Short Communication

A Novel Microbial Fuel Cell for the Sensing of Sodium Acetate in Soil

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Abstract

In this study, a new soil-based microbial fuel cell was developed that can be used for biological remediation in areas with soil pollution. Electricity generation was studied with the developed soil-based microbial fuel cell. Voltage values were measured depending on time and the effects of sodium acetate at different concentrations (20, 40, 60, 80, 100 mM) were investigated. Our results showed that up to 396 mV electricity generation is possible with the new soil-based microbial fuel cell. The voltage values gradually increased with increasing sodium acetate concentration. The half-saturation constant was found to be 75.99 ($R^2 = 0.97$). In conclusion, the developed soil-based microbial fuel cell has shown that it has biosensor potential and can be used in the detection of various environmental pollutants.

Keywords: bioremediation, electricity, microbial fuel cell, soil

Introduction

The need for energy in the world has been increasing rapidly in recent years and the global climate change reveals important environmental problems along with the energy crisis [1, 2]. Most of the energy needs are supplied by fossil fuels, but these resources are decreasing day by day and they also cause environmental pollution problems. As a result of the consumption of fossil fuels, gases such as carbon dioxide, carbon monoxide and sulfur dioxide that cause environmental pollution are released into the atmosphere [3]. The greenhouse effect emerges and causes global climate change [4]. The gradual decrease of fossil fuels in the

world, water scarcity and environmental pollution problems also require sustainable improvement of novel technologies [5]. Microbial fuel cell technology, which is one of the prominent environmentally friendly technologies in recent years, is an alternative technology used in the biological remediation of polluted water and soils and simultaneous electricity generation [6]. One of the reasons why microbial fuel cells are considered a renewable energy source is that they release carbon, which is stable to the environment, through the oxidation of organic wastes [2]. Microbial fuel cells run with exoelectrogenic microorganisms and the chemical energy in organic materials is converted into electrical energy [7]. In addition, they can biologically treat environmental pollutants such as antibiotics, dyes, drug metabolites, and heavy metals [8-12]. With these features, it has been proposed to reduce the operating costs of these wastewater treatment plants by integrating

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microbial fuel cells into them [13]. In recent years, soilbased microbial fuel cells are a new approach developed especially for use in areas with soil pollution, and soilbased microbial fuel cells are devices that can be applied and generate energy in soils contaminated with various environmental pollutants such as phenol [14]. While improving the soils with bioremediation, energy needs can be met at the same time.

The number of researches with soil-based microbial fuel cells has been increasing in recent years. Reactors with different configurations have been developed and their performance in environmental research has been reported. For example, in a study using a cylindrical microbial fuel cell, anode and cathode were placed on conductive paint, and the maximum voltage amount was recorded as 390 mV at 0.99Ω in this study [15]. In the reactor design used in another study, the anode and cathode electrodes are placed perpendicular to the ground and some of the electrodes are left outside in contact with the air [16]. Researches on the use of soil-based microbial fuel cells as biosensors are increasing and there is a need to explore this potential with new configurations.

In this study, a new soil-based microbial fuel cell was developed for the first time for the sensing of sodium acetate in soils. Configuration and performance analyses of the developed microbial fuel cell were carried out. The effects of different concentrations of sodium acetate as a carbon source on electricity generation were investigated.

Material and Methods

Configuration and Operation of Soil-MFC

In the study, soil-based MFCs made of plexiglass were prepared and used for the first time. The soil-based microbial fuel cell consists of the following parts; titanium wire (1), resistor (2), cathode (3), anode (4), air flow holes (5), air pump (6) inner cylinder chamber (7) and main reactor chamber (8) (Figure 1). The anode electrode was cut into a circle (7 cm², Lot: 14032102, FuelCells, Texas, USA) and placed on the bottom of the

reactor using carbon cloth. A cylindrical tube (diameter 3,14 cm) was placed in the middle of the reactor. There are holes on the cylinder pipe (length, 6 cm) to allow air passage. Cathode electrode carbon cloth was used (7 cm², CTO32414, FuelCells, Texas, USA) and one surface was coated with Platinum catalyst (0.5 mg/cm², Brand Model) using Nafion solution (7 μ L per cm², CAS. No: 31175, Sigma-Aldrich, USA). The platinum coated surface is placed facing the inner surface of the cylindrical tube. The anode and the cathode electrode are connected to each other with an external resistance of 985 Ohm using titanium wire. Soil is placed inside the soil-based microbial fuel cell so that it does not enter the inner cylinder. The inner cylinder is ventilated continuously with the help of an air pump (EHEIM-100).

The soil-based microbial fuel cell was used to study electricity production by a mixed microbial culture enriched from an activated sludge sample obtained from a local domestic sewage treatment plant (Pasakoy Advanced Biological Wastewater Treatment Plant, Istanbul, Türkiye). First of all, to preserve the viability of microorganisms, sodium phosphate buffered (100 mM, pH 7.0) medium was added to microbial fuel cells in 47 mL volume. The medium consisted of the following components: NaH₂PO₄.7H₂O (15.47g/L), (5.84g/L), NH₄Cl (0.31g/L), KCl Na₂HPO₄.H₂O (0.13g/L), vitamin stock solution (12.5 mL/L) and a previously reported mineral stock solution (12.5 mL/L) [17]. Then, only distilled water was used to prevent salt accumulation in soil-based microbial fuel cells and sodium acetate (20 mM) was added as a carbon source. Sodium acetate was directly dissolved in distilled water and added into microbial fuel cells operated in batch modes. The following sodium acetate concentrations were examined: 20, 40, 60, 80, 100 mM in batch modes. Fresh medium was added when voltage production decreased. Soil-based microbial fuel cells were operated in batch mode and at room temperature (~22°C).

Analyses and Calculations

Soil samples were obtained from below the soil surface and transferred to the laboratory in plastic containers. Soil samples brought to the laboratory were

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Fig. 1. Illustration of the soil-based microbial fuel cell.

a)



weighed after thinning with the help of a sieve. Soil sample was characterized and analyzed by Biotar Co. (Ankara, Türkiye) according to traditional methods. Soil-based microbial fuel cells were connected to a data acquisition system (ADC24, Picolog; Cambridgeshire, UK) and voltage was recorded on a computer every 11 minutes.

The following equation was used in modeling of substrate concentration (S) and voltage as

$$V = \frac{V_{\max}S}{K_s + S} \tag{1}$$

where V_{max} , the maximum voltage and K_s (S), the halfsaturation constant were determined using the Excel Solver (Microsoft, version 2007) [18].

Results and Discussion

The soil sample used in the study contained major impotant minerals and the electrical conductivity of the soil was 3,02 dS/m (Table 1). Fig. 2 shows the time dependent voltage generation in a ground-based microbial fuel cell. With the addition of a medium solution containing acetate to microbial fuel cells, electricity generation began. With the feeding with the medium containing 20 mM acetate, the voltage hovered around 0.150 V and then decreased. The volume of the addition solution was increased from 5 mL to 10 mL and the acetate concentration was gradually increased in each batch. A voltage generation of 0.1 mV was achieved with a concentration of 20 mM acetate. With increasing concentration, voltage generation increased in parallel (40, 60, 80, 100, 120 mM acetate with 182 mV, 261 mV, 294 mV, 379 mV, 396 mV respectively). These results showed that electricity generation is possible with the soil-based microbial fuel cells we developed in this study. The voltage values we reached within the scope of our study are similar to the voltage generation performances of other soil-based microbial fuel cells. The voltage values of 0.45 V were achieved in the previously conducted single-chamber microbial fuel cells at the same external resistance level [6]. However, the presence of soil between electrodes in soil-based microbial fuel cells can complicate proton transfer. Therefore, despite the advantage of using it in areas with soil pollution, there is a need for new approaches to increase electricity generation performance.

Table 1. Chemical characterization of soil sample.

| Analysis Parameters | Unit | Analysis Results | Methods |
|---------------------------------|-------------------|------------------|--|
| Nitrogen (N) | % | 0,43 | Theoretical |
| Phosphorus (P) | kg/da | 12,34 | TS 8340 (Olsen) |
| Potassium (K) | kg/da | 175,70 | TS 8341 (Ammonium Acetate) |
| Organic Matter | % | 8,55 | TS 8336 (Walkey-Black) |
| Clay | % | 38,99 | Richards, L.A. 1954 |
| Sit | % | 26,36 | Richards, L.A. 1954 |
| Sand | % | 34,65 | Richards, L.A. 1954 |
| pН | Power of Hydrogen | 7.05 | Mt5.4.2.T.55 pH Analysis Method in Saturation Sludge |
| Electrical Conductivity (EC) | dS/m | 3,05 | TS ISO 11265 |
| Salt | % | 0,2366 | TS 8334 |
| Lime | % | 1,32 | Mt5.4.2.T.4 Lime Analysis Method in Soil |
| Calcium (Ca) | ppm | 5805,00 | ICP-OES-(Ammonium Acetate) |
| Magnesium (Mg) | ppm | 393,40 | ICP-OES-(Ammonium Acetate) |
| Sodium (Na) | ppm | 803,90 | ICP-OES-(Ammonium Acetate) |
| Iron (Fe) | ppm | 18,31 | TS ISO 14870 ICP-OES (DTPA) |
| Copper (Cu) | ppm | 2,73 | TS ISO 14870 ICP-OES (DTPA) |
| Zinc (Zn) | ppm | 11,25 | TS ISO 14870 ICP-OES (DTPA) |
| Manganese (Mn) | ppm | 11,75 | TS ISO 14870 ICP-OES (DTPA) |
| Boron (B) | ppm | 1,26 | Spectrophotometric |



Fig. 2. Time dependent voltage generation plot at 985 Ohm external resistance using acetate solution in a soil-based microbial fuel cell (A: 20 mM 5ml acetate solution, B: 20 mM 10 ml acetate solution, C: 40 mM 10 ml acetate solution, D: 60 mM 10 ml acetate solution, E: 80 mM 10 ml acetate solution).

Fig. 3 shows the concentration-dependent changes in voltage generation. The relationship between voltage generation and substrate concentration was similar to Michaelis-Menten kinetics, and a linear relationship was found. The effect of sodium acetate concentration on the voltage generation of soil-based microbial fuel cell, Michaelis-Menten equation was used as a model and the semi-saturation constant was determined in order to better evaluate [18]. The semi-saturation constant determined in the study was found to be 75,99 mg/L. These results showed that the theoretical maximum voltage value is limited by other limiting factors. In previously reported papers, comparable semisaturation values such as 110 mg/L to 725 mg/L ($R^2 = 0.826 - 0.995$) have been reported in microbial fuel cells [18]. Soil-based microbial fuel cells can be used as microbial biosensors in soil polluted areas. Sensitivity, which is one of the most important parameters in sensors, is also affected by the external resistance value applied in this technology. The semi-saturation constant determined in our study may be useful for comparison purposes in the future for detection of different target molecules using microbial fuel cells.

The bioremoval of various pollutants such as phenol and their effects on electricity generation were investigated in soil-based microbial fuel cells



Fig. 3. Graph showing the effect of different acetate concentrations on voltage generation in a soil-based microbial fuel cell at an external resistance of 985 Ohm.

| Concentration (mM) | Power density (mW/m ²) | Current density (mA/cm ²) |
|-----------------------|---------------------------------------|--|
| 40 | 48.04 | 0.0263 |
| 60 | 98.79 | 0.0378 |
| 80 | 125.36 | 0.0426 |
| 100 | 208.32 | 0.0549 |
| 120 | 227.43 | 0.0574 |

Table 2. Performance values of soil-based microbial fuel cells.

[14]. Thus, such contaminants require new sensor approaches in bioelectrochemical systems [10, 19]. It is very risky because pollutants in the environment cause mass diseases and deaths [20] and the effects of environmental contaminants on public health are important. It is extremely important to minimize and precisely predetermine the negative effects of environmental pollution on public health. Considering the direct relationship between the performance of soilbased microbial fuel cells and the quality of the soil and the pollutants in the soil, it will become more valuable in the development of bioremediation strategies. Recently, promising studies have been proposed regarding the potential of microbial fuel cells to be used as a biosensor in the detection of various environmental pollutants such as antibiotics, heavy metals, drug metabolites, including chemical oxygen demand [6-9]. Time-dependent voltage data produced by microbial fuel cells can be used as signals, and biosensors need such signals and are critical [21]. In the presence of a pollutant, the electrical energy produced by microorganisms and the performance of microbial fuel cells decrease [8]. Research is underway on using microbial fuel cells to power environmental sensors, and the energy generated by fuel cells can be used to power sensors [22]. Previously, self-powered microbial fuel cell was developed as an autonomous biological oxygen demand (BOD) chemical oxygen demand (COD) biosensor and was used to detect organic pollutants in fresh water. This sensor relies only on the power produced by microbial fuel cells and can operate continuously without maintenance [23]. For the future, the interest in the production strategies of biomass resource, which is defined as green energy, by using microorganisms found in nature and the use of microbial fuel cells for soil improvement research is increasing in the literature.

Conclusions

In conclusion, the results of our study showed that the voltage values produced by the soil-based microbial fuel cell at different acetate concentrations can function as a signal. Our results show that the new soil-based microbial fuel cell produces electricity up to 396 mV and the voltage values increase up to 120 mM with increasing substrate concentration. These results suggest that microbial fuel cells can be used to detect various environmental pollutants that cause soil pollution. With the development of such a system, a new approach can be put forward that can function as a biosensor in areas where there is environmental pollution that harms the environment and life, while electricity is produced. In addition, the developed system can be a new potential electricity generator technology for efficient use and biological improvement of volcanic areas where industry or mining is common. However, soil microbial fuel cell should be fed with water regularly and the air flow should be provided continuously for effective operation.

Conflict of Interest

The authors (B. Kilinc, T. Catal) declare patent application (Turkish Patent and Trademark Office, 2023/000797 – submitted).

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