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Hydrogen production from wastewater using a microbial electrolysis cell

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Abstract−A Microbial electrolysis cell (MEC) was designed to produce a useful and valuable product, hydrogen gas, during the wastewater treatment process. Hydrogen can be produced using the MEC with an applied voltage of over 0.4 V, and the hydrogen yields gradually increased with the increasing of applied voltage. A maximum overall hydrogen efficiency of 21.2% was achieved at an applied voltage of 1.0 V with acetate as substrate, corresponding to a volumetric hydrogen production rate of approximately 0.095 m^3 H_2/m^3 reactor liquid volume/day. A volumetric hydrogen production rate of 0.061 m^3 H_2/m^3 reactor liquid volume/day was achieved when piggery wastewater was fed to the MEC, and the chemical oxygen demand removal rate ranged from 45 to 52%. The results demonstrated that the wastewater, especially an organic-rich item such as piggery wastewater, could be feasibly treated based on this MEC system.

Key words: Microbial Electrolysis Cell, Hydrogen Production, Organic Removal

INTRODUCTION

Renewable energy production technologies are currently gaining great attention in the society, due to the depletion of fossil fuels and the threat of global warming. Hydrogen is an entirely carbon-free fuel with a high combustion enthalpy of 185 kJ L^{-1} [1,2], thus considered to be a feasible alternative to fossil fuels. While around 96% of the world hydrogen production is made from fossil fuels [3], which also results in the release of CO_2 and contributes to the climate change. For hydrogen to become a more sustainable and green source of energy, it must be produced renewably. Sustainable hydrogen production could be achieved through water electrolysis using energy gained from renewable sources such as wind, solar or biomass, but the energy requirements are high (5.6 kWh/m^3 H_2) [4] and the typical electrolyzer efficiencies are as low as 56-73% [5], which shows less promise for economical production of hydrogen.

Renewable hydrogen can be generated from biomass by biological fermentation, but yields are low, with acetate or butyrate as fermentation dead-end products. The highest hydrogen production from fermentation is 4 mol H_2/mol glucose if acetate is produced, while only 2 mol H_2/mol could be produced if butyrate is generated as the sole end product, despite a stoichiometric potential of 12 mol H_2/mol glucose [6,7]. Fermentation is not capable of converting the produced volatile fatty acids (VFAs) to hydrogen, for the conversions involve endothermic reactions [8]. Additional energy has to be added to the system to overcome the thermodynamic limit. One method is the photo fermentation process using photosynthetic bacteria [2]. However, the process is restricted by the low efficiency and the high cost associated with the need of light provision and the requirement of large surface area [5,9]. Furthermore, when wastewater is taken as substrate for biological hydrogen production, the process must be carried out with sterilized wastewater to suppress the methanogenic bacteria, which is not practical or energy efficient for the waste treatment process [7].

Microbial fuel cells (MFCs) have been discovered as a completely new method for renewable electricity production simultaneously with organic compounds removal from wastewater [10-13]. In the MFC system, substrate is oxidized by the microorganisms and the produced electrons are transferred to the anode, which then flow to the cathode through the external wire, where they normally combine with oxygen and protons to form water [14-17]. While in MFCs, the maximum voltage that could be obtained is less than 1.14 V [18,19], and the voltage limitation restricts the energy recovery. The need of oxygen in the cathode chamber is another disadvantage of MFC [20], for oxygen may leak into the anode chamber through the membrane, and either lower the energy recovery or inhibit the growth of obligate anaerobes [6]. Based on the MFCs technologies, by removing the oxygen from the cathode chamber and applying a small voltage to the circuit, hydrogen can be produced directly from protons and electrons generated by the bacteria [6]. This hydrogen evolution process is referred to as microbial electrolysis cells (MECs). By operating the system as MECs for hydrogen production, the voltage limitation of MFCs could be bypassed. And the use of oxygen in the cathode chamber could also be omitted, for MECs are completely anaerobic systems.

As the direct production of hydrogen from the hydrolysis of ace-

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tate is not thermodynamically feasible, in the MEC system, the thermodynamic barrier has to be overcome by applying an external voltage of over 0.11 V; however, a voltage of over 0.25 V is needed due to the electrode overpotentials [21-23]. With an external voltage supply of over 0.25 V added to the −0.30 V (versus a standard hydrogen electrode) generated by the bacteria in the anode chamber, a potential of −0.42 V can be obtained for hydrogen production in the cathode chamber [24]. The working mechanism of MEC is given in Fig. 1(a). And the half reactions of each chamber can be deduced as the following equations:

$$\text{Anode: } C_2H_4O_2 + 2\,H_2O \rightarrow 2\,CO_2 + 8\,e^- + 8\,H^+ \quad (1)$$

$$\text{Cathode: } 8\,H^+ + 8\,e^- \rightarrow 4\,H_2 \quad (2)$$

The objective of this study was (1) to experimentally enrich the electrochemically active bacteria that function as the direct electron transfer from the substrate to the anode; (2) to study the performance of microbial electrolysis cell in hydrogen production and organic removal with artificial wastewater; and (3) to investigate the COD removal efficiency, hydrogen production rate and input electricity efficiency with piggery wastewater.

MATERIALS AND METHODS

1. Experimental Set-up

The microbial electrolysis cell used in this study was a two-chamber reactor separated by a Nafion 424 Membrane (projected area 52 cm^2, Aldrich, Germany). The membrane was sequentially boiled for 1 h in deionized water, 30% (w/w) H_2O_2 aqueous solution, deionized water, 0.5 M H_2SO_4 aqueous solution, and finally kept in deionized water until use. The volume of each chamber, with the electrode, was approximately 360 ml. Graphite felt (6.5×3.4×1.2 cm) which adhered to a carbon rod by conductive glue was used as anode. The cathode consisted of a square-shaped perforated titanium plate electrode (7.0×3.0 cm, 2 mm thickness, Labco Co., South Korea), with 1.0 mg/cm^2 platinum coated as catalyst.

A voltage range from 0.2 V to 1.0 V was applied to the circuit by connecting the positive pole of a power supply to the anode, and the negative pole to the cathode. The external resistance (R) which connected to the circuit in series was 10 Ω. Both the chambers were continuously mixed using magnetic stirrers. The photograph of experimental apparatus is given in Fig. 1(b).

2. Inoculation

The anode chamber of MEC was inoculated by a mixture of bacteria enriched in a conventional MFC together with anaerobic digester sludge (Yongin Wastewater Treatment Plant, Gyeonggi Province, Korea), at initial MLSS concentration of 1 g/L. The anode chamber was fed with synthetic wastewater modified from Lee et al. [25] with phosphate concentration of 50 mM (pH 7.0) and sodium acetate as sole substrate, while the cathode chamber contained only buffer (50 mM, pH 7.0).

Piggery wastewater was also fed to MEC for hydrogen production. Piggery wastewater was collected from the effluent of an anaerobic digestion process and kept in a refrigerator at 4 °C before use. The feed for MEC was diluted from raw wastewater by ten-times with tap water and buffered (50 mM phosphate buffer). Table 1 shows the characteristics of the feeding piggery wastewater.

3. Analytical Methods

The current and voltage of the reactors were measured (30 min intervals) with a multimeter and a data acquisition system (Keithley 2700, USA) connected to a personal computer. The anode and cathode potential were measured by Ag/AgCl reference electrode equipped to each chamber which was also recorded by the multimeter. The pH of the electrolyte was measured with a pH meter

Table 1. Characteristics of feeding piggery wastewater

Iteams	Average value	Unit
pH	7.3	-
Alkalinity	114	$mgCaCO_3/L$
$SCOD_{cr}$	842	mg/L
$TCOD_{cr}$	1298	mg/L
NH_4^+-N	270	mg/L
NO_3^--N	3.4	mg/L
NO_2^--N	0.1	mg/L

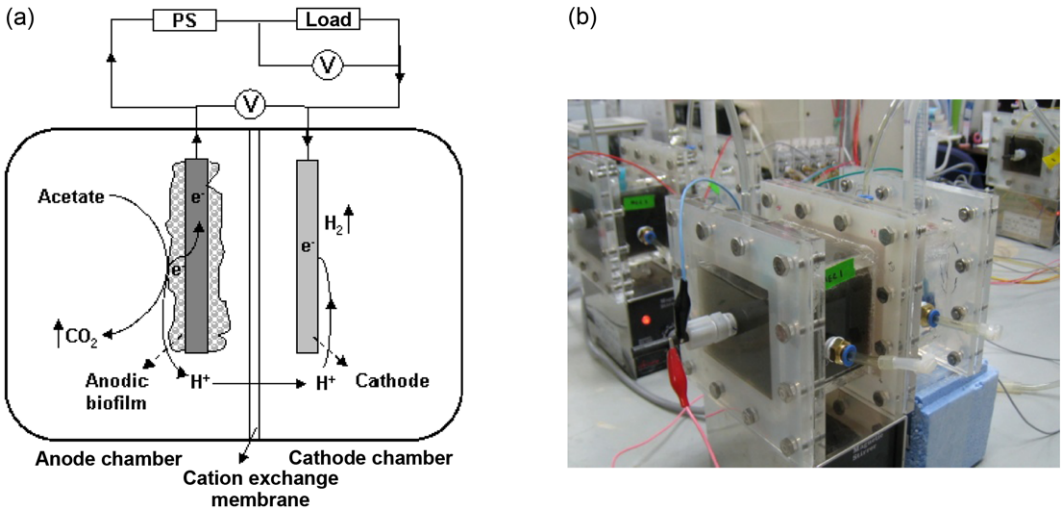

Fig. 1. Schematic diagram and photograph of the microbial electrolysis cell.

(ion LAB WTW). The chemical oxygen demand (COD) was quantified using Hach COD measurement system and kit, and the entire procedure for pre-treatment of samples was done in accordance with the Standard Method. The hydrogen concentration was analyzed with a gas chromatograph (GC-17A, Shimadzu, Japan) equipped with a thermal conductivity detector (TCD). A Molecular Sieve 5A column (Alltech corporate, USA) with argon as carrier gas was used to separate the gas.

4. Calculations

The current is calculated as follows: $I=V_R/R$, where V_R is the voltage across the resistor; and the current density could be calculated by current normalized the surface area of electrode (A, in square meter). The coulombic hydrogen recovery is calculated as: $r_{CE}=n_{CE}/n_{th}$. n_{CE} is the moles of hydrogen that could be recovered from the measured current, given by: $n_{CE}=C_P/2F$, where C_P is total coulombs calculated by integrating the current over time, F is Faraday's constant (96,485 C/mol electrons). n_{th} is the total theoretical number of moles of hydrogen that could be recovered based on substrate. The cathodic hydrogen recovery is as follows: $r_{Cat}=n_{H2}/n_{CE}$, where n_{H2} is the number of moles of hydrogen recovered during a batch cycle. The overall hydrogen recovery is calculated according to $R_{H2}=r_{CE}$ r_{Cat} [26].

The energy added to the system by power source, adjusted for losses across the resistor (W_E), can be calculated as: $W_E=\sum_1^n(IE_{ap}\Delta t-I^2R_{ex}\Delta t)$, where E_{ap} is the voltage applied using the power supply, Δt is the time increment of n data points measured during a batch cycle, and R_{ex}=10 Ω is the external resistance. The energy balance approach based on heats of combustion, which is commonly used for electrolyzers and for estimating the energy content of organic matter, was used in this study. The amount of energy added by the substrate is given by $W_S=\Delta H_S n_S$, where ΔH_S=870.28 kJ/mol is the heat combustion of the substrate, and n_s is the number of moles of substrate consumed during a batch cycle based on COD removal. The amount of energy output as hydrogen is calculated as $W_{H_2}=\Delta H_{H_2} n_{H_2}$, where ΔH_{H_2}=285.83 kJ/mol is the energy content of the hydrogen based on the heat of combustion (upper heating value), and n_{H_2} is the number of moles of hydrogen produced during a batch cycle [26].

RESULTS AND DISCUSSION

1. Inoculation and Start-up

To enrich the electrochemically active bacteria (EAB) which could transfer electrons directly to the anode, the reactors were inoculated in microbial fuel cell mode with oxygen as electron acceptor in the cathode chamber for about 30 days with an applied external resistance of 10 Ω in the circuit. The reactors were first operated in batch mode, and the voltage began to increase after 24 hours of MFC operation. Substrate addition was repeated for several times until a maximum voltage was achieved, and the inoculation was changed to continuous mode for further enrichment. Polarization tests were conducted on Day 30 by varying the external resistance from 10 to 1,000 Ω (Fig. 2). The highest power output of 39.2 mW/m^2 was achieved at a current density of 241.5 mA/m^2. Based on the current-voltage curve, internal resistance was calculated to range from 51 to 64 Ω. The polarization test proved that the reactors were satisfactory to proceed to the hydrogen production test.

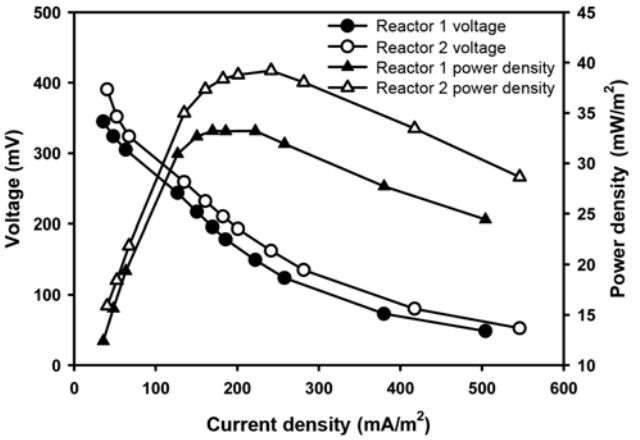

Fig. 2. Polarization curve obtained in microbial fuel cell mode.

2. Hydrogen Production from Acetate

The reactors were then transferred to microbial electrolysis cell mode for hydrogen production. Both compartments were flushed with N_2 gas for 30 minutes prior to the experiment to get a totally anaerobic atmosphere. A voltage ranging from 0.2 V to 1.0 V was supplied to the circuit, and the cathode chamber was sealed to collect the hydrogen gas.

Fig. 3 shows the profiles of hydrogen production, current density and electrode potential of the MEC in response of 4 mM sodium

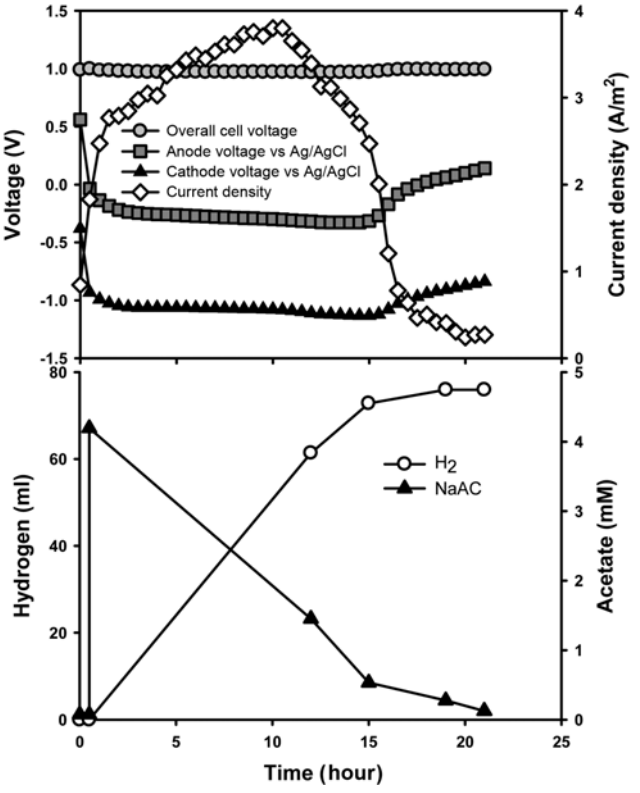

Fig. 3. Electrode potential, current density and H_2 production in response of 4 mM sodium acetate with an applied voltage of 1.0 V.

acetate with an applied voltage of 1.0 V. With the applied voltage and background level of substrate, the anode potential showed a value of about 500 mV, while it decreased sharply to −300 mV in response to the substrate addition, stabilized over 15 hours, and increased again due to the consumption of substrate. Following the addition of substrate, there was a rapid increase in current density, while the trend line declined constantly with the substrate consumption. Up to the current generation, hydrogen production could be detected in the cathode chamber.

In this batch, 3.39 mM of hydrogen gas was produced by the consumption of 4 mM sodium acetate, and the n_{CE} (moles of hydrogen that could be recovered from the measured current) was calculated to be 4.73 mM in accordance with the current. Based on the data obtained, the cathodic hydrogen recovery and coulombic hydrogen recovery of this process were calculated to be 71.7% and 29.6% respectively, corresponding to a recovery efficiency of 21.2% for hydrogen. The accumulation of CH_4 gas was detected in the anode chamber, which might lower the coulombic hydrogen recovery and thus the overall hydrogen recovery in this process.

To further evaluate the reactor performance, the current densities were measured with the reactors which had been run for over 8 months for hydrogen production. All of the data was obtained in duplicate by stepwise increase of the applied voltage.

As Fig. 4 shows, for the reactor with the presence of substrate in the anode chamber, the current density increased with the increasing of applied voltage from 0.64 to 3.19 A/m^2. To confirm the electron source for current generation, the reactor was operated without acetate as substrate in the anode chamber, while other parameters were kept the same as the system with the presence of substrate. In this case, the current generated was negligibly low (0.11-0.37 A/m^2), and no hydrogen gas was detected in the cathode chamber. The results proved that acetate was taken by the EAB (electrochemically active bacteria) in the anode chamber as substrate for current generation and then for hydrogen production.

Hydrogen can be produced with an applied voltage of 0.11 V theoretically; however, greater voltage is needed in practice to overcome the overpotentials. In this study, only negligible amount of hydrogen could be produced with an applied voltage low than 0.4 V.

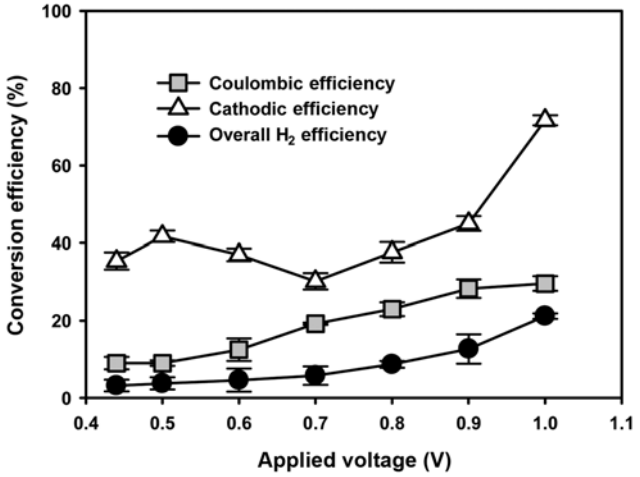

Fig. 5. Coulombic efficiency, cathodic efficiency and overall H_2 efficiency as a function of applied voltage.

Fig. 5 shows that with an applied voltage of more than 0.4 V, the recovery of electrons as hydrogen (cathodic efficiency) was over 30%. While the coulombic efficiency, defined as the recovery of total electrons in acetate as current, ranged from 9 to 29.6%. The overall hydrogen efficiency (recovery of electrons from acetate as hydrogen) increased with the increasing of applied voltage, and achieved a maximum of 21.2% at the applied voltage of 1.0 V. Assuming a maximum possible production of 4 mol H_2/mol acetate, the overall hydrogen yield was 0.8 mol H_2/mol acetate. This corresponded to a volumetric hydrogen production rate of approximately 0.095 m^3 H_2/m^3 reactor liquid volume/day, which is 1.8 times higher than the 0.052 m^3 H_2/m^3/day reported by Chae et al. [27], and is 4.7 times higher than the 0.02 m^3 H_2/m^3 reported by Rozendal et al. [28].

Fig. 6 shows the input electricity efficiency, substrate efficiency and total efficiency with different applied voltages. The energy efficiency of MEC was calculated to be from 78 to 117%, which is higher than the typically efficiencies of hydrogen production with water electrolysis (50-70%). The power source for this MEC for hydrogen production could be obtained by other methods, such as microbial fuel

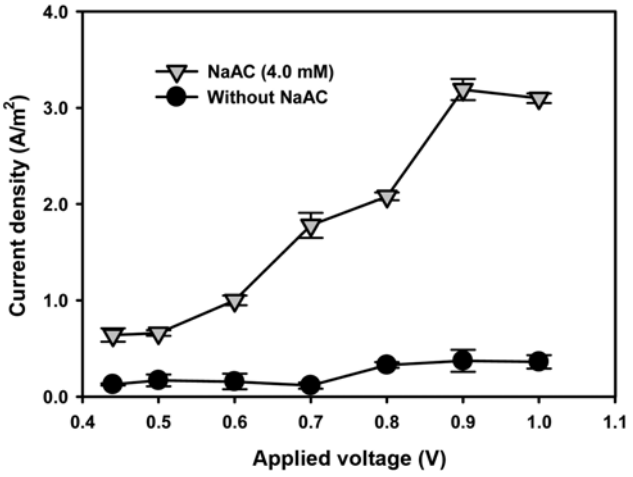

Fig. 4. Current densities as functions of the applied voltage in the MEC in both the presence and absence of substrate.

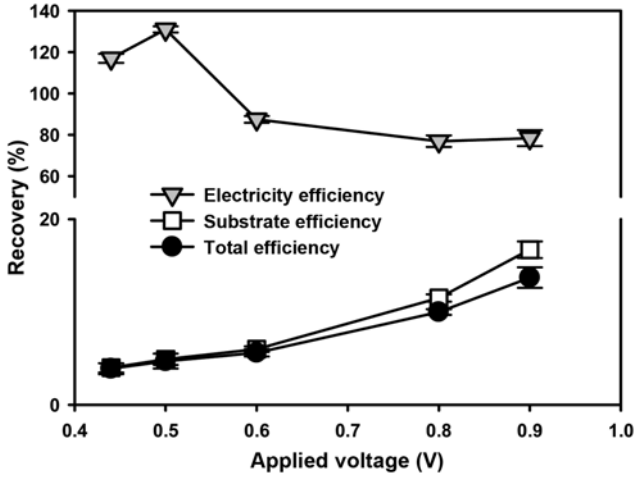

Fig. 6. Input electricity efficiency, substrate efficiency and total efficiency as a function of applied voltage.

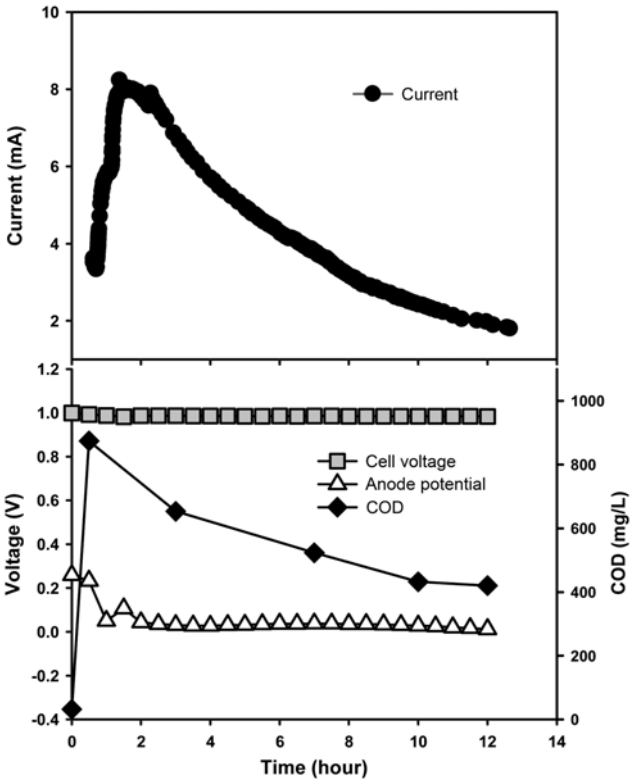

Fig. 7. Overall cell voltage, anode potential and current density using piggery wastewater with an applied voltage of 1.0 V.

cell, or other renewable energy, such as solar cell. By these methods, a clean and renewable energy production process combined with the wastewater treatment could be achieved. The efficiency relative to the substrate input ranged from 4 to 16.7%, while the total efficiency based on both energy and substrate input ranged from 3.9 to 13.7% within the range of applied voltages.

3. MEC Performance with Piggery Wastewater

Piggery wastewater was fed to MEC for hydrogen production in batch mode with an external voltage of 1.0 V. As shown in Fig. 7, with the fed of wastewater as fuel, the anode potential decreased until a minimum value of −200 mV, which is higher than the value obtained using acetate as substrate (−400 mV). This might because the complex organics such as polymeric and particulate substrates which exist in the piggery wastewater are difficult to be digested. For the higher anode potential, the current generated is lower, with the highest current density of 1.75 A/m^2 compared with the 3.8 A/m^2 using acetate as substrate. Up to 22 ml of hydrogen gas was generated in this batch, corresponding to a volumetric hydrogen production rate of 0.061 m^3 H_2/m^3 reactor liquid volume/day, following with the 45 to 52% (48% in average) COD removal from the wastewater. The input electricity efficiency was calculated to be 124%.

CONCLUSIONS

A dual-chamber microbial electrolysis was designed in this study, and its performance in both hydrogen production and organic removal was investigated:

- Hydrogen can be produced by using the MEC with an applied external voltage of over 0.4 V, and the hydrogen yields gradually increased with the increasing applied voltage. The maximum overall hydrogen efficiency of 21.2% was achieved at an applied voltage of 1.0 V with acetate as substrate, corresponding to a volumetric hydrogen production rate of approximately 0.095 m^3 H_2/m^3 reactor liquid volume/day. The energy efficiency of MEC was calculated to be from 78 to 117%, which is higher than the typical efficiencies of hydrogen production with water electrolysis (50-70%).
- A volumetric hydrogen production rate of 0.061 m^3 H_2/m^3 reactor liquid volume/day was achieved when piggery wastewater was fed to the MEC as fuel, and the chemical oxygen demand removal rate was 48% in average; the input electricity efficiency was calculated to be 124%.
- Molecular analysis will be done to characterize the difference of microbial communities between microbial electrolysis cell and microbial fuel cell.

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