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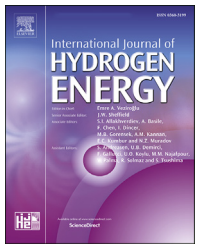

Hydrogen evolution in microbial electrolysis cells treating landfill leachate: Dynamics of anodic biofilm

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ABSTRACT

This study investigates the potential opportunities of hydrogen evolution treating landfill leachate in a set of two microbial electrolysis cells (MEC-1 and 2) under 30 °C and 17 ± 3 °C temperatures, respectively. The system achieved a projected current density of 1000–1200 mA m^{-2} (MEC-1) and 530–755 mA m^{-2} (MEC-2) coupled with low cost hydrogen production rate of 0.148 L La^{-1} d^{-1} (MEC-1) and 0.04 L La^{-1} d^{-1} (MEC-2) at an applied voltage of 1.0 V. Current generation led to a maximum COD oxidation of 73 ± 8% (MEC-1) and 65 ± 7% (MEC-2) with ≥100% energy recovery. The system also exhibited a high hydrogen recovery (66–95%), pure hydrogen yield (98%) and tremendous working stability during two months of operation. Electroactive microbes such as *Pseudomonadaceae*, *Geobacteraceae* and *Comamonadaceae* were found in anodophilic biofim, along with *Rhodospirillaceae* and *Rhodocyclaceae*, which could be involved in hydrogen production. These results demonstrated an energy-efficient approach for hydrogen production coupled with pollutants removal.

Introduction

Environmental pollution and energy shortages are two major global puzzles of the time. The present energy mainly comes from burning fossil fuels; however, depletion of fossil reserves with burgeoning global energy demand and increasingly environmental pollution is a matter of concern. Hence, the demand of renewable energy resources to replace fossil fuels has attracted worldwide attention. Hydrogen gas (H_2) is a preferred alternate energy source since it is clean and renewable energy carrier. Nowadays, H_2 gas is mostly produced from certain processes such as gasification, pyrolysis, thermochemical water splitting, steam reformation, electrolysis, fermentation and photo-fermentation [1]. One very promising technology to generate bio hydrogen gas is the use of microbial electrolysis cell (MEC), a viable alternative for wastewater treatment as well [2–4]. The H_2 evolution rates are significantly higher in MECs (80–100%) as compared to the fermentation process and water electrolysis [5]. In an MEC, a group of electroactive bacteria utilize the potential energy

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Nomenclature

BES	bioelectrochemical system
MEC	microbial electrolysis cell
DNA	deoxyribo nucleic acid
rRNA	ribosomal ribonucleic acid
PBS	phosphate buffered solution
PCR	polymerase chain reaction
r_{cat}	cathodic hydrogen recovery
OTUs	operational taxonomic units
Anammox	anaerobic ammonium oxidation
CEM	cationic exchange membrane
HRT	hydraulic retention time

stored in the organic compounds to metabolize and grow, donating electrons to the anode which then transport to the cathode with anaerobic environment, through electrolyte in a circuit and generate H_2 gas electrochemically (i.e. electrohydrogenesis) by certain endergonic reactions [3,6], as described in Eq. (1).

$$2H^+ + 2e^- \rightarrow H_2 \quad E^0 = -0.414\ V \tag{1}$$

The voltage produced by the exoelectrogenic bacteria is not sufficient for H_2 gas evolution, therefore in most cases, MECs a certain external voltage is added to the circuit to drive the redox reactions because no oxygen (or oxidative agent) is available in the cathode chamber electrochemical H_2 production [7]. Theoretically, a very low potential input (−0.414 V) is required to drive the process (Eq. (1)), but in practice it is substantially increased (i.e. 0.5–1.0 V) due to over potentials of the system. The H_2 production increases with the amplitude of applied potential (Eap, 0.7–1.0 V), which still is quite lesser than required for water electrolysis (1.8–2.0 V) [4,6,8].

The electrohydrogenesis proficiencies differ significantly with the nature of substrates employed. The MEC system with easily biodegradable organic compounds would have high hydrogen yield and energy output. Nevertheless, upon employing wastewater as substrate, the performance might be worse due to the high vulnerability of electrochemically active microbiota [9]. As shown in Table 1, beside simple substrates, a broad range of complex substrates have been tested so far in MECs for electrohydrogenesis such as human urine, glycerol, starch, winery, food processing, domestic and industrial wastewaters. However, less attention was given to use landfill leachate as anodic substrate in MECs. Landfill leachate is a high strength wastewater with excessive COD, NH_4-N and volatile fatty acid contents (VFAs). Organic content present in landfill leachate and its composition vary depending on the type of landfill waste materials and age of the leachate. High COD (>5 g L^{-1}) and NH_4-N (>0.4 g L^{-1}) content, and low BOD_5/COD ratio (<0.1) makes biological treatment of landfill leachate very difficult [10,11].

Employing landfill leachate as raw material for production of energy and chemicals is a novel approach. It is likely that landfill leachates with unique physiochemical characteristics and more complex components have higher difficulties in hydrogen production. Whether or not MEC system can catalyze landfill leachate to produce H_2 gas is still dubious owing to least attention. Anode respiring bacteria (ARB), the key microbes that colonize the anode of BES, can oxidize only a few simple compounds as electron donors. In this regard, Mahmoud et al. [12] employed pre-fermentation of mature landfill leachate (BOD_5/COD ratio of 0.32) for enhanced current density, CE and organics removal in MEC. The fermentation reactions produce the mixture of simpler compounds that ARB can oxidize. During fermentation, the complex organic compounds in the leachate were converted to simple VFAs, mainly succinate and acetate in batch tests, but mostly acetate in semi-continuous fermentation. The degree of conversion to VFAs improved by 4-fold, which led to a 68% increase in CE and a maximum current density of 23 A m^{-3} (or 1.7 mA m^{-2}). In another study [13], Fenton-based pre-treatment was employed to improve the biodegradability of landfill leachate that is subsequently fed to an MEC. It led to higher MEC performance: 52 ± 10% BOD_5 removal, 29 ± 3% CE, and 1.42 ± 0.27 A m^{-2} current density as compared to 3 ± 0.3% BOD_5 removal, 1.8 ± 0.5% CE, and 0.11 ± 0.06 A m^{-2} current density for the raw leachate.

Kargi et al. [14] employed landfill leachate for H_2 production applying DC voltage in the range of 0.5–5.0 V (i.e. electrohydrolysis) using aluminum electrodes. The highest cumulative H_2 evolution (5 L), H_2 yield (2.4 LH_2 g^{-1} COD), daily H_2 gas production (1.27 Ld^{-1}), and percent H_2 (99%) in the gas phase coupled with 77% COD removal were attained applying 4 V DC voltage. However, only 22 mL H_2 gas was generated within 96 h applying 0.5 V DC voltage. It indicated that the H_2 production was driven by electrohydrolysis other than bacterial decomposition of the leachate.

Since no MEC study has been employed for hydrogen production using landfill leachate as substrate. Herein, we investigate the potential opportunities of efficient clean hydrogen production treating simulated landfill leachate without any pre-treatment approach either biologically, physico-chemically or electro-chemically. To the best of our knowledge, this is the first study for H_2 evolution using landfill leachate as substrate. Series of batch scale experiments were conducted under different operational and electrochemical conditions to see the overall system performance including organic and nitrogen content removal, energy consumption and yield. At the end, microbial community was studied for a better understanding of the H_2 generation mechanism.

Materials and methods

MEC set up

A set of dual chambered rectangular reactors (MEC-1 and MEC-2) having 1.0 L and 0.5 L of total working volume, respectively as explained in previous work [15] was employed in this study. The schematics of experimental set-up is illustrated in Fig. 1. For hydrogen collection and measurement, the gas port at the top of cathode chamber was connected to an inverted measuring cylinder in a water tub. The anode of MEC-1 and MEC-2 consisted of 1.0 cm thick carbon