INFLUENCE OF BIOELECTROCHEMICAL SYSTEM ON BIOGAS PRODUCTION

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ABSTRACT
Integrating a bioelectrochemical system (BES) into an anaerobic reactor enhances methane yield, improves organic matter decomposition, and stimulates the growth of electroactive bacteria within the consortium.
The present study investigated the impact of an integrated BES on a vinasse biomethanation reactor in more depth. The type of separator strongly influences biogas yield and the decomposition of organic matter. An analysis was made of 6 AD-BES variants, with different types of membranes and without a membrane, in two operating modes - as a microbial electrolysis cell (MEC) and as a microbial fuel cell (MFC). The obtained data on the kinetics of biogas production and its composition, the rates of chemical oxygen removal, and the degradation of lactic and acetic acid were compared under different regimes. For 12 days, the daily biogas yield almost doubled, and the biomethane content increased from 60 % to 70 % in the AD-MEC variant without a membrane. The values of Coulombic Efficiency (CE) and Methane Recovery Efficiency (MRE) were determined, and in the most favourable variant (MEC- without a membrane), they were 16.6% and 4.4% respectively.
Key words*: bioelectrochemical systems, anaerobic digestion, vinasse, biomethanation, anion and cation exchange membranes.*

Introduction

An integrated bioelectrochemical system (BES) to an upflow anaerobic sludge blanket (UASB) improves the removal of organic matter and volatile fatty acids that accumulate in excess, which can inhibit the biomethane production process. In addition, methanogens can use them as a carbon source and produce energy in a microbial fuel cell (MFC). In a microbial electrolysis cell (MEC) mode, hydrogen is produced at the cathode, which can be converted to methane and improve the composition of the biogas (Weld and Singh, 2011; Vrieze et al., 2018). Unlike MFCs, which generate electricity directly, MECs require an external voltage to support electrolytic reactions at a lower potential (Choi et al., 2017).

An important element in such systems is the separator, which separates the anodic and cathodic zones and provides ion transport to close the electrical circuit. Most often, a cation exchange membrane (CEM) or an anion exchange membrane (AEM) is used. They allow maintaining specific chemical conditions in both compartments, prevent unwanted back diffusion of gases and increase the selectivity of cathodic reactions.

Despite these advantages, the presence of a membrane often leads to significant disadvantages: increased internal electrical resistance, limited ion transport, the need for higher external voltage (in the MEC), and potentially reduced energy efficiency. Several studies have shown that membrane-free systems can achieve comparable or even better results due to lower internal resistance and more efficient electron utilization (Rozendal et al., 2008; Call and Logan, 2008). However, other studies have highlighted that membranes are necessary in situations where it is critical to avoid back diffusion of oxygen or sulfur compounds, or when a specific course of cathodic reactions is aimed at (Villano et al., 2010).

If an anion exchange membrane is used in the integrated system, excess volatile fatty acids will pass through it and can be recovered. High concentrations of total ammonia and ammonium ions also inhibit methanogenesis. Often, a cation exchange membrane is used in BES to remove them and other cations. This increases the efficiency of their removal and recovery (Xu, 2005; Andersen et al., 2014; Vrieze et al., 2018). A disadvantage of membranes is that they increase the internal electrochemical resistance of the system, which requires the application of a higher external voltage to maintain the desired current. However, this effect can

be minimized by using thin, well-hydrated and structurally optimized membranes (Kadier et al., 2016). Systems with a multilayer "sandwiched" structure show a significantly lower internal electrochemical resistance, which leads to a higher current density (Guo et al., 2017). This is of key importance for the efficient degradation of organic matter and increasing the yield of intermediate products such as hydrogen.

Microbial electrolysis cells integrated with anaerobic digestion (AD–MEC) represent a promising technology for the organic waste utilization with increased biomethane yield. In these hybrid systems, part of the electrons released during the degradation of the organic substrate are directed to electrodes by exoelectrogenic microorganisms and can subsequently be used to stimulate methanogenesis (Lee et al., 2022). To evaluate the efficiency of electron transfer and transformation of the organic substrate in such systems, some key parameters are used, such as Coulombic Efficiency (CE) and Methane Recovery Efficiency (MRE).

Coulombic Efficiency is defined as the ratio of electrons reported as current through the external electrical circuit to the total number of electrons available from the oxidized organic matter. CE is a well-established parameter in microbial fuel and electrolysis cells and reflects the ability of the microbial community to direct electrons to the anode. However, in AD–MEC, CE often remains low because a significant portion of the electrons are used for direct or indirect methanogenesis, which is not reported as electrical current (Fornero et al., 2010). Therefore, CE is complemented by the Methane Recovery Efficiency, which expresses the fraction of electrons recovered as methane in biogas. MRE provides important information about the competing electron pathways that lead to methane synthesis through direct electron transfer or hydrogen as an intermediate carrier (Villano et al., 2010). Combining CE and MRE allows us to determine how much of the electron flow passes through the electrodes and how much through alternative pathways to the methanogens, giving a more complete picture of the distribution of electrons.

The combination of these parameters (CE, MRE) is vital for AD–MEC, as they reflect different aspects of electron transfer and its conversion into useful energy. While CE indicates the efficiency of electrogenesis, MRE emphasizes the contribution of methanogenesis (Dash et al., 2024). Therefore, the evaluation of AD–MEC systems by these indicators not only reveals the internal bioelectrochemical dynamics but also allows for optimization of the processes for maximum energy recovery from waste substrates.

The present study aims to determine the influence of the type and presence of a separator in a microbial fuel and electrolysis cell integrated to an anaerobic digestion reactor on the biomethanation process, the degree of organic substrate utilization and the AD-BES efficiency parameters.

Materials and methods

For conducting the experiments, a substrate from the ethanol production was used – vinasse. It is characterized by chemical oxygen demand (COD) between 15 and 65 gO_2/l, a low pH (3.5-5.0) and a balanced content of macro- and microelements. It also contains easily degradable organic matter, which makes it a potential substrate for methanization with the generation of methane-rich biogas (Moraes et al., 2015). The vinasse used in the present study has a pH of 3.33, a COD of 60 gO_2/l, 0.6 g/l glucose, 2.2 g/l lactic acid and an absolute dry matter of 3.0%.

For the experiment, a laboratory installation was constructed (Fig. 1), including – anaerobic UASB for biomethanization with a working volume of 3.0 dm^3 (7), a bioelectrochemical system operating in the microbial electrolysis cell mode with an external resistance (R) of 10 Ω and a constant current source (E) with a stabilized voltage of 0.8V. The used value of the external voltage was found in a previous study to be the most suitable in terms of the degree of biomethanization in the particular AD–MEC system (Velichkova et al., 2022).

In the microbial fuel cell (MFC) mode, the external power source (E) is removed and shunted in the circuit (Fig. 1), and the value of the load resistance (R) is changed to 100 Ω. The value of the selected load resistance is comparable to the expected internal resistance of the MFC. The input flow of wastewater (vinasse diluted with distilled water in a ratio of 1:1) entered the cathode chamber of the BES via a dosing pump (4), then passed through the UASB reactor and was recirculated by a pump through the volume of the anode chamber of the BES. The contact residence time of the incoming wastewater in the AD-BES system was 10 days.

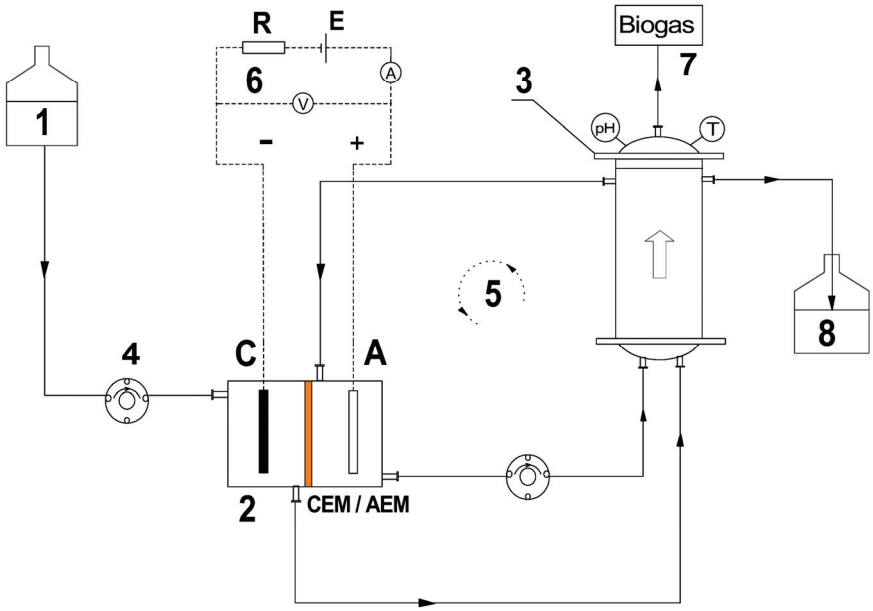

Fig. 1. Laboratory installation.

1- input substrate, 2- BES, 3- UASB-reactor, 4- dosing peristaltic pump, 5- recirculation loop between UASB and anode zone of BES, 6- loading circuit of BES, 7- biogas, 8- output spent substrate.

A two-chamber construction of the BES type “sandwich” was used. For the planned experiments, two types of separators were used, separating the cathode from the anode zone: anion exchange membrane type AMI-7001S and cation exchange membrane type CMI-7000S. Before the start of the experiments, the membranes were treated with a solution of 0.5 M NaCl at T = 25 °C for 72 hours. Graphite plates with dimensions of 100x100x6 mm and a geometric area of 0.021 m^2 were used for electrodes, with the area of the membranes being 0.01 m^2. The volumes of the cathode and anode sections were the same - 100 ml. 2 groups of experiments were conducted in 6 variants - without including BES in the UASB biogas reactor, and with including BES in the UASB reactor. BES, on the other hand, operated as an MEC (with an external voltage of 0.8V) with anion-exchange, cation-exchange membrane and without a membrane and as an MFC with anion-exchange and cation-exchange membrane. Before each series of experiments, the membrane and electrodes were replaced with new ones.

In the laboratory installation, pH, Eh and electrical conductivity (EC) were measured. The organic content was estimated by measuring the chemical oxygen demand (COD) with a HANNA INSTRUMENTS kit. Organic acids were analyzed by high-performance liquid chromatography with an Acclaim Organic Acid column connected to a UV-Vis detector. As the eluent, 0.1 M Na_2SO_4 was used with a flow rate of 0.6 mL/min and an injection volume of 5 µL. The volume of the separated gas was measured using a MilliGascounter "Ritter MGC-1", and the content of CO_2 and CH_4 in the biogas was determined using a portable gas analyzer “Draeger X-am 7000”

The electrical parameters of the BES were measured with a digital multimeter – Fluke 115, and a precision potentiometer with a range of values from 10 Ω to 11 kΩ (in MFC mode) was used for the load resistance. In this range of external resistance variation, the polarization characteristics and power curves were also taken.

The power density (P), referred to the geometric anode surface, was calculated using the equation $P=U^2/(R_T.A)$, where A(m^2) is the anode surface, R_T (Ω) is the external load resistance, and U (V) is the BES voltage.

The value of the Coulombic efficiency (CE) was determined by establishing the value of ΔCOD, as the difference between the COD values at the inlet and outlet of the system and the average current value during the experiment. The following formula is used to calculate CE:

$$CE = \frac{M.I.t}{F.b.V.\Delta COD.} x100\,\% \quad (1)$$

Where: M= 32 - the molar mass of O_2, t(s) - substrate residence time in AD-MES, I- average current value during the experiment (A), F (Faraday constant) = 96845 C/mol, b= 4 – number of electrons needed to oxidize 1 mol O_2, ΔCOD – difference between the initial and final value of COD (gO_2/L), V – working volume of AD-MES (L).

Similarly, the following formula was used to calculate Methane Recovery Efficiency (MRE):

$$MRE = \frac{8.M.n_{CH_4}}{b.V.\Delta COD.} x100\,\% \quad (2)$$

Where: 8 - the number of electrons needed for the reduction of 1 mol CO_2 to CH_4, M= 16 - the molar mass of CH_4, b= 4 – number of electrons needed to oxidize 1 mol O_2, n_{CH4} — moles of methane produced (or equivalent volume converted to moles), ΔCOD – difference between the initial and final value of COD (gO_2/L), V – working volume of AD-MES (L).

It should be noted that $n_{CH_4} = \frac{V_{CH_4}}{22.4}$ (3)

Where: 1 mole of an ideal gas occupies 22.4L/mol at standard temperature and pressure (STP), and V_{CH4} - is the generated, cumulative volume of CH_4 (L) over the time of the experiment.

Results and discussions

The kinetics of biogas production in the 6 modes are shown in Fig. 2. The process is more stable in the BES-integrated modes compared to the control. On the 12th day, the amount of biogas generated in the MEC mode without a membrane (31.7 L) is 1.5 times greater than in the system without BES (20.1 L). The results with the membranes mode slightly outperform the kinetics until day 8, after which they almost overlap with the control. A small advantage is noted in MEC with AEM (20.9 L) compared to MEC with CEM (19.1 L). In the MFC mode, the difference is more visible, with AEM yield being 28 liters vs CEM - 23.4 liters.

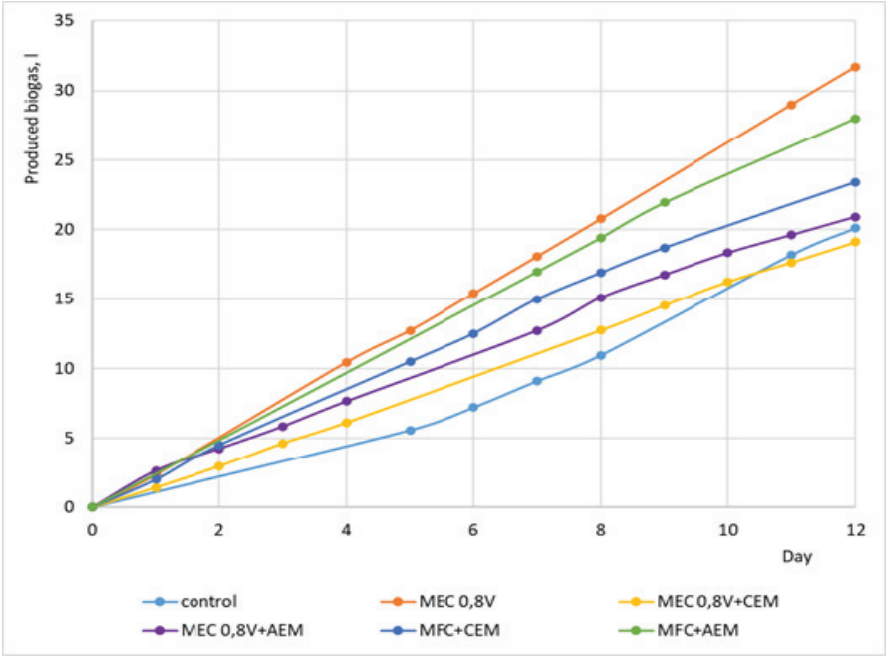

Fig. 2. Kinetics of biogas production from vinasse in an anaerobic reactor and an integrated BES system with and without a membrane

According to the results obtained for a 12-day cultivation period (Fig. 2), biogas yield increased in almost all studied variants compared to the control, 58.5% in MEC (0.8V), 40.1% in MFC+AEM, 17.2% in MFC+CEM and 4.5% in MEC+AEM, respectively.

Fig. 3 shows the methane content in the produced biogas. Table 1 presents data on the daily biomethane yield. The methane content in biogas was increased by 10% by integrating MEC into the reactor, with the daily yield almost doubling compared to the control (1.85 vs 1.00 L/day). The presence of MEC with CEM increased the methane content by 4%, whereas AEM-only increased it by 2%. In the MFC mode (with AEM and CEM), the methane content is 60 % as in the control without BES. Although this, the daily biomethane yield was higher for the MFC (1.18-1.40 L/day) compared to the MEC regimes with a separator (1.12-1.17 L/day), due to an increase in the amount of biogas produced.

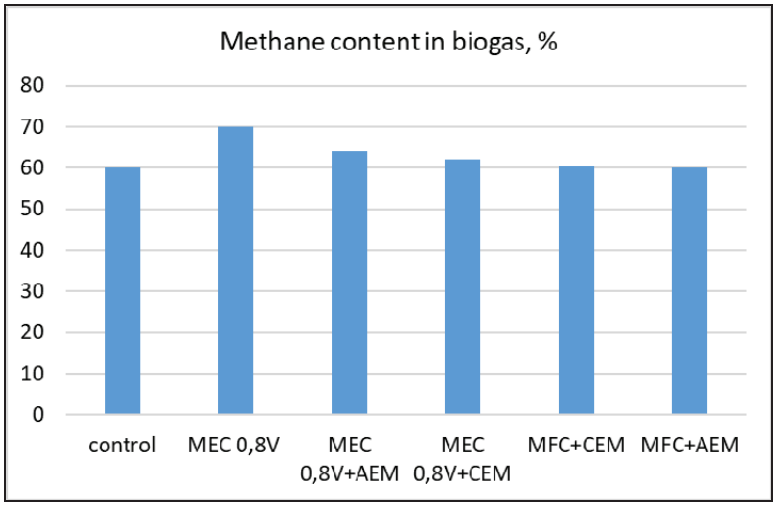

Fig. 3. Methane content in the produced biogas from different operating modes of the installation

Table 1. Daily biomethane yield in different operating modes

Mode	Biomethane production, L/day
Control	1.00
MEC 0.8V	1.85
MEC 0.8V+CEM	1.12
MEC 0.8V+AEM	1.17
MFC+CEM	1.18
MFC+AEM	1.40

To determine more specifically how the presence of a membrane in the system affects the organic matter degree removal, like COD, Coulombic efficiency and Methane recovery efficiency (Table 2), and the presence of lactic and acetic acids at the inlet and outlet of the reactor (Fig. 4), were determined.

Table 2. COD removal rate, average Current (I), Coulombic efficiency (CE) and Methane recovery efficiency (MRE) under different operating modes

Mode	COD, %	ΔCOD, g/l	I, mA	CE, %	MRE, %
Control	91.50	32,5	-	-	6.45
MEC 0.8V	95.86	25,2	14.1±1,1	4.42	16.6
MEC+CEM	90.50	23,2	2.5±0,1	0.65	9.76
MEC+AEM	91.06	27,8	3.4±0,2	0.75	10.01
MFC+CEM	92.23	24,8	0.2±0,05	0.04	10.96
MFC+AEM	94.74	25,6	0.4±0,09	0.08	12.05

The analysis of the results regarding the efficiency of AD-BES shows the highest CE (4.42 %) at MEC 0.8V and significantly lower values for the other variants, which is expected due to the significantly higher current in MEC without membrane (Table 2). This, in turn, is due to the significantly higher internal resistance (Rint) of the bioelectrochemical system in the variants with cation exchange (CEM) and anion exchange (AEM) membranes. The higher internal resistance due to the presence of a membrane in MEC has also been reported in other studies (Kadier et al., 2016). On the other hand, in many cases when treating complex substrates, such as wastewater with high concentrations of nitrates and sulfates, the use of AEM or CEM separators is justified, in order to detoxify the substrate before and during the biomethanization process (Vrieze et al., 2018). The MFC-AD systems show an extremely low CE (<0.1%), which is typical for systems without external voltage integrated into the anaerobic digestion process. The difference between MEC+CEM and MEC+AEM is minimal (0.65% vs. 0.75%), which suggests that the membrane type has a moderate influence under these conditions. However, in AEM membranes compared to CEM, both in electrolysis (MEC-AD) and fuel cells (MFC-AD), higher MRE and CE values were found, which was also confirmed by Tom et al. (2013), who concluded that this is due to the higher internal resistance of CEM compared to AEM. Evidence for the high internal resistance of the membranes used is the significant difference in the current value between the variant without a membrane and the other variants (Table 2).

With regard to the MRE parameter, in all variants with the presence of separators, 2 to 3 times higher values were observed compared to the control, where there was no methane electrogenesis. The highest MRE values were again reported at MEC 0.8V (16.6 %), followed by BES with AEM separator (~10–12 %), despite the low CE, which suggests that the microbial consortium contributes more to methanogenesis than to electrogenesis.

It should also be noted that the high levels of COD removal in all variants (over 90%), with some of the variants (MEC 0.8V and MEC+AEM) reaching 95-96 %. From this, it can be concluded that the integration of BES with AD has a significant positive effect, both on biomethane yield and on the reduction of the organic content of wastewater.

Overall, the obtained CE and MRE values are relatively low compared to other similar studies (Vrieze et al., 2018). This may be due to various reasons – high internal resistance of the membranes used, the use of a complex substrate (vinasse), insufficient electrochemical activity of the biofilms formed on the electrodes, the presence of competing metabolic pathways such as microbial sulfate reduction and nitrate reduction in the presence of nitrates and sulfates in the environment, the use of ordinary graphite electrodes with a small specific surface area close to the geometric one, etc.

From the data in Fig. 4, it can be seen that in the MEC 0.8 V and MFC+AEM mode, lactic acid is degraded to the highest degree, which also corresponds to the highest COD removal values (Table 2). By MEC+CEM and MFC+CEM, the lactic acid is at higher values at the end of the process. Before that, the control and MEC+AEM are placed. Acetate decreased to the highest extent in the MFC+CEM regime, followed by MFC+AEM, control, MEC+AEM, MEC 0.8V, MEC+CEM.

Volatile fatty acids are substrates for electroactive bacteria, and their decomposition generates an electric current at the bioanode in the BES, which can be used at the biocathode to produce methane and other valuable substances (Liu et al., 2020). For this reason, the methane content in the MEC modes (with and without a membrane) is higher in the produced biogas compared to the MFC mode. Acetate is used not only as a substrate for methanogenic bacteria but also as an electron donor in the BES. In addition, the organic acid ions pass through the AEM to the cathode, while in the CEM, they remain in the anode, which is why there are higher values of lactic acid at the outlet of the reactor. The second type of membranes is suitable for the passage of ammonium ions from the anode to the cathode, which at high values would inhibit the methanization process (Liu et al., 2020).

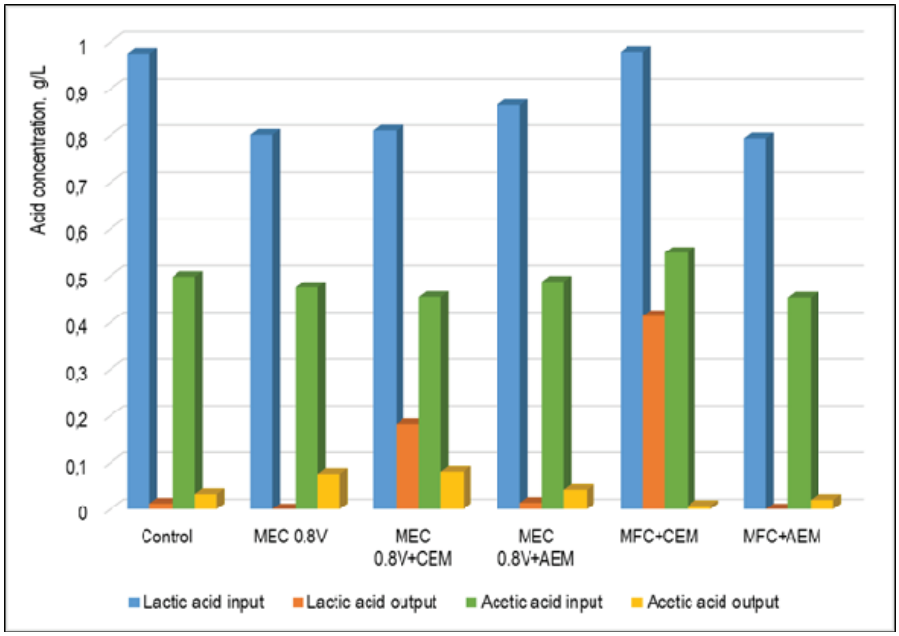

Fig. 4. Lactic and acetic acid content at the inlet and outlet of the installation under different operating modes

Conclusion

The application of bioelectrochemical systems in the anaerobic digestion of wastewater with complex composition is an innovative approach to increase biomethane yield and reduce organic content. The results obtained from 5 variants of BES with CEM, AEM and without membrane in two modes, such as MEC and MFC, show a significant improvement in the biomethanation process with an increase to 58.5 % and an increase in the share of biomethane in the gas mixture to 70 %. The electrical resistance of the membranes used is a limiting factor because it leads to a significant decrease in CE and MRE in these systems, and hence their efficiency.

Acknowledgements

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