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Innovative treatment of livestock manure by a single – compartment microbial fuel cell with air-breathing cathode

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Livestock manure (LM) is characterized with high level of organic matter, suspended solids, phosphorus and nitrogen. The application of LM as a fertilizer in agriculture is often restricted by pathogen organisms contained in this waste, as the waste fluids are often used as fertilizers after their stabilization. In this sense, developments of methods for LM stabilization by alternative approaches are of great interest. One way for such stabilization of LM is the application of bio-electrochemical systems (BES). Microbial fuel cell (MFC) as a typical BES can be used for conversion of the organic matter into electricity by electrogens activity.

The study is focused on monitoring of a MFC behavior. LM was used as a fuel, whilst oxygen from the air acted as an oxidizer. The process was monitored via the potential generated. The open circuit potential (OCP) was measured against different resistance- loads (closed circuit, CCP). It was found that at an applied resistance of 1000 Ω the output voltage was 0.547 V. After a few days of microorganism acclimation, the generated voltage was found to be 0.5 V. Over a period of 264 h, the organic matter content (assessed through the chemical oxygen demand, COD) decreased substantially from the initial value of 15.92 g O_2/L down to 0.03 g O_2/L per hour.

***Keywords**: livestock manure, wastewater treatment, microbial fuel cell*

INTRODUCTION

During the past few years, microbial fuel cells have been of great interest since they can find application for simultaneous waste water purification and electricity generation. The basic role in these systems is played by the biofilm which is formed on the anode surface and, on one hand, microorganisms oxidize organic substances to end products (CO_2, H^+, electrons), while on the other hand, biofilm participates in the transfer of generated electrons to the anode surface [1]. Classic microbial fuel cell consists of anode and cathode space divided by a separator (proton-exchange membrane, cation-exchange membrane); however, due to the weaker internal resistance and better system behavior, systems have recently been without separation, and the cathode is directly exposed to the air [2, 3]. Air-breathing cathode consists of the following layers: electrode, oxygen reduction reaction (ORR) catalyst layer, and air-diffusion layer [4].

The optimization of cathodes and anodes through different catalysts, the number of layers and new structures, aims at increase of the initial resistance and the productivity of MFC, increase of the activity of the anode biofilm, reduction of the internal resistance, and improvement of the efficiency of the processes [5, 6].

A classis method is permanently searched for characterization and understanding of the complex biochemical processes in the biochemical stimulators. Cyclic voltammetry (CV) is such a method which helps to conduct an optimal kinetic analysis of the cathode as an independent section, and of the anode biofilm [7, 8].

Cyclic voltammetry provides useful thermodynamic information as well as quality information on the nature of electronic transfer, bioelectrocatalytically active factors, and on other processes. The analysis of kinetic parameters through CV can give us important information, assessment of the mechanisms, and of the complex microbe-electrode interactions. Such experiments are conducted by Harnisch and Freguia who review cyclic voltammetric measurements with different basic techniques of Geobacter biofilms [9, 10].

Manure is one of the biggest pollutants which is directly dumped into the soil or waters as eutrophication. Waste waters from animal breeding contain significant quantities of organic substances, nutrients (nitrogen, phosphorus), heavy metals, pathogenic microorganisms [11, 12]. There are different methods of treating these deposits, as their application as fertilizer [13], after their initial

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stabilization through composting, is a conventional method. This process aims to reduce the organic contents of the obtained compost, the ratio C/N, pH, the temperature, the inorganic nitrogen, the contents of carbon [14, 15] is changed. Anaerobic digestion is a method applied for stabilization of deposits under the influence of microbiologic activity when organic matter turns into methane, carbon dioxide, hydrogen sulfide, ammonia, other organic substances, etc. Anaerobic digestion is the basic process of treating the so-called anaerobic lagoons [16]. There are also methods of treatment like wet extraction, phosphorus recovery by struvite precipitation, nitrification-denitrification, deammonification [17].

Despite for generating electricity, bio-electrochemical systems can be also used for treating waste waters. There is a statement of a microbial fuel cell of tubular type, charged with deposits from a big breeding farm, which has a generated power density of 1.143 W m^{-3} [18], while another analysis has applied air-breathing cathode for improving the process, and the reached power density is 4.725 W m^{-3} [19]. The maximum values of power density is up to 20.2 W m^{-3} when applying waste waters from dairy factories and up to around 15.1 W m^{-3} from waste waters originating from dairy farms [20,21]. Along with electricity generation, the values of organic pollution, nitrogen and phosphorus are reduced. Zhang *et al* [22] have reached to an effect of removing nitrogen from the anolite in the bio-electrochemical system with 83.4% and of phosphorus – with 52.4 % as well as to 95 % reduction of the organic matter for a period of 144 hours. Another analysis has reached values of removing nitrogen and phosphorus with 96 % and 64 %, respectively [23].

EXPERIMENTAL

Laboratory single-chamber microbial fuel cell (MFC)

The structured system is a plastic cylindrical corpus (with a capacity of 130 cm^3), without separation between the two electrodes, the anode is from a carbon brush (with a surface of 200 cm^2), while the cathode is of air type, with a surface of 3.77 cm^2 (VITO-Belgium), directly exposed to air contact. The cathode consists of the following layers: activated carbon and polytetrafluoroethylene in ratio 40:60.

The two electrodes are connected in an electric circuit with external resistance R=1000 **Ω**. Waste waters of a buffalo farm are used as a fuel of organic matter and microbiological culture in the cell. Initially, the deposit which is taken after anaerobic digestion is centrifuged under laboratory conditions (centrifuge JANETZKI, for 15 minutes, 3000 rpm). The obtained centrate is used for the experiments. The principal scheme of the process is presented in Fig. 1, and the real laboratory single-chamber microbial fuel cell is presented in Fig. 2. Table 1 shows the initial contents of this centrate:

Table 1. Characteristics of livestock manure

Analysis / Sample	PO_4–P, g/L	PO_4, g/L	NH_4-N, g/L	NH_4, g/L	COD, gO_2/L	TSS, g/L
Centrate of buffalo manure	0.94	2.88	1.21	1.56	15.92	17.8

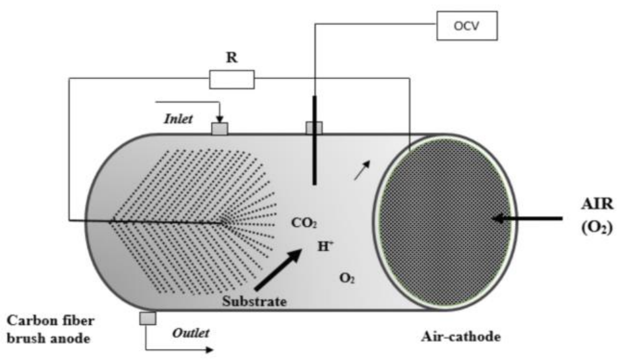

Figure 1. Schematic representation of the single-compartment microbial fuel cell with air-breathing cathode.

Figure 2. Laboratory prototype of the MFC.

The experiment lasts 15 days, as the concentrations of nitrogen (g/L), phosphorus (g/L), COD (chemical oxygen demand) (g/L) in the anolite is measured every 3 days. Spectrophotometric cuvette test is used for this purpose (HACH LANGE 3900 spectrophotometer).

The potential between an anode and a cathode is measured with a multimeter (MASTECH MY-66). Cyclic voltammetry (potentiostat/galvanostat Metrohm Autolab) is used for the electrochemical characteristics of the process.

Electrochemical cell for testing electrode materials:

The test cell used for conducting electrochemical tests consists of a glass reactor with electrolyte background (250mM water solution of NaCl). 3 stationary electrodes are put in it (working, comparative and referential) so that to create conditions analogical to the MFC structure. The first electrode is VITO Belgium 40:60 (air-breathing cathode), the second electrode consists of a carbon canvas the carbon brush is made of (anode). The silver-silver chloride electrode: Ag/AgCl/KCl (saturated aqueous solution) with 0.222 V potential (vs. SHE) is used as a reference. Cyclic voltammograms are recorded with AUTOLAB PGSTAT101 device with step 0.00244 and scanning rate of $0.1 Vs^{-1}$ at room temperature (25 ± 2°C). In order to receive more complete information on the stability of electrodes two more methods with linear change of the potential with time are applied – the so-called Linear polarization – LP and the so-called Linear sweep voltammetry – LSV.

RESULTS AND DISCUSSION

The laboratory microbial fuel cell was tested over a 15 days period, as up to the 11th day a reduction of the indicators monitored in the residual fluid, namely – nitrogen, phosphorus, COD was observed. Fig. 3 presents the results regarding these pollutants and their change over time. The chart shows that after the acclimation of the microbiological culture in the system, reduction of the content of nitrogen, phosphorus and organic matter (like COD) is observed. It was found that for a period of 264 hours the initial organic substances content (estimated as COD of 30 mgO_2/L) decreased with up to 54.8 %, whilst the starting levels of phosphate and ammonia ions were reduced with 37.5 % and 74.2 % (4.1 and 4.3 mg/L) respectively.

The change of the concentration of the COD, the ammonia and phosphate ions with time can be presented with the respective polynomial equations, as the coefficients (R^2) show that there is a very high correlation:

$$COD = 0{,}0403.t^2 - 1{,}2325.t + 16{,}335, \quad R^2 = 0.97$$

$$NH_4^+ = 0{,}0051.t^2 - 0{,}1546.t + 1{,}518, \quad R^2 = 0.95$$

$$PO_4^{3-} = 0{,}0059.t^2 - 0{,}1703.t + 2{,}8096, \quad R^2 = 0.95$$

where: COD – organic content in wastewater presented as COD (COD, gO_2/L); NH_4^+ - ammonia ions concentration, g/L; PO_4^{3-}—phosphate ions concentration, g/L; R^2 – correlation coefficient.

The process is also followed in accordance with the change of the potential between an anode and a cathode on a daily basis, and the results are presented in Fig. 4. An initial value of the voltage of 0.547 V is reported, as the following 7 days the potential was reduced to a value of around 0.4-0.45 V. The reason for this is the period of adaptation of microorganisms during the first few days. On the 7th day the potential is again observed to increase up to 0.54 V. By the end of the 15-day experiment, the potential is relatively stable, with values of around 0.55 V. The maximum power density was calculated to be $2.33 W/m^2$. This value is comparable with the reported power densities of bio-electrochemical systems fueled with the deposits of animal breeding [12, 13].

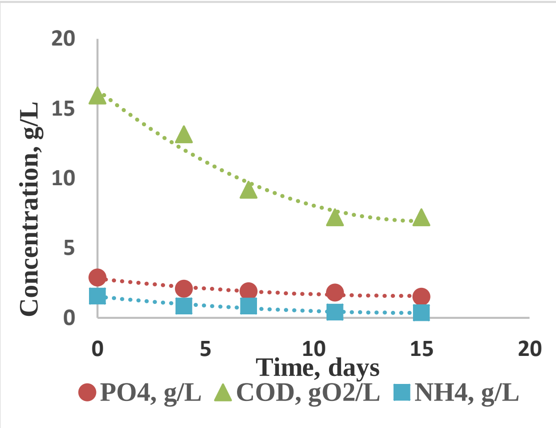

Figure 3. Changes in the concentrations of phospahtes, ammona ions and COD with time

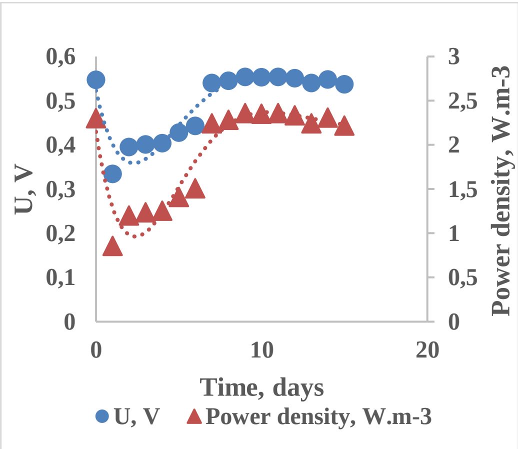

Figure 4. Variations of the cell voltage and power density over time

The electrochemical analyses were carried out on an apparatus: "*AUTOLAB POTENTIOSTAT-*

GALVANOSTAT", product of METROHM AUTOLAB B.V. The voltammogram of air-breathing cathode VITO represents a typical cyclic polarization curve, the forward scan of which corresponds the increased potential. The increased potential is accompanied by reduced surface concentration and mass transfer to reaching the maximal current which is then reduced due to the effect of exhaustion (resulting from slower diffusion). As a result, the current reaches its maximum and starts falling. After passing the maximum current, the scan of the potential reverses, (Fig. 5).

This result is was most probably due to some catalytic effect of the carbon black and the activation of cathodic reactions. The reported peak shifts in the voltammogram [24] is related to the improved reduction of oxygen resulting from the presence of the catalysts.

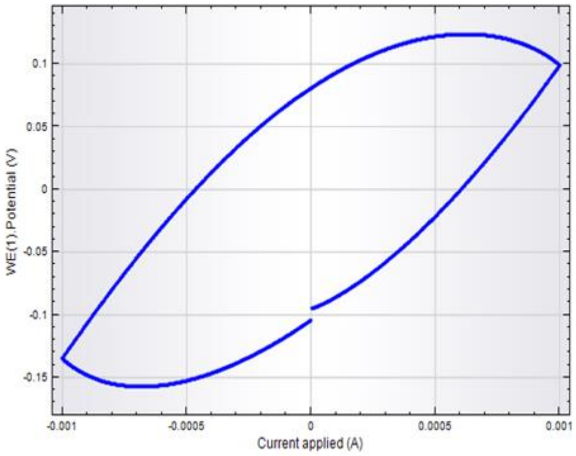

Figure 5. Dependence of the potential of the VITO electrode on the applied current over the range from -1 mA to + 1 mA.

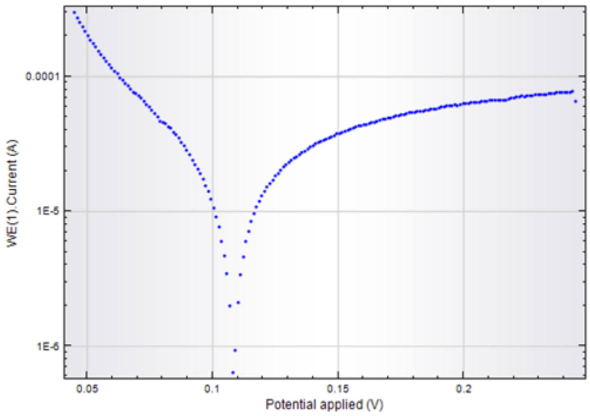

Figure 6. The Linear polarization curve (dependence of the current on the potential applied) for the air-breathing cathode VITO.

The dependence of the current on the applied potential of the air-breathing cathode VITO and the obtained curve of linear polarization is depicted in Fig. 6 This curve suggests that at ca. 0.11 V oxygen reduction takes place on the cathode – a clear reduction maximum is present.

CONCLUSIONS

Bio-electrochemical systems are an alternative of the conventional, expensive methods of purifying waste waters, as, together with the reduction of the pollutants, there is a generation of electricity. The constructed single-chamber fuel cell shows the abilities of these systems to reduce organic pollution and the phosphate and ammonium contents in waste waters from animal breeding by simultaneously generating a potential of around 0.5 V with the help of microbiological conenoses with the residual fluid. The system is stable within the test period of 15 days. Future studies shall be necessary in order to improve the work and to prove the resistance of the constructed microbial cell.

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