applied sciences

MDPI

Article

An Effective Energetic Application of Orange Waste in Multi-Component Co-Digestion with Municipal Sewage Sludge

Aleksandra Szaja [1,*], Joanna Czarnota [2], Adam Masłoń [2] and Magdalena Lebiocka [1]

[1] Faculty of Environmental Engineering, Lublin University of Technology, Nadbystrzycka 40B, 20-618 Lublin, Poland; m.lebiocka@pollub.pl
[2] Department of Environmental Engineering and Chemistry, Rzeszow University of Technology, Powstańców Warszawy 6, 35-959 Rzeszów, Poland; askalucz@prz.edu.pl (J.C.); amaslon@prz.edu.pl (A.M.)
* Correspondence: a.szaja@pollub.pl; Tel.: +48-81-538-4408

Abstract: A strategy allowing for the application of orange waste (OW) in anaerobic co-digestion with municipal sewage sludge (MSS) has been proposed. For this purpose, the introduction of an additional component represented by ice-cream processing waste (IPW) has been chosen. The experiment was conducted in batch mode at a temperature of 37 °C. Four series were conducted: S1—the mono-digestion of MSS; S2—two-component co-digestion of MSS and 1.5 g of OW; S3—two-component co-digestion of MSS and 1.0 g of IPW; and S4—three-component co-digestion of MSS, 1.0 g of IPW, and 1.5 g of OW. The obtained results indicate that the highest methane production was achieved in the presence of IPW in two- and three-component mixtures (S3 and S4). It was also accompanied by improved kinetics, enhanced organic removal, and stable process performance. The related methane yields were 407.6 and 401.6 mL/g VS in S3 and S4, respectively. In turn, in S1 and S2, this parameter was established at the level of 351.3 and 344.3 mL/g VS. Additionally, as compared to MSS mono-digestion (S1), the energy profit was enhanced by 54 and 62% in S3 and S4, respectively. The obtained results indicate the possibility of effective management of OW with energy recovery in the anaerobic digestion process (AD).

Keywords: orange peels; ice-cream processing waste; sewage sludge; methane production; kinetics modeling; energy balance

Academic Editors: Carmine Lubritto and Maria Rosa Di Cicco

Received: 15 January 2025
Revised: 28 January 2025
Accepted: 1 February 2025
Published: 3 February 2025

Citation: Szaja, A.; Czarnota, J.; Masłoń, A.; Lebiocka, M. An Effective Energetic Application of Orange Waste in Multi-Component Co-Digestion with Municipal Sewage Sludge. *Appl. Sci.* **2025**, *15*, 1537. https://doi.org/10.3390/app15031537

1. Introduction

Recently, the growing energy demand as well as the depletion of traditional fuels has resulted in the constant search for new solutions for sustainable energy production. Therefore, the application of food waste in the anaerobic digestion (AD) process has gained increasing attention. This is the dominant technology that allows various organic by-products to be converted into biogas as an energy carrier [1].

Importantly, the food sector is recognized as one of the most energy- and water-/raw material-intensive industries [2]. Simultaneously, it generates a significant amount of valuable by-products. The use of these wastes in AD is dictated by many factors, including a significant content of organic matter and the presence of many micro- and macro-elements that might stimulate AD microbes [3]. Another important factor in favor of the application of such wastes is the reduction of its management costs. This technology aligns with a circular economy model by converting food waste into valuable resources, e.g., biogas and nutrient-rich digestate, thus limiting the negative impact of this industry on the environment [4].

Despite significant developments in this technology, there are still many gaps in the use of specific wastes in AD. This group includes orange juice processing by-products, represented mainly by orange peel, accounting for about 40–50% of the total fruit weight [5]. It mainly contains essential oils, flavonoids, pectin, and fibers. It might be a source of essential oils or pectin [6,7]. Therefore, it has many applications in cosmetics, food, and pharmaceutical industries, as well as in biomaterial production [8]. However, those applications entail additional financial outlays. Additionally, due to its high lability and significant moisture content, as well as its minor calorific value, conventional methods of orange waste disposal, such as animal feed, landfilling, incineration, composting, and thermal treatment, are inadequate in terms of investment, environmental effect, and sustainability [2]. Simultaneously, according to the U.S. Department of Agriculture Foreign Agricultural Service (USDA FAS), in the coming years, a continuous increase in orange production is expected. In 2023–2024, approx. 48.8 million tons is forecast, which will result in huge amounts of waste that will need to be effectively managed. However, the previous studies indicated that mono-digestion is still challenging mainly due to the presence of essential oils, e.g., d-limonene, a natural compound present in orange peels that can inhibit microbial activity during its AD [9]. Other factors that make it difficult to use these wastes in mono-digestion include phenols, a significant content of organic substances, and the presence of barely biodegradable lignins.

Several strategies have been proposed to overcome the mentioned difficulties. The first includes the use of a pre-treatment strategy to reduce the d-limonene content, such as steam distillation [10], ensiling [11], or leaching of limonene using hexane as solvent [12]. Another possibility is the reduction of toxic compounds by using carbonaceous sorbents, e.g., biochar, that adsorb the toxic agents onto their surface [13,14]. However, those methods require additional financial outlays.

In recent years, the co-digestion strategy has gained increasing attention mainly because of the relatively low cost and ease of implementation, possibility of using a wide range of various organic wastes, and environmental friendliness [15]. However, the crucial benefits of implementing this strategy are enhanced methane production as well as providing valuable nutrient-rich digestate [16]. Nevertheless, the main challenge for successful application is the selection of a suitable additive with complementary composition to the main component, as well as the adoption of adequate operational parameters [17]. This strategy allows for optimization of the C/N ratio and dilution of toxic compounds present in substrates, ensuring the buffer capacity and hence providing synergistic effects on microbial growth [18].

With regard to OW, this strategy allows for balancing the nutrient composition and mitigates the inhibitory effects of d-limonene. Thus far, OW has been successfully co-digested with glycerol [19], organic fraction of municipal solid waste [20], fruit and vegetable wastes [21,22], and marine seaweed with cattle manure [23]. Importantly, its co-digestion with municipal sewage sludge might also result in low biogas production, indicating the occurrence of the d-limonene inhibition phenomenon [24,25]. The development of technology should be further investigated due to the widespread availability of anaerobic digesters at many municipal wastewater treatment plants. Additionally, WWTPs are interested in the implementation of strategies to increase methane production, which would allow the facilities to become energy self-sufficient [26]. Generally, mono-digestion of MSS indicates low methane production and efficiency of volatile solids reduction, additionally requiring a long retention time [18]. Therefore, there is still a need to find a new available substrate that will allow the difficulties related to anaerobic bioconversion of both orange wastes and MSS to be overcome.

In this study, a novel strategy allowing for effective energetic application of orange waste in co-digestion with municipal sewage sludge (MSS) was developed. To overcome the problems of two-component co-digestion of those wastes, the implementation of ice-cream processing waste (IPW) as an additional component was proposed. Thus far, the effectiveness of co-digestion of those substrates has not been the subject of research. Importantly, in this study, several factors were investigated, e.g., removal of organic compounds, process stability, and methane production, including its kinetics. Moreover, energy gains resulting from the implementation of this technology were estimated. Importantly, the proposed technology will allow for both energy recovery and effective management of selected groups of waste.

2. Materials and Methods

2.1. Substrate Characteristics

In this study, the following substrates were applied: municipal sewage sludge, oranges waste, and by-products from ice-cream production. The first component was obtained from the Hajdów WWTPs, Lublin, Poland. It consists of primary and excess sludge mixed in a volumetric ratio of 60:40% v/v. Those types of sludge were taken separately from WWTPs, and then, under laboratory conditions, they were mixed in the adopted proportion using a low-speed stirrer. The inoculum was taken from mesophilic digesters from the same WWTPs.

Orange waste was obtained as a by-product of juice processing, and it consisted mainly of peel and fibers. Before suppling it to the reactor chamber, this waste was shredded to a fraction of 0.5 cm. IPW was obtained from an ice-cream production company. The composition of all applied substrates is presented in Table 1.

Table 1. The composition of materials applied in this experiment (average values with standard deviation are shown).

Parameter	Unit	IPW	MSS	OW	Inoculum
COD	g/L	464 ± 7.8	47.4 ± 6.2	10.9 ± 1.2	
sCOD	g/L	449.8 ± 12.3	2.48 ± 0.04		
TS	g/kg	989.5 ± 33.1	43.4 ± 3.7	940.3 ± 23.4	24.45 ± 5.8
VS	g/kg	979.6 ± 25.1	34.0 ± 4.1	874.5 ± 60.1	14.37 ± 3.7
VFA	mg/L	121 ± 8.9	715 ± 21.4	470 ± 14.2	
TA	mg/L	4375 ± 56.3	735 ± 47.3	30.1 ± 8.9	
pH		3.52 ± 0.5	5.62 ± 0.7	4.94 ± 0.9	7.36 ± 2.1
TP	mg/L	19.6 ± 5.4	474 ± 44	16.3 ± 2.3	
TN	mg/L	1542 ± 30.1	1701 ± 36	90.1 ± 9.8	
$N\text{-}NH_4^+$	mg/L	2850 ± 17.2	102 ± 10.1	36.1 ± 5.8	
$P\text{-}PO_4^{3-}$	mg/L	11.2 ± 1.4	265 ± 8.9	12.3 ± 3.2	
Phenols	mg/L	1.3 ± 0.4	7.4 ± 1.1	64.1 ± 4.5	
D-limonene	ppb	nd	nd	312.7 ± 11.3	

2.2. Experimental Procedure and Labotatory Installation

The anaerobic digestion experiments were conducted in batch mode using laboratory stand BioReactor Simulator provided by BPC Instruments (Lund, Sweden). This device consisted of 6 anaerobic reactors, each with an active volume of 1.8 L. The reactors were placed in a water bath to keep the adopted temperature.

Each digester was provided with a mechanical agitator working on a cycle of 5 min and 25 min of mixing and rest, respectively. Prior to the experiments, all reactors were purged of inert gas to achieve anaerobic conditions. The volume of generated biogas was continuously monitored through the system provided by BPC Instruments.

Each reactor was supplied 1.4 L of inoculum and 0.4 L of the main component e.g., MSS. In this research, four experimental series with differing feedstock configurations were provided:

- S1—control series, mono-digestion of MSS;
- S2—two-component co-digestion of MSS and 1.5 g of OW;
- S3—two-component co-digestion of MSS and 1.0 g of IPW;
- S4—three-component co-digestion of MSS, 1.0 g of IPW, and 1.5 g of OW.

The adopted doses of the co-substrates were established on the basis of substrate-to-inoculum ratio to achieve the highest methane production. In this study, this ratio varied between 0.68 and 0.72. In turn, the total organic load varied from 13.6 to 14.4 g VS/L depending on the feedstock composition.

This batch anaerobic digestion was performed under mesophilic conditions (37 °C) and lasted 21 d. The experiments were repeated three times under the same operational conditions.

2.3. Analitical Methods

In the applied substrates, the following parameters were controlled: total chemical oxygen demand (COD), soluble chemical oxygen demand (sCOD), total nitrogen (TN) and total phosphorus (TP), volatile fatty acids (VFAs), alkalinity (TA), pH, ammonia nitrogen (NH_4^+-N), orthophosphate phosphorus ($PO_4^{3-}-P$), and phenols. These indicators were determined by involving the spectrophotometric method using Hach Lange UV–VIS DR 3900 (Hach, Loveland, CO, USA). Each of the above-mentioned parameters was determined using standard cuvette tests according to the protocols provided by the producer and available on the website [27] (Hach Loveland, CO, USA). The sCOD, VFAs, TA, NH_4^+-N, and $PO_4^{3-}-P$ were measured in the soluble fraction that was obtained by centrifugation of the samples at 4000 rpm for 30 min. In turn, TS and VS were determined according to the procedure presented in the Standard Methods for the Examination of Water and Wastewater [28]. The pH values were controlled using a CP-511 multimeter (Elmetron, Zabrze, Poland).

The biogas composition, e.g., CH_4 and CO_2, was established be means of a Thermo-Trace GC-Ultra gas chromatograph (Thermo Fisher Scientific, Milan, Italy). The conditions of analysis were as follows: 50 °C and 100 °C for the injector and the detector, respectively; carrier gas—helium (flow rate of 1.5 cm^3/min); and divinylbenzene packed columns (RTQ-Bond). The d-limonene content was also determined chromatographically. The Supelco, characterized by 30 m × 0.25 mm ID × 0.25 µm, was applied as a capillary column. The parameters of detection were as follows: carrier gas—helium, initial temperature—40 °C, temperature measurements—250 °C maintained for 3 min.

2.4. Kinetic Evaluation

To perform the kinetic evaluation, the hyperbolic model (HM) [29] (Equation (1)) and the logistic growth model (LGM) [30] (Equation (2)) were chosen. Both indicated the best fit to the experimental data, which was confirmed by the high coefficient of determination values (R^2). The adopted formulas with descriptions are presented below:

$$M(t) = M_p \cdot \left(\frac{k \cdot t}{1 + k \cdot t} \right), \tag{1}$$

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

where M_p is the methane production (mL CH_4/g VS), R_m is the maximum methane production rate (mL CH_4/(g VS·d)), M(t) is the cumulative methane production (mL CH_4/g VS), λ is the lag phase (d), and k is the rate constant (1/d).

2.5. Energy Balance Evaluation

The energy gains obtained by using this technology were calculated for the existing digester operated under mesophilic conditions, with a capacity of 2500 m^3, an average feedstock flow rate of 125 m^3/d, and an HRT of 20 d. To perform this evaluation, the following equations were used:

$$Q_m = Y_m \cdot L_{VS}, \tag{3}$$

$$Q_t = Q_m \cdot Q_i, \tag{4}$$

$$Q_1 = V \cdot \left(T - T_f\right) \cdot CSS, \tag{5}$$

$$Q_2 = 24 \cdot (T - T_a) \cdot U \cdot F, \tag{6}$$

$$F = 3.14 \cdot D^2, \tag{7}$$

$$Q_c = \beta \cdot (Q_1 + Q_1), \tag{8}$$

$$Z = \left(\frac{Q_t - Q_c}{Q_c}\right) 100\%, \tag{9}$$

$$E_d = Q_m \cdot Q_{ie}, \tag{10}$$

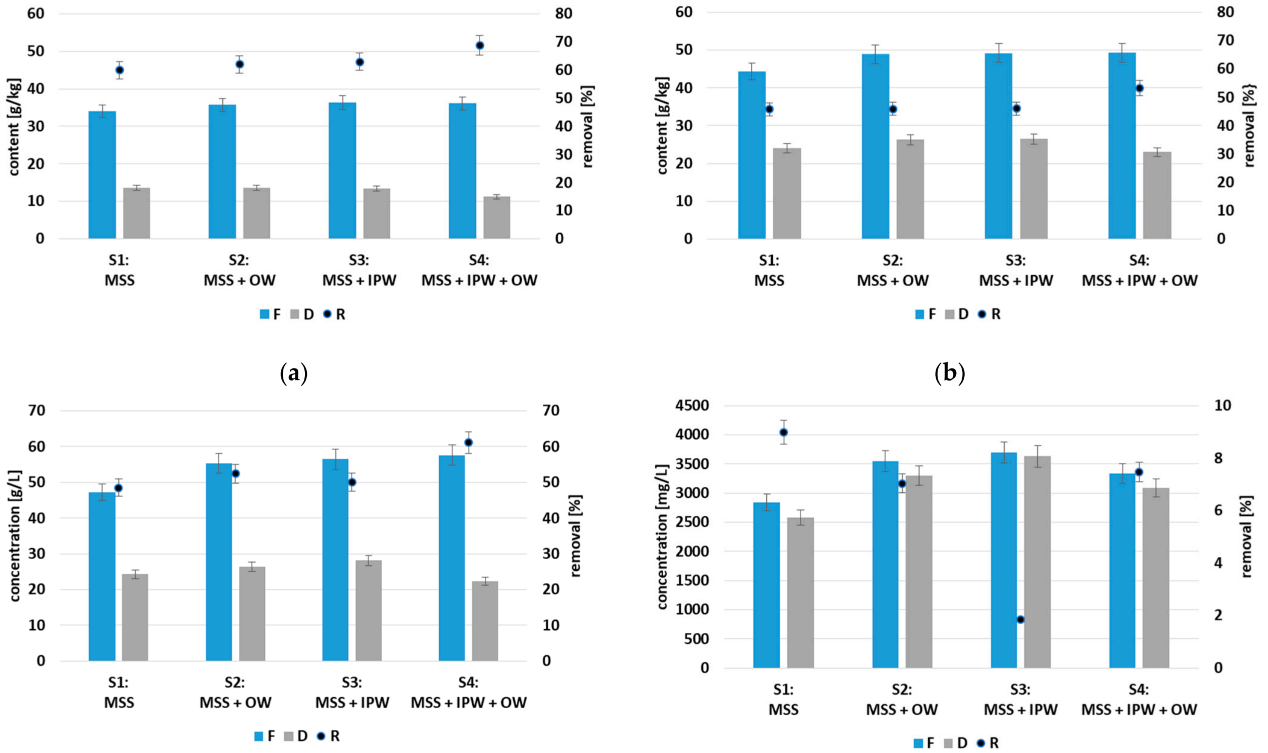
$$N_{t/e} = Q_m \cdot Q_{ie} \cdot \eta_{t/e} \tag{11}$$

where Q_m is the daily methane production (m^3 CH_4/d), L_{VS} is the volatile solid (VS) load in the feedstock (kg VS/d), Q_t is the theoretical amount of thermal energy obtained from the combustion of methane (MJ/d), Q_1 is the thermal energy required for heating the feedstock(kJ/d), Q_2 is the thermal energy required to cover the heat loss through the walls of the digester (kJ/d), CSS is the specific heat of the sewage sludge (4200 kJ/m^3 K), D is the diameter of the cylindrical part of the digester (m), E_d is the daily energy production (kWh/d), F is the surface of the digester walls (m^2), $N_{t/e}$ is the theoretical electric/thermal power production (kW), Q_c is the thermal energy demand (kJ/d) Q_i is the heating value of methane (35.8 MJ/m^3), Q_{ie} is the calorific value of methane (10 kWh/m^3), T is the anaerobic digestion temperature (K), Ta is the air temperature (K), T_f is the temperature of the feedstock in two- and three-component digestion (K), U is the heat loss coefficient by permeation through the walls of the digester (4.0 kJ m^2/h K), V is the feedstock flow rate (m^3/d), Z is the profit of thermal energy (%), β is the margin factor (1.1), and ηt/e is the thermal/electric efficiency of the CHP engine (η_t = 0.43, η_e = 0.38)

3. Results and Discussion

3.1. Process Performance

The performance of the AD process was evaluated based on the efficiency of removing organic compounds expressed as VSs, TS, COD, and sCOD (Figure 1). Regarding the first two parameters, the introduction of co-substrates resulted in improvements in their removal. As compared to MSS mono-digestion, a major growth of approx. 15% was observed in multicomponent co-digestion of IPW and OW (S4). A similar trend occurred in the case of COD; therein, its removal in S4 was enhanced by 26%, as compared to the control series (S1). These facts indicate the effective decomposition of organic compounds in multi-substrate AD. Previous studies indicated that the application of fat-rich wastes to MSS resulted in higher microbial activity that might have led to an enhanced degradation rate [31–33]. In the research conducted by Tandukar in MSS and fat–oil–grease co-digestion, a degradation rate improved by 17% was achieved [33].



(**a**) (**b**)

(**c**) (**d**)

Figure 1. Content/concentration of VSs (**a**), TS (**b**), COD (**c**), and sCOD (**d**) in feedstock (F) and digestate (D) in corresponding experimental series and also the effectiveness of their removal (R); MSS—municipal sewage sludge; OW—orange waste; IPW—ice-cream processing waste.

It should be pointed out that this tendency occurred despite providing a significant load of organic substances in the feedstocks. A different tendency was recorded only for sCOD (Figure 1d)—in this case, the deterioration of its removal. However, the highest decrease was obtained for two-component AD in the presence of IPW.

The stability of anaerobic digestion might be influenced by several factors, and maintaining it requires a balance of these factors to ensure optimal microbial activity and prevent system failure. In this study, process stability was evaluated on the basis of pH, ALK, and VFAs. Importantly, in all experimental series the mentioned parameters reached values indicating a stable process performance (Table 2).

Table 2. The pH value and alkalinity (TA), volatile fatty acid (VFA), total nitrogen (TN) and phosphorus (TP), and ammonia nitrogen ($N\text{-}NH_4^+$) and phosphate ($P\text{-}PO_4^{3-}$) concentrations in feedstock (F) and digestate (D) in corresponding experimental series (average values ± standard deviation are presented).

Parameter	Unit	S1		S2		S3		S4	
		F	D	F	D	F	D	F	D
TA	mg/L	635 ± 19.1	4896 ± 120	680 ± 18.9	4590 ± 135	694 ± 15.7	4916.5 ± 135	732 ± 12.3	4915.5 ± 140
VFA	mg/L	715 ± 35.2	224.5 ± 9.8	725 ± 29	314 ± 7.9	694 ± 21	275 ± 17	742 ± 15.1	237 ± 14.1
pH	-	5.62 ± 0.1	7.35 ± 0.2	5.5 ± 0.1	7.25 ± 0.3	5.75 ± 0.2	7.38 ± 0.4	5.75 ± 0.1	7.4 ± 0.07
TP	mg/L	474 ± 9.5	648.5 ± 12.3	550 ± 10.2	690 ± 14.5	650 ± 18.1	760 ± 16.2	655 ± 21.4	628 ± 11.3
TN	mg/L	1701 ± 85.1	2065 ± 80	1954 ± 54.1	2300 ± 47	2033 ± 39.5	2290 ± 37.1	2087 ± 39.1	2064 ± 38.2
$N\text{-}NH_4^+$	mg/L	80.2 ± 3.2	248.25 ± 10.2	100 ± 9.7	312 ± 9.9	109 ± 7.8	173.3 ± 7.9	89.7 ± 5.9	242.9 ± 4.7
$P\text{-}PO_4^{3-}$	mg/L	176 ± 13.3	111.7 ± 8.9	258 ± 5.7	114 ± 4.4	264 ± 5.5	116 ± 5.7	266 ± 4.8	116 ± 7.8

One of the most important factors affecting the AD process is the concentration of VFAs in the reactor. This group of compounds includes acetic, propionic, butyric, valerian, and caproic acids, among others [34]. These are substances that show toxicity only after exceeding a certain threshold value. The non-dissociated forms of these acids show toxic effects against methanogens. They can penetrate the cell membrane of microorganisms, where they dissociate when neutral, releasing a hydrogen ion that disrupts the acid–base balance in the reactor [35]. In almost all reactors, low VFA concentrations below 300 mg/L were observed, with the exception constituting the S2 supplied by OW. In this case, in the digestate an enhancement of its content by 40% was observed as compared to the control series (S1). An increase in the VFA concentration might have been the result of the presence of toxic substances in the feedstock, mainly d-limonene.

Alkalinity informs about the buffer capacity of the digesters. It allows for a quick assessment of the stability of the process under the conditions of VFA accumulation. Values in the range of 2000 to 5000 $gCaCO_3/m^3$ are considered favorable [36,37]. As in the case of VFA, the deterioration of this parameter was found only in two-component co-digestion of OW and MSS. Importantly, the supplementation of feedstock in IPW ensured adequate buffering capacity in the digester (S4).

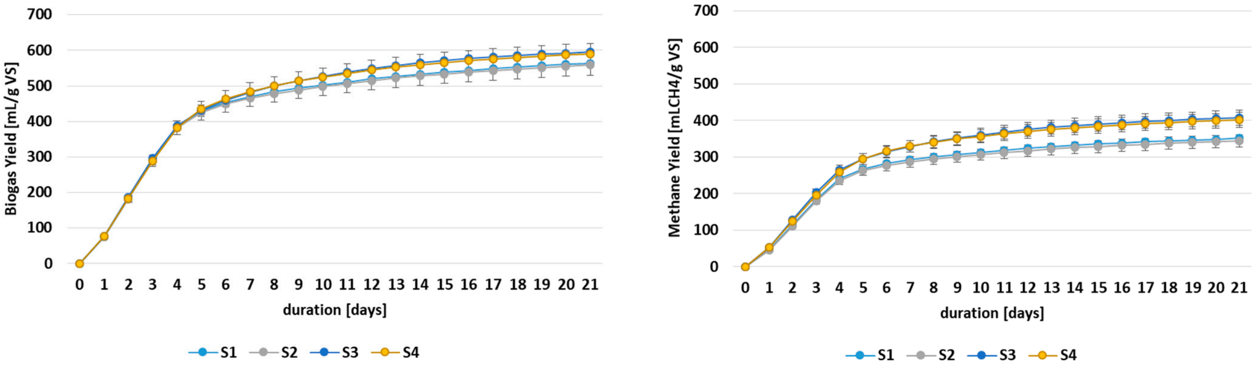
As a result of the AD process, the release of ammonium nitrogen was observed. Major 3.1-fold growth was achieved in S1 and S2. Importantly, the highest concentration was obtained in two-component MSS and OW co-digestion. A different trend was noticed in the case of phosphates, wherein a reduction in this parameter was observed. In all co-digestion series, the removal efficiency was established at a similar level of 56%; in turn, in MSS mono-digestion, it reached a value of 36%.

Another important parameter that was analyzed in this study was the COD/TN ratio, which is considered a key factor for a balanced performance of the AD process [38]. It should be pointed out that the introduction of co-substrates resulted in an improvement in this ratio, with the greatest in S4 supplied by both ICW and OW, wherein the COD/TN ratio was established at the level of 29.7, while in the control it was 26.1. In both co-digestion series (S2 and S3), comparable results were achieved, reaching a value of 28.4.

Additionally, in this research, the variation in nutrients during AD was investigated. In the presence of co-substrates, increased contents of both nitrogen and total phosphorus were observed. Major enhancements were achieved in three-component series supplied by both OW and IPW. Regarding TN, in almost all series (S1–S3) an enhancement in its content was achieved during AD. The exception was S4, wherein comparable concentrations in feedstock and digestates occurred. In the case of TP, an analogous tendency was observed, e.g., in S1–S3 there was an improvement in concentration during AD. In turn, comparable concentrations in feedstock and digestates were observed in S4. Considering the possibility of further use of digestates for fertilizing, it is worth mentioning that the highest contents of both TN and TP were achieved in S3 supplied by IPW. Previous studies indicated that digestate from co-digestion of fat–oil–grease (FOG) and sewage sludge has better fertilizing properties due to an additional nutrient content provided by those wastes.

3.2. Methane Production and Its Kinetics

The results in terms of biogas and methane production are presented in Figure 2 and Table 3. With regard to biogas production, the introduction of co-substrates did not lead to significant changes in biogas production compared to MSS mono-digestion. However, the key factor in assessing the efficiency of co-digestion of selected wastes is methane production. As compared to the control series (S1), significant improvements in the methane yield of S3 and S4 were achieved in the presence of IPW, reaching 16 and 14%, respectively. In turn, in MSS and OW co-digestion, a minor deterioration of this parameter was observed. The decrease in methane production occurred despite the improved COD/TN ratio in feedstock. For this reason, this fact might indicate the phenomenon of d-limonene inhibition present in OW (Table 1). Previous studies confirmed that this essential oil has a toxic effect on methanogens, which are responsible for producing methane in the final stages of the anaerobic digestion process [39,40]. D-limonene, being a hydrophobic compound, might disrupt microbial cell membranes and interfere with cellular functions [41]. High concentrations of limonene can inhibit methanogenic activity, leading to a decrease in biogas production. Another adverse effect of this essential oil is related to hydrolytic and acidogenic bacteria inhibition, which are microbes responsible for the initial breakdown of organic materials into simpler compounds, e.g., fatty acids and alcohols. This inhibition can lead to slower degradation of organic waste and reduced methane production. Moreover, d-limonene might lead to an accumulation of VFAs that might finally result in process instability [42].



(**a**) (**b**)

Figure 2. Cumulative biogas (**a**) and methane (**b**) production in corresponding experimental series (average values and standard deviation are given).

Table 3. Results of kinetics evaluation in corresponding experimental series.

Description	Parameter	Unit	S1	S2	S3	S4
Experimental data	Biogas yield	mL/g VS	563.8	558.2	595.5	590.5
	Methane yield	mL/g VS	351.3	344.3	407.6	401.6
	CH_4	%	62.3	61.68	68.45	68.01
LGM	M_p	mL/g VS	329.9	323.3	384.8	379.1
	R_m	mL/g VS d	62.6	61.4	62.2	64.3
	λ	d	0.33	0.33	0.11	0.23
	R^2	-	0.9889	0.98733	0.98576	0.9879
HM	M_p	mL/g VS	337.2	330.6	400.2	394.1
	k	1/d	0.273	0.274	0.243	0.246
	R^2	-	0.98729	0.98729	0.99086	0.98936

Importantly, the introduction of IPW to OW and MSS overcame the difficulties related to the presence of OW. In this case, a major improvement in the COD/TN ratio also occurred. The balanced feedstock composition resulted in an improvement in methane production. IPW is waste rich in lipids that might be easily converted into methane by specific microbial communities, enhancing biogas yield. Moreover, the introduction of fat-rich wastes might improve the degradation of organic matter, leading to higher methane production and improved system performance. A previous study indicated that such wastes contain long-chain fatty acids (LCFAs), which are readily degraded by specific hydrolytic and acidogenic bacteria. These bacteria can work in concert with other microorganisms in sewage sludge to break down a broader range of organic matter, improving the overall degradation process. In particular, the moderate lipid levels might be easily converted into methane through the acetoclastic pathway without VFA accumulation [43]. In a study conducted by Demirel et al. [44], in the co-digestion of wastewater with ice-cream production residues mixed at a ratio of 9:1, the methane production was established at the level of 396 mL CH_4/g VS; in turn, in the control, with mono-digestion of wastewater, it was only 91 mL CH_4/g VS. This indicates the significant potential of using such wastes as a co-substrate in the AD process. Other studies show that supplementation of FOG improved biogas production by nearly 30% [32]. However, its implementation on a technical scale might be challenging mainly due to several operational problems, including digester foaming, blockade of pipes and gas collectors, process inhibition by LCFAs, and sludge flotation [45,46]. Therefore, its application should be particularly controlled and preceded by laboratory-scale tests.

A similar effect to those obtained in these studies was also achieved by Guedes et al. [19]. Therein, to avoid d-limonene inhibition, crude glycerol was proposed as an additional substrate to orange peel. The biochemical methane potential (BMP) of mixed wastes was established at the level of 501.3 mL/g VS, while for OW it was only 160.5 mL/g VS. Another example of successful co-digestion with orange by-products was found in the author's previous studies—in this case, supplementation with brewer's spent grain, resulting in a methane production of 395 mL CH_4/g VS, compared to MSS mono-digestion, which showed an increase of 12% [47]. Another strategy enabling the d-limonene inhibition to be overcome was its adsorption as well as microbial immobilization by biochar. BMP, depending on the biochar type and adopted doses, varied from 163.9 to 186.8 mL/g VS, while for citrus peel, it was only 165.9 mL/g VS [13]. In other studies, such as the one by Wikandari et al. [12], it was demonstrated that the extraction of d-limonene from OW using hexane can significantly influence biogas production. The highest biogas yield was achieved with an orange waste and hexane ratio (*w*/*v*) of 12:1 at a temperature of 20 °C for 10 min, resulting in more than a threefold increase in methane production, from 61 to 217 mL/g VS.

Kinetic evaluation is an indispensable tool that allows the biogas production rate to be predicted. It allows for an efficient operation of digesters, as well as prediction of how the system will respond to various indicators, e.g., co-substrate introduction. Such an evaluation involves the analysis of potential maximum methane production, its production rates, and the lag phase [48,49]. Thus far, several models have been developed to simulate AD as well as to indicate the rate of methane production. However, in particular in the case of mono-digestion of complex organic substrates or co-digestion systems, the models should include more parameters that take into account the variable rate of decomposition during the AD process [49]. The results obtained in terms of methane production in both models correspond to the experimental data. This fact confirms the possibility of using both models, e.g., hyperbolic and logistic growth, to predict methane production from multi-component mixtures [50]. Importantly, the experimental results are higher than those obtained in both models, which also proves the accuracy of the selected operating parameters. As can be seen in Table 3, a major improvement was achieved in S3 supplied by IPW. In this case, as compared to MSS mono-digestion, enhancements of 17 and 19% for the LGM and HM were observed. It is worth mentioning that in the three-component series, a significant improvement in Rm was achieved as compared to both S1 and S2. In the case of lag phase, the introduction of IPW resulted in its shortening. However, major changes were noticed in IPW and MSS co-digestion (S3). Therein, the lag phase was reduced by 65% in comparison to the control series (S1). This effect was achieved by other researchers, and it resulted from the introduction of readily biodegradable substrates. Shortening of the lag phase was also observed in biochar addition, suggesting a beneficial effect related to counteracting the impact of d-limonene on methanogenesis [51].

Another beneficial effect was observed with regard to the rate constant in the HM. This is one of the most important parameters, and it describe the hydrolysis rate of the particular substrate. Generally, higher values are desirable for effective methane production with AD [52,53]. In this case, an enhancement in this parameter occurred in the presence of IPW. Conversely, the supplementation with OW resulted in the deterioration of both R_m and k. This fact might be related to the presence of barely biodegradable compounds, e.g., lignin, that are typically present in OW and are difficult for microorganisms to access [54]. Additionally, in both models, the M_p was slightly reduced, as compared to MSS mono-digestion (S1).

3.3. Energy Balance Evaluation

The energy balance analysis was completed to estimate the potential energy gains that might be obtained as a result of using this technology. As can seen in Figure 3, in all cases, the thermal energy calculated on the basis of experimental data will entirely cover the digester demand used for heating the feedstock and covering the heat losses through the walls of the tank. However, the most beneficial results were achieved in IPW in two- and three-component AD. Therein, as compared to MSS mono-digestion (S1), the energy profit was enhanced by 54 and 62% in S3 and S4, respectively. A similar trend was observed in multi-component co-digestion in the presence of grease trap sludge; in this case, an increase of 125% in energy profit was achieved [46]. The generated energy surplus can be used within WWTPs or sold to an external recipient. The presented results indicate that the proposed technology might be a profitable solution for WWTPs.

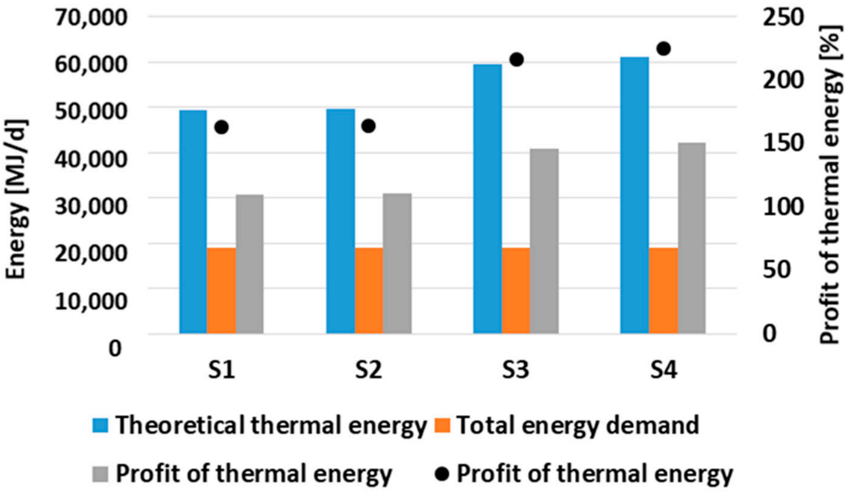


Figure 3. The results of energy balance in corresponding experimental series.

4. Conclusions

In this research, an effective strategy for energetic application of OW in co-digestion with MSS was evolved. For this purpose, the application of IPW as an additional co-substrate was chosen. In three-component co-digestion, significantly enhanced methane production and its kinetics were achieved, as compared to both MSS mono-digestion and OW and MSS co-digestion. It was accompanied by improved organics removal and stable process performance. In three-component co-digestion, the methane yield was established at the level of 401.6 mL/g VS, while its production rate was 64.3 mL/g VS d. In this case, a significant VS organic removal of 68% was also achieved. Importantly, the results of the energy balance evaluation indicate that energy profit was boosted by approx.

62%, proving that the application of those wastes into digesters at WWTPs might be a profitable solution at those facilities. However, a key factor allowing for the development of this technology is the availability of the raw materials used in the local market to avoid expensive transportation or long storage of raw materials.

Author Contributions: Conceptualization, A.S., J.C. and A.M.; methodology, A.S., J.C. and A.M.; software, A.S.; validation, A.S., J.C. and A.M.; formal analysis, A.S., J.C. and A.M.; investigation, A.S., J.C., A.M. and M.L.; resources, A.S., J.C. and A.M.; data curation, A.S. and J.C.; writing—original draft preparation, A.S., J.C. and A.M.; writing—review and editing A.S., J.C., A.M. and M.L.; visualization, A.S. and M.L.; supervision, J.C. and A.M.; project administration, J.C. and A.M.; funding acquisition, A.S. All authors have read and agreed to the published version of the manuscript.

Funding: The authors extend thanks for the financial support provided by the Ministry of Science and Higher Education in Poland (grant numbers FD-20/IS-6/036).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The original contributions presented in the study are included in the article; further inquiries can be directed to the corresponding author.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Ngabala, F.J.; Emmanuel, J.K. Potential substrates for biogas production through anaerobic digestion-an alternative energy source. *Heliyon* **2024**, *10*, e40632. [CrossRef] [PubMed]
2. Corigliano, O.; Algieri, A. A comprehensive investigation on energy consumptions, impacts, and challenges of the food industry. *Energy Convers. Manag. X* **2024**, *23*, 10661. [CrossRef]
3. Bernet, N.; Escudié, R.; Steyer, J.P. Anaerobic Digestion: Application to the Energy Recovery of Agricultural Co-products and Food Industry Waste. In *Green Chemistry and Agro-Food Industry: Towards a Sustainable Bioeconomy*; Baumberger, S., Ed.; Springer: Cham, Switzerland, 2024; pp. 85–103. [CrossRef]
4. Duan, Y.; Wang, Z.; Ganeshan, P.; Sar, T.; Xu, S.; Rajendran, K.; Sindhu, R.; Binod, P.; Pandey, A.; Zhang, Z.; et al. Anaerobic digestion in global bio-energy production for sustainable bioeconomy: Potential and research challenges. *Renew. Sust. Energ. Rev.* **2025**, *208*, 114985. [CrossRef]
5. Manakas, P.; Balafoutis, A.T.; Kottaridi, C.; Vlysidis, A. Sustainability assessment of orange peel waste valorization pathways from juice industries. *Biomass Conv. Bioref.* **2024**, 1–20. [CrossRef]
6. Bocker, R.; Silva, E.K. Pulsed electric field technology as a promising pre-treatment for enhancing orange agro-industrial waste biorefinery. *RSC Adv.* **2024**, *14*, 2116–2133. [CrossRef]
7. Kalengyo, R.B.; Ibrahim, M.G.; Fujii, M.; Nasr, M. Utilizing orange peel waste biomass in textile wastewater treatment and its recyclability for dual biogas and biochar production: A techno-economic sustainable approach. *Biomass Conv. Bioref.* **2024**, *14*, 19875–19888. [CrossRef]
8. Ahmad, T.; Danish, M.; Dadi, M.; Siraj, K.; Sundaram, T.; Raj, D.S.; Majeed, S.; Ramasamy, S. Potentials of orange wastes in wastewater treatment technology: A comprehensive review. *J. Water Process. Eng.* **2024**, *67*, 106113. [CrossRef]
9. Calabrò, P.S.; Fazzino, F.; Folino, A.; Paone, E.; Komilis, D. Semi-Continuous Anaerobic Digestion of Orange Peel Waste: Effect of Activated Carbon Addition and Alkaline Pretreatment on the Process. *Sustainability* **2019**, *11*, 3386. [CrossRef]
10. Martín, M.A.; Siles, J.A.; Chica, A.F.; Martín, A. Biomethanization of orange peel waste. *Bioresour. Technol.* **2010**, *101*, 8993–8999. [CrossRef]
11. Calabrò, P.S.; Fazzino, F.; Sidari, R.; Zema, D.A. Optimization of orange peel waste ensiling for sustainable anaerobic digestion. *Renew. Energy* **2020**, *154*, 849–862. [CrossRef]
12. Wikandari, R.; Nguyen, H.; Millati, R.; Niklasson, C.; Taherzadeh, M.J. Improvement of biogas production from orange peel waste by leaching of limonene. *Biomed. Res. Int.* **2015**, *2015*, 494182. [CrossRef] [PubMed]
13. Fagbohungbe, M.O.; Herbert, B.M.J.; Hurst, L.; Ibeto, C.N.; Li, H.; Usmani, S.Q.; Semple, K.T. The challenges of anaerobic digestion and the role of biochar in optimizing anaerobic digestion. *Waste Manag.* **2017**, *61*, 236–249. [CrossRef] [PubMed]
14. Zhang, J.; Zhao, W.; Zhang, H.; Wang, Z.; Fan, C.; Zang, L. Recent achievements in enhancing anaerobic digestion with carbon-based functional materials. *Bioresour. Technol.* **2018**, *266*, 555–567. [CrossRef] [PubMed]

15. Nayeri, D.; Mohammadi, P.; Bashardoust, P.; Eshtiaghi, N. A comprehensive review on the recent development of anaerobic sludge digestions: Performance, mechanism, operational factors, and future challenges. *Results Eng.* **2024**, *22*, 102292. [CrossRef]
16. Sakaveli, F.; Petala, M.; Tsiridis, V.; Darakas, E. Enhancing Methane Yield in Anaerobic Co-Digestion of Primary Sewage Sludge: A Comprehensive Review on Potential Additives and Strategies. *Waste* **2024**, *2*, 29–57. [CrossRef]
17. Ahmad, A.; Yadav, A.K.; Singh, A.; Singh, D.K. A comprehensive machine learning-coupled response surface methodology approach for predictive modeling and optimization of biogas potential in anaerobic Co-digestion of organic waste. *Biomass Bioenergy* **2024**, *180*, 106995. [CrossRef]
18. Li, P.; Zhao, H.; Cheng, C.; Hou, T.; Shen, D.; Jiao, Y. A review on anaerobic co-digestion of sewage sludge with other organic wastes for methane production: Mechanism, process, improvement and industrial application. *Biomass Bioenergy* **2024**, *185*, 107241. [CrossRef]
19. Guedes, M.T.J.C.; Soroka, V.D.; Marder, M.; Stacke, C.N.G.; Konrad, O.; Silva, M.C.D.A. Biogas generation through anaerobic digestion of orange peel waste and crude glycerol in single-stage and two-stage batch system. *Environ. Qual. Manag.* **2024**, *34*, e22234. [CrossRef]
20. Bouaita, R.; Derbal, K.; Panico, A.; Iasimone, F.; Pontoni, L.; Fabbricino, M.; Pirozzi, F. Methane production from anaerobic co-digestion of orange peel waste and organic fraction of municipal solid waste in batch and semi-continuous reactors. *Biomass Bioenergy* **2022**, *160*, 106421. [CrossRef]
21. Lane, G.A. Laboratory scale anaerobic digestion of fruit and vegetable solid waste. *Biomass* **1984**, *5*, 245–259. [CrossRef]
22. Bouallagui, H.; Lahdhed, H.; Romdan, B.E.; Rachdi, B.; Hamdi, M. Improvement of fruit and vegetable waste anaerobic digestion performance and stability with co-substrates addition. *J. Environ. Manag.* **2009**, *90*, 1844–1849. [CrossRef] [PubMed]
23. Negro, V.; Alvarado-Morales, M.; Tsapekos, P.; Fino, D.; Ruggeri, B.; Angelidaki, I. Co-digestion of orange peels and marine seaweed with cattle manure to suppress inhibition from toxicants. *Biomass Conv. Bioref.* **2022**, *12*, 3209–3218. [CrossRef]
24. Serrano, A.; Siles López, J.A.; Chica, A.F.; Martín, M.A.; Karouach, F.; Mesfioui, A.; El Bari, H. Mesophilic anaerobic co-digestion of sewage sludge and orange peel waste. *Environ. Technol.* **2014**, *35*, 898–906. [CrossRef]
25. Carvalho, A.; Fragoso, R.; Gominho, J.; Duarte, E. Effect of Minimizing D-Limonene Compound on Anaerobic Co-digestion Feeding Mixtures to Improve Methane Yield. *Waste Biomass Valor.* **2019**, *10*, 75–83. [CrossRef]
26. Masłoń, A.; Czarnota, J.; Szczyrba, P.; Szaja, A.; Szulżyk-Cieplak, J.; Łagód, G. Assessment of Energy Self-Sufficiency of Wastewater Treatment Plants—A Case Study from Poland. *Energies* **2024**, *17*, 1164. [CrossRef]
27. LCK Cuvette Test System. Available online: https://uk.hach.com/lck (accessed on 27 January 2025).
28. American Public Health Association (APHA). *Standard Methods for the Examination of Water and Wastewater*, 22nd ed.; APHA: Washington, DC, USA, 2012.
29. Koch, K.; Lippert, T.; Drewes, J.E. The role of inoculum's origin on the methane yield of different substrates in biochemical methane potential (BMP) tests. *Bioresour. Technol.* **2017**, *243*, 457–463. [CrossRef]
30. Ware, A.; Power, N. Modelling methane production kinetics of complex poultry slaughterhouse wastes using sigmoidal growth functions. *Renew. Energy* **2017**, *104*, 50–59. [CrossRef]
31. Kabouris, J.C.; Tezel, U.; Spyros, G.; Pavlostathis, S.G.; Engelmann, M.; Todd, A.C.; Gillette, R. The anaerobic biodegradability of municipal sludge and fat, oil and grease at mesophilic conditions. *Water Environ. Res.* **2008**, *80*, 212. [CrossRef]
32. Kabouris, J.C.; Tezel, U.; Spyros, G.; Pavlostathis, S.G.; Engelmann, M.; Dulaney, J.A.; Todd, A.C.; Gillette, R. Mesophilic and thermophilic anaerobic digestion of municipal sludge and fat, oil and grease. *Water Environ. Res.* **2009**, *81*, 476–485. [CrossRef]
33. Tandukar, M.; Pavlostathis, S.G. Anaerobic co-digestion of municipal sludge with fat-oil-grease (FOG) enhances the destruction of sludge solids. *Chemosphere* **2022**, *292*, 133530. [CrossRef]
34. Rahimieh, A.; Nosrati, M.; Zamir, S.M. Anaerobic Digestion of a Curious VFA Complex Feed for Biomethane Production; A Study on ANN Modeling Optimized with Genetic Algorithm. *Desalination Water Treat.* **2024**, *317*, 100257. [CrossRef]
35. Zhao, W.; Jeanne Huang, J.; Hua, B.; Huang, Z.; Droste, R.L.; Chen, L.; Wang, B.; Yang, C.; Yang, S. A new strategy to recover from volatile fatty acid inhibition in anaerobic digestion by photosynthetic bacteria. *Bioresour. Technol.* **2020**, *311*, 123501. [CrossRef] [PubMed]
36. Gerardi, M.H. (Ed.) Alkalinity and pH. In *The Microbiology of Anaerobic Digesters*; Wiley: Hoboken, NJ, USA, 2003. [CrossRef]
37. Wu, D.; Li, L.; Peng, Y.; Yang, P.; Peng, X.; Sun, Y.; Wang, X. State indicators of anaerobic digestion: A critical review on process monitoring and diagnosis. Renew. *Sust. Energy Rev.* **2021**, *148*, 111260. [CrossRef]
38. Syaichurrozi, I.; Budiyono; Sumardiono, S. Predicting kinetic model of biogas production and biodegradability organic materials: Biogas production from vinasse at variation of COD/N ratio. *Bioresour. Technol.* **2013**, *149*, 390–397. [CrossRef]
39. Trujillo-Reyes, Á.; Pérez, A.G.; Cuéllar, S.G.; Serrano, A.; Cubero-Cardoso, J.; Jeison, D.; Fermoso, F.G. Evaluation of toxic effect of monoterpene compounds on anaerobic digestion. *J. Environ. Chem. Eng.* **2024**, *12*, 112035. [CrossRef]
40. Chubur, V.; Hasan, G.; Kára, J.; Hanzlíková, I.; Chernysh, Y.; Sedláček, J.; Wang, J.; Roubík, H. Utilization of citrus, date, and jujube substrates for anaerobic digestion processes. *Biofuels Bioprod. Bioref.* **2024**, *18*, 1917–1929. [CrossRef]
41. Ruiz, B.; Flotats, X. Effect of limonene on batch anaerobic digestion of citrus peel waste. *Biochem. Eng. J.* **2016**, *109*, 9–18. [CrossRef]

42. Gutiérrez, M.C.; Serrano, A.; Alonso-Fariñas, B.; Siles, J.A.; Martín, M.A. Impact of D-Limonene in the technical and economic feasibility of the anaerobic digestion applied in biorefineries. *Biomass Conv. Bioref.* **2024**, *14*, 14877–14888. [CrossRef]
43. Liu, Y.; Xi, Y.; Li, Q.; Dzakpasu, M.; Chen, R.; Li, Y.Y. Biokinetic and microbial insights into regulatory mechanisms of long-chain fatty acid degradation during food waste-lipid co-digestion within anaerobic membrane bioreactor. *Bioresour. Technol.* **2024**, *408*, 131223. [CrossRef]
44. Demirel, B.; Örok, M.; Hot, E.; Erkişi, S.; Albükrek, M.; Onay, T. Recovery of biogas as a source of renewable energy from ice-cream production residues and wastewater. *Environ. Technol.* **2013**, *34*, 2099–2104. [CrossRef]
45. Worwąg, M.; Neczaj, E.; Grosser, A.; Krzemińska, D. Methane production from fat-rich materials. *Civ. Environ. Eng. Rep.* **2011**, *6*, 147–162.
46. Grosser, A.; Neczaj, E.; Singh, B.R.; Almås, Å.R.; Brattebø, H.; Kacprzak, M. Anaerobic digestion of sewage sludge with grease trap sludge and municipal solid waste as co-substrates. *Environ. Res.* **2017**, *155*, 249–260. [CrossRef] [PubMed]
47. Szaja, A.; Montusiewicz, A.; Pasieczna-Patkowska, S.; Lebiocka, M. Technological and Energetic Aspects of Multi-Component Co-Digestion of the Beverage Industry Wastes and Municipal Sewage Sludge. *Energies* **2022**, *15*, 5395. [CrossRef]
48. Khadka, A.; Parajuli, A.; Dangol, S.; Thapa, B.; Sapkota, L.; Carmona-Martínez, A.A.; Ghimire, A. Effect of the Substrate to Inoculum Ratios on the Kinetics of Biogas Production during the Mesophilic Anaerobic Digestion of Food Waste. *Energies* **2022**, *15*, 834. [CrossRef]
49. Ibro, M.K.; Ancha, V.R.; Lemma, D.B. Biogas Production Optimization in the Anaerobic Codigestion Process: A Critical Review on Process Parameters Modeling and Simulation Tools. *J. Chem.* **2024**, *1*, 1–25. [CrossRef]
50. Karki, R.; Chuenchart, W.; Surendra, K.C.; Sung, S.; Raskin, L.; Khanal, S.K. Anaerobic co-digestion of various organic wastes: Kinetic modeling and synergistic impact evaluation. *Bioresour. Technol.* **2022**, *343*, 126063. [CrossRef]
51. Parameswaran, P.; Rittmann, B.E. Feasibility of anaerobic co-digestion of pig waste and paper sludge. *Bioresour. Technol.* **2012**, *124*, 163–168. [CrossRef]
52. Shen, J.; Yan, H.; Zhang, R.H.; Liu, G.Q.; Chen, C. Characterization and methane production of different nut residue wastes in anaerobic digestion. *Renew. Energy* **2018**, *116*, 835–841. [CrossRef]
53. Shen, J.; Zhao, C.; Liu, Y.; Zhang, R.; Liu, G.; Chen, C. Biogas production from anaerobic co-digestion of durian shell with chicken, dairy, and pig manures. *Energy Convers. Manag.* **2019**, *198*, 110535. [CrossRef]
54. Smetana, G.; Grosser, A. Kinetic study of high-solids anaerobic co-digestion of pre-treated organic waste in terms of methane production. *Desalination Water Treat.* **2023**, *305*, 60–80. [CrossRef]