UFT Academic Publishing House, Plovdiv

Food Science and Applied Biotechnology
e-ISSN: 2603-3380

Journal home page: www.ijfsab.com
https://doi.org/10.30721/fsab2018.v1.i2

OPEN ACCESS

Research Article

Effect of the electrodes type on the energy efficiency of microbial fuel cells

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Abstract

Traditional methods for wastewater treatment are associated with high energy consumption. This is why biological treatment of water is more appropriate at the moment. In our previous study, oxidation and reduction of pollutants have been proposed to be carried out in a microbial fuel cell (MFC) designed by our laboratory that simultaneously purifies wastewater from sulfide and nitrate ions and generates electricity. The experiments were carried out with two types of electrodes, graphite rods and paddling of activated carbon using a Fumapem® FFA-3-PK-75 (OH- form) membrane. The results show that when the wad is used as an electrode in the anode compartment, the fuel cell power is 3 times the first hour compared to the use of electrodes in the form of graphite rods.

Key words: fuel cell, microbial fuel cell (MFC), wastewater treatment, sulfide oxidation, nitrate reduction;

Abbreviations:

MFCs - Microbial fuel cells

GAC - granulated activated carbon

AC - anode compartment

CC - cathode compartment

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Article history:
Received 1 December 2017
Reviewed 19 March 2018
Accepted 5 June 2018
Available on-line 10 October 2018

https://doi.org/10.30721/fsab2018.v1.i2.6

Introduction

Microbial fuel cells (MFCs) are unique in their ability to utilize microorganisms, rather than an enzyme or inorganic molecule, as catalysts for converting the chemical energy of feedstock directly into electricity (Rismani-Yazdia et al. 2008).The concept of employing microbial catabolic activity to directly generate electricity when treating wastewater provides access to cheap and environmentally friendly energy sources (Gil et al. 2003; Choi et al. 2003; Moon et al. 2006). The energy conversion can be achieved with the help of microbial fuel cells, in which microorganisms serve as biocatalysts and from which electrons are diverted and transferred to an electrode to generate electricity.The economic efficiency of converting wastes to bioenergy depends on the characteristics and components of the waste material (Park and Zeikus 2000; Angenent and Wrenn 2008; Pant et al. 2010). In a MFC, microorganisms interact with electrodes using electrons, which are either removed or supplied through an electrical circuit (Rabaey et al. 2007). The energy generation of MFC is influenced by many factors, including the type of electrode material (Liu et al. 2005). Using more efficient electrodes can significantly improve the reliability of microbial fuel cells. In their study, Schroder et al. (2003) report a current of 2-4 mA obtained with a platinized carbon cloth anode by using microbial culture E. coli in a glucose medium at 0.55 mmol.L^{-1}. Pt also has higher catalytic activity with respect to oxygen rather than the graphite materials. MFCs with Pt or Pt coated cathodes show higher power density than those with graphite ones (Jang et al. 2004; Oh et al. 2004; Moon et al. 2006; Zhuwei et. Al 2007). In their studies Park and Zeikus (2002, 2003) report a significant increase of nearly 100-fold in the energy generation using woven graphite and Mn (IV) graphite anode compared to textile using only a graphite anode; Mn (IV) serves as an electron mediator. Ions like Fe (III) and / or Mn (IV) incorporated into the cathode also catalyze catabolic reactions leading to improved efficiency. Four times high current can be achieved with the combination of Mn (IV) - graphite anode and Fe (III) - graphite cathode compared to ordinary graphite electrodes (Park and Zeikus 2000, 2003; Zhuwei et. al. 2007). The disadvantage of Pt or Pt black electrodes is the formation of a PtO layer on the surface of the electrode. Another significant disadvantage is their extremely high cost. Contrary to our previous study where CelGard® 3501 membrane is used (Stefanov et. al. 2017), currently we report the influence of two types of electrodes (graphite rods and paddling of activated carbon) on the energy efficiency of the microbial fuel cell using membrane Fumapem® FFA-3-PK-75 (OH- form). *Pseudomonas denitrificans* shown in Fig.1 reduces nitrates to nitrogen, passing sequentially through nitrites and nitrogen oxides in accordance with the following reaction scheme:

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2 \qquad (1)$$

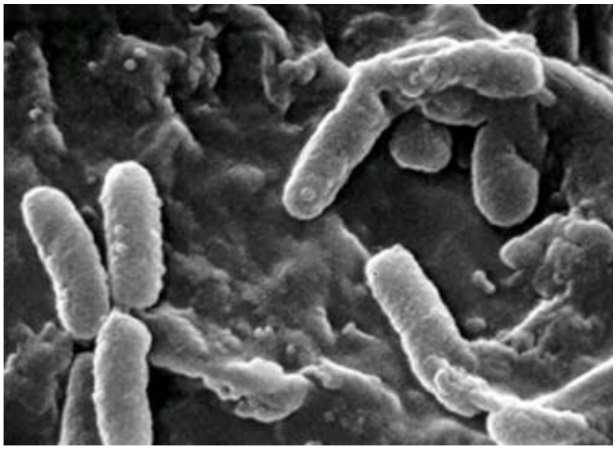

Figure 1. Microscopic photo of *Pseudomonas denitrificans*

According to Carlsson et al. nitrate reductases are bound to the cytoplasmic side of the cell membrane, while nitrite and N_2O reductases are associated with the periplasmic side. This model explains the easy release of NO_2^- and N_2O from the reaction medium under the passive transport mechanism in conditions unfavorable to the process (lack of an electron donor). In cases where the activity of nitrite reductases is lower than that of nitrate reductases, there is a significant accumulation of nitrite in the system.

Materials and Methods

Strain. A strain *Pseudomonas denitrificans* (NBIMCC 1625), provided from the Bulgarian National Bank of Industrial Microorganisms and Cell Cultures is used. The inoculum is cultivated in a medium containing: peptone – 10 g/l; yeast extract – 1 $g.l^{-1}$ NaCl – 10 $g.l^{-1}$ and is incubated at 30°C for 24 h in a rotary shaker at low stirring speed (50 rpm). The culture medium comprises of two solutions, each of which is sterilized separately:

-Phosphate buffer at pH= 7, containing also:

$MgSO_4.7H_2O$, 0.2 $g.l^{-1}$, $CaCl_2.2H_2O$, 0.2 $g.l^{-1}$; NaCl, 5 $g.l^{-1}$.

(2)

-Potassium nitrate stock solution – 10 $g.l^{-1}$.

The latter was added to the phosphate buffer after sterilization in a calculated amount to reach initial concentration of nitrate in the culture medium of 500 $mg.l^{-1}$.

Immobilization procedure. The immobilization of *Pseudomonas denitrificans* cells is done on granulated activated carbon (GAC). The preliminary cultivated bacterial suspension was mixed with the washed and dried to constant weight of GAC. Then the mixture was transferred to shaking flasks and they were incubated at 30°C for least 48 hours. The *Pseudomonas denitrificans* cells are capable to produce exo-polysaccharides in the biofilm layer, which serve as binding agents between carbon particles and microbial cells (Beschkov, V.).

GAC. Granulated activated carbon, (Fujikasui, Japan, specific surface area of 680 $m^2.g^{-1}$) is used. The principal fuel cell scheme is shown in Fig. 2. It consists of an anode compartment (AC) where sulfides are oxidized and a cathode compartment (CC) where nitrates are reduced. Contrary to our previous study where CelGard® 3501 membrane is used (Stefanov et. al. 2017), currently we report

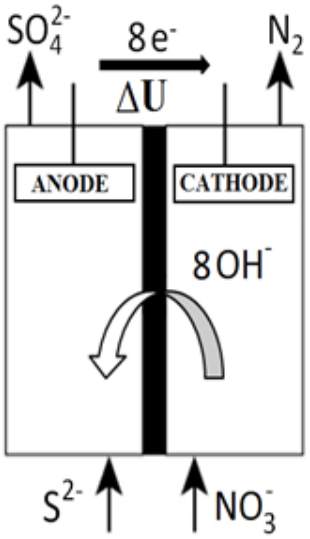

Figure 2. The fuel cell principle scheme.

the influence of two types of electrodes (graphite rods and paddling of activated carbon) on the energy efficiency of the microbial fuel cell using membrane Fumapem® FFA-3-PK-75, with the following characteristics: type of the membrane - anion exchange; thickness of the membrane – 55 μm; electrical resistance – 1.26 Ω. cm^2. The experimental design of our fuel cell is presented in Fig. 3 and Fig. 4.

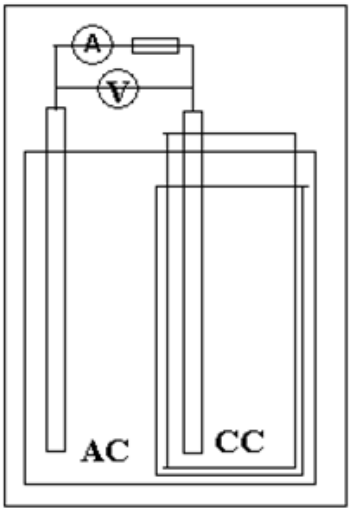

Figure 3. Constriction of the fuel cell.

Both compartments of the fuel cell are cylinders of different diameters (0.08 m and 0.1 m) located concentrically in one another. The membrane is placed at the bottom of the cathode (inner) compartment. The OH- conductive membrane used is with a working surface of 0.002 m^2.
Two types of electrodes (Fig. 4.) for the anode compartment are used:
-5 graphite rods with a total surface area of 0.1 m^2;
-paddling of activated carbon with total surface area of 0.1 m^2.
Supply solutions are prepared by dissolving analytical grade $Na_2S.9H_2O$ and KNO_3. The solutions prepared are 0.3 l each.

Figure 4. Standard cylindrical graphite rods**.**

Analysis

pH
During the experiments, the pH value is measured periodically.

Nitrate concentration
The concentration of nitrates is determined by UV-spectrophotometry (Goldman and Jacobs 1961) Samples are centrifuged for 10 minutes at 14000 rpm. Then, appropriate volume of the supernatant is diluted to 50 ml and 1 ml of 1N HCl is added. The absorption of the sample light is measured at $\lambda = 220$ nm on a UV spectrophotometer (VWR® UV-1600 PC spectrophotometer). To avoid the interference of dissolved organic substances the absorbance of the samples is also measured at $\lambda = 275$ nm. Corrected absorption of nitrate sample (A_{corr}) is calculated using the following equation:

$$A_{corr} = A_{220nm} - 2*A_{275nm} \quad (3)$$

Sulfide concentration
The concentration of the sulfide solution is determined photometrically by converting the sulfide ion to methylene blue by addition of N, N-p-phenylenediamine (T.D. Rees at al. 1971).

Sulfite and nitrite ions
The generation of sulfites and nitrites is monitored qualitatively. By adding $BaCl_2$ to the sample solution in the presence of sulfite and sulfate ions, opalescence occurs due to the formation of $BaSO_3$ and $BaSO_4$ precipitate. Upon addition of 2M HCl, $BaSO_3$ is dissolved and any residual opalescence is due to the presence of undissolved $BaSO_4$. When KI or $KMnO_4$ is added to a sample containing nitrate ions in an acid medium results in a color reaction for the former or discoloration the latter.

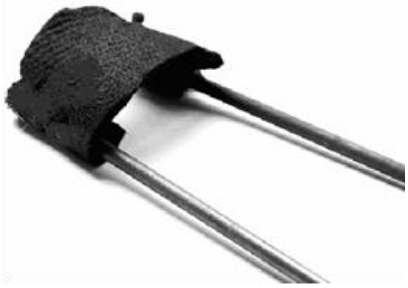

Figure 5. Paddling of activated carbon.

Results and Discussion

Two very important properties of the GAC are used: first, the *Pseudomonas denitrificans* cells are easily attached to the carbon surface; second, the toxic compounds are adsorbed by the activated carbon. As a result, the high concentrations of the substrate are reduced to not dangerous values for the microbial cells and therefore avoiding inhibition caused by high concentrations of the pollutant. (Beschkov 2008) The reactions are as follows:

Anode:

$S^{2-} + 6\ OH^- \rightarrow SO_3^{2-} + 3\ H_2O + 6e^-$

$SO_3^{2-} + 2\ OH^- \rightarrow SO_4^{2-} + H_2O + 2e^-$

Total:

$S^{2-} + 8\ OH^- \rightarrow SO_4^{2-} + 4\ H_2O + 8e^-$ (4)

Cathode:

$2\ NO_{3-} + 2\ H_2O + 4e^- \rightarrow 2\ NO_{2-} + 4\ OH^-$

$2\ NO_{2-} + 4\ H_2O + 6e^- \rightarrow N_2 + 8\ OH^-$

Total:

$2\ NO_{3-} + 6\ H_2O + 10e^- \rightarrow N_2 + 12\ OH^-$ (5)

The reactions indicate that the 8 electrons generated in the anode compartment are more than the 5 necessary for the cathode reactions. For this purpose the experiments are carried out at approximate sulfide:nitrate ions ratio of 5:8. Demirbas A. (2009) reports that oxidation of sulfide ions results in elemental sulfur as the final product. In our case, the production of sulfates prevents the risk of passivation of the anode and produces more energy. Fig. 6. shows the power output at a 100 Ω load on the fuel element with simultaneous sulfide oxidation and nitrate reduction as a function of time using both types of electrodes - carbon rods and paddling of activated carbon.

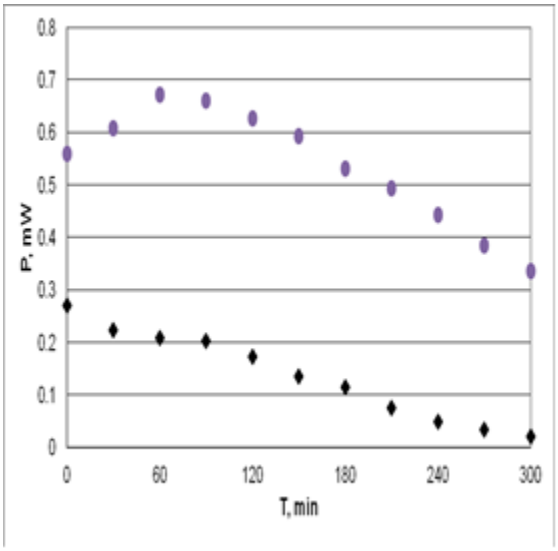

Figure 6. Power output over time of the electrodes tested:
● - carbon paddling, ♦ - graphite rods.

The latter are prepared by patented technology (Ljutzkanov and Atanasov, BG patent № 63594 / 26.06.2002). The results show that using activated carbon paddling yields 3 times more power output at the first hour mark compared to the power output obtained by using graphite rods as electrodes. The generated power at the beginning of the process is low due to the adsorption capabilities of the activated carbon paddling. The oxidation of sulfides in the anode compartment using activated carbon paddling as an electrode is 80% at the first hour mark, compared to 70% when using graphite rods (Fig. 7.).

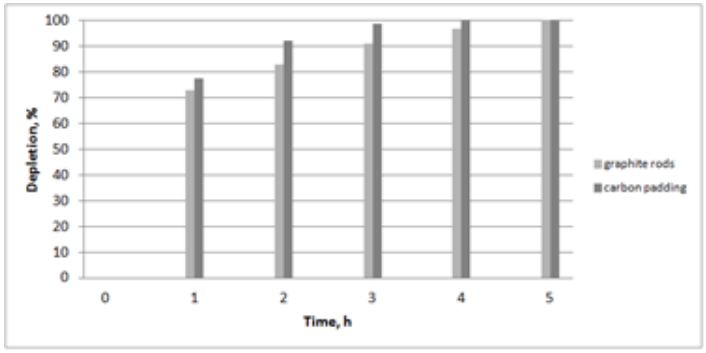

Figure 7. Depletion of sulfides over time.

Similarly, nitrates in the cathode compartment are also exhausted

Similarly, nitrate reduction using activated carbon paddling shows better results compared to the graphite rods (60% reduction for the former and 50% for the latter) (Fig. 8.).

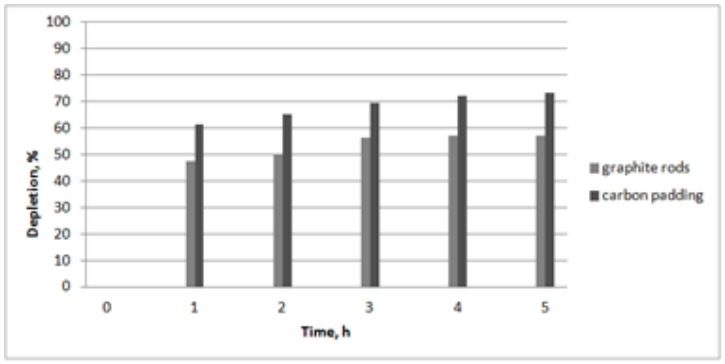

Figure 8. Depletion of nitrates over time.

Conclusions

The purification of wastewater from sulfide and nitrate ions is simultaneously carried out in a fuel cell, chemical in the anode compartment and microbiological in the cathodic compartment, where *Pseudomonas denitrificans* is immobilized on activated carbon. The activated carbon paddling is a good electrode that can be used for adsorption of other pollutants too. It shows approximately 20% higher depletion rate of the sulfide ions leading to their full elimination at the end of the process. The results show that MFCs are a reliable alternative for wastewater treatment combined with energy generation.

Acknowledgments

This work is supported under project E 02. 15 / 12. 12. 2014. The authors would like to thank the National Science Fund, Ministry of Education and Science of the Republic of Bulgaria.

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