ENHANCED METHANE PRODUCTION USING AN INTEGRATED ANAEROBIC DIGESTION AND BIOELECTROCHEMICAL SYSTEM

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ABSTRACT

Energy sustainability is becoming an integral part of New Zealand's society as the country is moving towards carbon-neutral approaches and a net-zero carbon emissions target by the year 2050. In particular, through decarbonisation of energy and industry emission. As a result, many industries, such as dairy producers, have pledged to change their energy source from fossil fuel to renewables and biomass energy. Biomethane via waste-to-energy is a potential source of renewable energy that can be produced on-site and can replace the coal and petrol used in industry.

Anaerobic digestion (AD) is a well-known technology that have been used world-wide for wastewater treatment as well as biogas production. Anaerobic digestion not only treats wastewater but also generates renewable gas that can be used for heating and electricity generation. Biogas composition can vary depending on the source of wastewater; however, in general, biogas contains 50-60% methane gas, and the rest is mainly carbon dioxide.

The ability to convert waste to valuable energy, as well as treat wastewater, makes anaerobic digestion an interesting process for industries and local government. However, due to the relatively low methane content of the biogas, there is interest for studying ways to improve AD performance in terms of methane output. In this regard, bioelectrochemical systems have been introduced as a potential means of improving biogas composition as well as improving the treatment process. The aim of this research is to study the potential of a bioelectrochemical system integrated to an anaerobic digester to improve methane production efficiency.

Results show that the integrated system does improve the performance of the anaerobic process including higher biogas methane content, COD removal, and solids removal. Methane yield is improved by 17.5% compared to an anaerobic digester alone. COD removal is also improved by 7.3 % while less solids were produced in the integrated system. The results show that integrated AD with bioelectrochemical systems can lower the carbon dioxide content of the biogas and provide a high calorific source of energy obtained from waste.

KEYWORDS

Renewable Energy, Microbial Electrolysis Cell, waste-to-energy

PRESENTER PROFILE

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INTRODUCTION

The world is moving towards a net zero carbon economy and countries have pledged to reduce carbon emission by 2050. New Zealand is amongst the countries that has an emission reduction target to reach net zero emission of all GHG other than biogenic methane by 2050 (MfE, 2022). In New Zealand, energy use accounts for 40% of the country's greenhouse gas emissions. This comprises of burning fossil fuels, producing electricity and travelling by plane or driving petrol cars for a short trip. It is therefore important to implement more renewable energy sources and decarbonise the use and production of energy (EECA, 2022).

To reach the goal of net zero greenhouse gas emission, the future energy scenario modelling in New Zealand shows that by 2050 the demand for fossil fuels must be halved, as such more renewable sources of energy must be implemented for production of heat and power (EECA and BEC, 2021). Waste-to-energy has shown that it can contribute to the path towards net zero carbon as not only it can minimise the waste management and its handling but also it can create renewable fuels. In this direction, anaerobic digestion is an effective means for valorisation of waste and producing renewable energy (WBA, 2021).

The world biogas association (2021) highlights the potential of anaerobic digestion as a technology to generate renewable energy, abate GHG emissions as well as the role it can play in meeting the waste/wastewater management. Anaerobic digestion can capture and store methane that would otherwise escape to the atmosphere from the degradation of food waste, sewage, and agricultural wastes. Instead of escaping to the atmosphere to negatively contribute to climate change, this methane can be captured and used as a source of renewable energy. However, we are currently harnessing only 2 % of the global potential. In 2019, there were only 18,943 biogas plants and 725 biomethane plants across Europe (EBA Statistical Reports, 2019).

BIOGAS POTENTIAL IN NEW ZEALAND

New Zealand has a history of using biogas since the 1970's when the global oil crisis forced the country to investigate local energy sources. New Zealand started looking into localising energy production by implementing more renewable energy sources. As a result, 16 agricultural biogas plants were installed on farms for biogas production making New Zealand a pioneer in adaptation of biogas in the world which inspired some European countries to follow the lead (EECA and Beca, 2020). However, the focus shifted away from AD plants with a change in

government in the following years and resulted in less focus on biogas plant nationwide.

To date, the majority of New Zealand's biogas generation occurs at wastewater treatment plants (WWTPs), a few private companies like Fonterra (at their Tirau and Darfield sites), small piggeries and from landfill gas capture operations. The most recent biogas plant is the one at Reporoa. The construction of this plant is underway and it will be New Zealand's first large scale food waste to bioenergy plant in New Zealand. This plant will have the capacity to power up to 2500 households in the region. Other products of this plant will be providing enough CO_2 and heat for local glasshouses to grow tomatoes. EECA estimated that New Zealand has a biogas production capacity of 12.6 – 16.9 PJ/year with the feedstock consists of food waste, municipal wastewater, industrial wastewater, agricultural waste. However, only 0.6 PJ/year is being produced.

ANAEROBIC DIGESTION

Anaerobic digestion (AD) occurs in four stages, via biological reactions involving a mixed culture of microbial communities. AD consists of hydrolysis, acidogenesis, acetogenesis, and methanogenesis. Anaerobic digestion can valorise energy embedded in organic wastes such as food waste, animal waste, wastewater treatment sludges, crop residues, and organic-loaded industrial waste.

The last stage of anaerobic digestion involves methanogenic reactions driven by acetoclastic methanogens and hydrogenotrophic methanogens which uses acetic acid and hydrogen, respectively, to produce methane gas. Figure 1 shows the stages of the AD process and the product of each stage. Methanogens are usually slow growers that cause the AD to suffer from VFA accumulation when the digester is overloaded, high HRT when the digester is completely mixed (HRT=SRT), and instability of AD systems.

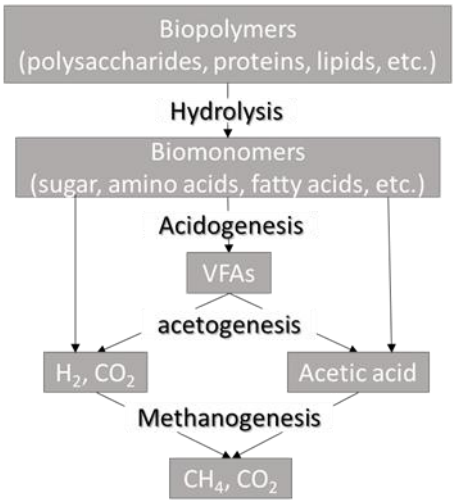

Figure 1 Anaerobic digestion process

The resultant biogas mainly consists of methane and carbon dioxide and, depending on the type of biopolymer (i.e., substrate), the methane content of the biogas can vary (Persson, Jönsson et al. 2006). Table 1 represents biogas yield and methane content of AD depending on the carbon source used in the process.

Table 1 methane content and yield as a function of carbon source in AD (adapted from Wllinger, 2006)

Substrate	Biogas yield (L/kg VS)	Methane content (%)
Fat	1000-1250	70-75
Protein	600-700	68-73
Carbohydrate	700-800	50-55

Several new technologies including microbial electrolysis cells (MECs) have been considered to improve the efficiency of conventional anaerobic digesters. MEC is a technology related to microbial fuel cells (MFCs). While MFCs produce an electric current from the microbial decomposition of organic matter, MECs is the process of producing hydrogen or methane from decomposition of organic matter by applying an electric current for microorganisms. The following section explains the MEC process.

MICROBIAL ELECTROLYSIS CELLS (MEC)

Microbial electrolysis cell is a derivative of microbial fuel cell where all the reactions happen anaerobically. The difference between these two systems is that in MEC, due to absence of oxygen, the reactions do not occur spontaneously therefore an external voltage is required to drive the reaction for degradation of the organic matter into renewable energy (CH_4).

MEC consists of a pair of electrodes (cathode and anode) where an external source of energy drives the anodic and cathodic reactions. The degradation of organic carbon compound occurs in the anodic area (or anodic chamber in the 2 chamber MEC) and the produced electrons travel via the closed circuit from the anode to the cathode. Concurrently the produced protons travel in the bulk towards the cathode. Finally, at the cathode, the electrons and protons along with carbon dioxide react to produce methane gas. Figure 2 shows reactions that occur in an MEC.

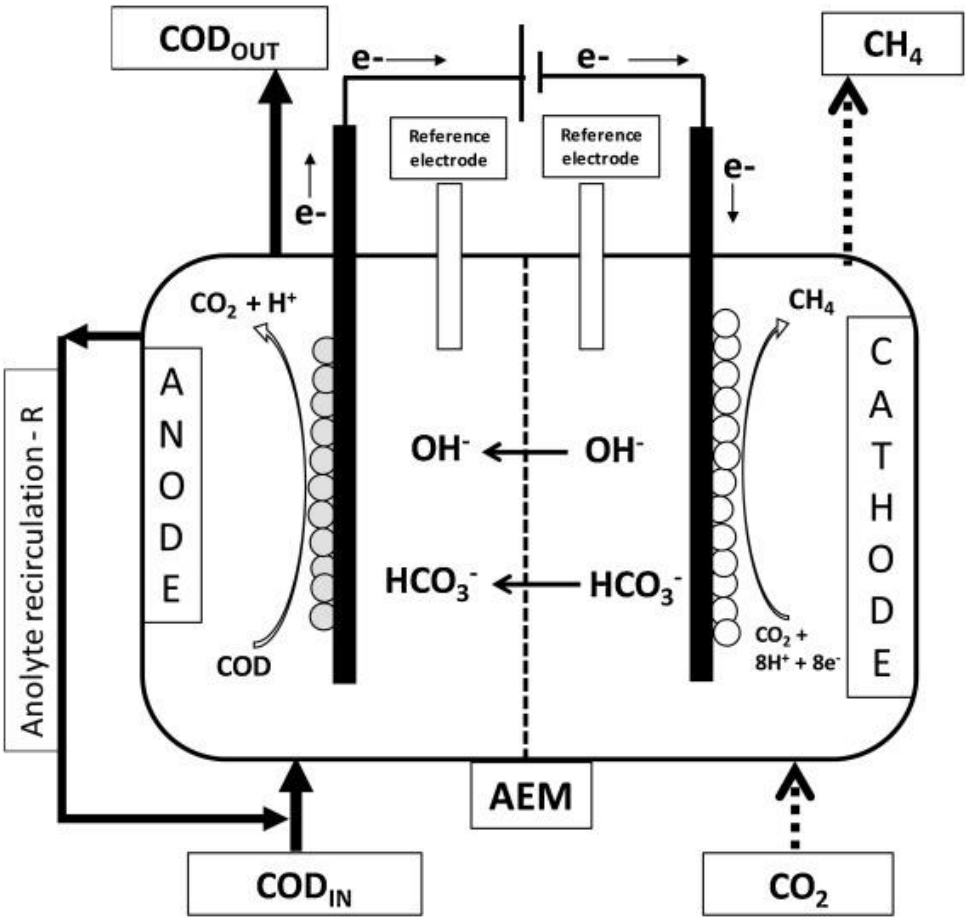

Figure 2 MEC reactions (adapted from Zeppilli et al., 2019)

Bioelectrochemical methane production in MEC uses additional energy (external voltage) to support the degradation of organic material and to facilitate electron transfer between the microorganisms and the substrate, making electron flow from electrodes easier. It has been noticed that homoacetogens and hydrogenotrophic methanogens drive the metabolic reactions, and direct methanogenesis via methanogenic archaea are the main reactions in MEC (Table 2).

In MEC, methane production occurs via methanogens that usually belong to acetotrophs and hydrogenotrophic methanogens. One chamber MEC plays an important role in methane production and anaerobic degradation of organic waste as this approach produces a renewable fuel that is easy to store, compress and transport.

The objectives of this study were to determine the stability and methane production improvement of a MEC-assisted anaerobic digestion system. Glucose was used as a model substrate since it has a high energy content and it is readily biodegradable, so it can upset the stability of the AD system via immediate production of VFAs.

Table 2 Anaerobic reactions and the microorganisms involved

Stage	Reaction	Microorganisms involved
Stage 1 Hydrolysis	$(C_6H_{10}O_5)_n + nH_2O = n(C_6H_{12}O_6)$	Clostridium, Proteus, Vibrio, Bacillus, Peptococcus, Bacteriodes, Staphylococcus
Stage 2 Acidogenesis	$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH+4H_2+2CO_2$ $C_6H_{12}O_6 + 2H_2 \rightarrow 2CH_3CH_2COOH +2H_20$ $C_6H_{12}O_6 \rightarrow CH_3CH_2CH_2COOH + 2H_2 + 2CO_2$ $C_6H_{12}O_6 \rightarrow 2CH_3CH_2OH + 2CO_2$ $C_6H_{12}O_6 \rightarrow 2CH_3CHOHCOOH$	Lactobacillus, Escherichia, Bacillus, taphylococcus Pseudomonas, Sarcina, Desulfovibrio, Selenomonas, Streptococcus, Veollonella, Desulfobacter, Desulforomonas, Clostridium, Eubacterium
Stage 3 Acetogenesis	$CH_3CH_2OH + H_2O \rightarrow CH_3COOH +2H_2$ $2\ CH_3CH_2OH + CO_2 \rightarrow CH_4 +2\ CH_3COOH$ $CH_3CH_2COOH +2\ H_2O \rightarrow CH_3COOH +3H_2+CO_2$ $CH_3CH_2CH_2COOH +2\ H_2O \rightarrow 2CH_3COOH+2H_2$ $CH_3CHOHCOOH+ H_2O \rightarrow 2\ CH_3COOH+ 2H_2+CO_2$	Clostridium, Syntrophomonas
Stage 4 Methanogenesis	$CH_3COOH \rightarrow CH_4+ CO_2$ $CO_2 +4H_2 \rightarrow CH_4 + 2H_2O$	Methanobacterium, Methanobrevibacter, Methanoplanus and Methanospirillum

MATERIAL AND METHODS

A microbial electrolysis cell coupled with anaerobic digestion and two anaerobic digesters were prepared using 3-L glass bottle reactors with a working volume of 1.5 L each. The reactors were inoculated with digestated sludge obtained from mesophilic anaerobic digesters at the Christchurch Wastewater Treatment Plant. The reactors were prepared with anaerobic medium to provide nutrients and minerals for microbial growth according to Angelidaki et al. (2004). The carbon source used in this experiment was glucose with a concentration of 15 g/L and an organic loading rate of 0.5 g COD/L reactor.day. This resembles a high strength and easily degradable waste.

The microbial electrolysis cell was equipped with 3 sets of electrodes; the cathode was made of carbon cloth with 5% Pt and the anode was made of carbon brush.

The external voltage was controlled at 0.5 V using a power supply, and the current generation was monitored via a data acquisition system continuously logging the data on a computer connected to the system.

The reactors were mixed continuously using a magnetic mixer and kept in a temperature-controlled room at 37.5 ℃. The systems were fed semi-continuously once every day with glucose as the carbon source along with nutrients to keep the COD:N:P at a ratio of 250:5:1.

Biogas production was continuously measured using a gas flow meter connected to the gas port of the reactor. The biogas was then collected in 1-L Tedlar bags for further analysis.

The conventional anaerobic digesters and the MEC were regularly monitored by analysing the influent and effluent samples on a daily basis for pH, and weekly for total suspended solids (TSS), volatile suspended solids (VSS), soluble chemical oxygen demand (sCOD), and volatile fatty acids (VFA). All analyses were done according to standard methods (APHA 2005).

Fifty-mL samples were collected from the effluent port of the reactors for VFA analysis. Samples were then filtered through a 0.22 µm filter and acidified with phosphoric acid to a pH around 2 before analysis. A gas chromatograph (Nexis GC-2030, Shimadzu, Japan) equipped with a flame ionization detector and a capillary column (30 m × 0.25 mm ×0.25 µm; HP-INNOWAX USA) was used to measure VFAs in mg/L (i.e. acetic acid (HAc), propionic acid (HPr), and butyric in the iso or n-butyric acid forms (HBu)).

Biogas composition was analysed with a gas chromatograph fitted with a thermal conductivity detector (Agilent 7820A, China). The setup of the GC-TCD method is as follows: Agilent 19095P-Q04 stainless steel column with 30 m× 530 µm× 40 µ; Helium carrier gas 10 mL/min with pressure 10.6 psi, oven temperature 30 °C; injector temperature 70°C; TCD temperature 155°C. The retention time for standard nitrogen (10%) methane (60%) and carbon dioxide (30%) was 1.44, 1.591 and 2.123 min.

RESULTS AND DISCUSSION

DAILY METHANE PRODUCTION

Daily methane production was monitored in all the reactors and the results showed that the MEC reactor produced more methane than the conventional anaerobic digesters (Figure 3). The daily methane production at the voltage of 0.5 V was 17.9% higher than the conventional ADs (228.2 mL methane/day compared with 193.6 mL methane /day). Choi, Kondaveeti et al. (2017) found similar results in their study on batch MECs for degrading glucose and methane production at various voltage levels. Their results showed approximately 12% improvement in daily biogas production when a 0.5 V was applied on the system compared with

their control. The current experiment has been running over several months;

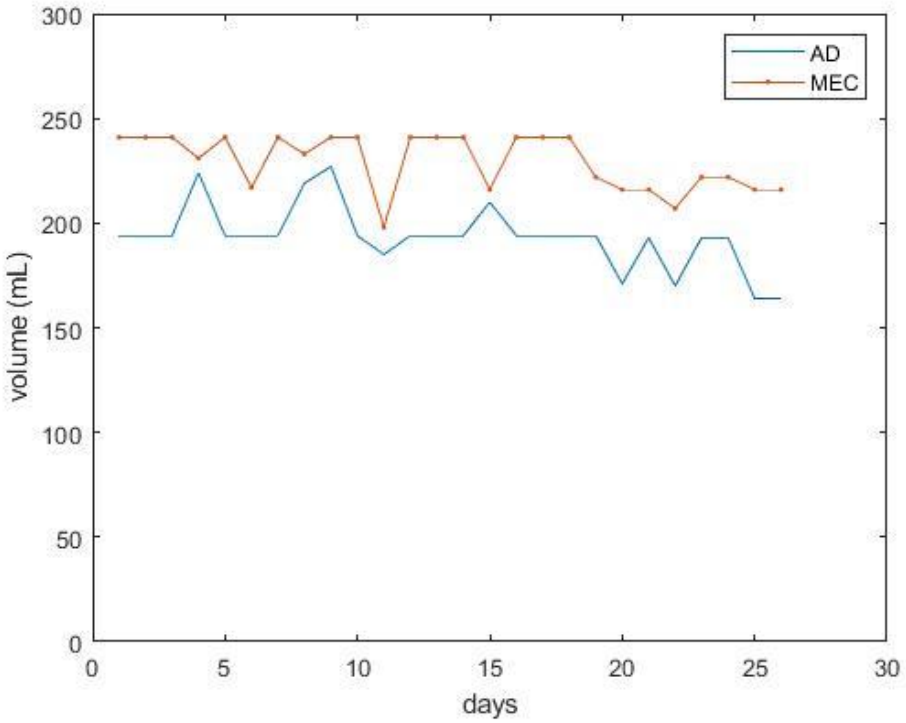

Figure 3 shows the daily methane production monitored over a selected month during the course of the experiment.

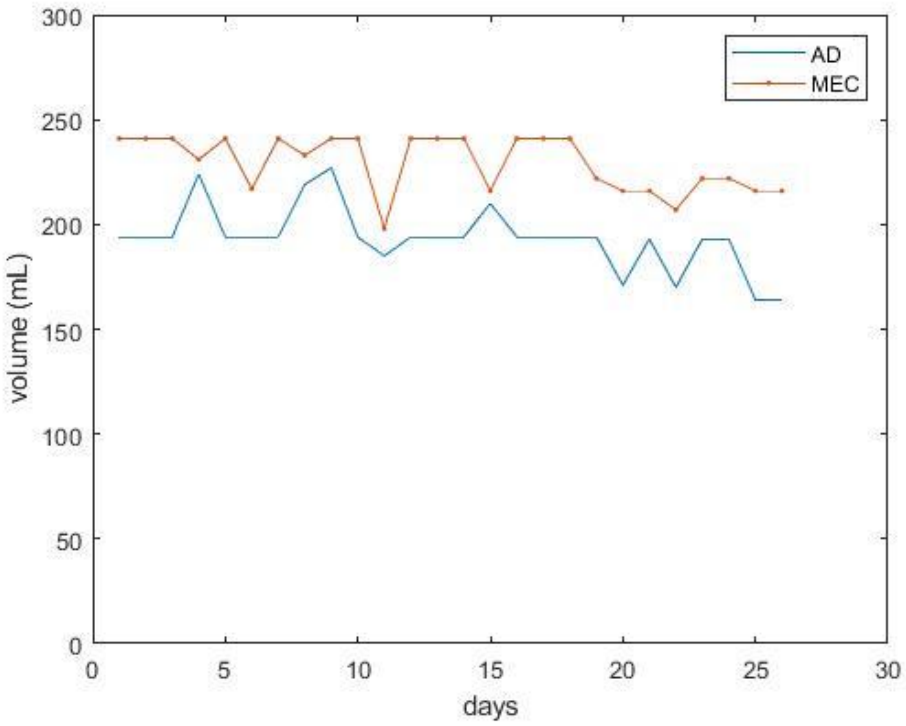

Figure 3 daily methane production in the MEC and AD reactors

BIOGAS METHANE CONTENT

During the course of the experiment, the MEC produced biogas with a more consistent methane content than the conventional ADs. Methane content in the biogas from the MEC reactor was higher (58%) than that of the AD reactors (50%) (Figure 4). Gajaraj et al. (2017) found similar methane content of biogas when they used glucose as the substrate for running MEC reactors at voltages of 0.3 and 0.6 V.

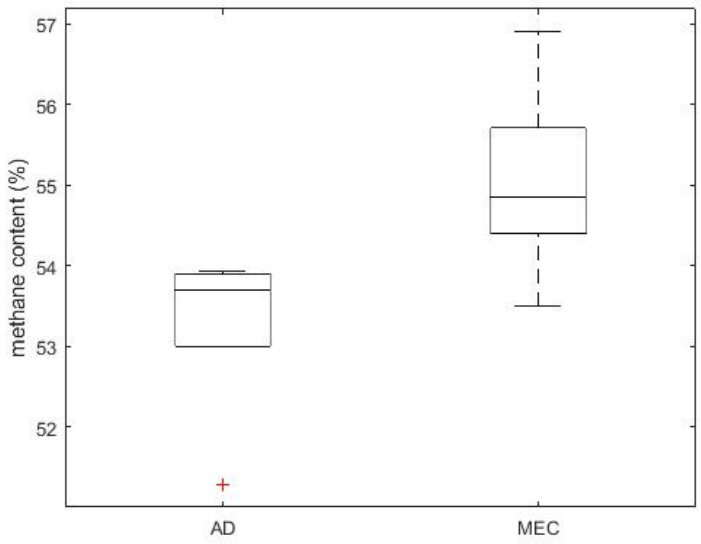

Figure 4 Methane content of biogas in the AD and MEC reactors

METHANE YIELD

Methane yield was assessed by fitting the modified Gompertz model to experimental data. The results showed that methane yield was higher in the MEC reactor compared to the AD reactor. The specific methane yield was improved by 17.5 % in the MEC reactor compared with the conventional AD reactor the results are also in agreement with the findings of Flores-Rodriguez, Nagendranatha Reddy et al. (2019). **Error! Reference source not found.** shows modified Gompertz model fitted to the methane production in one feeding cycle of the reactors.

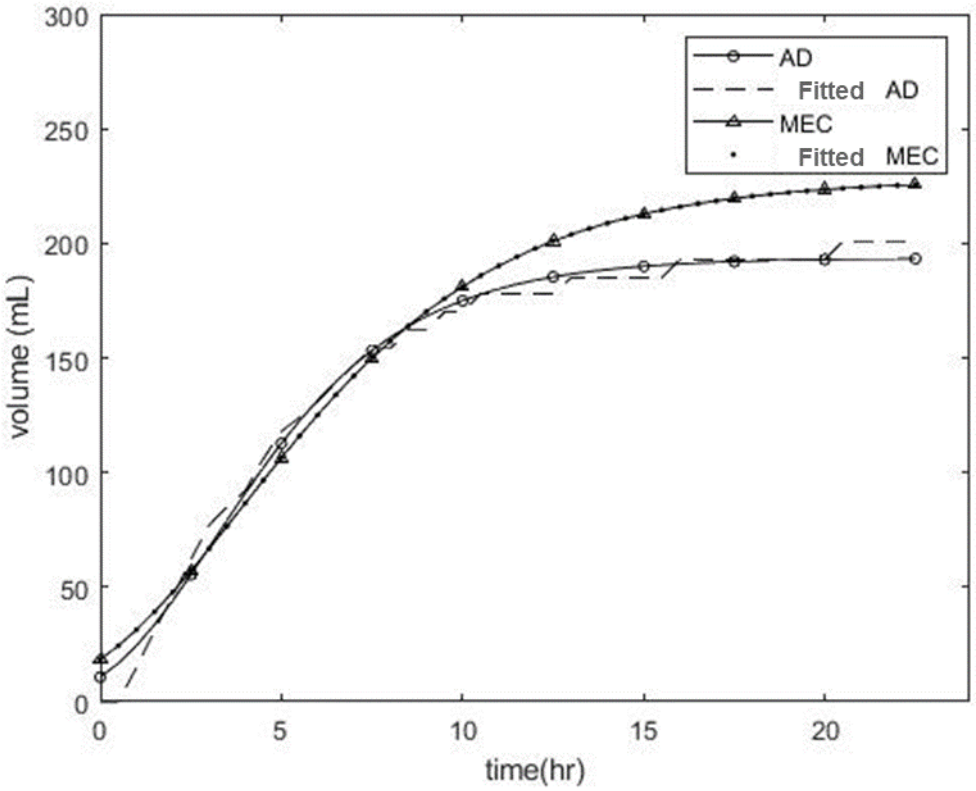

Figure 5 methane production in one feeding cycle (24hr)

The modified Gompertz model suggests that the AD reactor has a slightly faster approach to degrade the glucose (**Error! Reference source not found.**) and slower VFA utilisation, which is in agreement in the accumulation of more VFAs in AD in the first hours of feeding the reactors . However, MEC has a greater capacity for converting the produced VFA to methane gas (Logan et al., 2008). According to Lee et at. (2017) MEC reactors activate acetoclastic methanogens, which results in higher methane productions. Kinetic parameter values from fitting the modified Gompertz model to experimental data are presented in **Error! Reference source not found.**.

Table 3 modified Gompertz model parameters

	P (maximum methane yield, mL)	R (rate, hr^{-1})	L (lag phase, hour)	R^2
AD	193.6	23.8	0.19	0.991
MEC	228.2	20.0	-	0.991

VOLATILE SUSPENDED SOLIDS

All reactors (MEC and conventional AD reactors) were prepared with the same inoculum (digestated sludge). The initial concentration of microorganisms, represented by mass of volatile solid in the reactor (VSS), were similar in the MEC and AD reactors. However, after running the reactors for several months, the VSS reduced to 1208 mg/L for the MEC reactor and 1500 mg/L for the AD reactor. Lower VSS in the MEC reactor can be explained due to some of the biomass growing on the surface of the electrodes rather than in the bulk of the reactor. MEC has also shown greater removal of volatile suspended solids. A study carried out using MEC-assisted anaerobic digestion showed that volatile solids removal was approximately 10% higher in the AD-MEC reactor compared with AD reactor (Lee et al., 2017). The results of their study are similar to what has been found in the current study where MEC showed lower VSS in the effluent compared with the conventional AD.

COD DESTRUCTION, pH, AND VFA

A high-strength substrate was used to represent a carbohydrate-rich and readily biodegradable waste. As such, a synthetic waste with a high COD value of 15 g/L was used with an organic loading rate (OLR) of 0.5 g COD/L.day and COD conversion rate was calculated at the end of each feeding cycle.

Effluent COD was measured to be lower in the MEC reactor than the AD reactor hence a higher COD destruction rate was obtained in the MEC reactor. This can be explained by enrichment of electroactive microorganisms by polarised electrodes in the MEC reactor which promotes greater COD destruction in the MEC (Feng et al., 2022).

The results showed that MEC can improve COD destruction rate as the effluent COD was 7.25 % lower than the AD. Figure 6 below shows the effluent COD concentrations in the MEC vs. conventional AD.

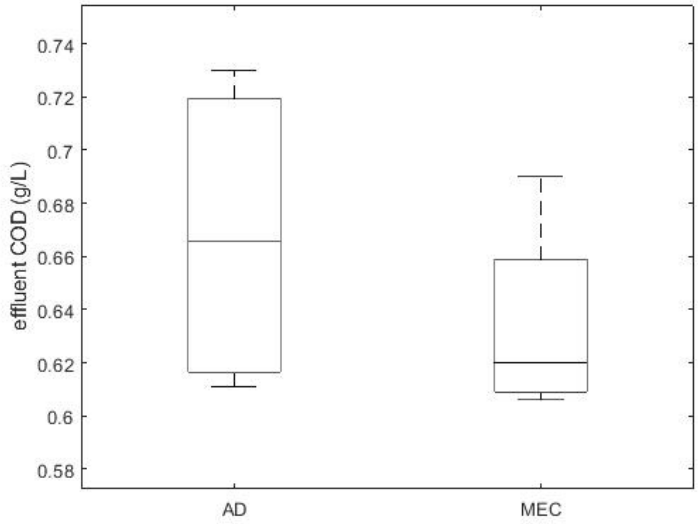

Figure 6 Effluent COD in the MEC and AD reactors

The pH in the reactors was monitored daily. While the AD reactors' pH fluctuated largely over the course of the experiment and during each feeding cycle, the MEC showed very stable pH levels. It was observed that a minor upset in the operation parameters had an adverse effect on the pH of the conventional AD, whereas the MEC's pH remained at a constant level of 6.7 during the experiment. The pH in this study was kept slightly below the pH range suitable for AD reactors (i.e., 6.8 -7.8) to examine the capability of the reactors in handling easily biodegradable wastes and rapid VFA production in the systems.

Similar to the COD destruction rate, VFA destruction rate was also higher in the MEC reactor. In most cases there was no propionic acid or butyric acid found in the effluent of the reactors. However, acetic acid was found in the effluent of the AD reactor, which suggests less process stability in the AD reactors where the acid production rate was not in line with acid consumption rate via methanogenic activity in the AD. These results compare well with those reported by Feng et al. (2022) where VFA accumulation was observed in the AD reactors. Figure 7 shows the effluent VFA concentration (acetic acid) in the effluent of the reactors.

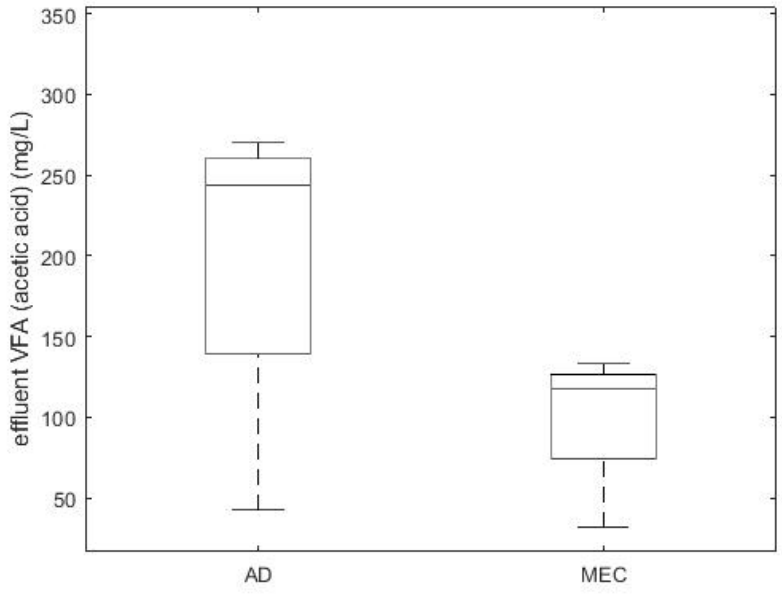

Figure 7 Effluent VFA (acetic acid) in the MEC and AD reactors

CONCLUSIONS

The methane production of a system consisting of a microbial electrolysis cell (MEC) and anaerobic digestion (AD) in a single reactor was evaluated. The MEC-assisted anaerobic digester had a methane production 17.5% higher than that of a conventional anaerobic digester. It also showed a greater process stability compared with conventional anaerobic digestion. The results of our study suggest that the performance of an anaerobic digester, such as substrate degradation rate, process stability and drifting due to system upsets, can be improved with the assistance of a MEC at a voltage as low as 0.5 V. The external energy requirement can be provided with renewable energy systems such as Microbial Fuel Cells (MFCs).

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