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Implementation of solidified carbon dioxide to anaerobic co-digestion of municipal sewage sludge and orange peel waste

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Introduction

The waste production is closely related with human activity. Various approaches have been applied to manage and reduce its increasing volume (Paranjpe et al. 2023). One of the possibilities that comply with the assumptions of circular economy is utilization of wastes in anaerobic digestion (AD) process. This technology is common worldwide and it is recognized as the cost-effective methods of energy generation that also allow for nutrient recovery, as well as effective waste management (Alharbi et al. 2023).

The biogas generated within this process is considered as a multifunctional renewable source that might be a promising alternative to the depleting traditional fuels. It finds various applications such as heat and power generation, fuel in automobiles, and substrate in chemical industry (Shitophyta et al. 2022, Pradeshwaran 2024). Typically, biogas contains 50–70% of CH_4, 30–50% of CO_2, and 1–10% of other trace gases like H_2, H_2S, CO, N_2. Its composition mainly depends on the feedstock characteristics, operational conditions, and adopted technology (Gani et al. 2023, Archana et al. 2024). Considering further application, the priority action should be increasing its volume and methane content. There are several strategies to achieve these goals, including implementing co-digestion strategy, adding additional component to the main substrate, introducing trace elements essential in AD, pre-treatment strategies, and introducing enzymes and microbial strains to digesters (Zhang et al. 2019). Each method has limits related to the implementation costs, changes in the adopted technology, operator training needs, and additional energy input, which might negatively influence the energy balance of wastewater treatment plants (WWTPs) (Meng et al. 2022). Therefore, recent scientific attention has focused on combining various strategies to achieve intended goals. Moreover, such combinations might allow for an effective utilization of various wastes, the earlier use of which in AD was difficult. Orange waste could be an example of such a substrate. The previous studies indicated that its application in AD resulted in poor process efficiency, mainly due to the presence of limonene, recognized as the main inhibitor of biological activity (Calabro et al. 2020, Bouaita et al. 2022).

In this study, the novel concept of implementing solidified carbon dioxide (SCO_2) in the anaerobic co-digestion of municipal sewage sludge (SS) and orange peel waste (OPW) has been proposed. This approach may help overcome the disadvantages of the two-component AD of these wastes. Importantly, such studies have not been conducted thus far. However, the recent studies indicated that application of SCO_2 to aerobic granular sludge improved biogas and methane yields and also enhanced the kinetics of biogas production (Kazimierowicz et al. 2023 a,b). Importantly, SCO_2 might be generated in biogas upgrading technologies (Yousef 2019). Such solution is consistent with the principles of the circular economy and contributes to reducing the carbon footprint of WWTPs.

Material and methods

Material characteristics

The sewage sludge used in this study was obtained from the WWTP located in Białystok city, Poland. This facility involves mechanical and biological treatments as well as sludge processing line. In the biological part, the conventional activated sludge process is employed. The capacity of this WWTP is 100,000 m^3/d. The sample used in this study was a mixture of thickened primary and waste sludge in the ratio of 60:40 v/v. The inoculum used in this study originated from anaerobic mesophilic digesters located at the same WWTP. The oranges used in this study originated from a local grocery store. Initially, they were washed. The obtained peel was then ground to obtain smaller particles, up to 5 mm in size. The characteristics of the materials are presented in Table 1.

Table 1. Characteristics of the materials used in this study (average values and standard deviation are given).

Parameter	Unit	OPW	SS	Inoculum
TS	g/kg	235.09±0.50	50.3±0.7	19.4±1.4
VS	g/kg-	224.41±0.87	38.7±1.2	9.9±0.5
%VS	%	95.46	77.9	-
pH		4.35±0.2	6.4±0.3	7.89±0.1
COD	mg/L	11 574±140	59 700±250	-
Limonene	ppm	297±12.4	-	-

The SCO_2 used in this study was in the form of granules with a diameter of 3 mm and was obtained from a company specializing in suppling this product for various purposes (eLod.pl, Bielsko-Biała, Poland). The specific gravity of SCO_2 was 1.6 kg/L and its temperature was -78.5°C.

Operational set-up and laboratory equipment

This study was divided into two experiments. In the first one, the influence of SCO_2 application on characteristics of the mixture of OPW and SS was investigated. SS and OPW were mixed at a ratio of 1:3.75 (SS volume, m^3: OPW additive mass, kg). In turn, the volumetric ratio of SCO_2 to the mixture of OPW and SS was 1:10 (S2). The adopted dose of SCO_2 was established according to literature data (Kazimierowicz et al. 2023b). Immediately after the addition of SCO_2, the mixture was homogenized using a low-speed stirrer. This sample was kept at a temperature of 20°C for about 6 hours.

In the second experiment, batch anaerobic digestion was conducted under mesophilic conditions. Three experimental series were carried out: S0, S1 and S2. In S0, the mono-digestion of SS was performed. In S1, the co-digestion of OPW and SS was examined. In turn, S2 was supplied with a mixture of OPW and SS with the addition of SCO_2. The experiments were performed using a BPC® BioReactor Simulator (BPC Instruments AB, Sweden). The simulator consisted of 6 small reactors, each with a total volume of 2.0 L and equipped with a mechanical stirrer, placed in a water bath to maintain the assumed temperature. These reactors were supplied with 1.4 L of inoculum and 0.4 L of feedstock.

Analytical methods

The analytical methods employed in the first experiment, assessing the influence of SCO_2 application on the properties of the mixture of OPW and SS, involved examining the solubilization degree (SD) and release degree (RD) of VS (volatile solids) and DOC (dissolved organic carbon). The following formulas were used:

$$SD = \frac{sCOD - sCOD_0}{COD_0 - sCOD_0} \text{ x } 100\%$$

where, sCOD is the soluble chemical oxygen demand of pre-treated mixture, COD0 is the total chemical oxygen demand of raw mixture, and sCOD0 is the soluble COD of the liquid fraction.

$$RD = \frac{P - P_0}{P_0} \text{ x } 100\%$$

where, P is the content of DOC (mg/L) or VS (g/kg) in pre-treated mixture, Po is the content of DOC and VS in untreated mixture.

Moreover, the presence of such inhibitors as phenols and limonene was analyzed in this part of the study.

In the second experiment, the effectiveness of SCO_2 application was assessed based on biogas/methane yields, organic compounds removal (R), and process stability. To evaluate these parameters, the following measurements were conducted on both the feedstock (F) and digestate (D): soluble chemical oxygen demand (sCOD), chemical oxygen demand (COD), total solids (TS), and volatile solids (VS). Additionally, stability parameters including alkalinity (ALK), volatile fatty acid (VFA), and VFA/ALK ratio were determined in both materials. Biogas/methane yields and the effectiveness of organic removal were determined following the procedure outlined in the study conducted by Szaja et al. (2022a,b).

The evaluate to concentrations of sCOD and DOC, the samples were first centrifuged at 4000 r min^{-1} for 30 minutes and then passed through a 0.45µm filter. Both TS and VS contents were analyzed according to the Standard Methods for the Examination of Water and Wastewater (APHA, 2012). The concentrations of COD and CODs, phenols, ALK, VFA were analyzed using an Hach Lange UV–VIS DR 6000 spectrophotometer (Hach, Loveland, CO, USA) with cuvette tests. The pH values were monitored using an HQ 40D Hach-Lange multimeter (Hach, Loveland, CO, USA). The TOC and DOC contents were determined using RC 612 LECO and TOC-L Shimadzu analyzers, respectively. Biogas composition and limonene presence were detected using a ThermoTrace GC-Ultra gas chromatograph (Thermo Fisher Scientific) and a Trace GC Ultra PolarisQ (Thermo Electron), respectively.

Kinetic evaluation

In this study, the kinetic assessment was also performed. Modified Gompertz (Eq. 1) and Logistic growth (Eq.2) models were applied.

$$M(t) = M_p \cdot exp\left(-exp\left(\frac{R_m \cdot e}{M_p} exp(\lambda - t) + 1\right)\right) \quad (1)$$

$$M(t) = \frac{M_p}{\left(1 + \text{exp } (4 \cdot R_m \cdot \left(\frac{\lambda - t}{M_p}\right) + 2\right)} \quad (2)$$

Where:
- M_p is the maximum methane production (mL CH_4/g VS);
- M (t) is the cumulative methane production (mL CH_4/gVS);
- R_m is the maximum methane production rate (mL CH_4/ gVS d);
- e is the constant (2.71828);
- λ is the lag phase (d);
- t is time (d).

Moreover, in this study, based on experimental data, biogas production rate (BPR) and methane production rate (MPR) were also calculated according to the procedure outlined in a previous study (Szaja et al., 2022a).

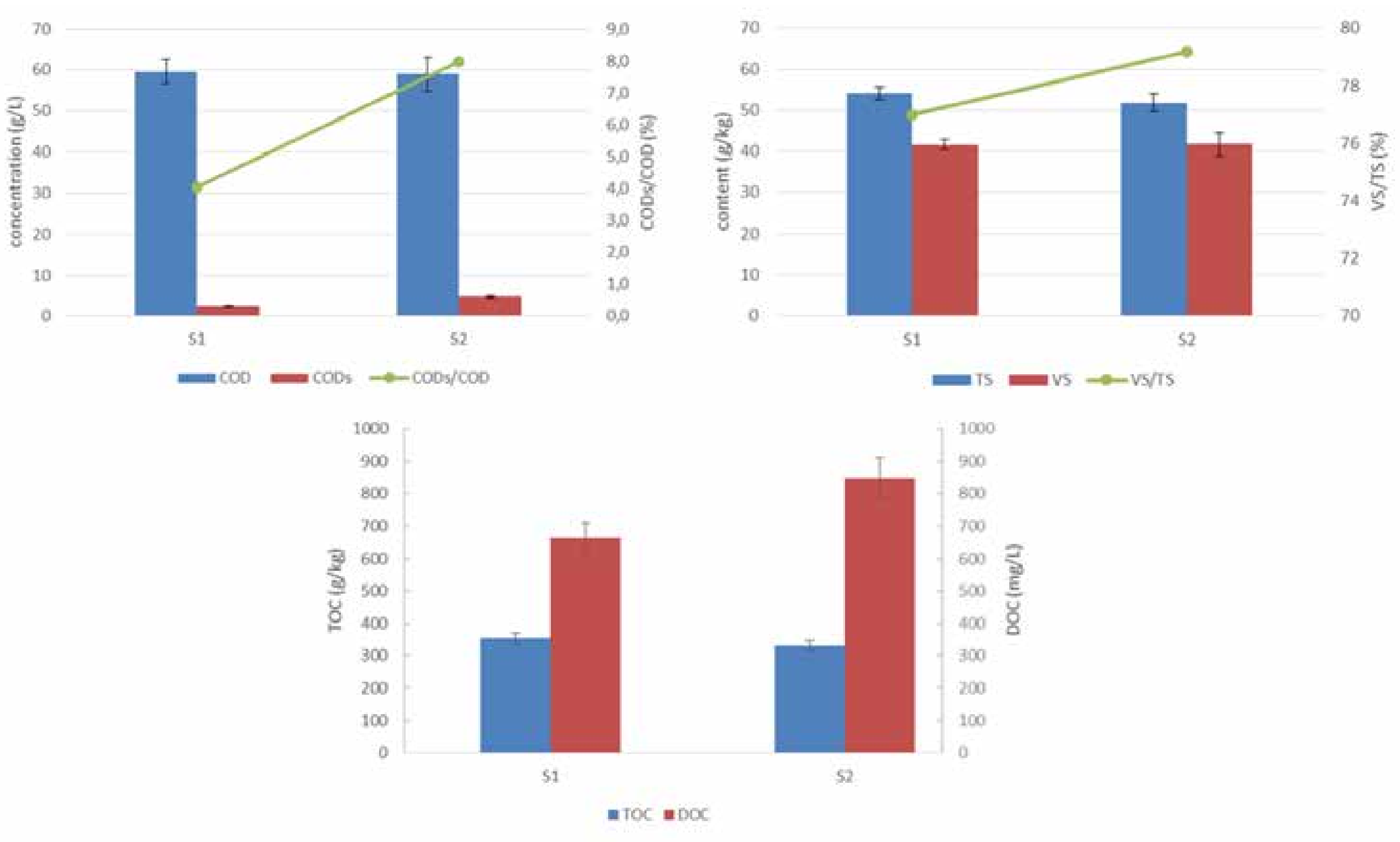

Figure 1. Content of COD, sCOD, TS, VS, DOC, TOC in un-treated samples (S1) and S2 (pre-treated samples, with SCO_2 addition) (average values, standard deviation are presented).

For statistical analysis, Statsoft Statistica software (v 14) was employed. The kinetic constants were evaluated using a nonlinear regression method.

Result and discussion

Experiment 1 - pre-treatment with SCO_2

The results regarding the application of SCO_2 on the properties of mixture of OPW and SS are shown in Figure 1. The introduction of SCO_2 to the mixture of OPW and SS resulted in a 2-fold increase in sCOD concentration. However, the SD reached a value of 4%. For comparison, this indicator for another pre-treatment method, i.e., sonification, is established at the level of 2 – 20%, depending on the adopted operational parameters (Pilli et al. 2011). A similar trend was observed in the case of DOC; however, a minor effect was noticed, the RD for this indicator established at the level of 28%. Concerning COD, TOC, TS and VS contents, there was no significant impact observed with its application, and the results comparable to untreated feedstock.

It should be noted that the application of SCO_2 led to a significant reduction of limonene content by 60% (Table 2). This effect may result from the properties of SCO_2 and limonene. Under atmospheric conditions, SCO_2 continuously sublimates, which is related to the fact that the carbon dioxide triple point pressure is higher than the atmospheric pressure (Purandare et al. 2023). On the other hand, limonene is recognized as a volatile compound (González-Mas et al. 2019). Therefore, during SCO_2 sublimation, an enhanced release of limonene to the atmosphere might be observed, ultimately resulting in losses in the analyzed mixture (S2). However, the pre-treatment resulted in a slight release of phenols, approximately 4%.

Experiment 2 – performance of the anaerobic digestion process

In experiment 2, the influence of SCO_2 on anaerobic digestion performance was examined. Firstly, the results in terms or organic removal were analyzed (Figure 2). It should be noted that in the presence of OPW in both raw and pre-treated mixtures, improvements in TS, VS and COD, sCOD removals were observed compared to SS mono-digestion. However, the most significant improvements were observed in the case of pre-treated feedstock (S2). In this case, enhancements of 7, 9 and 11% were achieved for VS, TS and COD removals, respectively. In turn, a notable increase in sCOD removal was observed, rising from 6.6% (control) to 57.5% (S2). This observation is related to a substantial concentration of this

Table 2. The contents of limonene, phenol and pH values in pre-treated mixtures.

Series	pH	Limonene (ppb)	Phenol (mg/L)
S0	6.06±0.01	4.2±0.4	4.8±0.12
S1	5.89±0.07	330±19.0	4.9±0.07
S2	6.14±0.04	123±12.1	5.3±0.06

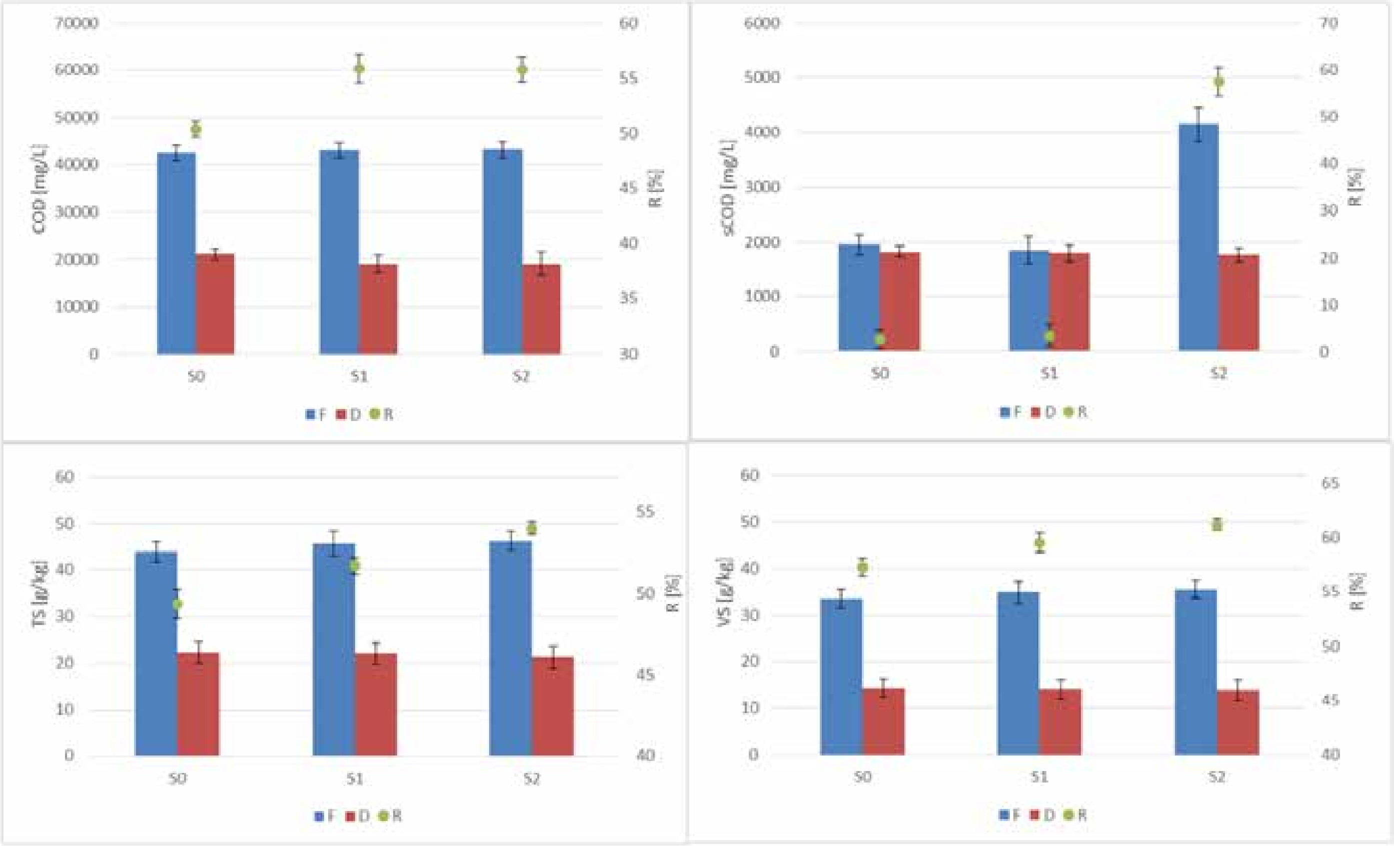

Figure 2. Content of COD, sCOD, TS and VS in feedstock (F) and digestate (D), with their removal efficiencies (R) (average values, standard deviation are presented).

parameter in the feedstock compared to both series S0 and S1, respectively. The achieved increases in the presence of SCO_2 are particularly beneficial, indicating the effective utilization of organic matter in the process, hence leading to increased biogas production (Figure 3).

In this experiment, stability parameters such as pH, VFA, alkalinity, and the VFA/ALK ratio were also monitored (Table 3). Evaluation of these parameters is particularly important due to the possibility of generating toxic products during pre-treatment. It is worth noting that all analyzed parameters are within the recommended range for the AD process (Wu et al., 2021). However, a negative impact on their values might be observed in the case of OPW. As shown in Table 3, a significant increase of 40% in the VFA/ALK ratio was found in S1 compared to the control, indicating process inhibition in the presence of untreated OPW. Such a high increase in this ratio is related to enhanced VFA concentration in the digestate compared to other series. This effect indicated that disturbances occurred in the untreated mixture of OPW and SS.

The results regarding biogas and methane productions are presented in Table 4 and Figure 3. It is worth mentioning that in the digester supplied with pre-treated feedstock, increases in both biogas and methane yields were observed. The biogas production was enhanced by 16% compared to SS mono-digestion. However, in the case of the untreated two-component digestion (S1), comparable results were achieved to control reactor, despite the improved feedstock composition. Importantly, an improvement in methane yield by 12% was noticed in the digester supplied with SCO_2 (S2). It should be noted that in the co-digestion series where SCO_2 was not added, similar results to SS mono-digestion were found. This observation was related to the inhibitory influence of limonene, indicating an antibacterial effect even at low concentrations (Rokaya 2019, Awasthi 2022, Hakimi 2023). Such observations were also reported in previous studies conducted by Szaja et al. (2022b), Serrano et al., (2014), Ruiz and Flotats (2014). It is worth mentioning that limonene indicates a toxic influence for methanogenic and hydrolytic–acidogenic bacteria. This

Table 3. The results of stability parameters in feedstock (F) and digestate (D) in experiment 2.

Series	ALK (mg/L)		VFA (mg/L)		pH (-)		VFA/ALK (-)
	F	D	F	D	F	D	
S0	715±12.1	5502±25	849±14.1	283±6.7	5.83±0.01	7.40±0.01	0.051
S1	852±14.2	4942±15	640±9.8	340±8.1	6.01±.0.2	7.49±0.03	0.071
S2	926±17.3	4984±19	737±10.1	281±5.1	5.70±0.01	7.29±0.03	0.056

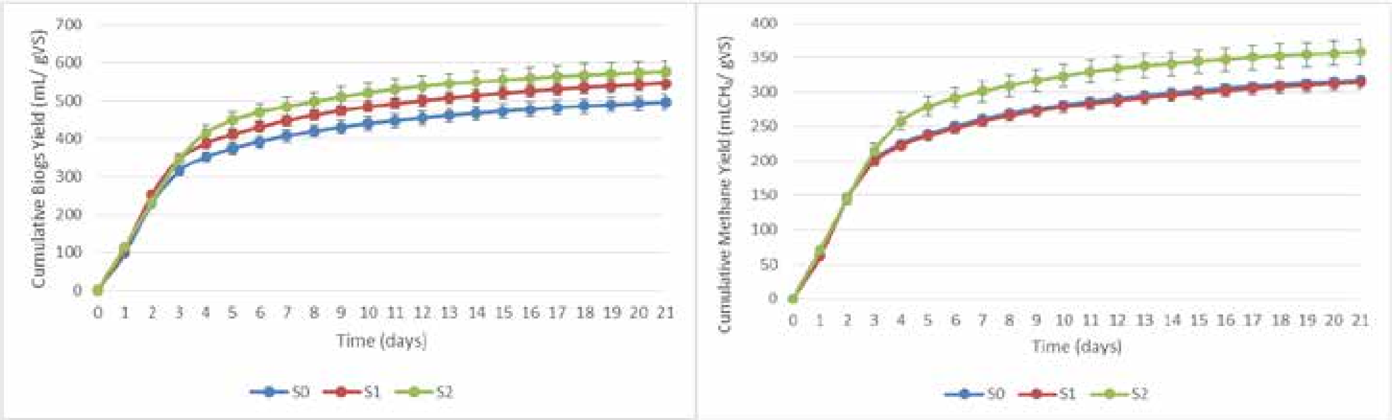

Figure 3. Cumulative biogas methane productions (average values and standard deviation are given).

essential oil might interact with their cell membrane, changing its structure and impairing a number of its functions, including selectivity, energy transducing, and being a matrix for enzymes. Finally, it leads to leakage of cell content (Fisher and Phillips 2008, Ruiz and Flotats 2014).

The application of low-temperature pre-treatment prior anaerobic digestion of SS has been widely investigated. It may enhance sludge dewaterability and the solubilization of organic matter from sludge (Nazari et al. 2017, Hu et al. 2011). In particular, the release of readily accessible organic matter for microorganisms might lead to enhanced biogas production (Montusiewicz et al. 2010). The main effect of low temperatures is related with the change in flock structure and the destruction of cell walls (Phalakornkule et al. 2017, Nazari et al. 2017). Some studies in the field of using of SCO_2 have also been performed. The use of SCO_2 resulted in enhanced methane production. Importantly, studies have not reported any negative impact of such pre-treatment on long-term digesters performance (Kazimierowicz et al. 2023a). Other investigations also confirmed the beneficial effect of this method on biogas production. In the study conducted by Zawieja (2019), this parameter was increased by 44% compared to the control. In turn, the use of SCO_2 combined with alkaline pre-treatment also led to enhanced biogas production by 15% (Grübel and Machnicka 2020).

So far, the impact of SCO_2 on the anaerobic co-digestion of OPW and SS has not been investigated. However, other pre-treatment strategies allowing for effective AD of citrus fruits have been applied. It should be noted that most of them concern only OPW itself, but not mixtures.

Rokaya, et al. (2019) evaluated the influence of hydrogen peroxide (H_2O_2) application on OPW. In this study, a significant enhancement in biogas production, from 170 mL/gVS to 750 mL/gVS was noted in the control and pre-treated sample, respectively. Among other applied strategies, steam distillation was also proposed. The use of this strategy allowed for recovering limonene and hence effective application of OPW in the AD process (Martín et al. 2010). Another pre-treatment strategy involved the use of ensiling, where limonene was removed up to 75%, resulting in enhanced methane yields (Calabro et al. 2022). In the case of biological methods, the application of *Penicillium genus* did not yield positive results in terms of methane production, despite the reduction of limonene content by 20%. This fact was related to the

Table 4. The results of kinetic evaluation in experiment 2 in terms of biogas and methane productions.

Model	Parameters	Unit	S0	S1	S2
Modified Gompertz	M_p	mL CH_4/gVS	295.6	292.2	337.8
	R_m	mL/gVS d	53.5	52.9	63.6
	λ	d	-0.281	-0.282	-0.037
	R^2	-	0.97475	0.97475	0.98397
Logistic growth model	M_p	mL CH_4 /gVS	298.7	295.3	341.3
	R_m	mL CH_4/ g VS d	55.7	55.0	65.0
	λ	d	-0.282	-0.282	-0.107
	R^2	-	0.98444	0.98444	0.9913
Experimental data	B_p	mL/gVS	496±11.4	546±16.4	576±17.8
	M_p	mL CH_4 /gVS	317±13.4	314±9.9	358±19.1
	GPR	mL/gVS d	23.6	26.0	27.4
	MPR	mL/ gVS d	15.1	14.9	17.1
	Methane content	%	63.99±2.3	58.0±1.7	62.13±3.1

generation of another inhibitor, e.g., α-terpineol, within pre-treatment (Ruiz and Flotats 2014). The problem of generating toxic by-products should always be investigated within the application of pre-treatment strategy. This fact is particularly important in the application of a pre-treatment method with multi-component mixtures. Another issue that should be considered is the energetic aspect and profitability of a given solution (Millati et al. 2020).

In this study, the effect of SCO_2 application on MBR and BPR was also analyzed (Table 4). In the case of BPR, the implementation of feedstock with OPW resulted in an improvement of this parameter by 10 and 16% in S1 and S2, respectively. A different trend occurred in the case of MPR; therein, in the digester supplied by OPW and SS, a decreased value was found. This fact also confirms the limonene inhibition. It is worth noting that the use of SCO_2 resulted in an improvement in this indicator by 13% as compared to control S0.

In this study, kinetic evaluation was also performed using two models: the modified Gompertz and logistic growth models. The validity of the choice was confirmed by the high value of R^2. As shown in Table 3, the results obtained in kinetic evaluation corresponded with the experimental data. In the presence of SCO_2 (S2), the maximum methane production was improved by 14% in both models compared to control (S0). Moreover, in both analyzed models, a significantly improved maximum methane production rate (R_m) was found in the presence of SCO_2. Compared to the control, growths of 19 and 16% for modified Gompertz and logistic growth models, respectively, were observed. Another important finding achieved in the presence of SCO_2 is the shortening of the lag phase. This kinetics constant describes the time of adaptation of microorganisms to process conditions (Howell et al. 2019). Such beneficial results in the case of SCO_2 are related to both the solubilization and limonene degradation observed during SCO_2 application. As in the case of experimental data, both M_p and R_m were decreased in the untreated mixture of OPW and SS (S1), confirming process inhibition.

Conclusions

The effective application of OPW in anaerobic digestion process remains a challenge; therefore, a novel strategy using solidified carbon dioxide has been proposed to overcome the difficulties of its utilization in AD process. The obtained results indicate that the application of this low temperature pre-treatment led to the release of sCOD and DOC concentrations, accompanied by a reduced content of limonene. This beneficial effect in the presence of SCO_2 resulted in improved biogas and methane production, as well as enhanced kinetics. On contrary, the AD of the untreated mixture of OPW and SS resulted in decreased methane yield and worsening stability parameters, indicating process inhibition. The proposed low temperature pre-treatment represents a breakthrough in studies in the field of citruses' application in anaerobic processes, enabling effective management with energy production.

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Zastosowanie zestalonego ditlenku węgla w procesie współfermentacji osadów ściekowych i opadów cytrusowych

Streszczenie: W przeprowadzonych badaniach zaproponowano zastosowanie niskotemperaturowej obróbki wstępnej z wykorzystaniem zestalonego ditlenku węgla (SCO_2) w celu przezwyciężenia trudności związanych z dwuskładnikową fermentacją odpadów odpadów cytrusowych (OPW) i komunalnych osadów ściekowych (SS). Przeprowadzono dwa eksperymenty, w pierwszym zbadano wpływ zastosowania SCO_2 na właściwości mieszaniny OPW i SS. W drugim przeprowadzono fermentację mezofilową w układzie porcjowym. Uzyskane wyniki wykazały, że zastosowanie SCO_2 spowodowało wzrost zawartości rozpuszczonej materii organicznej wyrażonej jako sChZT i DOC oraz spadek zawartości limonenu. Uzyskany korzystny efekt w obecności SCO_2 spowodował poprawę produkcji zarówno biogazu, jak i metanu. W tym przypadku uzyskano również korzystny wpływ na kinetykę produkcji metanu. Wydajność produkcji biogazu i metanu wyniosła odpowiednio 576±17,8 i 358±19,1 mL/ g smo. Z kolei, w reaktorze kontrolnym, w którym przeprowadzono fermentację osadów ściekowych wskaźniki te osiągnęły wartości odpowiednio 496±11,4 i 317±13,4 mL/ g smo. Dodatkowo, w przypadku zastosowania SCO_2 uzyskano wyższy stopień przefermentowania oraz stabilny przebieg procesu. Z kolei, w przypadku fermentacji dwuskładnikowej OPW i SS nie poddanej wstępnej obróbce w porównaniu do próby kontrolnej odnotowano zmniejszoną produkcję metanu oraz negatywny wpływ na stabilność procesu. Zaproponowana niskotemperaturowa obróbka wstępna z wykorzystaniem zestalonego ditlenku węgla stanowi przełom w badaniach w zakresie zastosowania odpadów cytrusów w procesach beztlenowych, umożliwiając ich efektywne zagospodarowanie z produkcją energii.