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Anaerobic organic matter degradation in Microbial fuel cell

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Abstract
Several studies have shown that Microbial fuel cell (MFC) converts organic matter of different nature into electrical power. However, the studies are usually focused on electricity production instead of describing the effects of mineralization. In this study the mixed microbial culture isolated from lake sediment sample was tested as an exoelectrogenic and organics degradation agent. The experiments were conducted in the conditions of Microbial Fuel Cell (MFC) designed as a cylindrical anode and cathode chambers, separated by cation-exchange membrane. Both electrodes were made of carbon cloth with circular section. The anode compartment was filled with activated carbon for expanding the anode surface and better electron collection and transport. Together with this, the large surface area provides conditions for formation of a stronger microbial culture through the formation of a biofilm. The MFC was fed with synthetic nutrient medium as an electron donor in the anode chamber and potassium ferricyanide as an electron acceptor in the cathodic reactions. In few sets of experiment a maximal current levels of 0.87 mA (with 100Ω resistor in the electric circuit) were obtained. This electricity generation was accompanied with strong mineralization of the organic medium irrespective of the anaerobic nature of the process. Due to the specific metabolic activity of the isolated microbial culture we established maximal degradation rate of 1.03 kg/m^3/d. The results demonstrate the potential of the MFC and tested microbial culture in water treatment and energy production. The biggest advantage of this technology is the ability of substrate mineralization in absence of oxygen i.e. without additional aeration of the fluids and related expenses.

Keywords: Microbial Fuel Cell; Wastewater treatment;

1. Introduction
Microbial Fuel Cells (MFC) are well known as bio-electrochemical systems which are capable to convert the chemical energy of organic substrates in to electricity. This is a result of specific biochemical activity in the so-called electrogenic microorganisms.
The typical MFC usually consists of anode and cathode, connected by an external circuit and separated in different compartments by proton exchange membrane. In the anodic chamber, microbial decomposition of the organic substrates (in strictly anaerobic conditions) generates electrons and protons that are transferred to cathode trough the circuit and membrane respectively. On the cathode surface they react with the final electron acceptor. Different ions and chemicals can be used as an acceptor of electron in cathodic semi-reactions - manganese and iron ions, nitrates, sulfates, oxygen etc [1,2,3].
The presence of appropriate electron acceptor plays important role in the electrochemistry of the process. Oxygen is the most preferred acceptor because of its availability in the environmental and high redox potential. The chemical electron acceptors as potassium ferricyanide ($Fe(CN)_6$) are relatively expensive but their application could increase the voltage and electric power significantly [4].
As an organic substrate in the anodic reactions, bacteria can utilize different compounds. There is lot of investigations reporting biological oxidation of pure carbon sources as glucose, acetate and lactate in MFC processes [5,6,7]. Together with this, there is the very promising alternative to apply different waste flows containing biodegradable organics as a growth medium in these systems. Recently, some positive results with domestic and industrial (mainly food production) wastewaters were reported [8,9,10]. The main benefit is the opportunity to mineralize organic matter to water and CO_2 in anaerobic conditions. This perspective is very promising since more that 50% of the wastewater treatment costs are formed by the energy demand of aeration systems [11].
Previously, few articles report positive results of application of MFCs in wastewater treatment. In experiments with domestic wastewater Liu *et al.* reported COD removal efficiency up to 80% [12]. The maximal COD

removal rates obtained in some other studies reach 0.412 and 0.88 kg /m^3/day, depending on the substrates applied [13].
The aim of this study was to observe and describe anaerobic mineralization of organic substrates in the conditions of MFC by bacterial culture isolated from bottom sediments of freshwater lake.

2. Materials and methods

2.1. Microbial fuel cell design

The MFC used in this investigation was designed as a cylindrical reactor with separated anode and cathode divided by cation exchange membrane (Fig.). Each compartment had ports for input and output flows. Both electrodes were made of carbon cloth with circular section (surface area - 38 cm^2) connected with an external electrical circuit loaded with 100Ω resistor. The anode compartment was filed by granular activated carbon for providing better biofilm formation and electron transduction within the volume of the reactor. The working volumes of anodic and cathodic chambers are 24 and 48 ml respectively. The cathodic chamber was connected by pump to a separate tank with the electron acceptor solution (total circulating volume 300 ml).

2.2. Experimental procedures

The electrogenic microorganisms were enriched in anaerobic conditions by inoculation of 0.5 ml sediment collected from the bottom of "Yasna Polyana" dam, situated near Burgas/BULGARIA in nutrient medium containing: glucose – 15g/dm^3; tryptone - 10 g/dm^3; yeast extract - 5 g/dm^3 and NaCl – 5 g/l and pH -7. After 96 hours of cell growth the enriched culture was suspended in fresh nutrient medium (without glucose) to a microbial concentration of 10^7 CFU/ml and loaded in the anode chamber of the MFC. As a electron acceptor in the cathodic reaction we applied Potassium ferrocyanide ($K_4[Fe(CN)_6]$) solution with concentration 10g/l which was circulated trough the cathodic chamber with flow rate of 27,78 ml/min. The process was conducted at a temperature between 14-18 ºC.

2.3. Analytic methods and data collection

During operation of the MFC the potential of electrodes and electric current were measured online by data acquisition devise *Meilhaus electronic Labjack U12* connected to PC and manually by *Auto ranging digital multimeter MY-66*.
The concentration of Total Organic Carbon (TOC) was measured daily by Hach *Lange* LCK 380 cuvette test kit and *Hach Lasa* DR 3900 automatic photometer.
All the measurements and analyses were performed in tri replicates and the values presented in the tables and graphics are the mean values of the experimental results obtained.

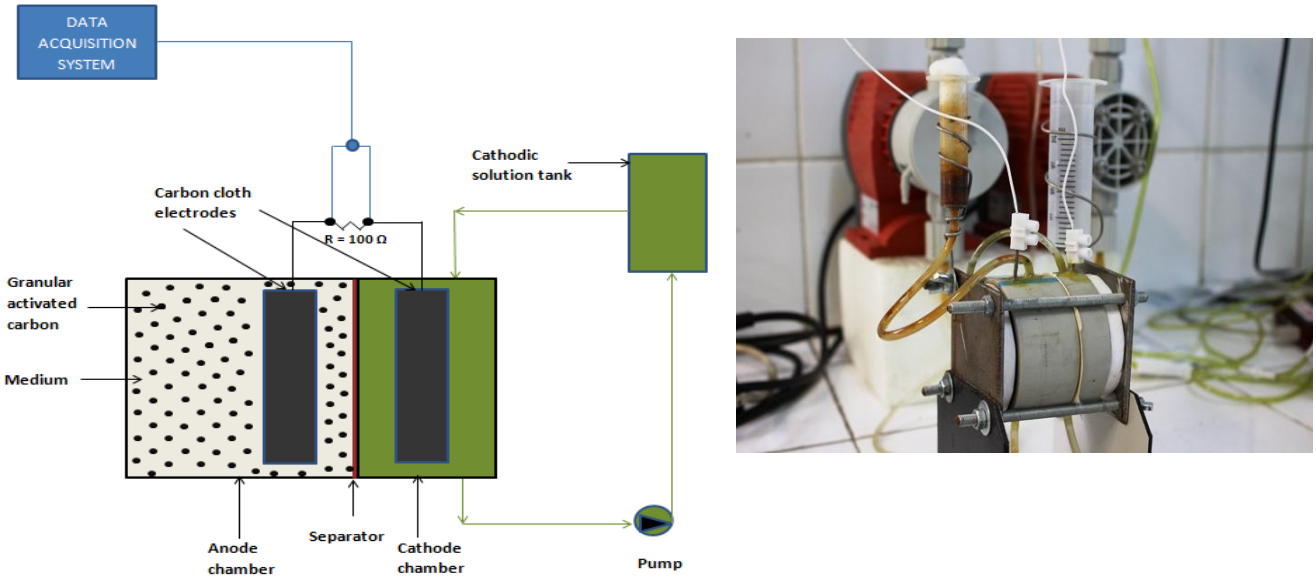

Fig. 1. Design of the Microbial Fuel Cell (left) and real reactor (right) used in this study

3. Results and discussion

By following the above mentioned experimental procedure we obtained the dynamics in the organics utilization and electricity production in the Microbial Fuel Cell. The results are presented in Figure 2.

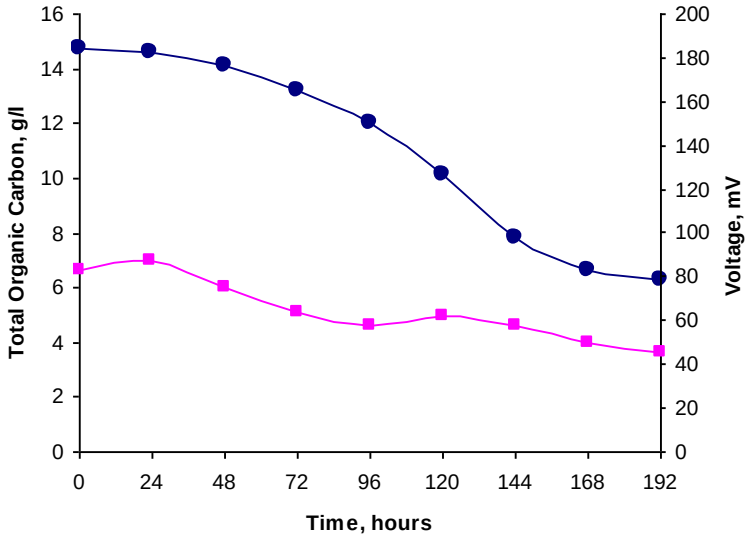

Fig. 2. Total Organic Carbon (●) and Voltage (■) vs. Time observed in the experiments with MFC

The characteristics of the electricity generated are changing in the time. The maximal voltage (87 mV) and electric Current (0.87 mA) were observed in the beginning of quick substrate degradation phase. After this point, the potential difference of the cell gradually decreases due to lower concentration of the substrate in the anodic chamber and exhausting of the cathodic solution. Evidence for such a process limitation and deterioration of the electrochemical conditions in the cell is the low coulombic efficiency calculated for the last stages of the investigated process (Fig. 3).

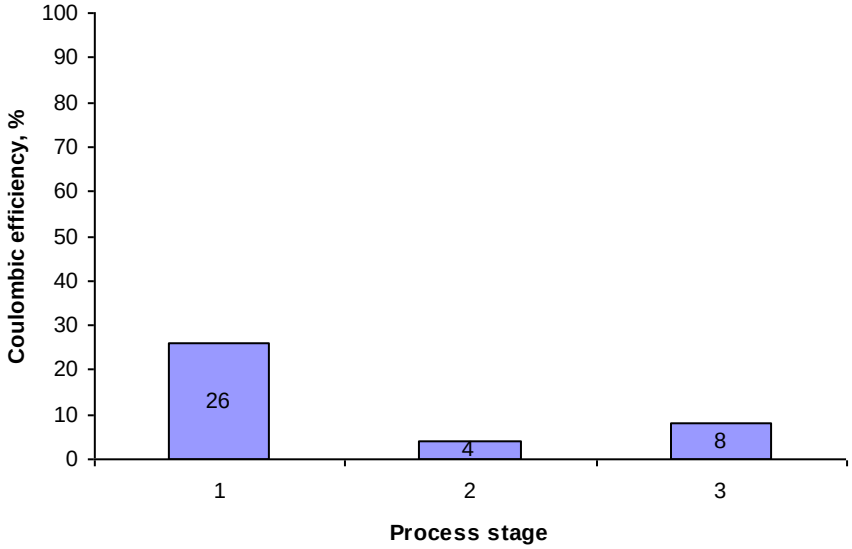

Fig. 3. Coulombic efficiency of the MFC during the different stages of the process
(1^{st} stage – 0 – 48h; 2^{nd} stage 48-168h; 3^{rd} stage 168-196h)

The mineralization curve has the typical character describing microbial utilization of substrates. We established that in 192 hours the nutrient medium was 60% mineralized with average degradation rate of 1.03 kg/m^3/d. This

degradation rates corresponds to COD reduction of 4.7 kgO_2/m^3/day (according to the TOC/COD correlation described and adopted by different authors - [14,15]. The maximal mineralization rate was observed between 48 and 144 hours – 1.65 kg/m^3/d (COD reduction - 7.67 kgO_2/m^3/day). Previously, other authors reported COD removal rates between 0.4 and 1.32 kgO_2/m^3/day [16].
Also, we have to keep in mind that this method could hides additional potential which can be unveiled after process optimization and application of different exploitation schemes. For example, the COD removal can be significantly increased by connecting several MFC reactors successively in cascade [17].
These results reveal the potential of MFC technology to be applied for mineralization and stabilization of organic wastes and to overcoming the main disadvantages of classic aerobic and anaerobic processes. On the first place, this process is independent of forced aeration and related expenses typical for aerobic degradation. From the other hand, unlike conventional anaerobic processes allows deep and rapid mineralization.

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