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Original Research Article

EFFECT OF USING VARIOUS CATHODE MATERIALS (carbon felt, Ni-Co, Cu-B, and Cu-Ag) ON THE OPERATION OF MICROBIAL FUEL CELL

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A b s t r a c t

Wastewater has high potential as an energy source. Therefore, it is important to recover even the smallest part of this energy, e.g., in microbial fuel cells (MFCs). The obtained electricity production depends on the process rate of the electrodes. In MFC, the microorganisms are the catalyst of anode, and the cathode is usually made of carbon material. To increase the MFC efficiency it is necessary to search the new cathode materials. In this work, the electricity production from yeast wastewater in membrane-less microbial fuel cells with a carbon felt, Ni-Co, Cu-B, and Cu-Ag cathodes has been analyzed. In the first place, the measurements of the stationary potential of the electrodes (with Cu-Ag catalyst obtained by the electrochemical deposition technique) were performed. Next, the analysis of the electric energy production during the operation of the membrane-less microbial fuel cell (ML-MFC). The highest parameters were obtained for the Ni-Co and Cu-Ag catalysts. The cell voltage of 607 mV for Ni-Co and 605 mV for Cu-Ag was obtained. Additionally, the power of 4.29 mW for both cathodes - Ni-Co and Cu-Ag was obtained. Moreover, Ni-Co and Cu-Ag allow the shortest time of COD reduction. Based on the test results (with selected MFC design, wastewater, temperature, etc.), it can be concluded that of all the analyzed electrodes, Cu-Ag and Ni-Co electrodes have the best parameters for use as cathodes in ML-MFC. However, based on the results of this study, it can be concluded that all the tested electrodes can be used as cathode material in MFC.

Keywords: bioelectricity, microbial fuel cell (MFC), bio-electro-chemical system, catalyst, cathode, environmental engineering, COD reduction, renewable energy sources

1. INTRODUCTION

The ongoing global population growth is contributing to a constant rise in waste and wastewater. Wastewater is primarily treated in wastewater treatment plants, incurring significant costs for its disposal [1,2]. Consequently, there is a continuous effort to develop new methods for both improved purification and the utilization of wastewater for alternative purposes [3-6]. Nowadays, the concept of waste reuse

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is more and more popular [7-10]. Thanks to the advancement of new technologies that enable the use of raw materials with lower content of required components, a growing amount of waste can now be regarded as valuable by-products suitable for reuse. By-products find applications in various sectors of the economy, including agriculture, construction, pharmaceuticals, cosmetics, and the food industry [11-14]. Although wastewater is primarily treated in wastewater treatment plants, there is a growing trend of utilizing it as a valuable by-product. This holds true for both municipal [15,16] and industrial wastewater [6,17]. Moreover, wastewater contains a significant amount of stored energy, primarily in chemical compounds. Theoretically, there is approximately nine times more energy stored in wastewater than is needed for its disposal [18]. Considering the amount of wastewater produced every year, the development of any technology allowing energy recovery from wastewater seems to be a necessity. It is important to recover each part of energy (even the smallest one) feasible to recovery. Furthermore, the development of a whole new energy platform that produces appropriate amount of energy while at the same time reducing negative impact of energy production on the environment it is necessary. The objective is to achieve carbon neutrality by 2050, while fully meeting energy needs [19-21]. But to achieve this goal, it will be necessary not only to change the energy system, but also to change our lifestyle [18]. It will be necessary to increase the use of electricity during periods of surplus production and to limit consumption during shortages. It appears that substantial educational initiatives and significant variations in energy prices will be required to instigate a shift in lifestyle, particularly during times of surplus production and energy shortages. To fulfill the energy demand, it will be necessary to harness every energy source that enables the provision of additional energy, with a special emphasis on renewable sources. As mentioned earlier, one of such sources is wastewater. A device capable of recovering energy from wastewater is a microbial fuel cell (MFC) [18,22]. MFC is a bio-electro-chemical system in which simultaneously generate electricity and purify wastewater (or polluted water) by oxidizing substrates with an anode biofilm. [23-25]. Examples of microorganisms which create the biofilm on anode are, e.g., bacteria from the groups of *Gammaproteobacteria, Clostridia, Bacteroidetes, Flavobacteria, Sphingobacteria, Deferribacteres, Spirochaetes, Planctomycetes,* or *Nitrospirales,* and fungi cells, e.g., *Saccharomyces* or *Pichia* [26-34]. However, there are in the anode chamber (of MFC) also other microorganisms, which present have not yet been fully determined [29,35]. For using in MFC the microorganisms are obtained mainly from soil, bottom sediments, wastewater treatment plants and from, e.g., previously operating MFC [18,35-42]. Both types of microorganisms (determined and undetermined) creating anode biofilm act together as a catalyst of anode [22,23,29]. The rate of the catalyst's action in this case depends on the metabolism of microorganisms. Unfortunately, the microorganism's metabolism is slow process, so the rate of energy production and wastewater treatment in the MFC are slow. However, their presence is necessary to use the substances contained in the wastewater. For this reason, anodes for MFCs are made of biocompatible materials, e.g., carbon, carbon felt, carbon fibers, etc. [18,23,42]. Whereas the cathodes for MFCs are can made from non-biocompatible materials [18,43-44]. Because cathode catalysts do not have to be microorganisms. If on cathodes occurs only chemical process, the oxygen reduction reaction occurs faster than when microorganisms are used. The material for cathodes can be both carbon material and metal electrodes or metal electrodes with a catalyst applied to the surface [45-51]. However, platinum has the best catalytic properties [52,53]. Unfortunately, it is also characterized by high price. That's why it is necessary to look for other catalysts that do not contain precious metals. Another example of a metal with good catalytic properties is nickel. However, pure nickel (Raney Ni, the most used) is difficult to use, e.g., it should never be exposed to air. Even after preparation, Raney Ni still contains small amounts of hydrogen gas and may spontaneously ignite when exposed to air [54]. Therefore, metal alloys should be easier (also safer) to use while maintaining good catalytic properties.

Substantial optimization and cost reduction are required before microbial fuel cells (MFCs) can be practically applied [55]. Therefore, it is necessary to constantly search for solutions to reduce costs and increase the efficiency of MFC. One of such directions is the selection of catalysts for MFC electrodes. In this work the effect of various cathode materials (carbon felt, and alloys: Ni-Co, Cu-B and Cu-Ag) on operation of membrane-less microbial fuel cell (with chambers one above the other) were analyzed.

2. MATERIALS AND METHODS

Due to the high costs of the proton exchange membrane, it was decided to use a membrane-less microbial fuel cell (ML-MFC) for the measurements. However, for comparison purposes, the choice of cell does not matter. It is important to maintain the same conditions for all analyzed electrodes (cathodes). The housing of ML-MFC (1-3 in Figure 1) was printed using the 3D technology. ABS plastic was used for printing. As an anode the carbon felt was used (9 in Figure 1). Whereas, as a cathode the various materials was used. For measurements as cathode was chosen some different materials: carbon felt and electrodes with Cu-B, Ni-Co, and Cu-Ag catalysts (7 in Figure 1). The alloys were obtained by the method of electrochemical deposition and were deposited on copper foam electrodes. The Cu-B alloy was deposited from a mixture of mainly $NaBH_4$ and $CuSO_4$ [46,51]. The Ni-Co alloy was deposited from a mixture of mainly $NiSO_4$ and $CoSO_4$ [56,57]. The Cu-Ag alloy was deposited from a mixture of mainly $CuSO_4$ and $AgNO_3$ [58-61]. The alloys were obtained at temperatures of 355–365 K and at a current density 1–3 $A \cdot dm^{-2}$. The composition of the mixture was selected experimentally. Table 1 shows the composition of the mixture applied for catalysts deposition.

Table 1. Composition of the mixture applied for catalysts deposition

Alloy	Component	Volume [$mol \cdot L^{-1}$]
Cu-B	$NaBH_4$	0.02
	$CuSO_4 \cdot 7H_2O$	0.05
	NaOH	1.00
	Trilon B	0.12
Ni-Co	$NiSO_4$ x $7H_2O$	0.92
	$CoSO_4$ x $7H_2O$	0.07
	H_3BO_3	1.03
	NaCl	0.25
Ag-Cu	$AgNO_3$	0.02
	$CuSO_4 \cdot 7H_2O$	0.05
	Trilon B	0.12
	NaOH	1.00

The cathode is constantly oxidized during the ML-MFC operation. Therefore, it is necessary to cathode pre-oxidize. There is a risk (in the case of pre-oxidation absence) of changing the catalytic properties of the electrodes during their operation. For measurements the cathodes pre-oxidized at a temperature of 673 K. The time of electrode oxidation was 6 h. The oxidation was performed with a laboratory furnace. The used ML-MFC was the dimensions of 70 mm × 70 mm × 130 mm (width x depth × height) with intake and outflow of the wastewater (10 and 13 in Figure 1). The electrical circuit of the ML-MFC was constantly connected with a 100 Ω resistor (R in Figure 1). For the research the mixed municipal wastewater (MWW) and process yeast wastewater (PYWW) from vacuum filters (mixed in a 1:1 ratio) was used [6,45,57]. Wastewater from vacuum filters is the least concentrated process wastewater in the yeast production line [6]. When mixed with municipal wastewater, they not only provide an additional source of nutrients for microorganisms, but also allow the mixed wastewater to flow more easily through

the ML-MFC. Initial COD concentration was 1455 mg·L^{-1}. The acidity of the wastewater was 6.8 pH. The conductivity of wastewater was 2.13 mS·cm^{-1}. The microorganisms were obtained from activated sludge from a wastewater treatment plant. The time of microorganism's acclimatization was 5 days [47,58,59]. During the ML-MFC operation the cathode was constantly aerated (5 L·h^{-1}) by bubbler (11 in Figure 1). Figure 1 shows the ML-MFC used in experiment.

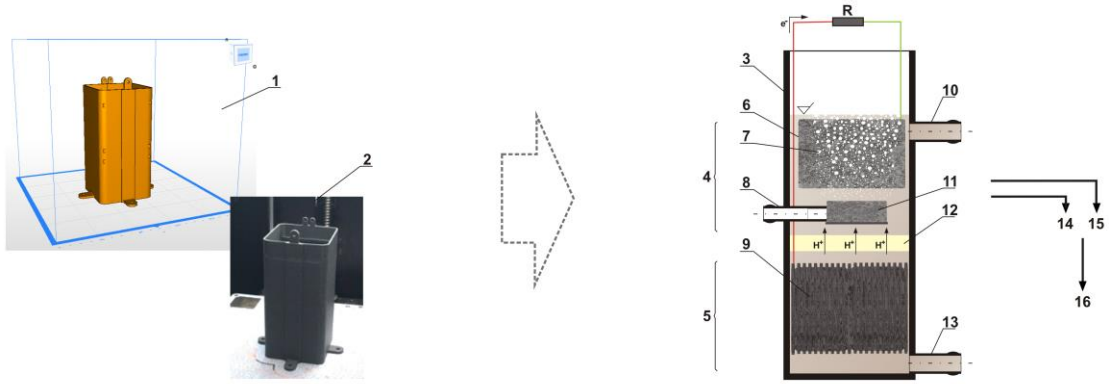

Fig. 1. Membrane-less fuel cell used in experiment: 1 – project of ML-MFC housing; 2 – ML-MFC 3D printout; 3 – housing; 4 – cathode chamber; 5 – anode chamber; 6 – cathode; 7 - air bubbles; 8 – air inlet nozzle; 9 – cathode; 10 – wastewater outflow nozzle; 11 - stone air bubble; 12 – glass wool; 13 - wastewater inflow nozzle; 14 – electrical measurements; 15 – COD measurements; 16 – data to computer

ML-MFC was combined with the external wastewater tank (9 in Figure 2). The wastewater was slow circulated in the direction from the anode to the cathode, by the external wastewater tank. This flow prevents the oxygenation of the anode. The rate of circulating was low (0.05 L·h^{-1}) to ensure stable conditions for the functioning of microorganisms in anaerobic conditions. The volume of wastewater in the entire system was 15 L (including an external tank). The wastewater in external tank was slowly mixed (200 rpm) by mechanical stirrer (8 in Figure 2). Figure 2 shows system including the ML-MFC and external tank.

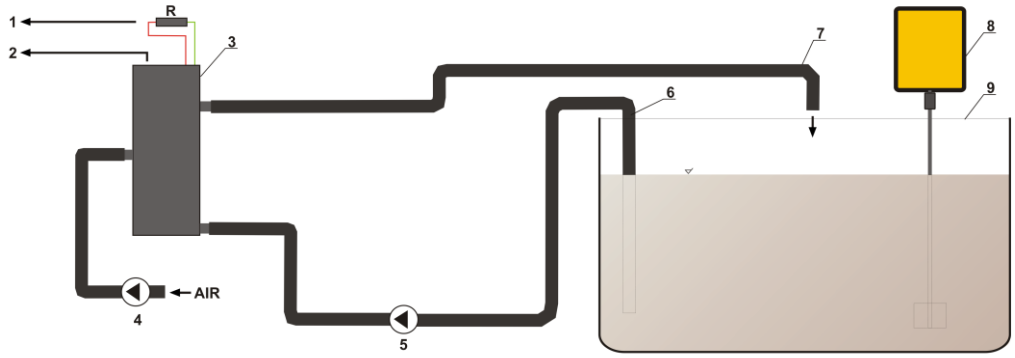

Fig. 2. System including the ML-MFC and external tank: 1 - electrical measurements; 2 - COD measurements; 3 – ML-MFC; 4 – air pump (for cathode aeration); 5 – wastewater pump; 6 - wastewater inflow; 7 - wastewater outflow; 8 – mechanical stirrer; 9 – wastewater tank

During ML-MFC operation the electrical parameters and COD reduction was recorded. The COD reduction in ML-MFC was comparison with wastewater aerated in another reactor. Both reactors were operated until 90% COD reduction was achieved [63]. The volume of this reactor was the same (15 L) as volume of the system with ML-MFC and external tank. The wastewater in this reactor was constantly aerated with capacity of 200 $L \cdot h^{-1}$. During ML-MFC operation the cell voltage and power was measured. The temperature of all measurements was 25 °C.

The electrodeposition was carried out with using a regulated power supply (PowerLab 305D-II, China). For printing and to smooth outsprints a M200 3D printer and Apoller smoothing device was used (devices with the Z-Suite software; Zortrax S.A, Olsztyn, Poland). For the electrode oxidation an LAC LH06/12 furnace (LAC s.r.o., Židlochovice, Czech Republic) were used. For COD reduction measurements a Hanna HI 83224 wastewater treatment photometer (HANNA Instruments, Woonsocket, RI, USA) was used. For the pH and conductivity measurements a HI 5522 (HANNA Instruments, Woonsocket, RI, USA). For the wastewater mixed in the external tank by a CAT R17 mechanical stirrer (Ingenieurbüro CAT M.Zipperer GmbH, Staufen, Germany). For the electrical measurements of ML-MFC, a Fluke 8840A multimeter (Fluke Corporation, Everett, WA, USA) and a PGSTAT302N potentiostat (Metrohm-Autolab BV, Utrecht, Holland) was used. For the temperature measurements a UNI-T UT33C multimeter (UNI-Technology, Hongkong) was used.

3. RESULTS AND DISCUSSION

In first step the electrical parameters during ML-MFC operation with various electrodes were obtained. During ML-MFC operation the cell voltage (average values), and power (maximum values) was measured. The results of cell voltage measurements are shown in Figure 3.

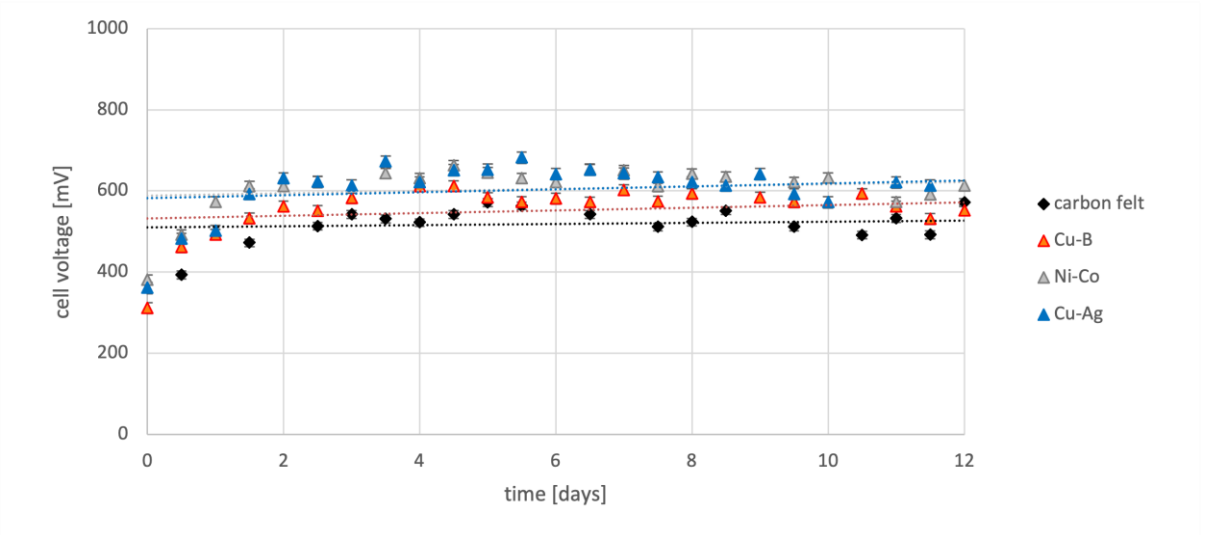

Fig. 3. Cell voltage of the ML-MFC in time, depending on the type of electrode

According to the obtained data, all three analyzed alloys (Cu-B, Ni-Co, and Cu-Ag), when used as cathode catalysts, resulted in an increased cell voltage compared to the carbon felt electrode (Figure 3; black markers). After the first day, it is evident that the cell voltage is consistently higher when using metal alloy electrodes compared to a carbon cathode. This trend persists throughout the entire measurement period. The average cell voltage using carbon felt cathode was 518 mV. When using the

Cu-B cathode, the cell voltage increased (Figure 3; orange markers). The average cell voltage increased by 7.0% to 554 mV. Furthermore, when utilizing Ni-Co and Cu-Ag cathodes, the cell voltage experienced another increase (Figure 3; gray and blue markers). The average cell voltage (for both cathodes - Ni-Co and Cu-Ag) increased by 9.4 % from value obtained for Cu-B to 607 mV (for Ni-Co cathode), and to 605 mV (for Cu-Ag cathode). However, the cell voltage increased by 16.9% for the Ni-Co cathode and by 16.8% for the Cu-Ag cathode, based on the values obtained from the carbon felt cathode. The results indicate that the average cell voltage for both cathodes (Ni-Co and Cu-Ag) is very similar.

Next, the power obtained in ML-MFC with various electrodes was analyzed. The results of power measurements are shown in Figure 4.

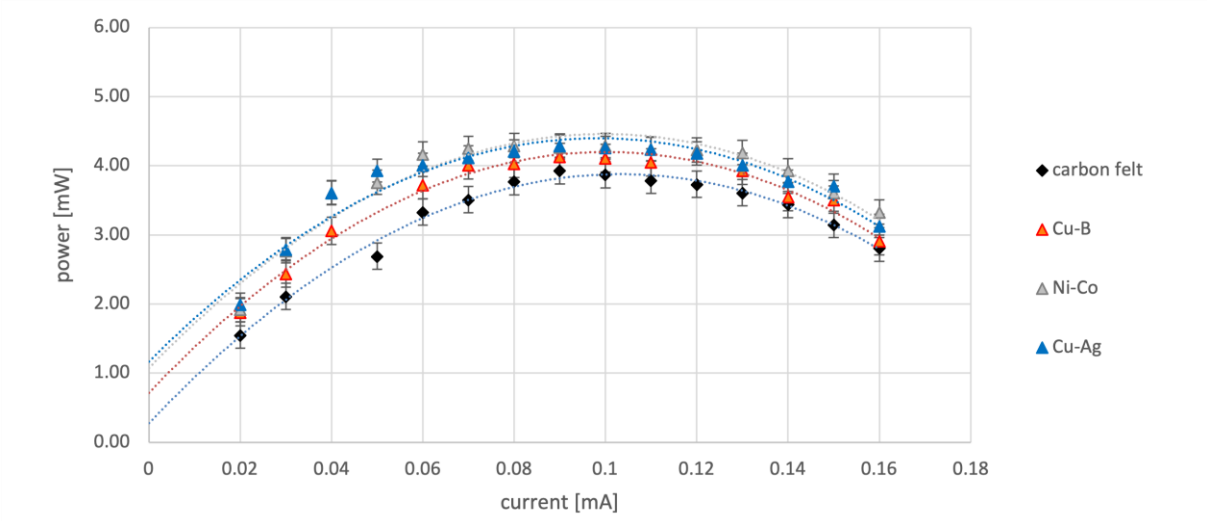

Fig. 4. Power curves of the ML-MFC, depending on the type of electrode

Similar to the cell voltage measurements, power measurements demonstrated that all metal cathodes (Cu-B, Ni-Co, and Cu-Ag) resulted in an increase in ML-MFC power compared to the use of a carbon felt electrode. When using the Cu-B electrode, a maximum power increase of 5.1% was achieved compared to the carbon electrode, from 3.93 mW (carbon felt) to 4.13 mW (Cu-B). While employing the Ni-Co and Cu-Ag cathodes, there was once again an increase in maximum power, like the observations in cell voltage measurements. Nevertheless, the disparity was not as substantial as observed in the case of cell voltage.

The maximum power (for both cathodes - Ni-Co and Cu-Ag) increased by 3.9 % from value obtained for Cu-B to 4.29 mW (for both cathodes - Ni-Co and Cu-Ag). Whereas from value obtained for carbon felt cathode the maximum power increased by 9.2 % for both cathodes (Ni-Co and Cu-Ag). The values of maximum power for Ni-Co and Cu-Ag were similar. However, there is a subtle distinction in the characteristics of the power curves, as illustrated in Figure 4 (gray and blue markers).
Summarizing the data obtained for average cell voltage (Figure 3) and maximum power (Figure 4) are summarized in Table 2.

Table 2. Cell voltage (average values), and power (maximum values) measured during the ML-MFC operation. Cathodes: carbon felt, Cu-B, Ni-Co, and Cu-Ag

type of electrode	cell voltage [mV]	power [mW]
carbon felt	518	3.93
Cu-B	554	4.13
Ni-Co	607	4.29
Cu-Ag	605	4.29

I the next step the reduction of COD concentration was analyzed in both reactors (ML-MFC, and reactor with aeration).

Both reactors were fed with the same wastewater, and measurements were carried out at a temperature of 25 °C. Figure 5 contains details of the reduction of COD over time for both types of reactors (ML-MFC, and reactor with aeration), and for all analyzed cathode materials (carbon felt, Cu-B, Ni-Co, and Cu-Ag).

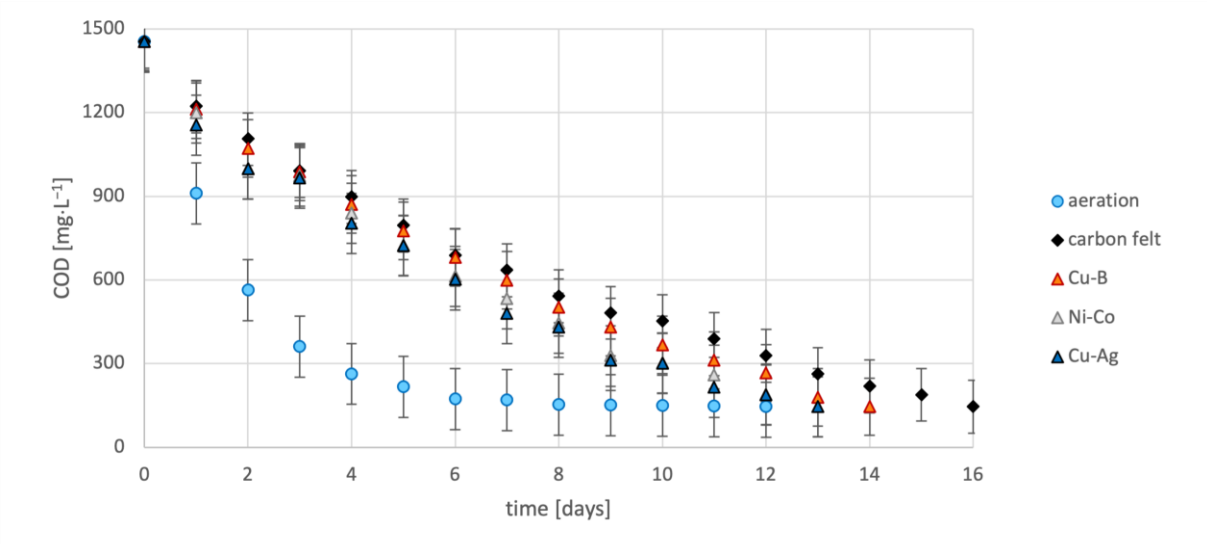

Fig. 5. Reduction of the COD in reactor with aeration, and in ML-MFC (with using various electrodes)

According to the data (Figures 5), a COD reduction of 90% was achieved for both reactors and the ML-MFC. It is noteworthy that a 90% COD reduction was attained for all electrode materials. In the case of the reactor with aeration, the reduction time was 12 days. Whereas the reduction time in ML-MFC, depending on the type of electrode, ranged from 13 to 16 days. The measurement using a carbon felt electrode was characterized the longest reduction time (16 days); (Figure 5; black markers). Whereas using a Cu-Ag and Ni-Co electrodes were characterized the shortest reduction time (13 days); (Figure 5; gray and dark blue markers). The COD reduction time (up to 90% effectiveness) for the Cu-B electrode was 14 days (Figure 5; orange markers). It should be noted that the characteristic of COD reduction curve for aeration is the most beneficial. Nevertheless, it is possible to achieve a similar reduction time using ML-MFC, which would also reduce the costs associated with aeration.

4. CONCLUSIONS

In the research a membrane-less microbial fuel cell (ML-MFC) was used, in which the impact of various types of cathodes on cell voltage, power and time of COD reduction. The choice of the cell type was driven by the necessity to reduce measurement costs, specifically by eliminating the high cost associated with a proton exchange membrane. However, for the purpose of comparison, the choice of the cell is not crucial. What matters is maintaining uniform conditions for all analyzed electrodes (cathodes). The housing of the ML-MFC was 3D-printed using ABS plastic, and subsequently, the surface of the printout was smoothed using a smart smoothing device. The carbon felt and three types of alloys (Cu-B, Ni-Co, and Cu-Ag) was used as cathodes. The alloys were obtained by the method of electrochemical deposition and were deposited on copper foam electrodes. The research has shown that all three analyzed alloys (Cu-B, Ni-Co, and Cu-Ag), used as cathode catalysts in ML-MFC, allowed to increase the power and voltage of the cell in relation to the carbon felt electrode. The best values of cell voltage were obtained for Ni-Co and Cu-Ag cathodes (607 mV and 605 mV, respectively). These values represent a 9.4% increase in cell voltage compared to the carbon felt electrode (518 mV). Similarly, for the cell voltage measurements, the power measurements showed that all metal cathodes (Cu-B, Ni-Co, and Cu-Ag) allowed an increase in ML-MFC power compared to the use of a carbon felt electrode. The best values of power were obtained for Ni-Co and Cu-Ag cathodes (4.29 mW for both cathodes - Ni-Co and Cu-Ag). Compared to the carbon felt electrode (3.93 mW), the power using Ni-Co and Cu-Ag electrodes increased by 9.2%. In the case of COD reduction, the shortest time of reduction also for Cu-Ag and Ni-Co was obtained (13 days). It should be noted that the characteristic COD reduction curve for aeration is the most favorable. However, aeration demands significant energy expenditure. Based on the test results, considering the selected MFC design, wastewater, temperature, etc., it can be concluded that, of all the analyzed electrodes, Cu-Ag and Ni-Co electrodes exhibit the best parameters for use as cathodes in ML-MFC. Nevertheless, the results of this study also suggest that all the tested electrodes can be employed as cathode materials in MFC.

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