HUNGARIAN JOURNAL OF
INDUSTRY AND CHEMISTRY
Vol. 50(2) pp. 23–26 (2022)
hjic.mk.uni-pannon.hu
DOI: 10.33927/hjic-2022-14

Separation of Dissolved Gases from Aqueous Anaerobic Effluents Using Gas-Liquid Membrane Contactors

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This study aimed to evaluate a gas-liquid membrane contactor for recovering the dissolved gases of methane (CH_4) and carbon dioxide (CO_2) from model aqueous anaerobic effluents. For this purpose, synthetic effluents were prepared by using the gas mixtures of SE-1: 100/0, SE-2: 0/100 and SE-3: 50/50 CH_4/CO_2 vol.% as well as DI water. The units in which the synthetic effluent was prepared were coupled with a dense hollow fiber membrane module by employing argon gas at atmospheric pressure. The desorption of the gases CH_4 and CO_2 dissolved in the effluents was investigated with a countercurrent flow of the liquid on the lumen side. The effect of the sweep gas flow rate on the removal rate was also investigated. The results showed that the recovery rate of CH_4 was slightly affected by increasing the sweep gas flow rate, while the recovery rate of CO_2 was enhanced considerably. By applying a sweep gas flow rate of 20 mL/min, the recovery rate of both gases from SE-3 exceeded 50%.

Keywords: gas separation; membrane contactor; biogas recovery; anaerobic effluent

1. Introduction

Anaerobic wastewater treatment is a widely used technology to convert organic waste into well-stabilized sludge. Compared to aerobic systems, the major advantages of anaerobic-based ones are that the process produces higher-quality effluent and has the potential to be a net energy producer by utilizing energy from the biogas produced. Raw biogas mainly consists of CH_4 and CO_2, moreover, may contain small quantities of hydrogen sulphide, moisture and siloxanes [1]. The composition of biogas can vary depending on the operating conditions and concentrations of organic compounds in the treated water. Typically, although the methane content in biogas is within the range of 50-70%, it can be as high as 90% depending on its interaction with the aqueous phase of the carbon dioxide [2]-[3]. Furthermore, important benefits of anaerobic treatment include the requirement of less nutrients as well as lower energy consumption and higher organic loads than most conventional biological treatments. Membranes are crucial for the separation of biomass and effluent as they enable higher concentrations of organic compounds to be used in reactors, generation less sludge as well as increase the rate of biogas production [4]. Therefore, an anaerobic membrane bioreactor system has emerged as a potential alternative technology for wastewater treatment by coupling anaerobic bioreactors with membrane separation, facilitating easy scaling up and selective separation with low energy consumption [5]. Biogas as a renewable fuel consisting of 50-70% CH_4 and 30-50% CO_2 can be produced with this method [6]. Since the treatment process occurs in a completely closed environment, it is crucial that the dissolved gases in the produced effluent are in equilibrium with the biogas in the headspace, resulting in a significant quantity of dissolved CH_4 and dissolved CO_2 being lost in the effluent solution [7]-[8]. Both dissolved gases are desorbed into the environment and contribute towards greenhouse gas emissions. Several researchers have reported that a considerable amount of the methane generated is dissolved and wasted in the liquid phase [1]-[2], [9]-[12].

Methane loss as a function of the temperature of bodies of municipal wastewater containing an average soluble COD of 200 mg/L is presented in *Fig. 1*. Since the

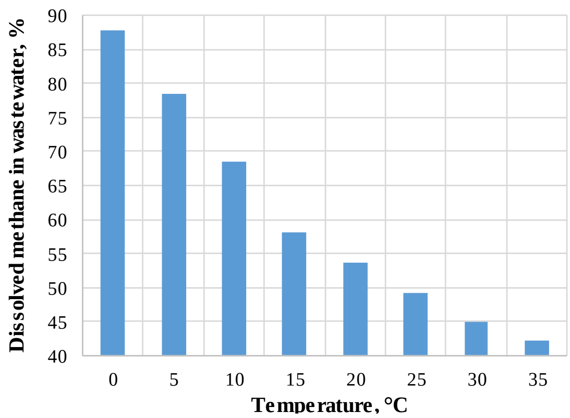

Figure 1. Dissolved methane in the wastewater as a function of temperature

Received: 19 Oct 2022; Revised: 24 Oct 2022; Accepted: 26 Oct 2022
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solubility of methane increases as the temperature decreases, the amount of dissolved methane is higher, even as high as 88% at 0°C, at lower temperatures. Methane is a greenhouse gas, its global warming potential is estimated to be 28–36 times higher than that of CO_2 over 100 years [13], moreover, is flammable with a lower explosive limit of 5 vol.% [2]. Consequently, the importance of recovering and utilizing methane entrapped in effluent during biogas production is significant in order for anaerobic treatment systems to be sustainable.

The membrane degassing technology using gas-liquid membrane contactors (GLMCs) has emerged as a potential approach for recovering entrapped methane in fermentation liquor [7]. Preferably, GLMCs are assembled into hollow fiber membrane modules since they yield a higher gas desorption rate by providing high volumetric mass transfer coefficients [14].

The goal of this research was to determine the recovery rates of CH_4 and CO_2 gas dissolved in synthetic effluents by applying a non-porous hollow fiber membrane. The effect of gas and liquid flow rates on the removal rate was also investigated.

2. Experimental

Pure CH_4 (98%)/CO_2 (99%) and deionized water were used to prepare the synthetic effluents (SEs) in glass bottles with a volume of 5 L. A peristaltic pump was used to displace the air from the bottle to create an anaerobic environment, which was confirmed with a dissolved oxygen analyzer. Saturation was achieved by bubbling CH_4 (SE-1), CO_2 (SE-2) or a mixture of CH_4 and CO_2 (50-50%: SE-3) into the deionized water for 3 hours.

The composition of the headspace was monitored by a Hewlett Packard HP 5890 Series II gas chromatograph equipped with a thermal conductivity detector (TCD). A capillary CarboPLOT® column was employed (Agilent Technologies, length: 60 m, ID: 0.32 mm, film thickness: 1.5 mm) with Ar (99.9 %) as a carrier gas at a flow rate of 15 mL/min. The applied split ratio was 100:1. The temperatures of the injector, column oven and detector were 130, 90 and 115°C, respectively. At the saturation point, the concentration of CH_4/CO_2 in the headspace was in a steady state. Once stability had been ensured, deoxygenated and CH_4/CO_2-saturated water was pumped against the membrane by a peristaltic pump. The units in which the synthetic effluent was prepared were coupled with a PermSelect® silicone, non-porous hollow-fiber membrane module with a surface area of 1.0 m^2. The membrane was operated with a countercurrent flow of the liquid on the lumen side to examine the desorption of CH_4 and CO_2 gases dissolved in the effluents. Argon (99.9%) was used as a sweep gas in the experiments.

The concentration of the outlet gas at the membrane module was measured by the gas chromatograph at regular intervals. Henry's law and the liquid flow rates were used to calculate the mass flow rate of gases entering the membrane module, while based on the ideal gas law, results obtained from GC and gas flow rates were used to calculate the mass flow rate of gases exiting from the membrane module. Based on the results obtained, the recovery rates of CH_4/CO_2 were calculated.

3. Results and Discussion

Based on the preliminary experiments, in this research, the liquid flow rate used was 15 mL/min, adjusted by a peristaltic pump and monitored with a balance. The sweep gas flow rate varied from 5-60 mL/min and was adjusted by a control valve as well as measured with a soap film flowmeter.

Recovery rates of CH_4/CO_2 from SE-1/SE-2 as a function of the sweep gas flow rate at a liquid flow rate of 15 mL/min are shown in *Tables 1 and 2* as well as summarized in *Fig.2*.

Table 1. Recovery rates of CH_4 from SE-1 as a function of the sweep gas flow rate

Liquid flow rate (mL/min)	Sweep gas flow rate (mL/min)	Recovery rate of CH_4 (%)
15	5	57.1
15	10	58.0
15	20	58.6
15	60	35.9

Table 2. Recovery rates of CO_2 from SE-2 as a function of the sweep gas flow rate

Liquid flow rate (mL/min)	Sweep gas flow rate (mL/min)	Recovery rate of CO_2 (%)
15	5	9.2
15	10	29.0
15	20	47.0
15	60	61.6

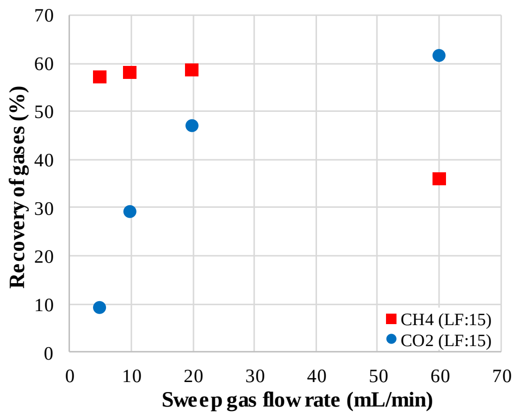

Figure 2. Recovery rates of CH_4/CO_2 from SE-1 and SE-2 as a function of the sweep gas flow rate

The results showed that the recovery rate of CH_4 at a sweep gas flow rate of 5-20 mL/min was almost constant (57.1-58.6%) and rapidly decreased to 35.9% by increasing the gas flow rate to 60 mL/min. Similar effects of the gas flow rate on the recovery ratios of the gases have been reported by Cookney et al. [15], where increasing the gas flow rate had little effect on the mass transfer coefficient of CH_4 due to mass transfer controlled by the resistance in the liquid phase. Rongwong et al. [7], [16] also reported that the CH_4 concentration is diluted in the outlet gas in the case of high gas flow rates, which was also observed in this study. Although the recovery rate of CO_2 was increased by increasing the sweep gas flow rate, these values were much lower than those of CH_4 except for at a gas flow rate of 60 mL/min.

SE-3 was prepared by purging a mixture of CH_4 and CO_2 gases (50:50) into deionized water for 3 hours to investigate the impact of this mixture on the recovery rate of the membrane module. The results were compared with those obtained from synthetic effluents prepared with pure gases. The recovery rates of CO_2 and CH_4 as a function of the sweep gas flow rate are given in *Table 3* and *Fig.3*.

Table 3. Recovery rates of gases from SE-3 as a function of sweep gas flow rate

Liquid flow rate (mL/min)	Sweep gas flow rate (mL/min)	Recovery rate of CH_4 (%)	Recovery rate of CO_2 (%)
15	10	61.3	36.2
15	20	53.1	55.0
15	60	11.9	62.9

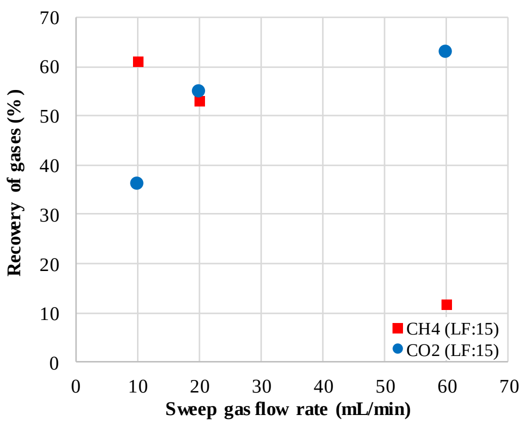

Figure 3. Recovery rates of CH_4 and CO_2 from SE-3 as a function of sweep gas flow rate

The results from SE-3 showed a similar tendency to those obtained in the case of individual gases. The recovery rate of CO_2 was increased from 36.2 to 62.9% by increasing the sweep gas flow rate, while these values for CH_4 at a gas flow rate of 10-20 mL/min were 53.1-61.3% but dropped drastically to 11.9% by applying a gas flow rate of 60 mL/min. At the latter gas flow rate, the recovery rate of the membrane module with regard to CH_4 from SE-1 was 35.9%, therefore, the presence of CO_2 in the synthetic effluent may have a negative effect on the recovery of CH_4. Nevertheless, by applying a sweep gas flow rate of 20 mL/min, the recovery rate of both gases from SE-3 exceeded 50%.

4. Conclusions

The anaerobic digestion of wastewater is a commonly used technology to produce biogas by converting organic waste into well-stabilized sludge. Since the process takes place in a completely closed environment, it is crucial that the dissolved gases in the produced effluent are in equilibrium with the biogas in the headspace, leading to a significant quantity of dissolved CH_4 and dissolved CO_2 being lost in the effluent solution. As a result, the recovery of dissolved CH_4 is critical to increase anaerobic energy production while minimizing the environmental impact of greenhouse gases. In this study, synthetic effluents were prepared by purging CH_4/CO_2 into deionized water. A membrane contactor was employed as a mass transfer device for measuring the recovery rates of CH_4 and CO_2 gases dissolved in synthetic effluents by applying a non-porous hollow fiber membrane. The effect of the sweep gas flow rate on the removal rate was also investigated. The results showed that the recovery rate of CH_4 was slightly affected by increasing the sweep gas flow rate, while the recovery rate of CO_2 was enhanced considerably.

Acknowledgements

This research was supported by the OTKA K 138232 research grant entitled “Stabilization of anaerobic effluents in a novel, integrated bioprocess towards controlled demethanization and energy recovery.”

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