Removal of COD by Two-Chamber Microbial Fuel Cells

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1. Introduction

Microbial fuel cells (MFC) are regarded as special bio-electrochemical systems which seem to have a high potential in the future technology for energy production in the section of renewable green energy sources [1-5].

A classical MFC in general [4-8] consist of an anodic and cathodic chamber divided by a proton (cation) selective membrane (Figure 1). Microbes in the anodic cell – mostly attached to the electrode surface forming a biofilm – oxidize the substrates and generate electrons and protons in the process. Then electrons are transported from the anode to the cathode through an external circuit (wire) resulting measurable electric current. Meanwhile protons are passing through the membrane and enter the cathode cell where they combine with oxygen to form water.

MFC-s can be operated by either monoculture (e.g. *Geobacter sulfurreducens* [5], *Shewanella oneidensis, Lactococcus lactis* [9], *Lysinibacillus sphaericus* [10]) – where the electrogenic species release electron to the anode electrode directly or with the use of electroactive metabolites –, or multiculture (microbe consortia) system, which can be found in e.g. anaerobic sewage sludge acting in a similar way. The substrates of the MFCs operated by sewage sludge can be provided from various wastewaters, thus electricity generation in the MFCs can be coupled with the degradation of organic matters even e.g. wastewater treatment processes [11-20].

Many types of wastewaters were investigated (e.g. beer brewery wastewater [22], food industrial wastewaters [22, 23]) where the degradation can be followed by COD removal determination [14]. In MFCs applied for treatment of organic matters, the feed can be enriched with various substrates. It has been noted that non-fermentable substrates are superior to fermentable substrate as the electron donor for power output and electron recovery. E.g. it was reported that an acetate enriched MFC produced higher power output than a glucose enriched



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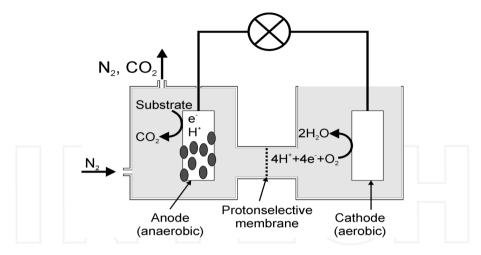


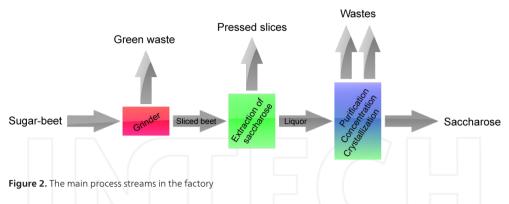
Figure 1. The scheme of a two-chamber microbial fuel cell

MFC [24, 25]. In contrast we found that certain carbohydrate substrates resulted in higher electricity generation [26]. Wastewaters from a sugar beet factory obviously consists of carbohydrates (mono-and/or disaccharides), which are probably suitable enrichments compounds for MFCs.

One of the application segments where extremely promising possibilities are visualised is the integration of the MFCs into wastewater treatment, since these systems are capable to consume organic material even from waste streams to produce power.

In Kaposvar (a city in Southern Hungary) there is a sugar factory, where saccharose (crystallized sugar) is produced from sugar beet [27]. It is an energy intensive process, thus the company has to make great efforts to optimise energy and resource usage, trying to apply environmentally sound, sustainable and waste minimising technologies, which cover water and air quality management as well as usage of by-products. Regarding air quality, the factory has taken extensive measure to decrease dust, smell and sound emissions in recent years, modern biofilters were installed. As to the water issue, special attention is payed to clean the wastewater streams generated during the manufacturing process. The by-products of the processes: the green leaves of sugar beet, the pressed slices (pulp) and other substances are used as components of fertilizers, soil conditioners and for other purposes.

In this factory the processing of all the by-product and waste streams is carefully designed and performed. The leadership of the factory felt responsibility to operate the plant according to environmental safe conditions, therefore they completed the sugar technology with composting – to handle the green parts of the plant –, with a wastewater treatment plant and recently even a biogas fermenter was installed (Figure 2). Inserting microbial fuel cells into this system direct electric power could be produced by reduction of the COD from the waste streams.



In this project the aim was to find out how to work and operate a two chamber microbial fuel cell by using wastewater from the sugar beet factory.

2. Materials and methods

A two-chamber MFC was used in the experiments (Figure 3). Both cells have a 240 cm³ volume, the membrane between them was a Nafion N115 proton selective membrane, its surface area was 50 cm² and thickness was 125 μ m. In the anodic cell a complex mesophilic anaerobic sludge (from a local working biogas plant, initial COD value was 70 000 mg/dm³), while in the cathodic cell distilled water was used. Both electrodes were carbon cloth, their surface area was 50 cm². The electrodes were connected via a resistor and the voltage data were continuously quantified by a parallel measuring system. It contained a 100 M Ω resistor and the voltage data were directly collected by a data acquisition device (National Instruments USB-6008/6009). The data were recorded by the LabVIEW program. Based on the voltage and resistance data the current values were calculated, thus the electric power (in mW units) was possible to provide. The cumulated electricity data were summarized (in mWh) taken into account the operating time.

The anaerobic sludge applied in the anodic cell was pretreated prior to usage, as it was reported [26]. The MFC was placed in a thermostated container, where the liquids in both cells were possible to circulate and stir. In the cathodic cell air was entered continuously by a pump to ensure aerobic environment, while N_2 was sparged through the anodic cell to assure the anaerobic conditions. The MFC reactor was initially inoculated with the pretreated anaerobic sludge. Then the microbial consortia started to operate in the cell and they were allowed to adapt the actual conditions and colonise locally.

To follow the processes various analytical methods: pH, total solid substance (TSS), COD were applied. COD values of the samples taken from the cells were determined by the potassium dichromate method, which is based on the following oxidation reaction in acidic environment:

 $K_2Cr_2O_7 + 4H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O$



Figure 3. The picture of MFC used

The organic substances in the samples were ravaged in the presence of potassium dichromate and catalysts (AgSO₄, HgSO₄) in sulphuric acid solution at 145 °C. The absorbance of the chromium (III) ions from the reduction of K₂CrO₇ during the oxidation process was determined by a spectrophotometer (Hach LANGE DR 3900) at 600 nm. The COD values of the samples were calculated using a calibration curve taken in the range of 750 – 4000 KOI mg/cm³.

3. Results

3.1. Experiments with model wastewater

To test the behaviour of the MFC, model substrates were used for the experiments. The composition of the model mixture – similar to the waste stream of the sugar beet factory – was carbohydrates (0.6 %) and inorganic substances (ash, 3 %).

The MFC operation was started by inoculation with the pretreated anaerobic sludge, then the processes were followed by recording the voltage data continuously (Figure 4). A 10 Ω resistor was used in the circuit. After certain intervals 100 cm³ fresh substrate was added (marked by the arrows) to the system to maintain the carbohydrate concentration. These additions mean 9000 mg/cm³ COD input each.

The voltage data have shown that the substrate addition enhanced the power generation and quite high voltage (current density) values were achieved (in the range of 10 and 24 mV).

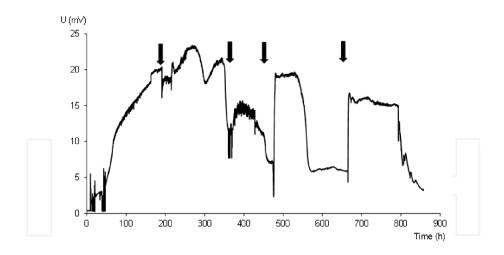


Figure 4. Power generation using model waste water

Samples were taken regularly and the COD values, pH and TSS were determined. The data are summarised in Tables 1 and 2.

Time (h)	COD (mg/	COD (mg/dm³)		
	Adding substrate	End of period		
1-192	19800	4900	75	
192-336	7150	2775	61	
336-480	5025	3075	39	
480-650	5325	1810	66	
650-880	4060	1250	69	
Time (h)				
	pH		TSS (g/dm ³)	
1	pH 6.70		TSS (g/dm³) 35.9	
1				
	6.70		35.9	
192	6.70 8.25		35.9 3.9	
192 336	6.70 8.25 7.65		35.9 3.9 1.9	

Table 2. TSS and pH values using model waste stream

As it can be seen remarkable TSS and COD decrease could be observed during the processes, while electric power was generated continuously. The drop in the pH at 880 h has shown that the operation of the MFC should be ceased due to the unfavourable biochemical processes. The values of current density, J (normalized to the 50 cm² carbon cloth electrode) and power density (calculated from the current density and voltage data; Pa and Pm, normalized to the surface of the carbon cloth electrode and the membrane surface area, respectively), moreover the cumulated energy data ΣP (taken into account the time period of the experiment) are summarized in Table 3.

Time (h)	J (mA/m ²)	P _a (mW/m ²)	$P_m (mW/m^2)$	∑P (mWh/m²)
1-192	260	3.380	4.023	649.0
192-336	416	8.652	10.300	1245.9
336-480	220	2.420	2.880	4114.0
480-650	240	2.880	3.428	4896.0
650-880	300	4.500	5.357	1035.0

Table 3. Results obtained using model waste stream

The values have shown that notable power density was achieved during the operation and finally altogether more than 10 thousands mWh/m² energy was generated by consuming the organic substances from the model waste water in the MFC.

3.2. Polarization curve

Our next purpose was to determine the polarization curve using the adapted microbe consortia (grown up in the experiments by the model wastewater). Therefore a serial of experiments were carried out applying various resistances (in the range of 5 and 500 Ω) built in the system and the voltage/current data were measured (Figure 5). Moreover the power density values were calculated.

It can be seen from the figure that voltage data decreased gradually as higher resistances were installed into the system up to 12 mA current, thus the MFC was in a stationer state in the given range from electrochemical point of view. With the growing resistance values, however, increasing power density values were possible to achieve, which mean that it is advisable to use higher resistances for the further measurements. The results shown in the Figure are similar as reported in literature [22].

3.3. Experiments with industrial wastewater

Wastewater from the sugar factory in Kaposvar was used in the next experiments of our work. It consisted of carbohydrates (others than saccharose: mainly glucose and fructose; altogether 0.6 %) and ash 3 %. The other features of the waste water were: pH 5.4, TSS 34.8 g/dm³ and COD value 12 075 mg/dm³.

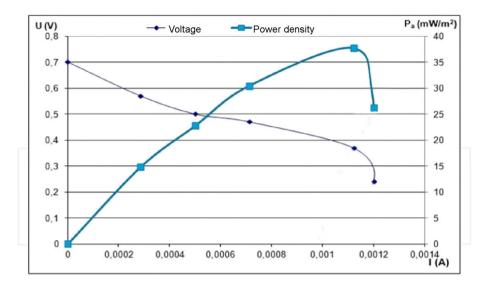


Figure 5. The variance of the voltage and power density in different resistances

Now the MFC was operated by a 330 Ω resistance built in the circuit, which was considered as a more effective operation condition point according to the polarization curve. The adapted microbial consortium was used to inoculate the cell. After certain intervals 100 cm³ fresh substrate (wastewater) was added (marked by the arrows) to the system. In Figure 6 the voltage data obtained in the MFC by the waste water from the sugar beet factory are presented.

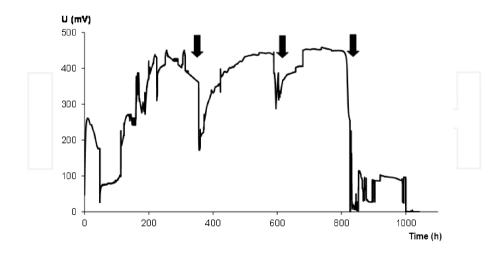


Figure 6. Power generation using industrial waste water from Kaposvar

The changes of COD values of the samples were determined and summarized in Table 4, while the TSS and pH data are shown in Table 5.

Time (h)	COD (mg/	COD (mg/dm ³) decrease of COD (%	
	Adding substrate	End of period	
1-330	21850	13850	37
330-600	13673	5225	62
600-840	7795	3875	50
840-1000	7975	5900	26

 Table 4. Changes of COD values using waste water from the factory

Time (h)	рН	TSS (g/dm³)
1	8.1	34.8
330	8.0	10.8
600	7.6	3.2
840	7.1	2.5
1000	4.1	4.2

Table 5. TSS and pH values using industrial wastewater

The values of current density, power density – which are higher here than in case of model waste water due to the higher resistance – and the cumulated energy data $\sum P$ are listed in Table 6.

Time (h)	J (mA/m²)	P _a (mW/m ²)	P _m (mW/m ²)	∑P (mWh/m²)
1-330	181	52	59.5	17 160
330-600	242	95	113	25 650
600-840	245	99.2	118.2	23 808
840-1000	51	4.2	5.0	642

Table 6. Results obtained using industrial waste stream

The current and power density values were outstanding compared to literature data [20-22] or the values obtained with the model wastewater. Altogether more than 60 thousands mWh/m² energy was generated during the over 800 hour operation. In the last interval (after 840 hour) the substrate addition did not result in any increase of voltage data, moreover the pH

decreased sharply, showing that the biochemical processes in the MFC have not been working properly any longer, thus the operation was ended.

4. Conclusion

A two-chamber MFC was designed and built in our laboratory where carbon cloth (fibres) were used as electrodes and Nafion 0125 protonselective membrane was placed between the two cells. Pretreated anaerobic sludge from a local biogas plant was applied in the anode chamber. Experiments with model and industrial wastewaters from a sugar beet factory were carried out to study the efficiency and stability of the system and to measure the electric power generated. It has turned out that it was possible to generate bioelectricity from the particular wastewater and the power data obtained were found similar or higher to the data published in literature, i.e. comparable performance was achieved in our MFC system. Our next purpose is to study the MFC for longer term operation, even in continuous mode of operation, so that we can insert the MFC into the processing scheme of the sugar beet factory [28].

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