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MICROBIAL FUEL CELL WITH Cu-B CATHODE AND $KMnO_4$ CATHOLYTE

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Abstract

The increasing of standard living causes the increases energy consumption and waste or wastewater production. The possibility to combine wastewater treatment and electricity production can accomplish a microbial fuel cell. The possibility of wastewater treatment using the Cu-B catalyst with $KMnO_4$ catholyte for microbial fuel cells is presented in this paper. The measurements covered comparison of changes in the concentration of COD, NH_4^+ and NO_3 – in the reactor without aeration, with aeration and with using a microbial fuel cell (with Cu-B cathode and $KMnO_4$ catholyte). The reduction time for COD with the use of microbial fuel cell with the Cu-B catalyst (and $KMnO_4$ catholyte) is similar to the reduction time with aeration. It has been shown that the Cu-B (with $KMnO_4$ catholyte) can be used as cathode catalyst in microbial fuel cells. Unfortunately in this case is needed to constant delivery of catholyte

Keywords: microbial fuel cell, wastewater treatment, cathode, Ni-Co alloy, renewable energy sources, environment protection, clean technology, sustainable development

INTRODUCTION

Wastewater treatment systems with activated sludge and aeration of wastewater can efficiently remove organic pollutants, but such systems are cost and

energy intensive. The United States spends approximately $23 billion annually on domestic wastewater treatment (US EPA 2008). So, it is important to reduce of wastewaters treatment costs. Technical device that can accomplish this task are microbial fuel cells (MFCs) (Logan 2008). The concept of MFC was created the 1960's (Davis and Yarbrough 1962). In MFC bacteria can be used for electricity production during wastewater treatment. Bacteria that were identified as capable of creating electricity in microbial fuel cell include a wealth of genera of bacteria e.g. *Geobacter, Shewanella* or *Pseudomonas* (Bond and Lovley 2003; Chaudhuri and Lovley 2003; Kim *at al.* 2002; Park *at al.* 2001; Pham *at al.* 2003). So, activated sludge is capable of producing electrons (e^-) and H^+ jones. MFCs are bio-electrochemical systems that are devices that use bacteria as catalysts to oxidize organic and inorganic matter and generate electric current (Berk and Canfield 1964; Logan 2008, Rabaey and Verstraete 2005). Electrons produced by the bacteria are transferred from the anode to the cathode through the electric current receiver. In MFC organic material is oxidized on anode, and the product of oxidation is carbon dioxide and electrons. Bacteria in the anode area transfer electrons to the electrode (anode). This occurs either through direct contact (by nanowires) or mobile electron shuttles. The electrons flow from the anode through an external resistance to the cathode. And next they react with oxygen and protons (Liu *at al.* 2004; Rabaey and Verstraete 2005; Wang *at al.* 2008). In MFC a catalyst of anode are microbes. So, it is important to find catalyst for cathode. In MFCs carbon is most often used as the electrode. It is also possible to use metal catalysts for electrodes of MFCs (Dumas *at al.* 2006; Martin *at al.* 2011). In real conditions the choice of catalyst is mainly carried out by experimental methods (Bockris and Reddy 2000, Twigg 1989). For this reason experimental researches on the search for new catalysts for MFCs have been conducted for a dozen or so years (Cheng *at al.* 2006; Dumas *at al.* 2006; Logan *at al.* 2006; Martin *at al.* 2011; Zhao *at al.* 2005; Włodarczyk and Włodarczyk 2015a; Włodarczyk and Włodarczyk 2015b; Włodarczyk and Włodarczyk 2015c; Włodarczyk and Włodarczyk 2015d; Włodarczyk and Włodarczyk 2016a; Włodarczyk and Włodarczyk 2016b; Włodarczyk and Włodarczyk 2016c; Włodarczyk and Włodarczyk 2016d; Włodarczyk and Włodarczyk 2016e; Włodarczyk and Włodarczyk 2017). Authors have attempted to demonstrate the possibilities of wastewater treatment using the Cu-B alloy as cathode catalyst for MFC and $KMnO_4$ as catholyte.

MATERIAL AND METHODS

The method of electrochemical deposition was chosen to obtain Cu-B alloy. The alloys were deposited on titanium electrode (mesh form). The alloys

were deposited from a mixture of mainly $NaBH_4$ and $CuSO_4$ (Włodarczyk and Włodarczyk 2016f). The alloys were obtained at temperature of 365K. Before the deposition of the alloy titanium electrode was degreased in 25% aqueous solution of KOH (after the degreasing the surface shall be completely wettable), digested in acetic acid and washed with alcohol. The chemical composition of Cu-B alloys was determined with the X-ray diffraction method (XRD). The alloy with 9% of B was selected for measurements.

The measurements have included changes in the concentration of COD, NH_4^+ and NO_3^-. The research was conducted in reactors with capacity equal 15l. Measurements of reduction of COD, NH_4^+ oraz NO_3 – was conducted without aeration, with aeration and with using a MFC with Cu-B cathode and $KMnO_4$ catholyte. $KMnO_4$ was chosen as catholyte due the good oxidizing properties (Logan 2008). The temperature of measurements was equal 293K. The measurements were carried out to obtain 90% effectiveness of COD reduction (Huggins at al. 2013). The municipal wastewater was used in measurements. Table 1 shows the parameters of analysed wastewater.

Table 1. Parameters of analysed wastewater

parameter	value
pH	6,3
ChZT [mg/l]	2172
NH_4^+ [mg/l]	11
NO_3 – [mg/l]	3

Source: Own compilation

The figure 1 shows view of measurement position.

In the first reactor the wastewater had contact with air only by water mirror. In the second reactor the wastewater was aerated (270l/h) and in the third reactor the wastewater was treatment with MFC (with Cu-B cathode and $KMnO_4$ catholyte). The carbon electrode was used as anode. The MFC was loaded with resistance equal 10Ω. The cover was printed on the 3D printer (layer thickness was equal 290μm). The Nafion 117 was used as PEM. The cathode was immersed in $KMnO_4$ catholyte. Figure 2 shows view and scheme of cathode in ABS cover.

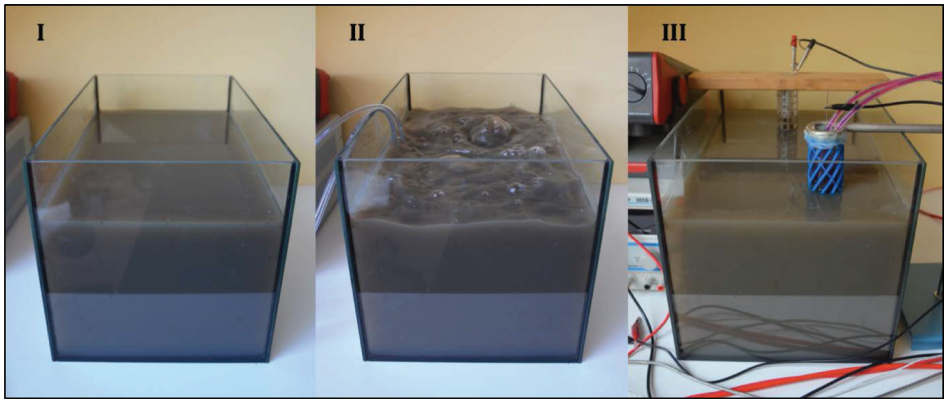

Figure 1. View of measurement position: I – without aeration, II – with aeration, III – MFC with Cu-B cathode and $KMnO_4$ catholyte [own compilation]

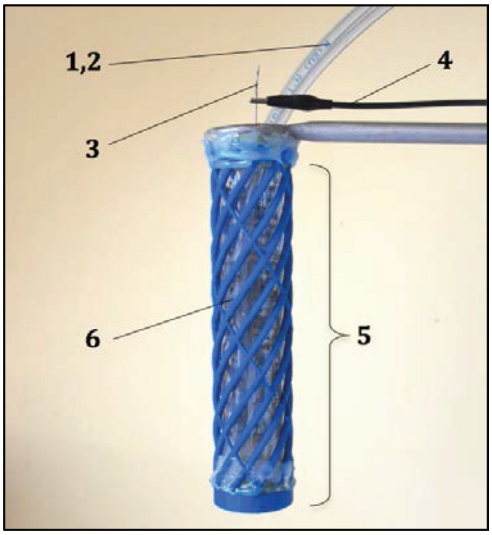

Figure 2. View of cathode in ABS cover [own compilation]
1,2 – inflow and outflow of $KMnO_4$ catholyte, 3 – cathode connector, 4 – electrical connection, 5 – ABS cover (blue), 6 – PEM.

RESULTS

Figure 3-5 shows the measurements of change of COD, NH_4^+ and NO_3 – concentration. All measurements were carried out at a temperature of 293K.

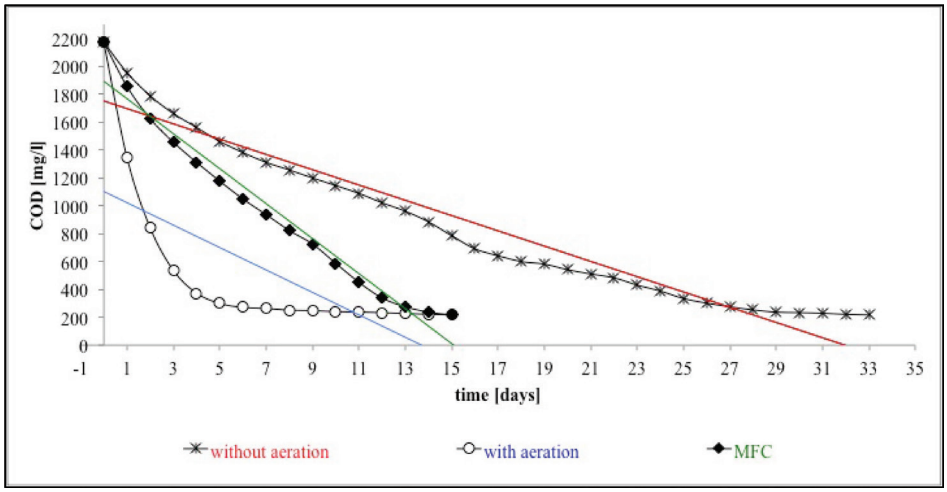

Figure 3. Change of concentration of COD during municipal wastewater treatment without aeration, with aeration and with using a MFC (with Cu-B cathode and $KMnO_4$ catholyte). The colours indicate the trend lines of individual data [own compilation]

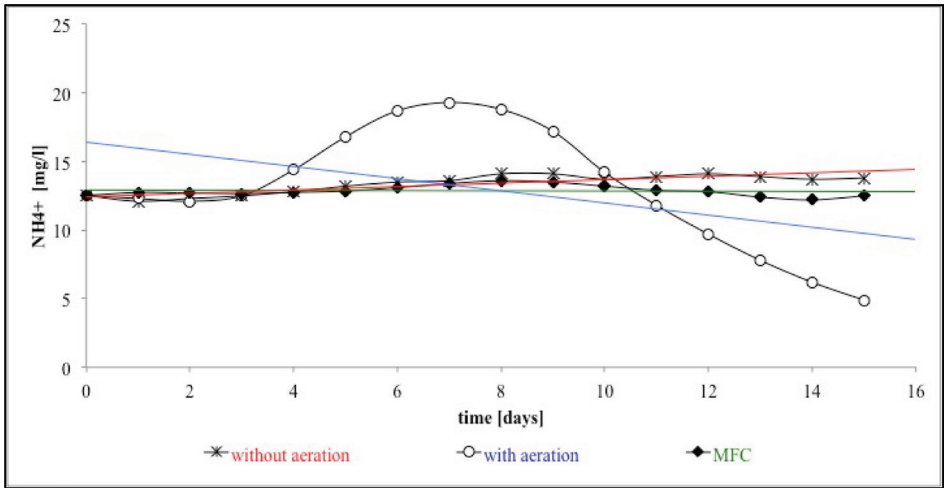

Figure 4. Change of concentration of NH_4^+ during municipal wastewater treatment without aeration, with aeration and with using a MFC (with Cu-B cathode and $KMnO_4$ catholyte). The colours indicate the trend lines of individual data [own compilation]

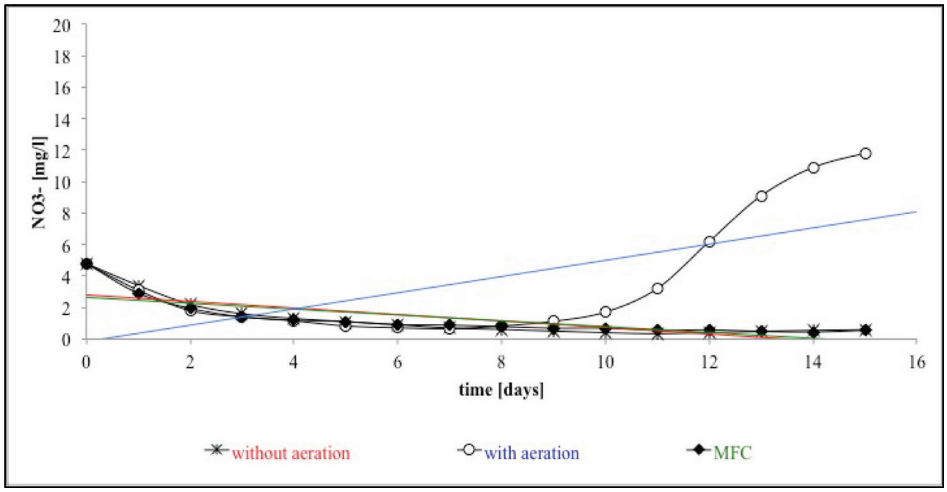

Figure 5. Change of concentration of NO_3 – during municipal wastewater treatment without aeration, with aeration and with using a MFC (with Cu-B cathode and $KMnO_4$ catholyte). The colours indicate the trend lines of individual data [own compilation]

CONCLUSIONS

In any cases (without aeration, with aeration and with MFC) the reduction of COD was 90% (fig. 3). So, measurements have shown the effectiveness of COD reduction. The reduction time for COD with the use of MFC (with Cu-B cathode and $KMnO_4$ catholyte) is similar to the reduction time with aeration (15 days) to obtain 90% effectiveness. But, unfortunately in this solution (MFC with KMnO4) is needed to constant delivery of catholyte. The characteristics of curves are different in any cases. The characteristic curve of aeration is more preferred than characteristic curve of MFC (with Cu-B cathode and $KMnO_4$ catholyte) because about 80% effectiveness of COD reduction after about 4 days. The measurement of NH_4^+ reduction shows almost no changes in cases measurement in MFC (fig. 4). The measurements (fig. 5) have shown also the effectiveness (about 90%) of NO_3 – reduction. Increasing of NH_4^+ concentration (during aeration) results from the attachment of hydrogen molecule to the ion ammonia (e.g. during putrefaction) (fig. 4) (McMurry at al. 2009). The increase of NO_3 – concentration (fig. 5) is the result of nitrification during the growth of bacteria (Łomotowski and Szpindor 2002). It has been shown that the Cu-B (with $KMnO_4$ catholyte) can be used as cathode catalyst in microbial fuel cells.

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