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Effect of Electrode Space on Internal Resistance and Wasted Sludge Removal of Low-cost Solid Phase Microbial Fuel Cell

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Abstract

Activated sludge process has been widely used in wastewater treatment plants. Excess sludge produced during the process has become a solid waste for many treatment plants to be managed. Solid-phase microbial fuel cell (SMFC) is a process which can remove the excess sludge as well as transform wasted sludge into electrical energy. In this research, 3 low-cost SMFCs were constructed and used to digest wasted activated sludge under the condition of 3 electrode spaces, i.e., 4 cm, 6 cm, 8 cm. The experiment was aimed to investigate the effect of electrode space on internal resistance and wasted sludge removal of the SMFCs. As a result, the relationship between electrode space and internal resistance was not always in direct variation. It changed along the operation period. In terms of sludge removal, the removal rates and efficiencies (6 cm<8 cm<4 cm) conformed to the electricity generation (6 cm<8 cm<4 cm) during 4-120-hr. operation period. At that period, SMFC with 4-cm electrode space displayed greatest performance in both electricity generation and wasted sludge removal. It removed 34.1% of the wasted sludge with the highest sludge removal rate (0.05-kgVS/L·day) and the lowest internal resistance (17.5-875.6 ohms). It also showed the highest electricity generation yield (83.7-μWhr/gVS) with 298.0-mW/m^3 maximum electrical power density (21.84 mW/m^2).

Keywords : Solid-phase microbial fuel cell; electrode space; internal resistance

Introduction

Activated sludge process is currently the most widely used biological wastewater treatment process in the developed world [1]. As certain amount of excess sludge is produced along with the operation of activated sludge process, high cost is required for the wasted sludge treatment [2]. It was reported that China spent 25-60% of the total typical wastewater treatment expenses in treatment and disposal of the excess sludge [2]. Most excess sludge treatment methods, e.g., landfill, composting, and incineration, generally include sludge digestion as the pretreatment process to stabilize and reduce the volume of wasted sludge [3]. Thus, it is worth challenging to modify the sludge digestion into the process which can remove the excess sludge as well as transform it into electrical energy.

Microbial fuel cell (MFC) is a clean technology which directly turns waste into electrical energy [4] without any combustion process [5]. Waste materials, such as wastewater, sludge, or other solid wastes are applied to an anodic chamber of MFC as food for microorganisms. When microorganisms degrade waste material, electrons and protons are removed from the compounds and released into an anodic medium. Some protons move across a separation compartment to a cathode chamber while some electrons enter an anode and flow via electrical wire to the cathode to perform chemical reactions with the protons and an electron acceptor, e.g., oxygen gas, at the cathode compartment. This phenomenon causes potential difference, namely voltage, which lead to an electricity generation of the MFCs.

In numbers of researches, MFCs were often applied for wastewater treatment using sludge as a microbial inoculum [6]. Out of numerous factors affecting electrical generation, electrode space is a basic factor which accumulated researchers' attention in the first period of MFC studies. It was often reported that MFCs provided higher power density when electrode space decreased due to the low internal resistance of solution inside the MFCs [7-10]. Several variations of electrode spaces were applied in their MFCs studies, i.e., 20 cm, 24 cm and 28 cm for synthetic wastewater treatment [7]; 10 cm, 12 cm and 15 cm for sago-processing wastewater treatment [8]; and 5 cm, 10 cm, 50 cm and 100 cm for benthic MFCs [10] However, other trends were also found in other researches. Lee et al. [11] have found that either increasing or decreasing of electrode space could both provide higher electrical power if COD concentration in the influent was suitable [11]. For example, at 300-mgCOD/L influent concentration, 5.8-cm electrode space caused the highest power density comparing to the cases of 10.2-cm, 15.1-cm, and 19.5-cm electrode spaces [11]. But when the influent concentration reduced to 100 or 50 mgCOD/L, the highest power density appeared in the condition of 10.2-cm electrode space [11]. And at 25-mgCOD/L influent concentration, 15.1-cm electrode space condition exhibited the highest power density [11]. This result suggested that decreasing electrode space did not always lead to the decreasing of MFCs' internal resistance, especially in the case of low concentration substrate. There seems to be a certain value of optimal electrode distance for each MFC reactor. Ibrahim et al. [12] treated salted boiled fish processing wastewater using their MFCs. Harvested electrical currents were highest (0.46±0.17 mA) at the 4 cm electrode space, and became relatively low at 6 cm (0.44±0.16 mA) and 2 cm (0.17±0.06 mA) electrode spaces [12]. Kondaveeti et al. [13] found that their air-cathode single chamber MFC with a low-cost polypropylene separator generated highest power density (488 mW/m^2) at 6-mm electrode space, following by 220 mW/m^2, 358 mW/m^2 and 370 mW/m^2 for electrode distance of 0 mm, 3 mm and 9 mm, respectively [13]. According to these findings, effect of electrode space on MFCs' internal resistance and power output should be examined case by case in order to define the optimal value for each MFC reactor.

Recently, several researchers are interested in using MFCs for solid-waste digestion. The solid-phase MFCs (SMFCs) have been widely used for the treatment of Livestock solid waste [14], excess activated sludge [15], food wastes [16], etc. [17] which provided comparable power densities (36.6-220,000 mW/m^3 m^3 ([14, 18]) to those of liquid-phase MFCs (200-200,000 mW/m^3 [19]). It was reported that a soil microbial fuel cell provided highest electrical power density (19.5 mW/m^2) at lowest electrode space (4 cm) comparing to that of the 7-cm (8.5 mW/m^2) and 9-cm (5.9 mW/m^2) electrode spaces [20]. However, due to the possibility of electrons' shortcut movement from anode to cathode under membraneless condition, the SMFCs could probably produce lower electrical power when the distance between electrodes become too short. Since the relationship between electrode space and internal resistance of membraneless SMFCs has not been well clarified, this study was performed to contribute that information. Low-cost SMFCs were constructed and used to digest wasted activated sludge in membraneless condition under various electrode spaces without mixing. Effect of electrode space on internal resistance and wasted sludge removal of the SMFCs were discussed.

Materials and Methods

Construction of low cost SMFCs

Each of 3 low-cost SMFCs was constructed by filling a 54-ml plastic tubes (2.5-cm diameter, 11.5-cm height) with 54.71-g wasted sludge collected from an activated sludge treatment plant located in Mahasarakham hospital. An air cathode made from 4-cm^2 graphite plate was placed on the surface of wasted activated sludge in each SMFC. For anode installation, a 4-cm^2 graphite plate was placed inside each tube with different distances from the cathode, i.e., 4 cm for SMFC1, 6 cm for SMFC2, 8 cm for SMFC3, as shown in **Figure 1**. It costed only 55 Baht to produce 1 SMFC.

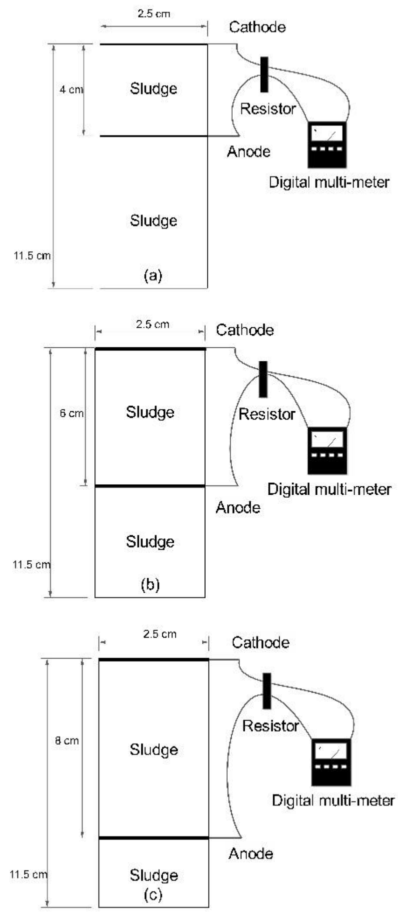

Figure 1 Schematic diagram of solid-phase microbial fuel cell (SMFCs) with three different electrode distance, i.e., 4 cm (a), 6 cm (b), 8 cm (c)

Polarization experiment

For practical SMFC operation, an anode of each SMFC should be connected to a cathode via an external resistor to produce electrical current (I, ampere). Polarization experiment was performed to determine a suitable external resistance (R_{EXT}, ohm) for each SMFC. Each of 10 different external resistors, i.e., 10000 Ω, 8400 Ω, 6800 Ω, 5100 Ω, 3300 Ω, 2200 Ω, 1000 Ω, 560 Ω, 250 Ω and 150 Ω was one by one applied to each SMFC for 5 minutes, respectively. Closed circuit voltage (CCV, Volt) dropping across each external resistor was measured by a multimeter (GW-INSTEK GDM-8255A) and used to calculate electrical power (P, Watts) and electrical power density (PD, mW/m^3) according to equation 1 and 2, where V_{SMFC} (m^3) is SMFC volume. A resistance value that led to the highest PD was selected as the suitable one for that SMFC's practical operation.

$$P = I \cdot CCV = \frac{CCV^2}{R_{EXT}} \quad (1)$$

$$PD = \frac{P}{V_{SMFC}} \quad (2)$$

SMFC operation

SMFC1, SMFC2 and SMFC3 filled with wasted sludge were placed in room temperature in open circuit condition until the open circuit voltages (OCV, Volt) of each SMFC became nearly stable. Polarization experiment was then done to choose an external resistor for each SMFC. With the selected external resistor connected to both electrodes, each closed circuit-SMFC was operated to digest wasted sludge. CCV dropping across each external resistor was measured throughout the operation and used to calculate P and PD. Total electrical energy (TE) harvested from each SMFC was estimated based on equation 3, where t is time, and t_{end} is operation ending time. Internal resistance (R_{INT}) of each SMFC was calculated using equation 4 [21].

$$TE = \int_{t=0}^{t_{end}} P dt \quad (3)$$

$$R_{INT} = \left(\frac{OCV}{I} \right) - R_{EXT} \quad (4)$$

Contents of volatile solids in wasted sludge before (VS_{before}, kg) and after (VS_{after}, kg) the operation were measured using gravimetric method and used to calculate wasted sludge removal rate (SR, kilogram/day) using equation 5

$$SR = \frac{VS_{before} - VS_{after}}{t_{end} - t_0} \quad (5)$$

Electricity generation yield (EY, Whr/g) of the SMFC was calculated based on equation 6, where TWR is total wasted sludge removal (kg)

$$EY = \frac{TE}{t_{end} - t_0} = \frac{TE}{TWR} \quad (6)$$

Results and Discussions

Polarization experiment

Figure 2 demonstrates the result of polarization experiment. A graph of voltage versus electrical current shows lines which their slopes represent the values of total resistance. A graph of power density versus electrical current displays suitable currents which allow SMFCs to produce maximum power densities. At very low electrical current (< 0.0001 mA), all SMFCs produced same level of voltages and power densities. But when the current boosted up from 0.0001 to 0.00018 mA, voltages and power densities of SMFC3 decreased with remarkable slopes comparing to those of the other 2 SMFCs. And when the current rose higher than 0.00018 mA, voltages and power densities of SMFC2 began to decrease with predominant slopes. Consequently, the graph-lines of 3 SMFCs had individual different slopes in the order of SMFC1<SMFC2<SMFC3 as shown in **Figure 2**. This result implied the direct variation between electrode space (SMFC1<SMFC2<SMFC3) and internal resistance (SMFC1<SMFC2<SMFC3) which was consistent with the result reported by other researches [7, 20]. As high internal resistance decelerates the movement of ions, it results in low power contribution of SMFC [22], the contrary relationship between electrode space

(SMFC1<SMFC2<SMFC3) and power density (SMFC3<SMFC2<SMFC1) in this experiment is rational.

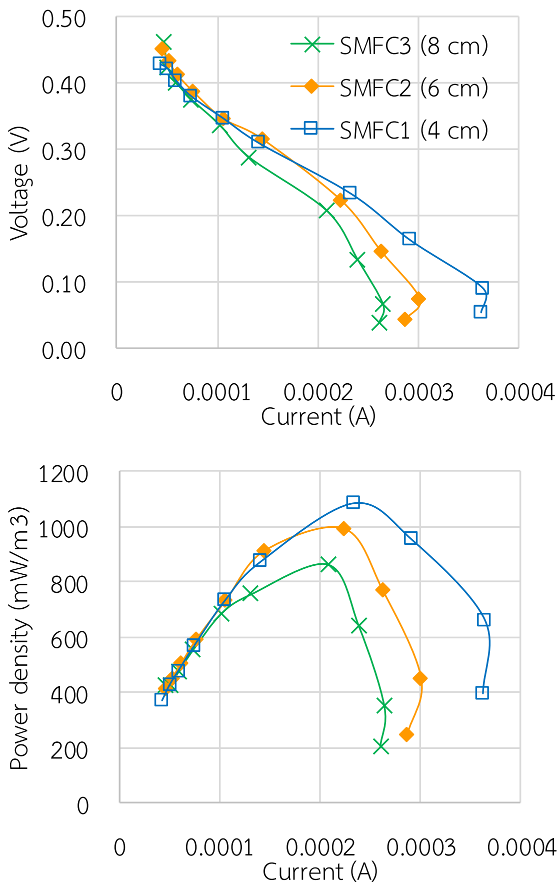

Figure 2 Power density and voltage during the polarization experiment

Comparing the voltage graph in Figure 2 to the theory of MFC potential loss [5], activation losses of 3 SMFCs are considered to occur at the current of 0-0.0001 mA and almost in the same level. As the activation loss occurs during the transfer of electrons from or to a compound reacting at the electrode surface [5], all SMFCs in this research were confirmed to have same qualities of electrode surfaces and anolytes. Ohmic losses of 3 SMFCs were considered to happen at the current of higher than 0.0001 mA. The highest ohmic loss was observed in SMFC3 which had the largest electrode space, following by SMFC2 and SMFC1, respectively. Consequently, the difference of internal resistance among 3 SMFCs (SMFC1<SMFC2<SMFC3) were considered to result from the difference of ohmic loss. According to the literature, ohmic loss includes both the resistance to the flow of electrons through the electrodes and interconnections, and the resistance to the flow of ions through membrane (if present) as well as the anodic and cathodic electrolytes loss [5]. Due to this result, it was assumed that when electrode space increased, numbers of protons transferred from anolyte to catholyte might decrease. This led to higher internal resistance as well as low power density. However, this result is not consistent with the explanation of another research that the reduction of electrode space enhances oxygen penetration from cathode to anode compartment [23]. Consequently, the oxygen will react with electrons in anolyte and cause high internal resistance and low power density [23]. This inconsistency can be explained that anodes of SMFCs in this research were installed in the location that oxygens from catholyte could rarely approach.

The polarization results further indicated that external resistors which caused maximum power density in 3 SMFCs were 1000 ohms, equally. As maximum power density occurs when the cell connects to an external resistor which has equal resistance to the cell's internal resistance [24], it can be said that, the 3 SMFCs equally had 1000-ohm internal resistance at the maximum power production state.

Production of electricity

An external resistor of 1000 ohm was selected and connected to both electrodes of each SMFC. During 120-hr. operation, voltages, electrical currents, and power densities of SMFCs were in the ranges of 0.0662-0.1221 V, 0.066-0.122 mA and 87.7-298.0 mW/m^3 for SMFC1; 0.0125-0.1130 V, 0.012-0.119 mA and 3.1-284.9 mW/m^3 for SMFC2; and 0.0465-0.0891

V, 0.046-0.089 mA and 43.2-158.8 mW/m^3 for SMFC3 as shown in **Figure 3**.

Due to values of the parameters, the graphs can be divided into 3 regions as shown by dashed lines in Figure 3. During 0-1 hr. operation period, voltages, currents as well as power densities of the SMFCs were in the order of SMFC3<SMFC1<SMFC2. But at 1-5 hr. operation period, the order became SMFC3<SMFC2<SMFC1, and changed into SMFC2<SMFC3<SMFC1 at 5-120 hr. operation period. This can be explained by values of internal resistance shown in **Figure 4**. As high internal resistance causes low electrical power [22], it is logical to have the order of power density at 5-120 hr. operation period (SMFC2<SMFC3<SMFC1) contrary to the order of internal resistance (SMFC1<SMFC3<SMFC2). Furthermore, at 1-4 hr. operation period, the order of internal resistance (Figure 4) was SMFC1<SMFC2<SMFC3 which was reasonably opposite to the order of power densities at 1-4 hr. operation period, i.e., SMFC3<SMFC2<SMFC1 (**Figure 5**). Here, it is interesting that the order of internal resistance at the 5th hour had changed into SMFC1<SMFC3<SMFC2 while that of the power densities at the 5th hour still remained in the same order as that of 4th hour (SMFC3<SMFC2<SMFC1). Consequently, there might be 1-hr. of time lag before the influence of internal resistance manifesting itself in terms of power density. Due to this assumption, high power densities of SMFC2 at 1st hour was possible although the order of internal resistance at 1st hour was SMFC1<SMFC2<SMFC3. It was possible that SMFC2 had moderate size of electrode space which might not be too large to decelerate the movement of protons from anode to cathode, and not be too small to enhance the short circuit of electrons' direct transfer from anode to cathode. Therefore, SMFC2 produced highest power density at the 1st hour (Figure 3). But during operation period of 1-4 hr., numbers of ions surrounding the anode and cathode of SMFC2 might become very scarce, thus the internal resistance of SMFC2 increased (SMFC1<SMFC2<SMFC3) and resulted in less power production (SMFC3<SMFC2<SMFC1). This deterioration of SMFC2 might continue after the 4th hour, therefore the order of internal resistance at 4-120 hr operation period became SMFC1<SMFC3<SMFC2 which cause opposite order in power densities (SMFC2<SMFC3<SMFC1). However, if the wasted sludge was fermented before entering SMFC process, SMFC2 might have had higher digestion rate and produced the highest power density throughout the operation period as it produced higher power density than the other 2 SMFCs at the same value of internal resistance (see Figure 5). These assumptions have to be proved later by further study.

To discuss more about internal resistance, the result of polarization experiment (Figure 2) was taken into account. According to Figure 3, SMFC3 had the highest internal resistance during the first 4 hours with electrical current of less than 0.0001 A (activation loss region). At that moment, SMFC1 and SMFC2 was in ohmic loss region with electrical current of 0.0001-0.00012 A, and the order of internal resistance was SMFC1<SMFC2<SMFC3 (Figure 3) which was the same as those in polarization experiment (Figure 2). But after the 4st hour, electrical current produced by SMFC2 reduced remarkably, and became in range of 0.00001-0.00004 A after the 28st hour (Figure 3) which was lower than the case of activation loss in the polarization experiment (Figure 2). Electrical currents of SMFC1 and SMFC2 also reduced after the 4st hour but were still in the range of 0.00004-0.00008 A at the 120th hour (Figure 3) which were counted among the range observed in the polarization experiment (Figure 2). This created special condition in SMFC2 that resulted in very high internal resistance during 4-120 hr. operation period. The special characteristic of SMFC2 was also observed in the estimated functions demonstrating the relationship between internal resistance and power density in Figure 5. According

to the graph, the line of SMFC1 and SMFC3 were almost in the same trend while the line of SMFC2 was obviously located in the separated region.

Comparing power densities of SMFCs in this study (19.8-37.3 mW/m^2, see **Table 1**) to other researches, they were higher than those of Wang et al. (3.97 mW/m^2) [25] and Sherafatmand & Ng (4-6 mW/m^2) [26]; comparable to those of Khater et al. (52 mW/m^2) [27]; and lower than those of Lv et al. (332.2-628.1 mW/m^2) [28].

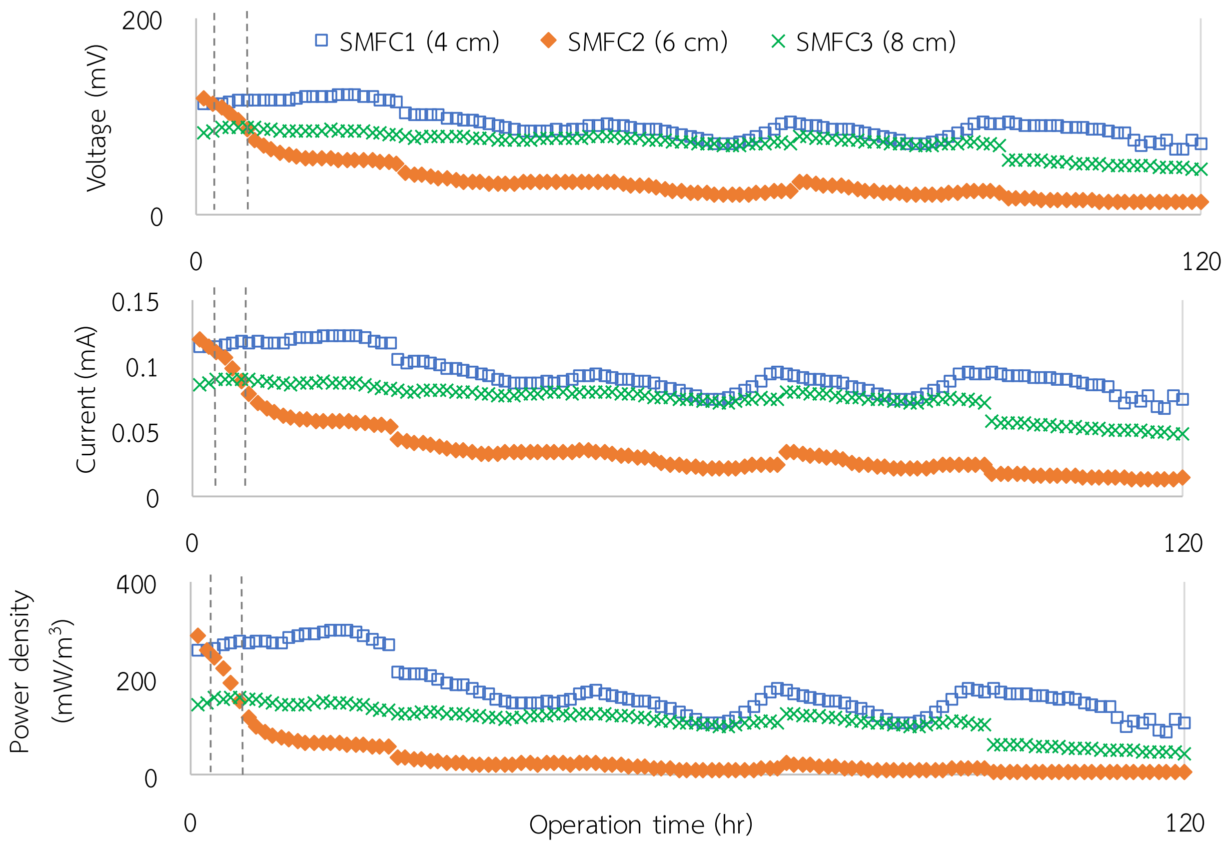

Figure 3 Voltages, currents and power densities of SMFCs during 120-hr operation

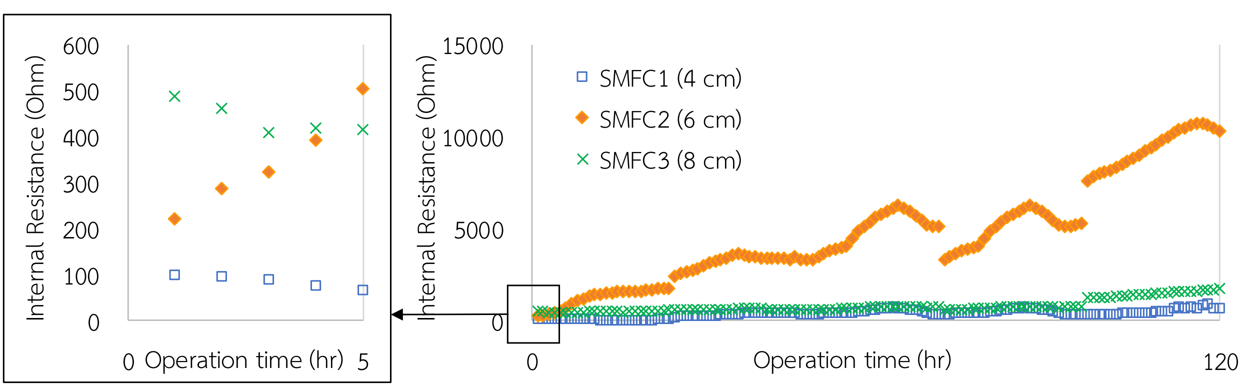

Figure 4 Internal resistance of SMFCs during 120-hr operation

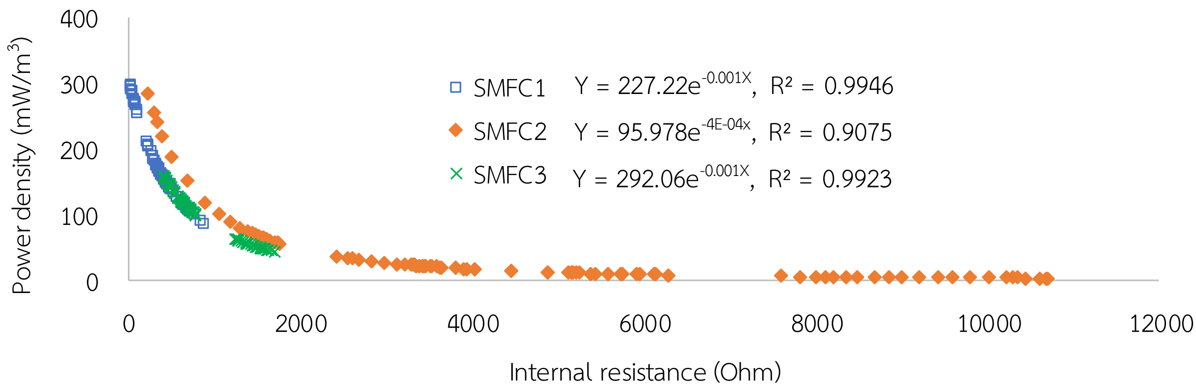

Figure 5 Relationship between internal resistance and power densities produced by SMFCs during 120-hr Operation

Wasted sludge removal

Wasted sludge with contents of 904.4-gTS/L TS and 734.0-gVS/L VS digested itself through SMFC process. After 120-hr operation, VS contents of SMFC1, SMFC2 and SMFC3 reduced to 483.71 gVS/L, 505 gVS/L, and 497.17 gVS/L, respectively. Sludge removal efficiencies and removal rates were calculated in the terms of VS, i.e., 34.10% and 2.502 gVS/day for SMFC1, 31.20% and 2.290 gVS/day for SMFC2, and 32.27% and 2.368 gVS/day for SMFC3. This result indicated SMFC1 as the fastest sludge digester, following by SMFC3 and SMFC2, respectively.

Figure 6 demonstrates the direct-variation relationship between total wasted sludge removal (gVS) and total electrical energy produced (mWhr) during 120-hr operation. It is possible that high electrical energy which refers to high power generation enhances the sludge digestion of SMFCs.

Table 1 Performance of SMFCs during 120-hr operation (* refers to standard deviation)

Parameters	SMFC1	SMFC2	SMFC3
Distance from anode to cathode (cm)	4.0	6.0	8.0
Max voltage (mV)	122.06	113.01	89.10
Max current (mA)	0.1221	0.1193	0.0891
Max Power (uW)	14.899	14.243	7.938
Max power density by volume (mW/m^3)	297.97	284.87	158.77
Max power density by anode area (mW/m^2)	37.25	25.61	19.85
Average electrical power (μW)	8.7±2.9*	1.6±2.5*	5.5±1.6*
Average electrical power density (mW/m^3)	174.72±58.42*	32.66±50.42*	109.03±31.85*
Average electrical power density (mW/m^2)	21.84±7.30*	4.08±6.30*	13.63±3.98*
Total electrical energy produced during 120 hours (mWhr)	1.048	0.196	0.654
Wasted sludge removal rate (gVS/day)	2.502	2.290	2.368
Total wasted sludge removal during 120 hours (gVS)	12.51	11.45	11.84
Electricity Generation Yield (μWhr/gVS)	83.77	17.11	55.24

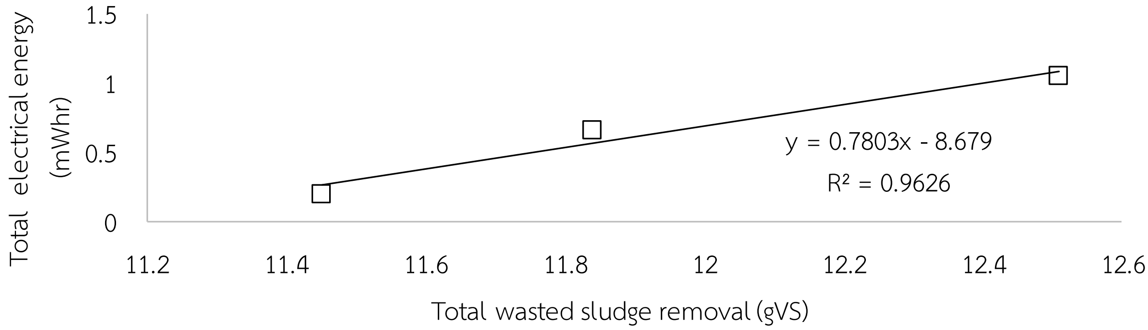

Figure 6 Relationship between total wasted sludge removal and total electrical energy produced by SMFCs during 120-hr operation

As electrons were well transferred during the state of high-power generation, the digestion reaction in an anode chamber should be expedited. Therefore, the sludge removal rates, sludge removal efficiencies, as well as total digested sludge varied directly towards the total produced electrical energy. As a cycle, the increase of digested sludge could then multiply numbers of released ions which resulted in the increase of energy production. Electricity generation yield (EY) of SMFCs were in the range of 17.1-83.8 μWhr/gVS as shown in Table 1. SMFC1 with 4-cm electrode space was found to have the highest EY of 83.8 μWhr/gVS.

Conclusion

Low-cost SMFCs in this research removed 31-34% of wasted activated sludge with 2.290-2.502 gVS/day removal rate for 120-hr operation. They generated 0.2-1.0 mWhr electrical energy with maximum power densities of 19.9-37.3 mW/m^2 as by-product of the process. Every 1 gVS of removed wasted sludge resulted in the generation of 17.1-83.8 μWhr electrical energy. The relationship between electrode space and internal resistance of SMFC during digestion was divided into 2 cases. During 1-4 hr. operation period, the internal resistance varied directly with electrode space, i.e., 4 cm<6 cm< 8 cm, which induced power density to be in the opposite order of 8 cm<6 cm< 4 cm. But at 4-120 hr. operation period, the order of internal resistance changed into 4 cm<8 cm< 6 cm which led the power density to be in the order of 6 cm<8 cm< 4 cm. Obviously, SMFC with electrode space of 4 cm exhibited the highest performance in both cases (37.3 mW/m^2 power density, 2.502 gVS/day removal rate). However, SMFC with electrode space of 6 cm generated highest power density at the first hour of the operation. It also showed higher power density than other 2 SMFCs at the same internal resistance value. Further study, such as an insertion of pretreatment before SMFC operation is required to optimize the electrode space for harvesting higher power output. In terms of sludge removal, SMFC with electrode space of 4 cm had the highest removal efficiency (34.10%), following by the cases of 8 cm electrode space (32.27%) and 6 cm electrode space (31.20%), respectively. SMFC's sludge removal ability appeared to be consistent with its ability of electrical generation during 4-120 hr. operation period.

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