic efficiency* of MFC designed for laboratory needs fed by clean substrate is even 80-99%, but this parameter for cells fed by heterogeneous substrate, e.g. wastewater from industry is even four times lower [12]. It is known that in order to get the maximum theoretical energy in the cell supplied substrate must be completely oxidized to CO_2 simultaneous with efficient transport of electrons to the electrode. Considering this first requirement and heterogeneous composition of the waste delivered to MFC obtaining high efficiency of cell seems to be very difficult. Regarding values of removed COD achieved in MFC, they oscillate between 40 and 60% in the case of heterogeneous substrate, in turn MFC fed with pure glucose gives removed COD on level of 90% [11, 13].

Despite considerable efforts an electrical voltage in an amount corresponding to the theoretical maximum efficiency of work of a single cell, which is 1,14V has not been received yet. So far, a single cell is able to generate only from 0.3 to 0.7 V [7, 14]. Therefore, lots of researchers are still working on improving performance of MFC technology. The objective of this is creation of such a cell, which produces the highest amount of energy with the contribution of external energy as low as possible [15].

There are many biological, physical and chemical parameters that influence the productivity of MFC. The parameters concern the mass transfer within the biofilm, the oxidation of substrate that is carried out by microorganisms, the electron transfer and the reduction reaction occurring at the cathode. However, the transfer of electrons issue as well as biological activity of microorganisms are the most frequently discussed and studied problems [16]. The amount of power generated by the MFC is primarily determined by the type and density of cells co-creating a consortium of bio-anode [17]. In contrast the rate of bioconversion process carried out by microorganisms depends on the temperature and pH conditions in the MFC. Among the advantages of the MFC functioning in the low temperatures (20-30 °C) is seen as very valuable compared with other methods of bioconversion, but these very low temperatures are sometimes regarded as a limiting factor [12].

An important parameter is also the pH of the solution which is particularly significant in the case of direct contact of bio-anode with supplied substrate. When wastewater is the feedstock it is very difficult to ensure constant pH range, optimal for the growth of microorganisms. On the other hand the oxidation of the organic substances present in the supplied feedstock produces protons, which in theory are transported to the cathode chamber. However, it is noted that this transportation may be difficult, and leads to acidification of the solution in anode chamber [16], what in turn reduces the biological activity of microorganisms and results in decreasing the amount of energy generated in the MFC. Another very important factor which influences the MFC performance is quality of the substrate. Theoretically the more reduced compound is used as the substrate the greater power can be obtained. It is confirmed by the fact, that much lower amount of electricity is produced by MFC supplied with liquid waste than by MFC supplied with pure substrates as glucose. It turns out that the amount of energy generated by the MFC increases with increasing of biodegradable fraction of wastewater. Amount of generated power in MFC also depends strongly on the concentration of oxygen in the cathode chamber and reduction reaction occurring at the cathode may be a limiting factor in its performance. Slight contact between the source of oxygen and the electrode could reduce efficiency of the process [15]. On the other hand admission of oxygen to the anode chamber may cause loss of productivity due to anaerobic metabolism of electrochemically active microorganisms. Therefore, to ensure high rate of reaction on the anode the possible leak of oxygen from cathode chamber must be prevented. An important parameter is also the kinetics of the reduction reaction which can be controlled by the addition of catalysts [12]. The use of MFC in industrial scale is limited by internal resistance of the MFC. Modifications of basic design seems to be necessary to overcome this problem.

Concerning fuel in MFC almost every biodegradable source of organic matter from pure compounds (e.g. acetate, glucose, cysteine, ethanol) to mixtures of organic compounds (e.g. wastewater, animal farm leachate, liquid waste from agricultural and industrial sectors) can be used for production of energy in MFC [3]. It happens due to ability of microorganisms to use different sources of organic matter. By that MFC seems to be the ideal technology for the production of energy from biomass.

Microorganism

The main sources of organisms in the MFC are usually sediments, soil and wastewater rich in bacteria [4,5]. Inoculum from previously activated sludge from wastewater treatment processes or from another previously operated MFC are often used [6,7]. Because of using various kinds of inoculum in the anode chamber representatives of various species of microorganisms could be found in the biofilm. Apart from many unidentified microorganisms there are bacteria belonging to the class: *Alfaproteobacteria, Betaproteobacteria, Gammaproteobacteria, Deltaproteobacteria, Clostridia, Bacteroidetes, Flavobacteria, Sphingobacteria, Deferribacteres, Spirochaetes, Planctomycetes, Nitrospirales* but also fungi, for example *Saccharomyces* and *Pichia* genus [8,9,10]. So far the highest value of the power generated by MFC is achieved with use of multi-species bioanode where microorganisms grow as a biofilm [11]. Mixed culture or microbial consortia seem to be more durable and efficient than single strains. Additionally their isolation from natural sources is much easier. The use of pure cultures have also some technical limitations, mainly due to necessity to ensure sterile conditions and according to this high cost of the process [6]. There are few species of microorganisms characterized below, which are used in MFC as pure cultures with satisfactory performance [42].

Shewanella species - Shewenella is a marine bacteria, which produces trimethylamines, from *Shewanellaceae* family. This bacteria is regular component of the surface flora of fish. Shewanella is implicated in fish spoilage and therefore is associated with the odour of rotting fish. Frequently used strain is fast-growing *Shewenella putrefaciens*. In solid and liquid media, this strain is often recognizable by its bright pink color.

Pseudomonas species - *Pseudomonas* is aerobic, Gram-negative genus of gammaproteobacteria from *Pseudomonadaceae* family. This genus demonstrates a wide range of metabolic diversity and by that can colonize a wide range of niches. *Pseudomonas aeruginosa* produces chemical mediators such as pyocyanin and related compounds which can shuttle electrons to an electrode and produce electricity in MFC without using exogenous mediators. [biocatalyst in MFC]

Geobacter species - *Geobacter* are anaerobic respiration bacterial species, from phylum proteobacteria, which can be useful in bioremediation. This species have been found in soils and aquatic sediment. It has got ability to oxidize organic compounds and metals (including iron, radioactive metals, petroleum compounds) into carbon dioxide while using iron oxide or other available metals as electron acceptor. *Geobacter* is also able to respire upon a graphite electrode.

Modification and optimization of typical MFC

Two-chamber cell was the first, simplest model of microbial fuel cell. However, MFC can be constructed also in other configurations. Modifications of basic model were started due to economic and technical aspects, to reduce the costs and increase MFC performance. For example single-chamber cell was designed, in which cathode chamber was removed and the cathode was in constant and direct contact with air. This structure was tested in order to ensure easier and cheaper access of oxygen to the cathode - in two-chambered MFC there is necessity of constant aeration of the solution in the cathode chamber, which provides to increasing in the costs of MFC performance. Many attempts is carried out to optimize the process in different ways such as: searching for a better and cheaper materials forming the ion-selective membrane, optimization of mass transfer in the MFC or designing a new cathode. New solutions lead not only to decrease the cost of production of MFC but also simplify the design and increase the efficiency of their work. Problematic attempts of up-scaling of those devices led designers to create complex systems combining several MFC in various configurations which offer opportunities for the use of microbial fuel cells on a large scale.

To obtain a greater amount of energy modifications of the electrodes were repeatedly attempted. Among others the size and shape of anode were changed and the best effects were obtained using the electrode with the shape of brush that providing increase in the porosity and making surface accessible for electrochemically active organisms [17]. As it was already mentioned the increasing of the anode surface allows bacterial growth in the form of biofilms which leads to higher production of energy by MFC [27]. Recent studies indicate that such improvement can increase fuel cells efficiency up to 150% [28].

Application of variety of materials was also tested in order to build the fuel cells that would be not only cheaper but also biocompatible and chemically stable. Not all of them characterise with such a good electric conductivity as metals, but using for example graphite in combination with nanoparticles of gold resulting in an up to 20-fold increase in voltage in the cell compared to the homogeneous electrode [17]. The expected results can also be supplemented with redox mediators on the electrode or medium. Unfortunately this method has restrictions on application: these substances in fact must be regularly added to the bioreactor or subjected to recycling. Exogenous redox mediators are very expensive and therefore beyond the study of small size MFC in the laboratory wider studies in this direction do not seem to be forward-looking.

Immersing the cathode in water rich in dissolved oxygen can be replaced by the constant exposure to air which is a passive oxygenation of this electrode (cathode-air) or by using a cathode connected to the semi-permeable membrane. In addition, those already mentioned catalysts are used in order to streamline the functioning. An example would be platinum, which increases the contact of oxygen with a cathode, what effectively reduces overpotential that appears on an electrode and as a result contributes to increase the voltage generated by the MFC [29]. However, the use of platinum significantly increases the cost of the project, and this metal turned out to be also sensitive to sulphides diffusing from the anode compartment by proton exchange membrane (PEM) [13].That is why lower-cost catalysts other than platinum, such as ferric cyanide [30] and potassium permanganate [31], potassium dichromate or manganese oxide are sought [7]. On the other hand the use of ferrocyanide as electron acceptor enabled further improvement of the functioning of the MFC, but this compound due to its toxicity is not a good contender for use on a large scale. So the alternative seems to be the use of metal oxides integrated with carbon or special materials such as fullerenes, as a material for the cathode structure which improves electrode contact with oxygen [32]. Tsai et al. (2009) in turn used carbon cathode with addition of carbon nanotubes instead of platinum catalyst in MFC powered with sewage. In these research an increase of voltage, power and coulombic efficiency generated by MFC was observed. Additionally resignation from catalyst enabled to reduce project costs [13]. Microbial fuel cells require stable pH in both anode and cathode chambers. To maintain the suitable conditions different anolythe and catholyte solutions are used [35]. The most commonly buffer applied in cathode compartment is phosphate. However, its utilization may occur too expensive and undesired due to depletion of phosphorus in a global scale. Therefore, recent attention is focused on application of other catholyte solutions as a replacement for phosphate. The studies performed in laboratory scale show the great potential of saline solutions applied for two-chamber MFC [36,37], or its mixtures with phosphate buffer [38]. New catholytes (i.e. sodium percarbonate) are also applied as an alternative electron acceptors [39].

Another promising approach is the use of biocathode, which has certain advantages over conventional abiotic cathodes. Besides lower costs of construction and operating, additional benefits are being achieved related to production of useful products by microorganisms growing on the surface, and the removal of unnecessary compounds from the cathode compartment [7]. Last development in the MFC design is maintaining anaerobic conditions in the cathode compartment. That allows to use other electrons acceptors like i.e. nitrate. Such modifications are successfully used for denitrification of wastewater in laboratory scale [40]. What is also very important, application of anaerobic conditions decrease the costs of MFC technologies [41].

Membrane is one of most important part of a MFC. It has to enable proton exchange but also separate the aerobic cathodic chamber from the anaerobic anodic compartment. As a result of this, main purposes of the membrane are [24]:

- to reduce the substrate flow from the anode to cathode chamber;
- to avoid the back-diffusion of the electron acceptor;
- to perform as a barrier to the transfer of other ions between the chambers;
- to increase the Coulombic efficiency (CE) by reducing the flow of the oxygen to the solution in the anode chamber;
- to ensure an efficient operation during a long time.

There are lots of membrane types used in microbial fuel cells. Most frequently used are characterized below.

Cation exchange membranes

Cation exchange membranes (CEM) are favoured to MFC's separators because they conduct protons direct from anode chamber, where protons are generated, to cathode chamber. Main types of CEM are: Nafion, Hyflon, Zirfon and Ultrex CMI 7000 [42]. Nafion is the most popular CEM. It is a synthetic, sulfonated copolymer of tetrafluoroethylene and ethanesulfonyl fluoride produced by DuPont. It has a good proton conductivity. There are two types of Nafion – thinner Nafion 112 and thicker Nafion 117. Nafion 112 membranes have higher maximum voltage, current and power densities because of lower resistance, but they also have higher permeability of oxygen which leads to deterioration of MFC's performance.

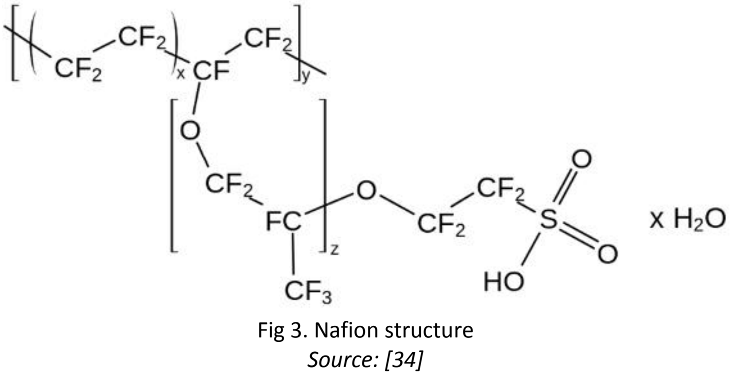

Fig 3. Nafion structure

Source: [34]

Hylfon is a membrane consisting of perfluorosulfonylfluoridevinyl ether. Zirfon is an ultrafiltration composite membrane that consists of an asymmetric polysulfone membrane structure and inorganic filter particles of ZrO_2. Main disadvantages of CEMs are pH difference between the anode chamber, where proton accumulation takes place, and the cathode chamber, oxygen diffusion from the cathode chamber to the anode chamber, where anaerobic conditions must be kept, loss of substrate and biofouling.

Anion exchange membranes

AEM (anion exchange membrane) is acting as proton carriers and facilitate proton transfer by conducting hydroxide (or carbonate) anions from the cathode chamber to the anode chamber. This transfer mechanism reduces pH difference, because it helps to avoid proton accumulation in the anode chamber. That makes MFC performance with AEM better than with Nafion membrane. But AEM also favours substrate crossover, which promote microbial growth in the cathode chamber and reduce MFC performance by that. This is major drawback of AEM. Most popular and most commonly used AEMs are Ultrex AMI-7001 and fumasep FAB [42].

Porous membranes

This type of membranes is used mainly because of their low cost. Glass wool is more cost effective for wastewater treatment and power generation instead of expensive PEMs. Microfiltration membranes have been used to decolorize azo dyes. [42] Main problem with porous membranes is that porous structure favours crossover of oxygen, substrates and other bigger molecules. Crossover rate is higher than in dense membrane, but lower than in membraneless MFC. Good property of this type of membrane is low membrane internal resistance. But biofilm is quickly forming on the surface of membrane, which increases its resistance. That makes porous membranes simply useless in long-term working MFC.

Membraneless MFC

The presence of membrane causes problems such as limited proton transfer, biofouling and high costs of the conventional and well-known membranes. There is a possibility to avoid it by removing the membrane from the MFC. There are some research which show that membraneless MFC has lower cell internal resistance and high proton transfer rate. But it is directly connected with high oxygen diffusion in the vicinity of anode, what causes the drastically drop of CE of the MFCs by about 20% [42]. Moreover, this type of MFC leads to form biofilms on cathode surfaces which limits oxygen diffusion to the cathode and by that reduces MFC efficiency. There are many advantages of membraneless technology like no membrane biofouling issues, zero membrane internal resistance and lower MFC operational costs. However, membraneless technology is inadvisable for long term MFC performance because of its high oxygen and substrate crossover rate which could result in significant decrease of MFC efficiency.

There are also some studies about alternative membranes such as:

- low cost agar membrane [24];
- polymer inclusion based on ionic liquids;
- composite materials (e.g. metal-polymer, metal-carbon).

The review of the problems posed by current membrane separators affecting MFC performance leads to identifying following main challenges to overcome in order to design very well performing MFC:

- low membrane resistance (improving proton transfer from anodic chamber to cathodic chamber);
- non-porous or dense membranes (preventing oxygen diffusion from the cathode chamber to the anodic chamber and substrate crossover in the opposite direction);
- high biofouling resistance (allowing MFC to be operated longer without serious drops in performance);
- cheaper membrane material (reducing MFC's cost).

Present and potential ways for application of MFC

Ways of industrial application of microbial electrochemical technologies (MET) depend of the type of the device. Below some of the possible applications of MET are shortly described.

On the beginning of MFC development, about over twenty years ago, there was speculation about application of this devices for power small vehicles or boats without having to charge the batteries, as a small power generators to use in areas without access to electricity or as additional equipment in small wastewater treatment plant in sugar factories or dairies [18]. Currently proposed application of microbial fuel cells are much wider: besides utilization of industrial waste MFC could be used for recovery of important biogens such as phosphorus from wastewaters, desalination of sea water [43,44], hydrogen production (MEC), bioremediation of soils, power portable electrical devices and telemetry stations or function as biosensors.

Such applications like power source for portable electrical equipment in the areas without access to the grid or traditional power generators are much more interesting than the originally proposed target of MFC. What is more in some cases this is no longer just a theory. Today there are studies and research in pilot scale in this area and some of them have already found their application in practice. The most spectacular examples are projects of autonomous mini-robots. One of the most interesting is "slugbot" - robot producing electricity from biomass which are the slugs, common pests of English fields. Produced energy robot used to move and capture another pest in the field [2].

The ability of microorganisms functioning in MFC to degrade a wide spectrum of environmental pollution can be even more valuable than the production of energy, especially in systems that allow for using of technology to treat the wastewater in situ [19]. It is known that the species of the genus *Geobacter* are able to degrading components of crude oil and leachate from landfills present in groundwater. The oxidation of these pollutants is associated with reduction of iron (III). Both oxidation and reduction can be improved by addition of mediators or chelators of Fe (III), so the addition of them to the reaction environment could enable utilization of these refuse. It has been proven that pure cultures of *Geobacter metallireducens* oxidize benzene and toluene using the electrode as a final electron acceptor [20], thus placing the electrodes in the soil with those hydrocarbons enables increase in the rate of degradation of toluene, benzene and naphthalene present in the environment.

MFC is also proposed as a device for monitoring contamination of wastewater with toxic compounds. Its operation is based on the inhibition of biological activity when in delivered liquid waste there are toxic substances, resulting in a decrease in the amount of energy generated by the MFC. Thanks to the dependence between the degree of inhibition of production of energy and the degree of contamination of the substrate there are ideas to use it as a preliminary warning device (indicator) from the toxic contamination of wastewater [21, 22].

Modifications of microbial fuel cells led to their application in the desalination of sea water. Moreover, recent modifications to these systems allowed for obtaining the simultaneous energy recovery from salt water [23]. The process of reverse electrodialysis is used for the direct production of energy from gradient of salinity created by freshwater and saline water. The electrodialysis cell uses many pairs of membranes to exchange anions or cations located between two electrodes. This membrane system is indispensable for the effective use of salinity gradient and energy production. But by that cost of construction of such cells increases significantly [23].

More advanced and innovative applications of MFC are biosensors, that means systems using biological reactions for detection of different compounds. The presence of the compound in the anode chamber activates the current flow which is recorded with electronic methods. It has been proposed to use biosensors for detection of compounds such as: glucose (with *Gluconobacter suboxidans* and *G. industrius*), glycerol (with *G. industrius*), ethanol (with *G. suboxidans* and *Acetobacter aceti*) [1], lactates (with *S. putrefaciens*) [25]. MFC are also used as biosensors for measuring pollutants in the environment, for example determination of BOD (biological oxygen demand). This parameter indicates the content of biologically degradable organic material in the sewage or water tanks [26]. Other proposed precise applications is use of miniature MFC to supply medical implants dosing medication for patients [44]. Such miniature MFC may be located directly in the blood vessel using glucose from blood as a fuel [2].

Another group of applications are maintenance-free telemetry stations, for example meteorological or monitoring the environment. An example of such devices is the EcoBotII - the device for monitoring of environment with temperature sensor transmitting information via radio powered by dead organic matter (e.g. dead flies) [33].

Conclusions

Development in field of knowledge concerning microbial fuel cells is growing fast. Year by year more researchers are concentrated on this topic. There are lots of ideas related to innovative applications of MFC in different sectors of industry - from wastewater treatment to biomedical processes. Therefore it is very important to conduct research about modifications and optimizations of these devices, because this technology could be breakthrough in many areas of our lives.

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