INCREASING METHANE YIELD DURING ANAEROBIC DIGESTION BY AN OUTSIDE INTEGRATED MICROBIAL ELECTROLYSIS CELL

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ABSTRACT. An integrated anaerobic reactor-microbial electrolysis cell system has been created, which has been moved out of the reactor volume. This has several advantages over the one integrated inside the anaerobic reactor: it does not disturb the working volume and is easier to operate and control. The kinetics of biogas production was monitored by comparing the data obtained from the hybrid system and the stand-alone anaerobic reactor. The results show an increased methane yield (from 75 to 88 %), better biodegradability of organic matter (from 66 to 89 %), and purification of ethanol stillage from sulphates in the integrated system (from 860 mg/l to <1 mg/l). In addition, the process of generating biogas in the hybrid system is more stable.

Key words: biomethane, microbial electrolysis cell, anaerobic digestion, ethanol stillage.

ПОВИШАВАНЕ ДОБИВА НА МЕТАН ПО ВРЕМЕ НА АНАЕРОБНО РАЗГРАЖДАНЕ ЧРЕЗ ИНТЕГРИРАНА ВЪНШНА МИКРОБНА ЕЛЕКТРОЛИЗНА КЛЕТКА

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РЕЗЮМЕ. Създадена е интегрирана система анаеробен реактор-микробна електролизна клетка, която е изнесена извън обема на реактора. Предимствата пред интегрирана в обема на анаеробния реактор са няколко – не се нарушава работният обем, процесът е по-лесен за работа и управление. Кинетиката на производството на биогаз беше наблюдавана чрез сравняване на данните, получени от хибридната система и самостоятелния анаеробен реактор. Резултатите показват повишен добив на метан (от 75 до 88 %), по-добра биоразградимост на органичната материя (от 66 до 89%) и пречистване на спиртната шлемпа от сулфати (от 860 mg/l до <1 mg/l) в интегрираната система. Освен това процесът на генериране на биогаз в хибридната система е по-стабилен.

Ключови думи: биометан, микробна електролизна клетка, анаеробно разграждане, спиртна шлемпа.

Introduction

The treatment of wastewater from various industries is an important step in protecting the environment. The ethanol stillage is a liquid waste obtained after ethanol distillation from alcoholic fermentation of starch-containing raw materials. It is a potential environmental pollutant because of its high acidity (low pH), organic load (COD), and sulphates, which disrupt soil structure and water quality. Due to the high content of reducing sugars and volatile fatty acids, it can be subjected to additional fermentation to generate bioethanol, but anaerobic digestion (in particular methanogenesis) would be most suitable for waste disposal because it also generates energy in the form of biogas (Choonut et al., 2015; Fuess and Garcia, 2015). The resulting biogas is a renewable energy source. After further purification of its methane from CO_2, H_2S, and other gases, it can be used for electricity and heat, as well as for automotive fuel.

In recent years, work has been done to optimise the process in order to reduce the cost of biogas treatment and increase methane production in it. One of the promising technologies is the integration of bioelectrochemical systems (BES) into the anaerobic reactor (Xie et al., 2021). They eliminate the disadvantages of conventional anaerobic digestion (AD), such as sensitivity to changes in environmental conditions, accumulation of volatile fatty acids, and others. CH_4 yield and biodegradability in AD remain low and in most processes only 50% to 60% of organic materials are converted to biogas, while the rest is converted to CO_2 and other intermediates.

In a microbial electrolysis cell (MEC), the organic substrate is oxidised by electrochemically active bacteria, which leads to the production of protons and electrons at the anode. Electrons are transferred to the anode surface by exoelectrogenic bacteria and protons are released into the solution. Thus, the electrons pass through the outer circuit to the cathode (Arvin et al., 2019). Previous studies have reported that applied voltages can increase COD removal, accelerate the conversion of volatile fatty acids, increase methane content, increase methane production, and maintain optimal pH levels for methanogenic growth (Guo et al., 2013). A hybrid AD-MEC system has high efficiency, low cost and is easier to operate. The MEC as a biosensor can be employed to monitor a biogas fermentation process by measuring a volatile fatty acids concentration (Yu et al., 2018).

Literature abounds in articles on integrated microbial fuel and electrolysis cells in the volume of an anaerobic reactor (Adekunle et al., 2019; Arvin et al., 2019; Bajracharya et al., 2017; Cerrillo et al., 2018; Cheng and Kaksonen, 2017; Logan and Rabaey, 2012; Pham et al., 2006), but there is no information on exported MECs outside the reactor volume.

This report presents an integrated microbial electrolysis cell outside the volume of an anaerobic digester and compares the biogas production kinetics between the AD-MEC hybrid plant and an unmodified stand-alone reactor.

Materials and methods

An integrated AD-MEC system outside the reactor volume

The scheme and photograph of a laboratory installation is shown in fig.1. The anaerobic reactor is made of stainless steel with a working volume 5 dm^3. Graphite plates measuring 100 × 100 × 6 mm were used for the electrodes. Recirculation pumps moved the flow. Biogas was collected in gas bags which were attached on the top of the anaerobic reactor. The cathode and anode electrodes were connected to the power supply, with an external resistance of 10 Ω.

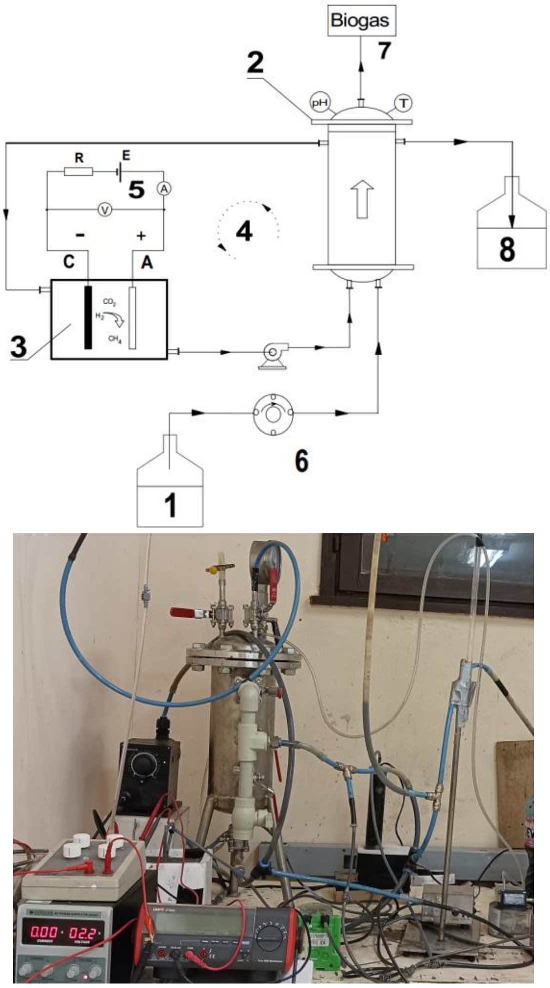

Fig. 1. The technological scheme and photograph of an integrated AD-MEC system.

Legend: 1- substrate input, 2-anaerobic reactor bioreactor (UASB), 3-microbial electrolysis cell (MEC), 4-recirculation flow, 5-load chain of the MEC, 6- substrate inlet pump, 7-biogas, 8- reactor outlet.

It was proved that the supplied voltage had positive effects on COD removal. Microorganisms can be inhibited when exposed to high electrical potential (> 1.0 V). Results indicated that the higher voltage (> 0.8 V) led to lower growth rate, lower metabolic activity, decrease of COD removal efficiency and methane yield. In conclusion, the optimal applied voltage for wastewater treatment was 0.8 V. Information provided will be useful to design a reactor and maintain industry practice (Ding et al., 2016). Ding et al. found that COD removal efficiency increased at 0.8 and 1.0, but it was more economical to apply 0.8 V due to costs. Therefore, we apply 0.8 V to the AD-MEC system.

Wastewater and activated sludge

Wastewater (ethanol stillage) was obtained from an ethanol plant in the village of Svetovrachene, Bulgaria. After obtaining the ethanol stillage, it was stored in a cool place at 4°C. Before using it, the wastewater was neutralised to pH 7.5 with NaOH.

The activated sludge was taken from a working methane tank in “Almagest”, the village of Verinsko, Bulgaria.

Analytical methods

Chemical oxygen demand (COD) was measured with a Hanna instruments kit. The contents of CO_2, CH_4, H_2S, and H_2 in the generated biogas were measured using a portable "Draeger X-am 7000" gas analyser. The biogas production was measured by Milli-gascounter MGC-1, Ritter. The sulphate concentration was determined employing the spectrophotometric method at λ 420 nm with the use of $BaCl_2$ as a reagent. The pH was measured using a pH meter (Hanna instruments) and was maintained around 7 with a solution of NaOH.

Results and discussion

Fig. 2 shows a comparative graph between the kinetics of biogas production from an ethanol stillage in an anaerobic reactor with and without MEC. The inoculum represents 10% of the volume of the wastewater in the reactor. The process of biogas generation was monitored for 15 days in a continuous mode of wastewater supply. The composition of the biogas was measured daily and chemical analysis was periodically performed - determination of COD and sulphates at the inlet and outlet of the installation, dissolved hydrogen sulphide in the liquid phase leaving the reactor.

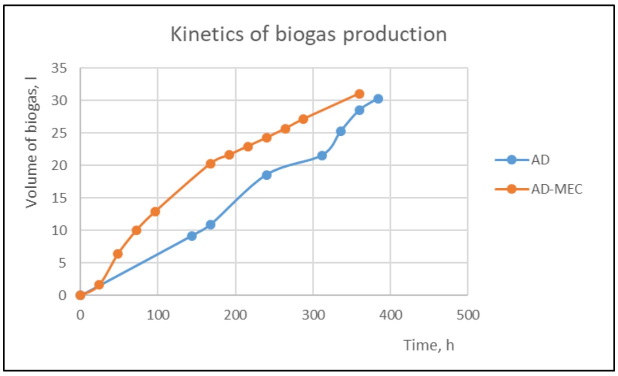

Fig. 2. Comparison between the kinetics of biogas production in an anaerobic reactor with and without MEC

As can be seen from the graph (fig. 2), in the combined AD-MEC system on the 7th day (168th hour), the biogas produced is almost twice as much as in the anaerobic reactor without MEC - 20 and 11 litres respectively. Then, the kinetics begins to slow down and equalise with that in a system without MEC, reaching a point of intersection after the 15th day (360th hour) - around 30 l. It is also noted that the process of generating biogas from the hybrid system is more stable than in a process without a MEC.

In fig. 3, the gas composition of the produced biogas in both modes is shown. The methane production has increased from 75 to 88 % with the integration of a MEC into the reactor. The methane generated in the course of 15 days is 21.392 l in a system without a MEC and 27.320 l in an AD-MEC system. The CO_2 content decreases from 4,848 l to 3,105 l after external voltage application, and along with hydrogen, they are converted into methane. Hydrogen sulphide disappears in the AD-MEC system, unlike the presence of 0.048 l in AD without a MEC. Also, hydrogen is measured as 1.140 litres in a system without a MEC, while when an external voltage is applied, it disappears. So, with the AD-MEC system, CO_2 and H_2 have been converted to methane.

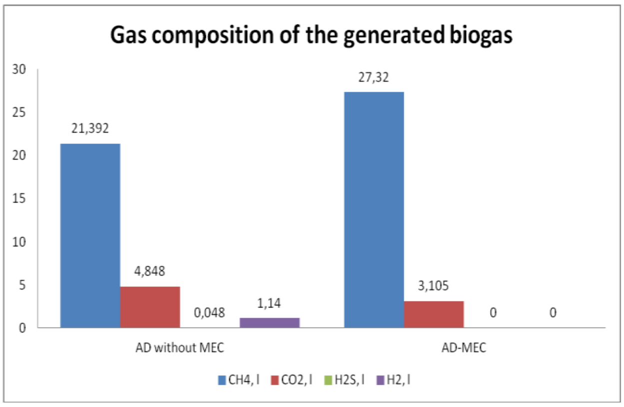

Fig. 3. Gas composition of the biogas generated from AD-MEC and AD-only systems

In table. 1, data on COD and sulphates at the entrance and exit of the installations are given. The data show that the biodegradability of organic matter (from 66 to 89 %) and the purification of ethanol stillage from sulphates (from 860 to <1 mg/l) in the integrated system has increased. H_2S in liquid phase is <1 mg/l at the outlet of the integrated system vs. 300 mg/l in an AD-only system. This means that, in addition to increasing the methane content in biogas, the ethanol stillage has been successfully purified from hydrogen sulphide. H_2S is a very dangerous, toxic and explosive gas. High concentrations of it are toxic to plants and inhibit their growth.

Table 1. *Characteristics of reactor inlet and outlet in two modes: with and without a MEC*

Parameters System	COD input, g/l	COD output, g/l	SO_4^{2-} input, mg/l	SO_4^{2-} output, mg/l
AD without MEC	99.44	34.08	847.45	450
AD-MEC	87.36	9.76	859.76	<1

The obtained results correspond to those obtained by Ding et al. (2016) at an internal MEC. COD removal efficiency and methane yield are better in a combined AD-MEC system than in a non-MEC system (*ibid*).

Conclusion

It can be concluded from the obtained data that the integration of a MEC outside the volume of an anaerobic reactor increases the methane yield in the generated biogas, purifies the ethanol stillage from sulphates, and reduces organic pollution by up to 89%. This system can be used mainly for the first 168 hours in a periodic biogas generation process and then the process can continue without external voltage. The obtained results overlap with those for an internal MEC, which means that the way of connecting a MEC to AD does not affect the stability of the process and operating parameters. A system with an external MEC has several advantages over an internal one, related to improving the work and controlling the process. Besides, it does not reduce the working volume of the reactor.

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