Single chamber microbial fuel cell with Ni-Co cathode

Barbara Włodarczyk[1,*], *Paweł P.* Włodarczyk[1], and *Antonina* Kalinichenko[1]

[1]University of Opole, Department of Process Engineering, Dmowskiego Street 7-9, 45-365 Opole, Poland

Abstract. The possibility of wastewater treatment and the parallel energy production using the Ni-Co alloy as cathode catalyst for single chamber microbial fuel cells is presented in this research. The research included a preparation of catalyst and comparison of COD, NH_4^+ and NO_3^- reduction in the reactor without aeration, with aeration and with using a single chamber microbial fuel cell with Ni-Co cathode. The reduction time for COD with the use of microbial fuel cell with the Ni-Co catalyst is similar to the reduction time with aeration. The current density (2.4 $A \cdot m^{-2}$) and amount of energy (0.48 Wh) obtained in MFC is low, but the obtained amount of energy allows elimination of the energy needed for reactor aeration. It has been shown that the Ni-Co can be used as cathode catalyst in single chamber microbial fuel cells.

1 Introduction

The energetic industry struggles with difficulties with producing more and more energy. Simultaneously the wastes and wastewater production increases very much, too. Both industrial and municipal wastewater is generated in huge amounts. Traditional wastewater treatment systems require lot of cost and energy to efficient work. The United States spends approximately $23 billion annually on domestic wastewater treatment, and another about $200 billion is needed for improving publicly owned treatment works [1]. So, it is important to reduce of wastewaters treatment costs. It is exist most different ways to use of wastewater [2]. At the same time new sources of energy are sought. Technical device that can combine electricity production with wastewater treatment is a microbial fuel cell (MFC) [3,4]. During wastewater treatment in MFC the activated sludge bacteria can be used for electricity production. The concept of microbial fuel cells was created the 60's of XX century [5]. Bacteria that were identified as capable of creating electricity (activated sludge is capable of producing electrons and H^+ jones) in MFCs include a wealth of genera of bacteria e.g. *Geobacter*, *Shewanella* or *Pseudomonas* [6-10]. Electrons are formed as a result of biochemical reactions catalysed by enzymes produced by bacteria. Next electrons are transferred from the anode (negative terminal) to the cathode (positive terminal) through the electric current receiver (load) [11]. In MFC organic material is oxidized on anode, and the product of oxidation are electrons (and CO_2) [12,13]. A bacterium in the anode compartment transfers electrons to the anode electrode. This occurs either through direct contact, nanowires, or mobile electron shuttles. During electron production protons are also produced in excess. These protons migrate through the proton exchange membrane (PEM) into the cathode area. The electrons flow from the anode through an external resistance to the cathode where they react with the final electron acceptor (oxygen) and protons [12-14]. So, MFCs are bio-electrochemical systems that are devices that use bacteria as catalysts to oxidize organic and inorganic matter and generate current [3,15].

The problems of using MFCs are slow process of reducing of some wastewater parameters and a low current density obtained in MFCs. But, it is possible to increase the current density by using different catalyst for electrodes (mainly for cathode). On anode the function of catalyst take over the microbes. In MFC's carbon is most often used as the electrode, but it is possible to use metal catalysts [16]. Theoretical the current density (obtained with using specific catalyst) can be calculated using the Butler-Volmer exponential function [17]. But, in real conditions the choice of catalyst is mainly carried out by experimental methods. For this reason experimental research of search a new catalysts for MFCs are still conducted [15, 16, 18-24]. Authors have attempted to demonstrate the possibilities of wastewater treatment with electricity production using the single chamber MFC (with Ni-Co alloy as cathode catalyst).

2 Material and Methods

The wastewater from municipal wastewater treatment plant was used in measurements. Research covered measurement of wastewater treatment level and electricity production. Research of wastewater treatment level covered reduction of COD, NH_4^+ and NO_3^- were conducted in the reactor without aeration, with aeration and with using a MFC [25]. Capacity of each reactor was equal 0.015m^3. In the first reactor the wastewater had contact with air only by wastewater mirror. In the second reactor the wastewater was aerated by air pump

* Corresponding author: barbara.wlodarczyk@uni.opole.pl

($0.27 m^3 \cdot h^{-1}$) and in the third reactor the wastewater was treatment with MFC. In test MFC the graphite brush as the anode (Chemviron Carbon) and Ni-Co alloy was used as catalyst of cathode. Ni-Co alloy were obtained by the method of electrochemical deposition and analysed by the XRD method. The alloys were deposited on mesh copper electrode. The alloys were deposited from a mixture of $NiSO_4$ and $CoSO_4$ [26, 27]. The alloys were obtained at temperature of 293K at current density of deposition id equal to 300 $A \cdot m^{-2}$ [26]. Composition of mixture for alloy deposited shows Table 1 [22].

Table 1. Mixture composition for deposited Ni-Co alloy on copper electrode.

Component	$NiSO_4 \times 7H_2O$ 195 $g \cdot l^{-1}$ $CoSO_4 \times 7H_2O$ 35 $g \cdot l^{-1}$
pH	2.0
Temperature	293 K
Current density	300 $A \cdot m^{-2}$
Co	50 %

Before the deposition of the alloy, mesh copper electrode was degreased in 25% aqueous solution of KOH (after degreasing, the surface shall be completely wettable with water), digested in acetic acid and washed with alcohol [26]. The time of the deposition was equal to 1 hour. The chemical composition of Ni-Co alloys was determined with the XRD method. The alloy with 50% of Co was selected for measurements [24, 26]. The Nafion 117 (183 μm) was used as PEM. The cathode with Ni-Co catalyst (in mesh form) was hot pressed into PEM. Cathode prepared in this way was used as one of reactor (MFC) wall (Fig. 1) [24].

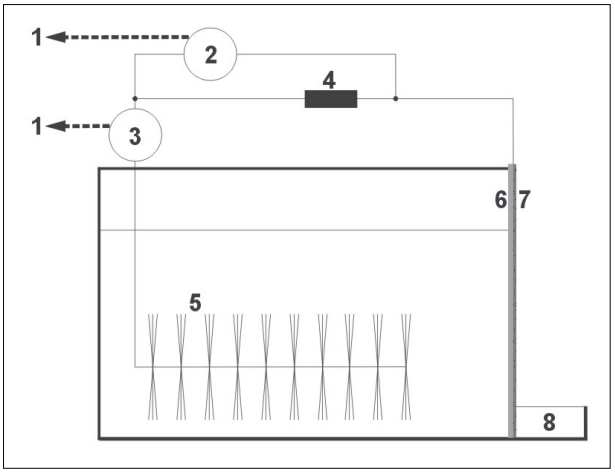

Fig. 1. Scheme of single chamber microbial fuel cell with graphite anode and Ni-Co cathode:
1 – to computer, 2 – voltmeter, 3 – ammeter, 4 – load, 5 – graphite anode, 6 – PEM, 7 – mesh cathode with Ni-Co catalyst, 8 – water (from cathode) container.

All three reactors were fed with the same wastewater with a COD concentration of 1755 ± 70 $mg \cdot l^{-1}$. The reactors were operated in batch mode till reaching 90% of COD removal (assumed reduction level) [25]. The temperature of measurements was equal 293K. During MFC operation, both voltage and current were also measured. The MFC was loaded with resistance equal 10Ω. The Fig. 2 shows scheme of measurement position.

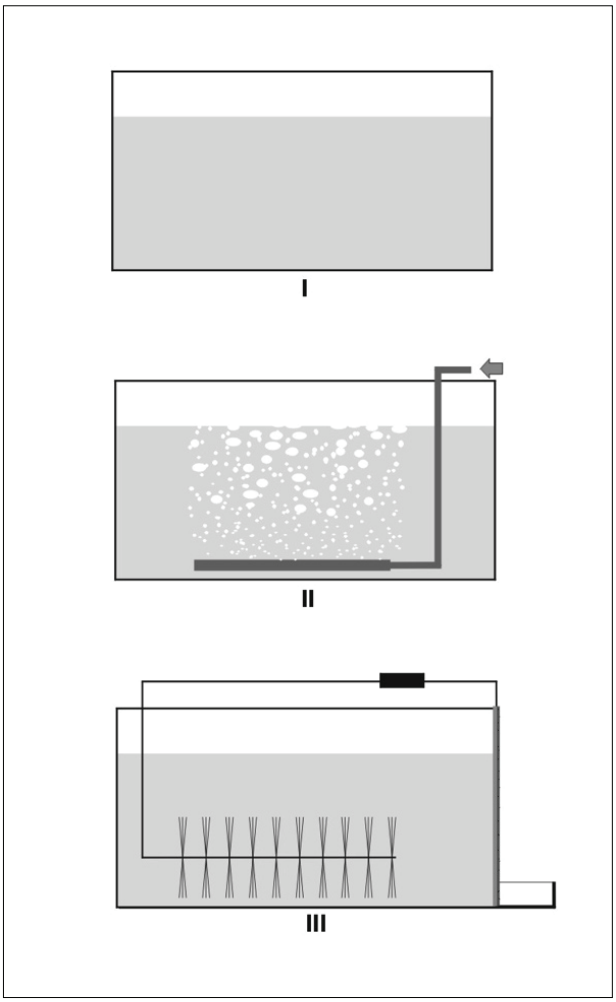

Fig. 2. Scheme of measurement position: I – without aeration, II – with aeration, II – with using MFC .

Table 2 shows the parameters of analysed wastewater.

Table 2. Parameters of analysed wastewater.

Parameter	**Value**
pH	6.7±0.1
COD $[mg \cdot l^{-1}]$	1,755 ± 70
NH_4^+ $[mg \cdot l^{-1}]$	11 ± 2
NO_3^- $[mg \cdot l^{-1}]$	4 ± 2

3 Results

Fig. 3 shows the decreasing the COD value during wastewater treatment without aeration, with aeration and with using a microbial fuel cell with Ni-Co cathode. Figs. 4 and 5 shows the change of concentration of NH_4^+ and NO_3^- during wastewater treatment without aeration, with aeration and with using single chamber MFC (with

Ni-Co cathode). All measurements were carried out at a temperature of 293K.

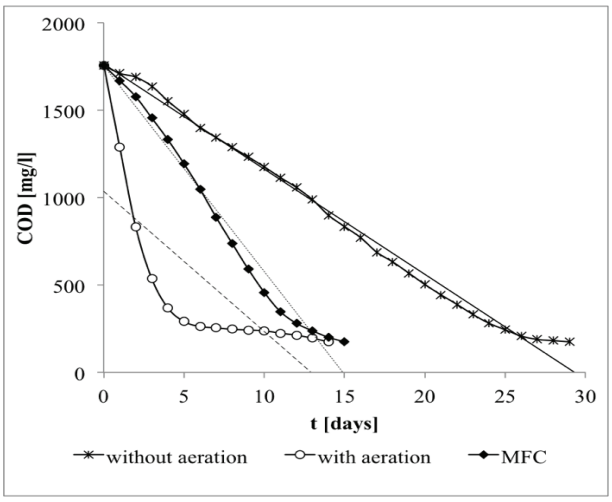

Fig. 3. COD reduction during wastewater treatment without aeration, with aeration and with using single chamber MFC with Ni-Co cathode.

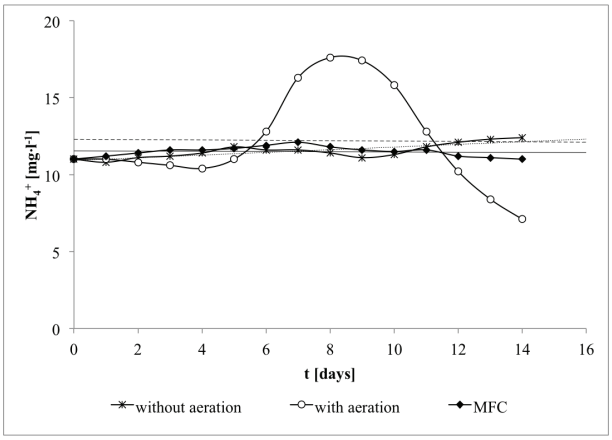

Fig. 4. Change of concentration in time of NH_4^+ during wastewater treatment without aeration, with aeration and with using single chamber MFC with Ni-Co cathode.

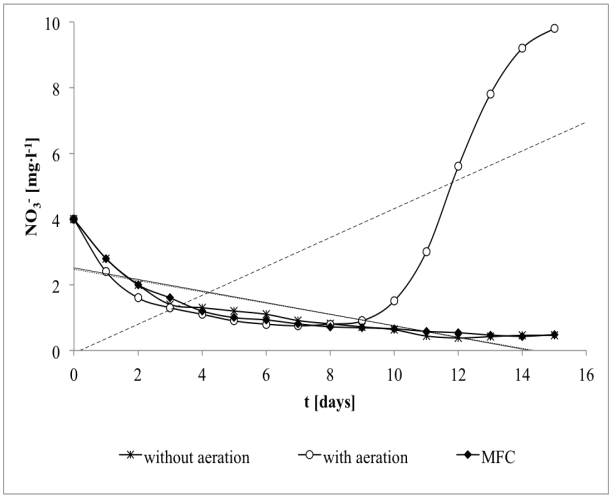

Fig. 5. Change of concentration in time of NO_3^- during wastewater treatment without aeration, with aeration and with using single chamber MFC with Ni-Co cathode.

The obtained current density was equal 0.24 $mA \cdot cm^{-2}$ and obtained amount of energy was equal 0.93 Wh. Based on voltage and current have been determined power curve. Figure 6 shows power curve of single chamber MFC with Ni-Co catalyst.

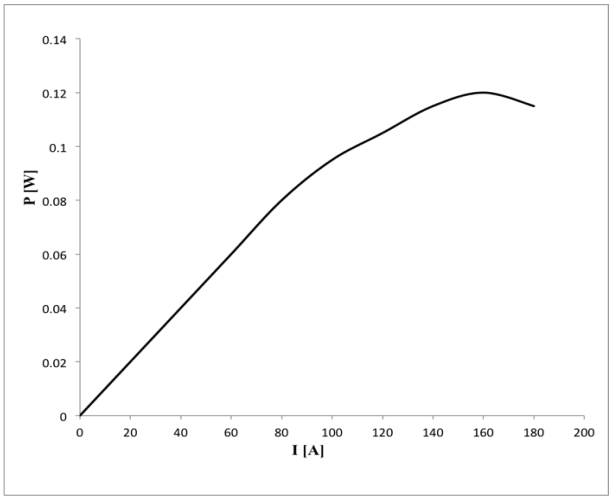

Fig. 6. Power curve of test single chamber MFC with Ni-Co catalyst.

4 Conclusions

The measurements show that in any cases (without aeration, with aeration and with single chamber MFC with Ni-Co cathode) was reached level 90% efficiency of COD reduction (Fig. 3). Measurements have shown the effectiveness of COD reduction in any cases (in any reactor) but the characteristics of curves are different. The characteristic curve of aeration is more preferred than characteristic curve of MFC (with Ni-Co cathode) because about 83% effectiveness of COD reduction after about 5 days (Fig. 3). But time for 90% (assumed reduction level) effectiveness reduction of COD with the use of single chamber MFC (15 days) is similar to the reduction time with aeration (14 days). The measurement of NH_4^+ reduction shows no changes in cases measurement in single chamber MFC (Fig. 4). The measurements (Fig. 5) have shown also the effectiveness of NO_3^- reduction (during 14 days). Increasing of NH_4^+ concentration (in II reactor - aerated) results from the attachment of hydrogen molecule to the ion ammonia (e.g. during putrefaction) (Fig. 4) [28]. The increase of NO_3^- concentration (Fig. 5) is the result of nitrification during the growth of bacteria [29,30]. The average current density (2.4 $A \cdot m^{-2}$) and amount of energy (0.48 Wh) obtained in test single chamber MFC are low. But, if can accept a longer COD reduction time, the obtained amount of energy will allow elimination of the energy needed for wastewater aeration. So, use of MFC should be considered as a support traditional wastewater treatment. The obtained results are comparable to the results using e.g. carbon or Cu-B alloy as cathode catalyst [25,31].

The fundamental possibility of using of Ni-Co alloy as cathode catalyst of single chamber MFC for municipally wastewater was obtained in this paper.

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