

## Article

# Possibilities of Biogas Upgrading on a Bio-Waste Sorbent Derived from Anaerobic Sewage Sludge

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**Abstract:** The development of biogas upgrading technologies is now an essential issue in recovering fuel-grade methane. Nowadays, trends in biogas upgrading include investigations of low-cost and renewable materials as sorbents for biogas enrichment to produce biomethane. Therefore, in this work, wastewater anaerobic sludge stabilized with calcium oxide was used as the bio-waste sorbent to capture carbon dioxide from biogas, employing a fixed bed column. The biogas flow rate was the parameter considered for examining the breakthrough responses. It was observed that breakthrough time decreases with increasing biogas inflow rate from  $570 \pm 10$  min at 5 mL/min to  $120 \pm 12$  min at 35 mL/min. The maximum sorption capacity of  $127.22 \pm 1.5$  mg CO<sub>2</sub>/g TS of sorbent was estimated at 15 mL/min. Biomethane concentration in biogas increased from  $56.5 \pm 1.7$  v% in the raw biogas to  $98.9 \pm 0.2$  v% with simultaneous low carbon dioxide content of  $0.44 \pm 0.2$  v%. A strong positive correlation ( $R^2 = 0.9919$ ) between the sorption capacity and the biogas flow rate was found in the range of biogas inflow rates between 5 mL/min and 15 mL/min. Moreover, the correlation analysis showed a strong negative relationship ( $R^2 = 0.9868$ ) between breakthrough time and the mass of carbon dioxide removal, and the biogas flow rates ranged from 10 mL/min to 20 mL/min.

**Keywords:** biogas upgrading; biomethane; wastewater sludge; calcium oxide; fixed-bed sorption; bio-waste sorbent



**Citation:** Zieliński, M.; Karczmarczyk, A.; Kisielewska, M.; Dębowski, M. Possibilities of Biogas Upgrading on a Bio-Waste Sorbent Derived from Anaerobic Sewage Sludge. *Energies* **2022**, *15*, 6461.  
<https://doi.org/10.3390/en15176461>

Academic Editor: Attilio Converti

Received: 11 August 2022

Accepted: 2 September 2022

Published: 4 September 2022

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## 1. Introduction

Renewable energy plays an important role in the energy policy of the European Union (EU). The EU 2030 Climate and Energy Framework set the key targets for the year 2030 to cut GHGs emissions by at least 40% compared to 1990 levels and reach at least 32% share of renewable energy in the total energy consumption [1]. Among many renewable energy sources, biogas is considered an excellent substitute for fossil fuels and one of the most useful and versatile forms of energy for providing electricity as well as heat [2,3]. Nowadays, commercial biogas production in biorefineries has highly increased, and a number of new technologies and improvements have been developed to raise the output and quality of the generated biogas [4–6]. According to the European Biogas Association estimation, biogas production in Europe reached over 200 TWh in 2021 [7].

Raw biogas without considerable pre-treatment can be directly used for combustion or combined heat and power generation (CHP) [8]. Enrichment of the methane content in biogas is essential for increasing its quality and heating value as well as making it suitable for other applications. By upgrading, a significant increase in methane content (over 95%) is achieved [9]. Upgraded biogas, which is called biomethane, can be converted to bio-compressed natural gas (bio-CNG), which can be easily stored and distributed via gas pipelines, thus counteracting fluctuations in other renewable energy supplies from wind or solar photovoltaic power [10,11]. It is also estimated that bio-CNG used as a fuel for vehicles will increase worldwide from 2% today to 27% in 2050 [2,12]. Currently, in the EU, biomethane is consumed as a natural gas substitute in the amount of 20 TWh/year,

resulting in a 0.4% share in the gas network and will further increase to 5–8% by 2030 to meet the European goals [13,14].

The available techniques for biogas upgrading can be generally divided into physico-chemical and biological methods. Most of the widely used full-scale technologies for biogas upgrading are based on physico-chemical processes (sorption and separation) [2,15]. According to the literature, sorption is the most widely used technology for biogas upgrading due to its versatility, efficiency (the methane loss is lower than 4%, and the biomethane purity in the output gas is 95–98%), as well as low energy requirement (0.24–0.6 kWh/m<sup>3</sup> upgraded biogas, 0.25 Euro/m<sup>3</sup> upgraded biogas) [9,12]. The full-scale upgrading plants typically contain several columns working in parallel, so when the sorbent in one column is saturated, the biogas is directed to another one. Regeneration of the sorption column is carried out by reducing the pressure in several steps, and the gas desorbed may be returned to the inlet of the raw biogas or, when it is methane free, released into the atmosphere. The most commonly used adsorbent is activated carbon, and the adsorption mechanism depends on its surface characteristics and interaction affinity toward carbon dioxide (CO<sub>2</sub>) molecules [16–18]. However, innovative, low-cost, and renewable resource sorption materials are intensively searched for to reduce the cost of commercial adsorbents and meet the circular economy requirements [19–23].

Sludge management is the most difficult and challenging issue for wastewater treatment plants due to its poor dewaterability, high methane emissions, and strict regulation for disposal [24]. According to EU Directives, raw sludge from municipal and industrial wastewater treatment plants cannot be deposited in any natural or even controlled environment; thus, it must be properly processed before further usage [25,26]. Sludge production in the EU was estimated at 13 million tons of dry matter in 2020 [27]. One of the most popular treatment methods is chemical stabilization, in which a controlled dose of hydrated lime (calcium hydroxide) as a liquid or quicklime (calcium oxide) as a dry powder is added to sewage sludge [28]. As in the chemical sorption technique, the packed column reactors include sodium carbonate, calcium hydroxide, or sodium hydroxide as an active material for CO<sub>2</sub> capture; stabilized sludge containing aqueous alkaline solutions seems to be a useful material in the CO<sub>2</sub> sorption process [29,30].

Thus, the main focus of this work was to investigate the usefulness of a newly developed bio-waste sorbent for CO<sub>2</sub> capture. For this purpose, the sludge from an anaerobic reactor stabilized with calcium oxide (CaO) was used as an active medium to construct a fixed-bed column for biogas upgrading. During the study, the sorption capacity of the newly developed sorbent and the concentration of biomethane in upgraded biogas were investigated.

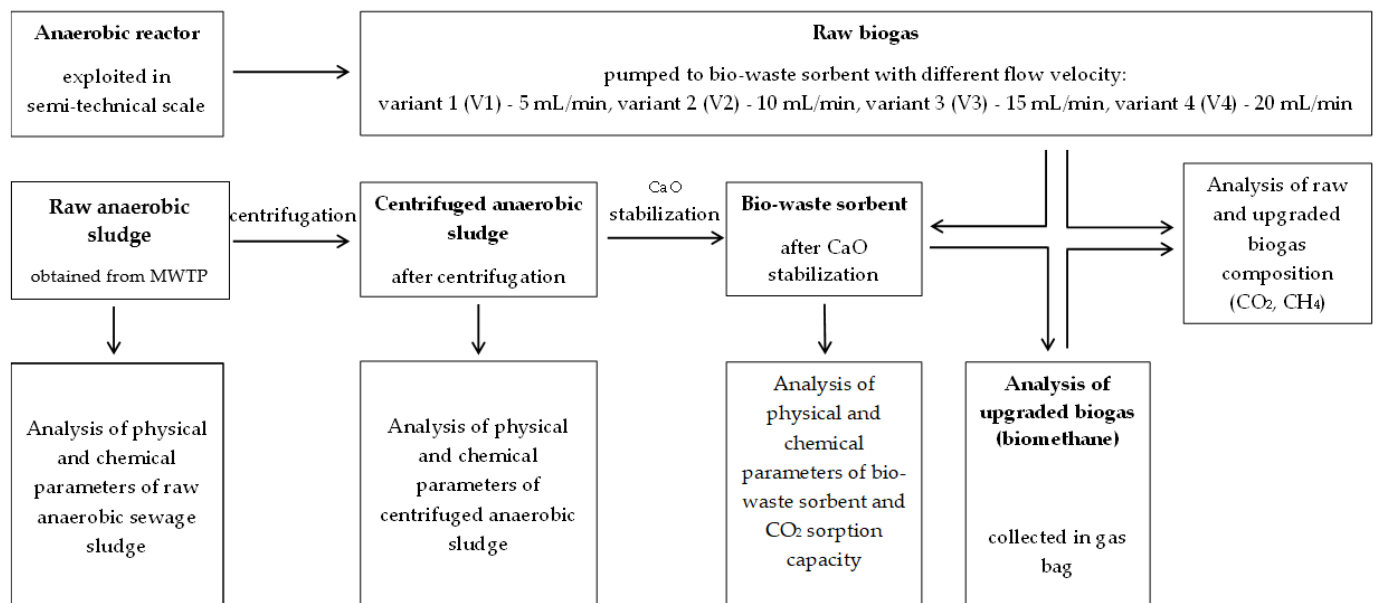
The proposed technology is a completely new and innovative approach for biogas upgrading. This method uses the bio-waste materials (i.e., the lime-stabilized excess sludge) from wastewater treatment plants as a natural sorbent for CO<sub>2</sub> capture. This approach aims to reuse and recycle waste products while simultaneously reducing the use of commercial materials, which completely meets the 3-R approach of the circular economy. In this way, the lime-stabilized sludge loses as little value as possible and becomes a valuable material in biogas upgrading.

## 2. Materials and Methods

### 2.1. Study Organization

The study on the effect of limed municipal sewage sludge use in biogas upgrading was carried out on a laboratory scale. The experiment was divided into 4 variants, which were identified depending on the inflow velocity of the raw biogas through a fixed-bed column reactor: variant 1 (V1)—5 mL/min; variant 2 (V2)—10 mL/min; variant 3 (V3)—15 mL/min; variant 4 (V4)—20 mL/min. Each variant lasted until the breakthrough of CO<sub>2</sub> was achieved. The breakthrough point and saturation time were set at 5% and 95% of influent CO<sub>2</sub> concentration, respectively. Additionally, the sorption capacity of the

centrifuged anaerobic sludge without the addition of CaO was also estimated. The study organization is shown in Figure 1.



**Figure 1.** The study organization.

## 2.2. Materials

The digested sludge for the preparation of the bio-waste sorbent was collected from the municipal wastewater treatment plant (MWTP) in Olsztyn with a daily average flow of 60,000 m<sup>3</sup>/day. In the MWTP, a multi-chamber activated sludge reactor was utilized for organic and biogenic compounds removal with the production of approx. 550 tons of dry mass surplus sludge MSS/day. Surplus sludge was stabilized in the 2 anaerobic digesters with an active volume of 10,000 m<sup>3</sup>. The operation parameters of the digesters were: organic load rate (OLR) of approx. 2.4 kg VS/m<sup>3</sup>·d; hydraulic retention time (HRT) of 20 days; temperature of 35 °C. The digested sludge was collected directly from the digesters. The characteristics of raw anaerobic sludge used in the experiment are presented in Table 1.

**Table 1.** Characteristics of the raw anaerobic sludge, centrifuged anaerobic sludge, and bio-waste sorbent.

| Parameter                      | Raw Anaerobic Sludge | Centrifuged Anaerobic Sludge | Bio-Waste Sorbent |
|--------------------------------|----------------------|------------------------------|-------------------|
| Total solids (%)               | 4.9 ± 0.7            | 22.4 ± 0.5                   | 35.1 ± 0.7        |
| Volatile solids (% TS)         | 72.7 ± 0.6           | 71.9 ± 1.3                   | 39.4 ± 0.9        |
| Total nitrogen (mg/g TS)       | 32.9 ± 2.7           | 33.8 ± 2.9                   | 17.1 ± 2.0        |
| Total phosphorus (mg/g TS)     | 1.7 ± 0.2            | 1.9 ± 0.4                    | 0.88 ± 0.13       |
| Total carbon (mg/g TS)         | 311 ± 21             | 317 ± 19                     | 165 ± 17          |
| Total organic carbon (mg/g TS) | 201 ± 37             | 204 ± 21                     | 107 ± 19          |
| Calcium (mg/g TS)              | 17.2 ± 3.7           | 17.1 ± 1.9                   | 351 ± 13          |
| Magnesium (mg/g TS)            | 5.8 ± 0.9            | 5.7 ± 0.2                    | 3.1 ± 0.3         |
| C/N ratio                      | 9.4 ± 0.1            | 9.4 ± 0.2                    | 9.6 ± 0.2         |
| pH                             | 7.2 ± 0.2            | 7.3 ± 0.2                    | 12.2 ± 0.3        |
| Proteins (% TS)                | 20.9 ± 1.8           | 20.1 ± 1.9                   | 10.1 ± 0.4        |
| Lipids (% TS)                  | 3.2 ± 0.7            | 3.3 ± 0.8                    | 1.6 ± 0.4         |
| Sugars (% TS)                  | 1.6 ± 0.4            | 1.4 ± 0.2                    | 0.75 ± 0.3        |

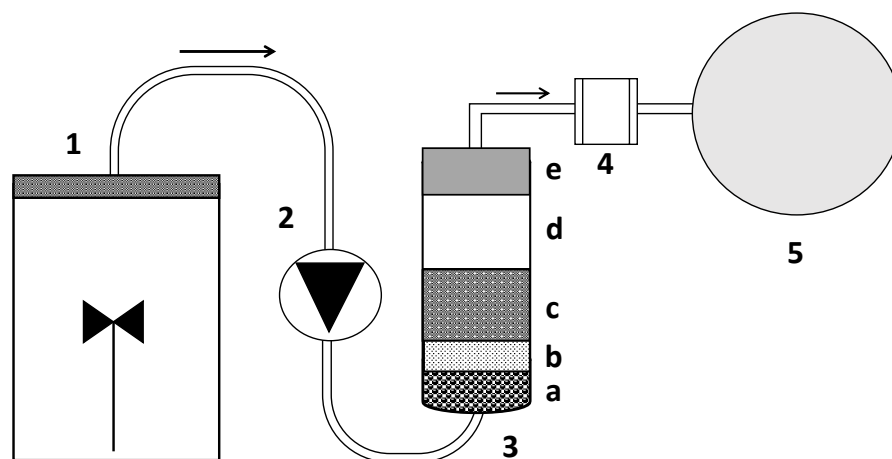
Then, 500 mL of the raw anaerobic sludge was centrifuged at 9000 × g rpm for 3 min (Rotina 380, Hettich, Tuttlingen, Germany) to separate the solids and supernatant with characteristics of centrifuged sludge presented in Table 1. The bio-waste sorbent was prepared from 5 g of separated solids mixed with 1 g CaO (0.9 g CaO/1 g TS of separated solids)

(Table 1). The applied dose of CaO was typical for stabilized wastewater sludge [30,31]. The CaO was produced by Trzuskawica S.A. (Sitkówka-Nowiny, Poland) and was characterized by relative density of 3.31 g/mL (at 20 °C) and water solubility of 1337.6 mg/L (at 20 °C). The mixing process took place in a reactor with a working volume of 1 L equipped with a vertical agitator (30 rpm, 24 h) (Microstar 30 control, IKA Werke GmbH & Co. KG, Staufen, Germany). Characteristics of the bio-waste sorbent are shown in Table 1.

The raw biogas was collected directly from an anaerobic cage-mixing reactor working on a semi-technical scale and fed with lignocellulosic biomass and cattle slurry [32]. The biogas produced was characterized by methane and carbon dioxide concentrations of  $56.5 \pm 1.7$  v% and  $42.2 \pm 2.1$ , respectively.

### 2.3. Fixed-Bed Column Construction and Exploitation

The fixed-bed column for biogas upgrading was constructed of three layers: plastic fittings as a support layer, glass wool, and biomass sorbent derived from anaerobic sludge (50 g), all placed in a glass bottle with a total volume of 250 mL (Figure 2). The bed height was 10 cm. The column was connected with a Tedlar Gas Bag (Sigma Aldrich, Taufkirchen, Germany) with a capacity of 500 mL, to which raw biogas from the anaerobic cage-mixing reactor was continuously fed by a peristaltic pump (Fast Load, VWR, Radnor, PA, USA) (Figure 2).



**Figure 2.** Scheme of the research station: (1) anaerobic reactor producing biogas; (2) peristaltic pump; (3) fixed-bed column for biogas upgrading; (a) support layer; (b) glass wool; (c) bio-waste sorbent; (d) gas phase; (e) tight cover with discharge valve; (4) gas flow meter; (5) gas bag for storing upgraded biogas.

The inflow of biogas was controlled by a digital gas flow meter (XFM17S, Aalborg Instruments & Controls, Inc., Orangeburg, NY, USA). The raw biogas was continuously fed downward into the filter bed. In the upper part of the column, there was a tee outlet for biomethane discharging, which ended with a Tedlar Gas Bag (Sigma Aldrich, Taufkirchen, Germany) with a capacity of 500 mL collecting biogas. The instantaneous and total biogas flow in the filter was measured using a digital gas flow meter (XFM17S, Aalborg Instruments & Controls, Inc., Orangeburg, NY, USA). The composition of biogas outflow was analyzed every 30 min.

### 2.4. Analytical Methods

The content of total solids (TS) and volatile solids (VS) was calculated according to the gravimetric method by drying the sample at 105 °C to a constant weight and then burning it at 550 °C for 2.5 h. TC, TOC, and TN were measured using a Flash 2000 analyzer (Thermo Scientific, Waltham, MA, USA). The total phosphorus (TP) and sugars (saccharides) contents were determined with a DR 2800 spectrophotometer (Hach Lange GmbH, Düsseldorf, Germany). Determination of lipids was performed using the Soxhlet method with an

extractor (B-811, Büchi AG, Flawil, Switzerland). Total protein was calculated as total nitrogen content  $\times 6.25$ . The pH of aqueous homogenized solutions was measured with a pH meter (1000 L, VWR, Radnor, PA, USA). Calculation of the calcium (Ca) concentrations in samples were performed according to the EDTA titration method in a solution of 0.1 M sodium hydroxide (pH 12–13) against murexide. Magnesium (Mg) was determined by EDTA titration in pH 10 against Eriochrome Black.

A gas chromatograph (GC 7890A, Agilent, Santa Clara, CA, USA) incorporating the two Haysep Q columns (80/100 mesh), two molecular sieve columns (60/80 mesh), and Porapak Q column (80/100) operating at a temperature of 70 °C was used to analyze the biogas composition. The GC was also equipped with a thermal conductivity detector (TCD). A sample injection and detector ports had a temperature of 50 °C and 250 °C, respectively. The carrier gasses were helium and argon (flow rate of 15 mL/min).

### 2.5. Calculation Methods

The behavior of the fixed-bed column sorption process was described by breakthrough curves using the Thomas model (1), which assumes Langmuir kinetics of sorption–desorption, no axial dispersion, and second-order reversible reaction kinetics:

$$\frac{C_e}{C_0} = \frac{1}{1 + \exp\left[\frac{k_{Th}}{Q} \cdot (q \cdot m - c_0 \cdot V)\right]} \quad (1)$$

where  $C_0$  and  $C_e$  are, respectively, the influent and effluent concentrations (mg/mL),  $k_{Th}$  is the Thomas rate constant (mL/mg·min),  $q$  is the maximum capacity of sorption (mg/g),  $m$  is the quantity of sorbent in the column (g),  $V$  is the volume of solution (mL), and  $Q$  is the feed flow (mL/min).

As a comparison, determination of CO<sub>2</sub> sorption capacity of the newly developed sorption material was also determined on the basis of the content of CO<sub>2</sub> in biogas inflow and outflow and using the Clapeyron equation as the basis for the calculations. CO<sub>2</sub> sorption capacity (g CO<sub>2</sub>/g) was obtained as the ratio of the weight of removed carbon and the weight of the sorbent.

### 2.6. Statistical Methods

The results were processed statistically with the Statistica 13.3 PL (StatSoft, Inc., Tulsa, OK, USA) routines. A confidence level of 95% was used in the statistical analyses, and the variables were considered as significant for the evaluated process when  $p < 0.05$ . Each experimental variant was conducted in three replications. The ability of the Thomas model to describe CO<sub>2</sub> sorption was assessed using the coefficient of determination  $R^2$ . The correlation coefficient between variables was also assessed.

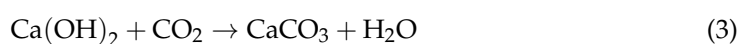
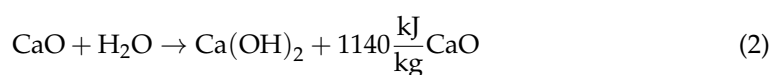
## 3. Results and Discussion

In the study, anaerobic sludge treated with CaO was used as active packing material to construct the fixed-bed column for biogas upgrading. The raw and centrifuged anaerobic sludge were characterized by VS concentration of approx. 72% TS. TS concentration after centrifugation was increased from  $4.9 \pm 0.7\%$  to  $22.4 \pm 0.5\%$  (Table 1). In bio-waste sorbent, the total solids content was on the level of  $35.1 \pm 0.7\%$ . The nitrogen concentration in the raw anaerobic sludge was  $32.9 \pm 2.7$  mg/g TS (Table 1), which was typical for anaerobically digested sludge from municipal treatment plants [33]. The phosphorus concentration in the raw sludge was at the level of  $1.7 \pm 0.2$  mg/g TS (Table 1). Górka and Cimochoicz-Rybicka [33] reported higher content of phosphorus in the digested sludge, which was from 14.67 mg/g TS to 33.04 mg/g TS depending on the type of wastewater sludge used for mesophilic anaerobic digestion. The digested sludge used for bio-waste sorbent preparation had a neutral pH. Ca and Mg contents were on the level of  $17.2 \pm 3.7$  mg/g TS and  $5.8 \pm 0.9$  mg/g TS, respectively (Table 1). According to the literature, the waste-activated sludge after mesophilic anaerobic digestion was characterized by lower Ca

and Mg concentrations, amounting to the level of 1.2–1.7 mg Ca/g TS and 0.64–0.95 mg Mg/g TS [34]. The addition of CaO to the centrifuged sludge resulted in a reduction in organic matter expressed as volatile solids from  $71.9 \pm 1.3\%$  TS in centrifuged sludge to  $39.4 \pm 0.9\%$  TS and as TOC from  $204 \pm 21$  mg/g TS to  $107 \pm 19$  mg/g TS. The concentration of Ca increased to  $351 \pm 13$  mg/g TS, while the pH raised to  $12.2 \pm 0.3$ .

A review of the world's scientific literature has shown that sewage sludge was used as a raw material to develop inexpensive sorbents for many substances. Monsalvo et al. [35] used drying and carbonization as the treatment methods of sewage sludge valorization into inexpensive sorbents potentially useful for the removal of some hazardous water pollutants (e.g., chlorophenols). The dried sludge showed a maximum adsorption capacity of 0.73 mmol 4-chlorophenol/g at pH 5.0 and 15 °C, while the carbonization process allowed to obtain 1.36 mmol/g. Other researchers used the excess activated sludge from a municipal sewage treatment plant as waste sorbent for dye removal [36]. The different models of sorption isotherm were examined, and the sorption capacity calculated on the Langmuir model was 434.8 mg/g for the dye of Acid Green 16 and 109.9 mg/g for Acid Red 18. A sludge-based activated carbon was developed as an efficient sorbent material for oil spilled on surface waters [37]. Sewage sludge activated chemically with  $\text{ZnCl}_2$  was also used as an adsorbent for the removal of ciprofloxacin from synthetic wastewater [38]. The researchers obtained 93% removal of ciprofloxacin and an adsorption capacity of 102 mg/g. The sludge biochar prepared by the pyrolysis was used for the removal of trace metals (copper, cobalt, and nickel) in an aqueous solution by optimization of the temperature and adsorbent particle sizes [39]. The study showed that higher temperature enhanced the surface (space and structure) of the sorbent, thus increasing the adsorption of metal ions up to 77.86%, 75%, and 56.25% of copper, cobalt, and nickel, respectively. The dried sewage sludge was also valorized as an adsorbent for dyes from aqueous solutions [40]. During the experiment, the sludge was characterized using several techniques such as scanning electron microscopy (SEM), Brunauer–Emmett–Teller (BET) analysis, X-ray diffraction (XRD) analysis, and Fourier Transform Infrared Spectroscopy (FTIR). The study proved that the innovative sorbent was an effective, economic, and environmentally friendly material and may be an alternative for commercial sorbents for dye removal. XRD, as well as scanning electron microscopes and energy-dispersive X-ray (SEM–EDX) analysis, were performed to characterize the sewage sludge ash as a sorption material for heavy metal ions removal [41]. It was observed that the sorbent had irregular-shaped particles of different sizes. Additionally, the EDX spectra analysis showed the presence of elements such as Ca, K, P, Si, Fe, Mg, and Al, which led to lower adsorption capacities for the tested metals. The Langmuir isotherms were used to describe the adsorption process with a maximum capacity of 25 mg/g for Pb (II) and 7.5 mg/g for Cu (II).

Biogas upgrading technologies based on  $\text{CO}_2$  sorption (adsorption and absorption) are divided into two categories, physical and chemical scrubbing [9]. Chemical techniques for  $\text{CO}_2$  capture use aqueous alkaline solutions (e.g., sodium hydroxide (NaOH), calcium hydroxide ( $\text{Ca(OH)}_2$ ), potassium hydroxide (KOH), or CaO) to upgrade biogas [19,42,43]. The exothermic reactions occur when CaO is added to water, and then the raw biogas is passed through the packed columns containing the reagents solution.  $\text{CO}_2$  reacts with chemicals in the solvent and is also absorbed into the liquid [42]. The reactions are as follows [19,29]:



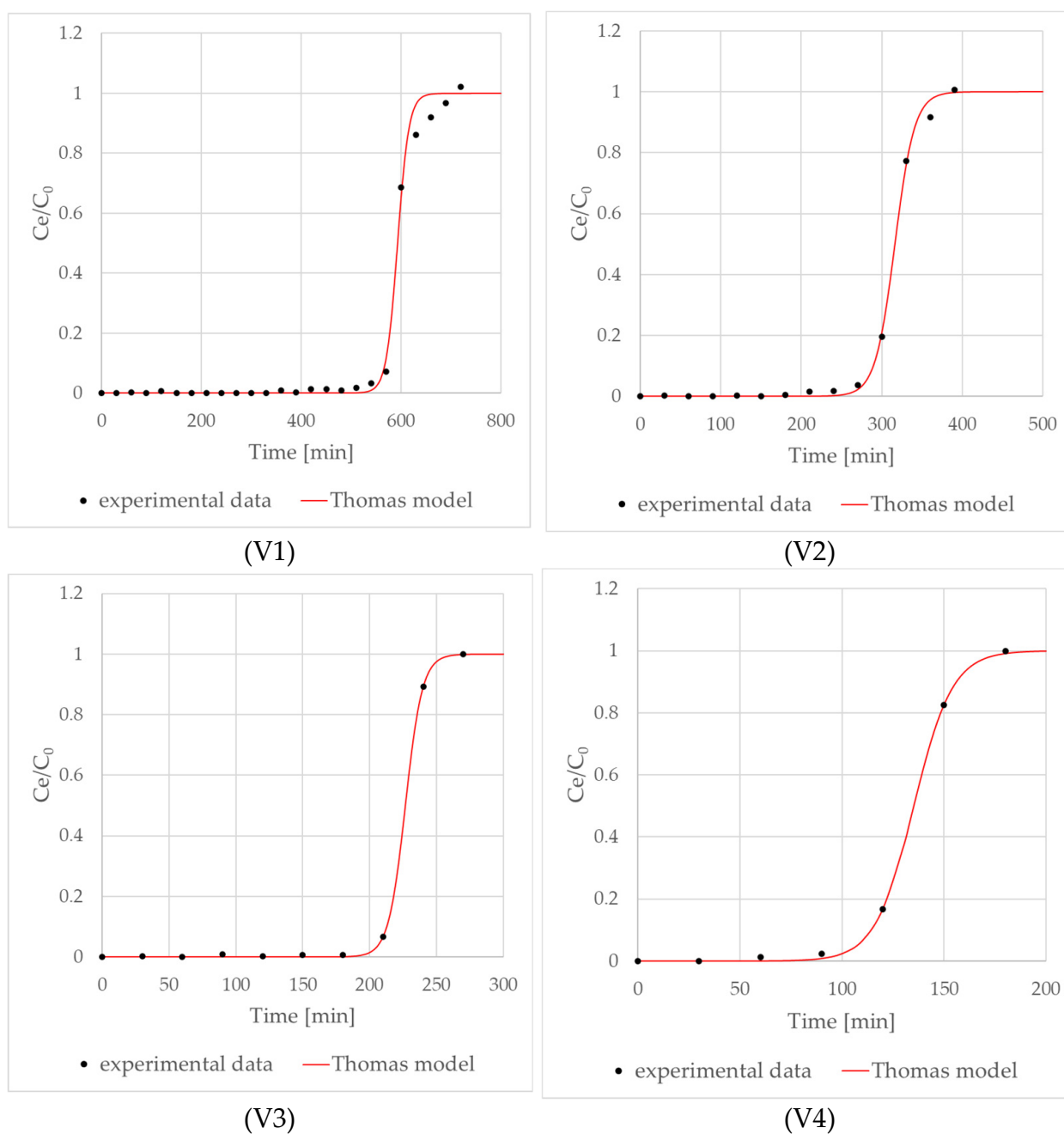
Kulkarni and Ghanegaonkar [42] investigated the biogas quality upgraded in packed column reactors with aqueous solutions of  $\text{Na}_2\text{CO}_3$ ,  $\text{Ca(OH)}_2$ , and NaOH. They found that  $\text{CO}_2$  removal efficiency from the raw biogas consisting of 57.52 v%  $\text{CH}_4$  and 26.28 v%  $\text{CO}_2$  was 99.85 v%. The upgraded biogas contained 96.91 v%  $\text{CH}_4$ . The biogas purification using  $\text{Ca(OH)}_2$  was studied by Srichat et al. [44]. They obtained 89.3 v%  $\text{CH}_4$  in purified biogas

with  $\text{Ca}(\text{OH})_2$  concentration of 0.2 mol and the raw biogas rate of 5 L/min. According to the literature, the concentration of  $\text{CH}_4$  in biogas upgraded with chemical scrubbing achieved 96–99.5 v% [9,12].

In the study, the effect of biogas inflow velocity on the sorption capacity was studied in breakthrough experiments (Figure 3). At every flow rate, a typical S-shaped curve was obtained. An increase in the biogas inflow rate influenced the duration of saturation time as well as the sorption capacities (Figure 3, Tables 2 and 3). The highest sorption capacities, ranging from  $110.03 \pm 2.1$  mg  $\text{CO}_2$ /g TS to  $127.22 \pm 1.5$  mg  $\text{CO}_2$ /g TS, were achieved with a biogas rate between 10 mL/min and 15 mL/min (Table 3). These values were similar to those predicted by the Thomas model (Table 2). At the highest and the lowest biogas inflow rates, the sorption capacities were, respectively,  $67.55 \pm 4.8$  mg  $\text{CO}_2$ /g TS and  $97.50 \pm 3.7$  mg  $\text{CO}_2$ /g TS (Table 3). The breakthrough time decreased with the increase in the biogas feed rate from  $570 \pm 10$  min at 5 mL/min to  $120 \pm 2$  min at 35 mL/min (Table 2). Similar findings were described by Srichat et al. [44], who tested the impact of biogas rates from 5 L/min to 15 L/min on its purification using a  $\text{Ca}(\text{OH})_2$  solution. They found the highest  $\text{CO}_2$  capture with the lowest biogas inflow rate. Generally, the breakthrough occurred faster with increasing flow rates due to the fact that the adsorbate phase did not have enough time to be in contact with adsorbent particles [45,46]. Rattanaphan et al. [22] obtained lower sorption capacity, ranging from 60.64–78.98 mg/g of 40%  $\text{CO}_2$ , from swine farm biogas on activated carbon prepared from modified waste tea. In turn, Karimi et al. [47] studied the potential of compost derived from municipal solid wastes, which was activated by sulfuric acid and thermally treated, as a bio-waste source of sorbent for  $\text{CO}_2$  capture. They found that the sorption capacity of the bio-waste material was 110.025 mg/g, which was in the range of commercial activated carbon materials. It was also noted that the sorption capacity of sawdust-activated carbon was 97.3 mg/g [48]. Acevedo et al. [49] found that the adsorption of  $\text{CO}_2$  in the activated carbons treated chemically with  $\text{Cu}(\text{NO}_3)_2$  presented values between 103 mg  $\text{CO}_2$ /g and 217 mg  $\text{CO}_2$ /g. The nitrogen-rich activated carbon treated with terephthalaldehyde and melamine for  $\text{CO}_2$  capture exhibited a  $\text{CO}_2$  uptake of 141 mg/g at 298 K and 0.1 MPa, which was one of the highest  $\text{CO}_2$  capture capacities among activated carbons [50]. In turn, the adsorption capacities of zeolite-based sorbents were around 114 mg  $\text{CO}_2$ /g sorbent at 30 °C and under atmospheric pressure and 190 mg  $\text{CO}_2$ /g sorbent and at 30 °C and 5 bar pressure [51]. Using modified mesocellular silica foams impregnated with tetraethylenepentamine (TEPA) ensured the adsorption capacities from 26.4 mg  $\text{CO}_2$ /g to 193.6 mg  $\text{CO}_2$ /g [52]. Thus, the adsorption capacities presented in the manuscript are in the range presented in the literature, which clearly demonstrates the potential of the bio-waste sorbent derived from anaerobic sewage sludge in commercial applications.

**Table 2.** Results of breakthrough curves and sorption capacities with the Thomas model for  $\text{CO}_2$  sorption onto the bio-waste sorbent in a fixed-bed column.

| Parameter                                  | Variant          |                  |                  |                 |
|--------------------------------------------|------------------|------------------|------------------|-----------------|
|                                            | V1               | V2               | V3               | V4              |
| $K_{\text{Th}}$ (mL/mg·min)                | 0.491            | 0.0391           | 0.0730           | 0.0625          |
| Sorption capacity (mg $\text{CO}_2$ /g TS) | $106.73 \pm 3.5$ | $132.85 \pm 3.2$ | $147.20 \pm 2.8$ | $91.19 \pm 4.4$ |
| $R^2$                                      | 0.998            | 0.998            | 0.999            | 0.999           |
| Breakthrough time (min)                    | $570 \pm 10$     | $270 \pm 5$      | $210 \pm 7$      | $120 \pm 12$    |
| $C_e/C_0$                                  | $0.07 \pm 0.01$  | $0.04 \pm 0.02$  | $0.07 \pm 0.01$  | $0.17 \pm 0.01$ |



**Figure 3.** Effect of biogas flow rate on CO<sub>2</sub> breakthrough curves: (V1) 5 mL/min; (V2) 10 mL/min; (V3) 15 mL/min; (V4) 20 mL/min.

**Table 3.** The sorption capacity calculated on the basis of carbon dioxide concentration in biogas inlet and outlet through the fixed-bed column.

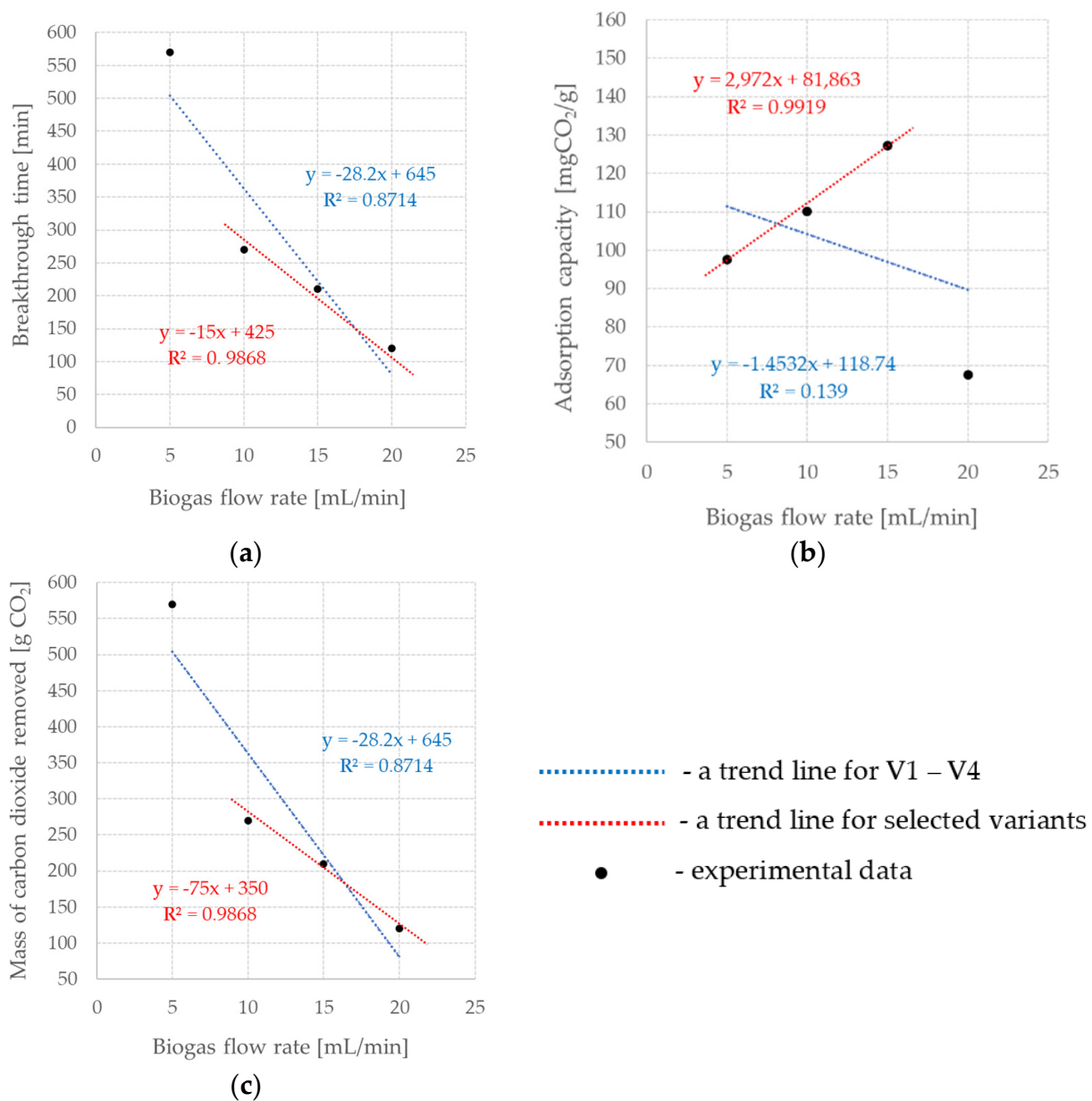
| Parameter                                           | Variant           |                   |                   |                   |
|-----------------------------------------------------|-------------------|-------------------|-------------------|-------------------|
|                                                     | V1                | V2                | V3                | V4                |
| Inlet carbon dioxide (g/L)                          | $1.84 \pm 0.08$   | $2.11 \pm 0.07$   | $2.16 \pm 0.09$   | $1.69 \pm 6.5$    |
| Outlet carbon dioxide (g/L)                         | $0.130 \pm 0.009$ | $0.076 \pm 0.008$ | $0.145 \pm 0.007$ | $0.281 \pm 0.008$ |
| Mass of carbon dioxide removed (g CO <sub>2</sub> ) | $4.87 \pm 0.06$   | $5.50 \pm 0.05$   | $6.36 \pm 0.04$   | $3.38 \pm 0.05$   |
| Sorption capacity (mg CO <sub>2</sub> /g TS)        | $97.50 \pm 3.7$   | $110.03 \pm 2.1$  | $127.22 \pm 1.5$  | $67.55 \pm 4.8$   |

According to the newest literature reports, the novel technologies for CO<sub>2</sub> capture not only remove it from biogas but also store it using waste from municipal solid waste incinerators containing calcium [53]. Other methods for biogas upgrading were also studied. For example, Aghel et al. [54] investigated the possibility of CO<sub>2</sub> separation and biogas upgrading using industrial wastewater (municipal, meat processing, water distillation, dairy, caustic, and fish pond wastewater). They found that the mass transfer coefficient of the presented method was at least 5 to 22 times greater than in chemical absorption.

The correlation analysis showed a strong negative relationship ( $R^2 = 0.9868$ ) between biogas flow rate and breakthrough time in variants V2–V4 (Figure 4a). When taking into account the whole range of tested flow rates (from 5 mL/min to 20 mL/min), the correlation was slightly weaker ( $R^2 = 0.8714$ ) (Figure 4a). The strong positive correlation ( $R^2 = 0.9919$ ) of sorption capacity with biogas flow rate was found in the range of rates between 5 mL/min and 15 mL/min, while the negative effect and weak correlation ( $R^2 = 0.139$ ) were achieved over the entire tested flow rates (Figure 4b). The strong positive correlation ( $R^2 = 0.9919$ ) of sorption capacity with biogas flow rate was found in the range of rates between 5 mL/min and 15 mL/min, while the negative effect and weak correlation ( $R^2 = 0.139$ ) were achieved over the entire tested flow rates (Figure 4b). This suggested that higher rates of biogas inflow negatively affected the capture of CO<sub>2</sub> in a fixed-bed column filled with bio-waste sorbent. In addition, the mass of carbon dioxide removed was strongly related to the biogas flow rate (Figure 4c). Regardless of the biogas inflow rate, there was no statistically significant efficiency of CO<sub>2</sub> capture by centrifuged anaerobic sludge ( $p > 0.05$ ). The CO<sub>2</sub> concentration in the biogas outlet was similar to the raw biogas and achieved  $41.9 \pm 2.5$  v%.

The biogas upgrading depending on the biogas inflow rate is shown in Figure 5. The inflow of biogas influenced the biomethane purity (Table 4). In the variant V3 (15 mL/min of the biogas inflow) the upgraded biogas contained  $98.9 \pm 0.2$  v% CH<sub>4</sub>, while in V2 (10 mL/min) it was slightly lower ( $98.6 \pm 0.2$  v% CH<sub>4</sub>), ( $p > 0.05$ ) (Table 4). Moreover, there were no statistically significant differences in methane contents in upgraded biogas obtained in variants V1–V3 ( $p > 0.05$ ). The fastest biogas velocity in V4 resulted in the reduction in biomethane to the value of  $96.9 \pm 0.2$  v% ( $p < 0.05$ ) (Table 4).

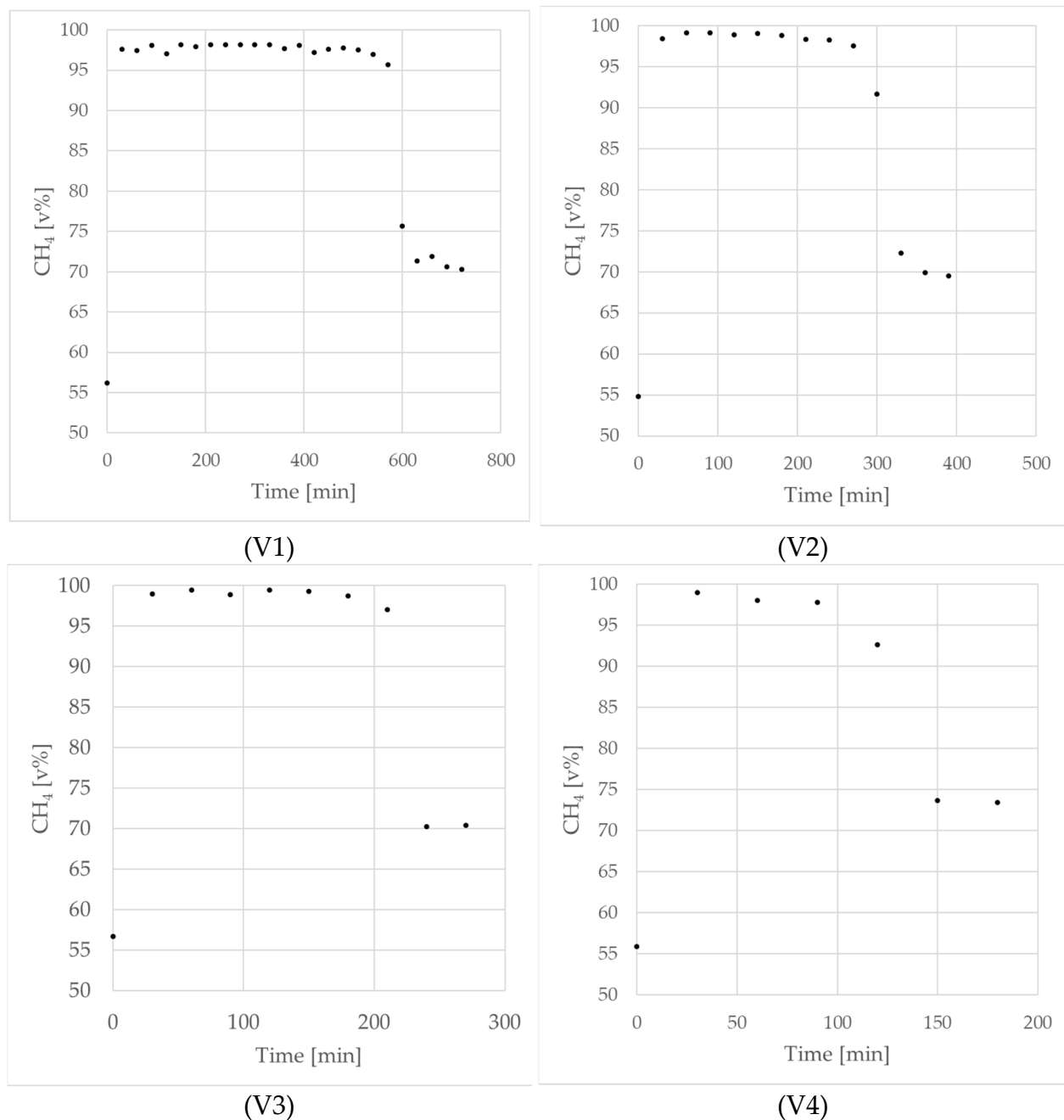
Sorption technologies for CO<sub>2</sub> capture ensure the methane concentration in biogas on the level of 93–98% [19]. In the study, the analysis of biogas composition showed that the highest methane concentration in the biogas outflow was  $98.9 \pm 0.2$  v% at a flow rate of 15 mL/min (Figure 5, Table 4). CO<sub>2</sub> uptake from biogas was effective during the breakthrough cycles in variants 1–3, providing biogas nearly completely devoid of CO<sub>2</sub> (the concentration of CO<sub>2</sub> was lower than 0.5 v%). However, in all experimental variants, the capture of CO<sub>2</sub> was high and ranged from 94.9% in V4 to 98.9% in V3. High flow rates lead to a reduced contact time between the gas molecules and the sorption bed, finally resulting in the reduction of the mass transfer rate and low CO<sub>2</sub> capture [47]. The treatment of the raw biogas (51 v% CH<sub>4</sub>, 39–36 v% CO<sub>2</sub>) with a solution of Ca(OH)<sub>2</sub> and biogas flow of 5 L/min resulted in a methane value of 89.3% [44]. The higher inflow rates of 10 L/min and 15 L/min ensured the methane content in upgraded biogas at the level of 87.4% and 84.3%, respectively. Bałys et al. [55] conducted breakthrough experiments using sorbents derived from bio-waste materials for biogas upgrading. They found that coconut shell activated carbon as the sorbent ensured the purity of biogas initially containing 25 v% CH<sub>4</sub> and 75 v% CO<sub>2</sub> on the level of above 95 v% CH<sub>4</sub>. Upgrading biogas using seawater solutions supplemented with modified zeolite and precipitates of phosphogypsum waste, plant clarifier, and water distillation at 30 °C, a liquid flow rate of 150 mL/h and a gas flow rate of 50 mL/min ensured the maximum CO<sub>2</sub> capture of 96.85, 96.01, 92.99, and 90.23%, respectively [56].



**Figure 4.** Correlation analysis of the effects of biogas flow rate on (a) breakthrough time; (b) sorption capacity; (c) mass of carbon dioxide removed.

**Table 4.** Upgraded biogas characteristics in comparison with raw biogas (as average).

| Parameter                            | % by Volume |                    |                    |                    |                    |
|--------------------------------------|-------------|--------------------|--------------------|--------------------|--------------------|
|                                      | Raw Biogas  | Upgraded Biogas V1 | Upgraded Biogas V2 | Upgraded Biogas V3 | Upgraded Biogas V4 |
| Carbon dioxide (v% CO <sub>2</sub> ) | 42.2 ± 2.1  | 0.53 ± 0.2         | 0.50 ± 0.2         | 0.44 ± 0.2         | 2.14 ± 0.3         |
| Methane (v% CH <sub>4</sub> )        | 56.5 ± 1.7  | 97.7 ± 0.3         | 98.6 ± 0.2         | 98.9 ± 0.2         | 96.9 ± 0.2         |
| Other gases (v%)                     | 1.3 ± 0.8   | 1.77 ± 0.06        | 0.9 ± 0.05         | 0.66 ± 0.07        | 0.96 ± 0.08        |



**Figure 5.** Effect of biogas flow rate on biogas upgrading: (V1) 5 mL/min; (V2) 10 mL/min; (V3) 15 mL/min; (V4) 20 mL/min.

The present study shows a simple solution for biogas upgrading that meets the circular economy requirements and material recycling, simultaneously reducing the costs of commercial sorbents [19]. The experiments are a novel approach to the valorization of organic waste materials such as wastewater sewage sludge, which is produced in large amounts in municipal and industrial wastewater treatment plants [24,27,57]. This solution seems to keep the cost of sorbent production and fixed-bed column exploitation low and, thus, may be competitive with conventional scrubbing methods. Further studies on a semi-technical scale should be conducted to establish the optimal technology parameters and estimate the process effectiveness and the real costs of the commercial solution.

#### 4. Conclusions

Developing sorbents from low-cost biomass residues for CO<sub>2</sub> capture is now a very important issue in the global climate strategy for renewable energy production as well as in the context of the circular economy. Sewage sludge from wastewater treatment plants is simultaneously the origin of hazardous contamination and a source of methane emissions; thus, its proper disposal is now a big challenge. Thus, in this work, these two environmental problems are solved by using sewage sludge as a bio-waste sorbent in biogas upgrading.

The potential of digested sludge derived from an anaerobic reactor as the bio-waste sorption material for CO<sub>2</sub> capture from biogas was studied. The fixed-bed column showed good performance at lower feed flow velocities from 10 mL/min to 15 mL/min. The maximum sorption capacity of  $127.22 \pm 1.5$  mg CO<sub>2</sub>/g TS was noticed at 15 mL/min. A strong positive correlation ( $R^2 = 0.9919$ ) of sorption capacity with biogas flow rate was found in the range of biogas inflow rates of 5 mL/min to 15 mL/min, while the negative effect ( $R^2 = 0.139$ ) was achieved over the entire tested flow rates (5–20 mL/min). This indicates that the higher rates of biogas inflow negatively affect the capture of CO<sub>2</sub> in a fixed-bed column filled with the bio-waste sorbent.

The breakthrough time decreased with the increase in biogas feed flow rate from  $570 \pm 10$  min at 5 mL/min to  $120 \pm 2$  min at 35 mL/min. The mass of CO<sub>2</sub> removed was strongly related to the biogas inflow ranging from 10 mL/min to 20 mL/min ( $R^2 = 0.9868$ ). The maximum mass of CO<sub>2</sub> removed ( $6.36 \pm 0.04$  g CO<sub>2</sub>) was achieved at 15 mL/min.

Biomethane concentration in the biogas outlet achieved a maximum of  $98.9 \pm 0.2$  v% at 15 mL/min with a simultaneous low CO<sub>2</sub> content of  $0.44 \pm 0.2$  v%. CO<sub>2</sub> uptake from biogas was effective during inflow rates from 5 mL/min to 15 mL/min, providing biogas nearly completely devoid of CO<sub>2</sub> (the CO<sub>2</sub> capture was over 98%). There were no statistically significant differences in the methane contents in upgraded biogas obtained at biogas velocities from 5 mL/min to 15 mL/min ( $p > 0.05$ ).

**Author Contributions:** Conceptualization, M.Z. and M.D.; methodology, M.Z.; investigation, A.K.; data analysis, M.Z., M.D., A.K. and M.K.; writing—original draft preparation, M.K. and A.K.; writing—review and editing, M.D. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was financially supported by the Minister of Education and Science in the range of the program entitled “Regional Initiative of Excellence” for the years 2019–2022, project no. 010/RID/2018/19, amount of funding: PLN 12,000,000, and project no. 29.610.023-110 of the University of Warmia and Mazury in Olsztyn funded by the Minister of Education.

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** Not applicable.

**Conflicts of Interest:** The authors declare no conflict of interest. The funders had no role in the design of the study, in the collection, analysis, and/or interpretation of data, in the writing of the manuscript, and in the decision to publish the results.

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