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# Algae cathode microbial fuel cells for electricity generation and nutrient removal from landfill leachate wastewater

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## ARTICLE INFO

### Article history:

Received 11 July 2017  
Received in revised form  
29 September 2017  
Accepted 3 October 2017  
Available online xxx

### Keywords:

Microbial fuel cell  
Landfill leachate  
Algae  
Nutrient removal

## ABSTRACT

Landfill leachate is one of the most toxic and difficult-to-treat wastewater due to its high level of contamination and complex composition. In this study, landfill leachate at different percentages (5–40%) was fed to algae cathode microbial fuel cells (MFCs) for electricity generation along with chemical oxygen demand (COD) and nutrient removal. Maximum cell voltage of  $300 \pm 11$  mV was obtained with 5% leachate, but the cell voltage decreased with an increase in leachate percentage. The maximum dissolved oxygen (DO) was 19.57 mg/L with 5% leachate. The COD in the anode chamber was almost completely removed (97%) with all leachate percentages, while the maximum COD removal was 52% with 10% leachate in the cathode chamber. Enhanced nitrogen and phosphorus removal was observed with leachate percentages less than 10%, but nitrogen removal efficiency was significantly reduced and even more phosphorus was observed with leachates higher than 25% ( $\text{NH}_4^+ - \text{N} = 651$  mg/L). This study suggests that leachate can be treated at an appropriate dilution with simultaneous electricity generation in algae cathode MFC.

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## Introduction

Microbial fuel cells (MFCs) are an innovative and environmentally friendly bioenergy technology, having great potential towards electricity generation with simultaneous wastewater treatment. The organic substrate in the anode chamber is oxidized by microorganisms present on the anode electrode with generation of protons and electrons. Then, these produced electrons move towards the cathode externally and protons diffuse through membrane and get reduced to water with the help of oxygen in the cathode. Economic feasibility is an important concern to be addressed, while considering the net energy production from an MFC system in order to reduce the energy consumption for aerating the MFC cathode. Several studies have previously been conducted to

supplement oxygen for the reduction process in MFC using ambient air, mechanical aeration, or algae growth in the cathode chamber [1,2].

MFC operation with aeration by algae growth in the cathode chamber has several advantages compared to other oxygen supply systems. Firstly, algae in the MFC cathode involve in photosynthesis (carbon fixation) with evolution of higher dissolved oxygen (DO) and generate more power output than mechanical aeration in MFC operation [3,4]. In previous studies, the maximum DO concentration with *Scenedismus obliquus* in the cathode chamber was 15.7 mg/L and the maximum power was 153 mW/m<sup>2</sup>, whereas the DO concentration and power value were 5.9 mg/L and 116 mW/m<sup>2</sup>, respectively, with mechanical aeration [1]. Algae aeration in their study obtained DO concentration approximately double

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<https://doi.org/10.1016/j.ijhydene.2017.10.011>

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times compared to the theoretical solubility of oxygen in water at 30 °C (7.56 mg/L) [5]. Secondly, algae are ubiquitous in nature and capable of growing in adverse climatic and ecological conditions with removing nutrients and toxic metal components by uptake [6,7]. Lastly, it can produce economically valuable biomass that can be used for synthesis of bio-fuels, bioactive compounds and nutrient supplements [8–10].

Large amounts of municipal and industrial wastes are produced annually due to increasing economy and population growth. The sanitary landfill method has emerged as an efficient solution to dump these wastes due to its low cost and simple operation. However, a large amount of leachate is produced from landfill sites, which needs to be treated before disposal in the natural environment. Landfill leachate generally contains excessive nutrients, strong organic chemicals, and other toxic pollutants, which are not effectively treated by conventional wastewater treatment technologies [11,12]. Several previous studies have investigated the feasibility of applying different types of MFCs for leachate removal, such as an air-cathode MFC [13–15], double chamber MFC [15], or three MFC columns fluidically connected in series [16]. However, a high amount of nutrients in leachate wastewater was not removed in previous studies and also power generation was limited by cathodic reduction process.

In this study, algae cathode microbial fuel cells (ACMFCs) were first operated to treat leachate (nutrients) by algae growth in the cathode and simultaneously supply oxygen to the cathode for high bio-electricity generation. Optimum leachate dilutions were investigated to obtain high nutrient (nitrogen and phosphorus) removal and electricity generation with algae growth in the cathode chamber. The half-cell potentials and DO concentrations were measured over time in the cathode at different leachate dilutions. Moreover, the ammonium, total phosphorus (TP), and soluble chemical oxygen demand (SCOD) removals were determined in both anode and cathode chamber to evaluate the overall removal efficiency at various leachate dilutions in MFC applications.

## Materials and methods

### Wastewater and landfill leachate

Wastewater was collected from the Giheung Respia Wastewater Treatment Plant (Yongin, Korea) and landfill leachate was obtained from the Metropolitan Landfill Management Corporation (Incheon, Korea). The average  $\text{NH}_4^+-\text{N}$  concentration of raw landfill leachate was approximately 2538 mg/L, but nitrate ( $\text{NO}_3^--\text{N}$ ) and nitrite ( $\text{NO}_2^--\text{N}$ ) were not detected. The total carbon (TC) and TP concentrations were approximately 2329 mg/L and 3.627 mg/L, respectively. Therefore, the measured C:N:P ratio of raw landfill leachate was 1659:1549:1. The optimum C:N:P ratio for better algae growth is known to be 106:16:1 [17]. Due to a high nitrogen concentration in the leachate, a dilution process may not be avoided in biological leachate treatment to prevent possible nitrogen inhibitions. So, diluted leachate using domestic wastewater was used to determine the optimum dilution ratio for algae growth in the cathode chamber. The characteristics of the landfill leachate and domestic wastewater are shown in Table 1.

**Table 1 – Characteristics of landfill leachate and wastewater used in this study.**

Parameters	Landfill leachate	Wastewater
TCOD (mg/L)	1938 ± 27	168 ± 8
SCOD (mg/L)	1883 ± 18	122 ± 3
$\text{NH}_4^+-\text{N}$ (mg/L)	2537.6 ± 6.3	34.0 ± 3.4
pH	8.53 ± 0.45	6.89 ± 0.34
Conductivity ( $\mu\text{S}/\text{cm}$ )	22,208 ± 1989	637 ± 25
TP (mg/L)	3.63 ± 0.30	3.21 ± 0.08
TC (mg/L)	2329 ± 42	77 ± 1
IC (mg/L)	1756 ± 43	50 ± 1
TOC (mg/L)	573 ± 20	27 ± 1

### Algae culture

The mixed algae culture was isolated from domestic wastewater and grown in 3-L Erlenmeyer flasks using Bold Basal Medium (BBM) [2]. Filtered air with the flow rate of approximately 400 mL/min was supplied as a carbon source for algae growth under alternating light and dark (14 h light/10 h dark) conditions at a temperature of  $28 \pm 4$  °C. During light conditions, the culture was mixed using a stirrer and illuminated by a fluorescent light of 1600 lux. While in dark conditions, the light supply and mixing of the algal culture were stopped [18]. The algae culture from the bioreactor (fresh algae) and the algae from the cathode chamber at the end of every cycle (old algae) were taken to prepare for the next cycle of the batch test. Every week, approximately 200 mL of the algae culture was collected from the bioreactor for the experiment and replaced by the same amount of fresh BBM. Then, the fresh algae solution from the bioreactor and the old algae solution from the previous cycle were centrifuged to obtain the settled algae. The old algae solution in particular was centrifuged 3 times with distilled water to remove all of the chemicals from the previous cycle. Two types of settled algae after this process were mixed with the ratio 2:1 (old algae: fresh algae) to obtain a total algae concentration of 2 g/L in leachate wastewater and this solution was used as catholyte in the MFC experiment.

### Microbial fuel cell configuration and operation

A double chambered cube MFC, which was made of Perflex sheets, was used in this study. A carbon fiber brush electrode ( $3 \times 2.5$  cm; Kemsung brush, Korea) was used as both the anode and cathode electrodes. The volume of anolyte was 290 mL (total volume of 295 mL) and the catholyte volume was 255 mL (total volume of 260 mL). The anode chamber was covered by aluminum foil to maintain dark conditions to prevent algal growth. The anode and cathode chambers were separated by a cation exchange membrane CMI-7000 (International Inc. USA) with dimensions of  $5 \times 6$  cm (W × H). A DO probe was inserted through the top of the cathode chamber and the gas outlet was connected to a gas sampling bag (Tedlar bag, US). During the startup period, the anode chamber was filled with domestic wastewater containing sodium acetate (2 g/L) for the development of biofilm on the anode electrode. The cathode chamber was supplied with domestic wastewater containing 2 g/L of algae. The total algae biomass of 2 g/L was prepared using previously cultured and fresh

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