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Impact of Hydrothermal Pretreatment Parameters on Mesophilic and Thermophilic Fermentation and Anaerobic Digestion of Municipal Sludge

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Abstract: Four parameters affecting hydrothermal pretreatment (HTP) of municipal sludge prior to anaerobic digestion and fermentation were investigated. Partial factorial design including several key HTP parameters at two distinct levels, including temperature (170 and 190 °C), retention time (RT) (10 and 30 min), pH (4 and 10), and solid content (SC) (4% and 16%), were studied. Further, the impact of HTP parameters on mesophilic and thermophilic fermentation was explored and compared. Results revealed a significant effect of all HTP parameters on COD solubilization, VFA, and methane yield. There were correlations between HTP parameters and process responses such as VFA yield and methane yield. HTP was found to increase COD solubilization and VFA production between 15 and 20% during thermophilic fermentation in relation to mesophilic treatment. All parameters, including SC, temperature, pH, and RT, were important contributing factors affecting methane production during anaerobic digestion. The highest methane production yield of 269 mL CH_4/g TCOD added was observed at the highest SC (16%) and pH (10) and at the lower temperature (170 °C) and RT (10). HTP is expected to be combined with other intensification routes to treat waste with high solid contents improving the fermentation and anaerobic digestion processes.

Keywords: anaerobic digestion; fermentation; hydrothermal pretreatment; pH; solid content; temperature; volatile fatty acids

Citation: Kakar, F.L.; Aqeel, H.; Liss, S.N.; Elbeshbishy, E. Impact of Hydrothermal Pretreatment Parameters on Mesophilic and Thermophilic Fermentation and Anaerobic Digestion of Municipal Sludge. *Fermentation* **2023**, *9*, 508. https://doi.org/10.3390/fermentation9060508

Academic Editor: Yutuo Wei

Received: 17 April 2023
Revised: 18 May 2023
Accepted: 20 May 2023
Published: 25 May 2023

1. Introduction

Municipal wastewater sludge is of interest as a raw material because it rises steadily with population growth and anthropogenic activity and represents opportunities for sustainable processes and products [1–4]. Furthermore, sludge disposal costs represent 40–60% of the operational budget of wastewater treatment plants (WWTP) [1].

Traditional approaches to wastewater solids management include anaerobic digestion (AD), the most widely used stabilization and solids reduction process for municipal sewage sludge. AD has various advantages, including producing value-added products such as methane and fertilizer. Furthermore, volatile fatty acids (VFA) can be recovered during the acidogenesis stage of AD [1]. However, AD and fermentation processes are limited by several factors, including the slow breakdown of complex organic waste [2,3]. Given substrates have a significant role in the performance of AD [4], co-digestion of organic materials such as waste-activated sludge, primary sludge, food waste, manure, and other readily and slowly biodegradable, carbon-rich, materials have been explored to overcome AD limitations [5,6]. Further, to enrich methanogens activities, new processes such as DIET (direct interspecies electron transfer) [7] are introduced to AD adding conductive materials to AD and facilitating hydrogenotrophic methanogens growth [8]. When digesting or fermenting complex substrates, such as biosolids, where organic material is not easily accessible to the bacteria, hydrolysis is an important rate-limiting step [9]. Therefore, significant efforts continue to focus on enhancing AD process performance. Pretreating the solids prior to AD ruptures the bacterial cell wall and membrane structures, releasing soluble organic substances and nutrients [10].

Various pretreatment methods (thermal, biological, and mechanical) have been demonstrated to effectively address the slow breakdown of complex wastes [10]. Hydrothermal pretreatment (HTP) has gained significant attention among different pretreatment techniques [11]. Studies on HTP attribute methane production improvements to the increased hydrolysis rate [12,13] and the effect of different parameters on HTP performance have been investigated. There has been little focus on the impact of pH and solids content (SC) compared to the attention to the effect of temperature and retention time (RT). For pH, researchers focused more on studying the alkaline pH with HTP than acidic pH [14–16]. Alkaline pH conditions have improved solubilization, VFA, and methane production. Liu et al. [16] compared the effect of thermo-alkaline (pH 12) and thermo-acid (pH 3) pretreatment of TWAS on solubilization, VFA, and methane production. They reported that thermo-alkaline pretreatment resulted in higher solubilization compared to thermo-acid pretreatment. However, there were no significant differences in VFA production between pretreatment methods, where there was a reported 60% increase in the VFA yield compared to the untreated sample. For SC, very few studies in the literature investigated the effect of SC on the TWAS in the HTP performance. Gong et al. [17] found that the highest COD solubilization was achieved at SC of 10%, whereas the highest increase in VFA production and methane yield compared to the raw sample was achieved for the sample with SC of 8%.

As discussed earlier, most of the research had focused mainly on optimizing pretreatment temperature and retention time. In contrast, other factors such as pH and solid content (SC) have received limited attention. This is the first paper to address the multi-factors (temperature, retention time, solid content, and pH) impact associated with HTP ahead of fermentation and AD and in mesophilic and thermophilic conditions. The novelty of the study is about investigating the HTP factors on fermentation that are crucial for the full application of fermentation. Currently, most HTP processes are combined with AD. The main objectives of this study were two-fold: (i) Investigations of the impact of SC, pH, RT, and temperature on sludge solubilization, fermentation, and AD performance; and (ii) Evaluating the interactions and relationships between these parameters.

2. Materials and Methods

2.1. Substrate and Inoculum

TWAS was the primary substrate for this study. TWAS and inoculum were obtained from Ashbridge's Wastewater Treatment Plant (WWTP), Toronto, Ontario. The substrate used for this study was collected after secondary treatment and thickening. The inoculum used in this study was also obtained from an anaerobic digestion tank at AWWTP that operates at a mesophilic temperature range (34–38 °C) and HRT of 18 days for the sludge [18]. Raw TWAS and inoculum had a total chemical oxygen demand (TCOD) of 40.0 ± 1.3 and 21.0 ± 1.2 g/L, soluble chemical oxygen demand (SCOD) of 6.2 ± 0.4 and 0.7 ± 0.2 g/L, volatile fatty acid (VFA) of 2.8 ± 0.1 and 0.060 ± 0.04 g COD/L, total suspended solids (TSS) of 24.0 ± 1.1 and 18.0 ± 0.5 g/L, volatile suspended solids (VSS) of 17.0 ± 0.4 and 12.0 ± 0.1 g/L, respectively.

2.2. Experimental Design and Sample Preparation

In this study, the interaction between four parameters affecting the HTP of the TWAS was investigated. A fractional factorial design was used with four factors and two levels (Table 1). The pH, temperature, retention time, and solid content levels were in the range of 4–10, 170–190 °C, 10–30 min, and 4–16%, respectively. In total, nine conditions with one center point were tested. For the sample preparation, the pH of TWAS was first adjusted using NaOH and HCl, then thickened with a Fisher Scientific Sorvall Legend XT centrifuge at 2907× *g* for 30 min, and subsequently pretreated. After the pretreatment, the pretreated and the raw samples were used as feedstock for the batch tests.

Table 1. Methane kinetics including the Gompertz model, First-rder Kinetics, and biodegradability.

Sample and Pretreatment Conditions					Gompertz Model				First-Order Kinetics		Biodegradability
Run Order	Temp.	Retention Time	pH	Solid Content	P	R_m	λ	R^2	k	R^2	
	°C	min	-	%	mL CH_4/g COD Added	mL CH_4/g COD Added.d	d	-	d^{-1}	-	%
1	170	30	4	16%	246	22	1.2	0.930	0.18	0.971	65
2	170	10	4	4%	189	25	0.6	0.978	0.17	0.979	49
3 (control)	180	20	7	10%	231	23	0.8	0.958	0.20	0.984	59
4	190	10	10	4%	199	19	0.7	0.897	0.16	0.993	52
5	190	10	4	16%	257	25	1.5	0.911	0.22	0.962	63
6	170	10	10	16%	272	28	2.0	0.944	0.22	0.961	67
7	190	30	4	4%	223	24	0.6	0.962	0.11	0.985	57
8	170	30	10	4%	237	24	0.1	0.985	0.12	0.994	60
9	190	30	10	16%	270	25	1.5	0.919	0.19	0.963	66

P: Ultimate methane production potential, R_m: Max methane production rate, λ: Lag phase, k: Hydrolysis coefficient.

2.3. Hydrothermal Pretreatment

Pretreatment of TWAS enhances the hydrolysis rate and increases biodegradability [19]. After adjusting the pH and the solids content for each sample, the samples were hydrothermally pretreated using a Parr 4848 Hydrothermal Reactor (Parr Instrument Company, Moline, IL, USA) with a capacity of 2 L. The procedure of the HTP has been described previously [20].

2.4. Batch Fermentation

The batch thermophilic and mesophilic fermentation tests were conducted to evaluate the VFA's production potential and compare the impact of the HTP on each process. The procedure, environmental conditions, design, and calculation of the process response parameters for mesophilic and theosophic fermentation were the same and described in our previous work [20]. The only difference between both fermentation processes was that the temperature of the thermophilic fermentation was adjusted to 55 °C.

2.5. Biochemical Methane Potential (BMP) Test

BMP tests are usually conducted to understand the methane production potential, the methane production rate, and biodegradability [21–23]. In the current study, we have used the same procedure and conditions for the BMP test described previously [24]. The BMP tests were conducted under mesophilic conditions in batch mode. The food to microorganism ratio was 1 g COD substrate/g VSS of Seed. The calculated amount of substrate was added to the degassed seed, and bottles were purged with nitrogen creating the anaerobic condition. The BMP test was run for 40 days.

2.6. Solubilization, Biodegradability, and Kinetics

The degree of solubilization and solids reduction are commonly used as indicators to evaluate the pretreatment performance [25]. The calculations of the degree of solubilization and the solids reduction due to pretreatment are described in our previous work [20]. The biodegradability calculations and the different kinetics models used in this study are described in our previous study [20]. The kinetics models used were Gompertz model and first-order kinetics.

2.7. Analytical Methods

All the water and gas quality analyses including TSS, VSS, TCOD, SCOD, carbohydrates, proteins, VFA, biogas production, and biogas compositions were conducted as described previously [24].

2.8. Statistical Analysis

One-way multifactor analysis of variance (ANOVA) evaluated the statistically significant effect of the experimental factors with a 95% confidence level ($\alpha = 0.05$). The analysis of ANOVA in a two-level interaction was performed to evaluate the effects of experimental factors [26]. The fisher's least significant difference was also calculated for all pairs of means.

3. Results and Discussion

3.1. Sludge Disintegration

3.1.1. Sludge Disintegration Due to HTP

Figure 1a illustrates the percentage solubilization for COD, carbohydrates, and proteins of the TWAS, the major organic constituents in municipal waste. Results revealed that regardless of the level of parameters (temperature, retention time, pH, and SC), HTP enhanced the sludge disintegration by 20–45%. The COD solubilization due to HTP ranged between 32% and 45%, whereas the control (control here refers to the middle point with HTP conditions of pH 7, SC 10%, 20 min, and 180 °C) demonstrated the highest COD solubilization of 45%. Further, analysis of the variance indicated that the order of the dominant factors for the solubilization was SC, temperature, pH, and retention time, respectively.

The results revealed that higher levels of SC, temperature, pH, and retention time were associated with higher COD solubilization. As seen in Figure 1, the four samples with high SC (10% and 16%) have higher SCOD solubilization than the samples at 4% SC. The COD solubilization for the samples with SC of 10% and 16% ranged from 39% to 45% compared to 32 to 37% for the samples with SC of 4%, which accounted for approximately a 10–20% improvement. The highest COD solubilization of 45% was achieved for the sample with an SC of 10%. The COD solubilization for the samples with an SC of 16% ranged from 39% to 43% based on the other pretreatment conditions. Gameiro et al. [27] found that the COD solubilization of the organic municipal solid waste (OMSW) was improved from an average of 30% to about 40% when the SC was increased from 5% to 10%, which was in agreement with our results.

Temperature has been proven to play a crucial role in sludge disintegration during HTP [20,22,27–29]. It was reported that temperatures above 100 °C improve the sludge disintegration drastically, whereas going beyond 200–220 °C produces refractory compounds such as melanoidins [30–32]. Therefore, temperature ranges of 170–190 °C have been utilized broadly by researchers and HTP technology providers, and thus this range was investigated in this study. It was observed that the temperature had a significant impact when it was combined with other parameters ($p < 0.005$). Higher temperatures led to higher solubilization when combined in similar scenarios. For instance, comparing samples with the same solid content and pH, it was observed that the sample with a higher temperature level (190 °C) had a higher disintegration than the lower level, indicating the impact of temperature.

Comparing samples with the same SC of 16% and pH of 10, it was found when the temperature changed from 170 °C to 190 °C, the COD solubilization increased from 40% to 43%. Jeong et al. [32] evaluated the effect of HTP on the solubilization of waste-activated sludge (WAS) at four different levels of solid content (1%, 3%, 5%, and 7%) over a temperature range of 100–220 °C. They observed an increasing trend in COD solubilization when increasing the HTP temperature for all SC. They found that the COD solubilization increased from 30% to 40% when the temperature increased from 160 °C to 180 °C in almost all scenarios. According to the literature, the solid portion of the municipal sludge has a lower specific heat capacity (1.95 MJ/ton °C at 20 °C) than that of water (4.18 MJ/ton °C) [20]. Accordingly, the higher the solid content of the sludge, the lower the specific heat capacity, resulting in lower energy input and increased economic efficiency [33].

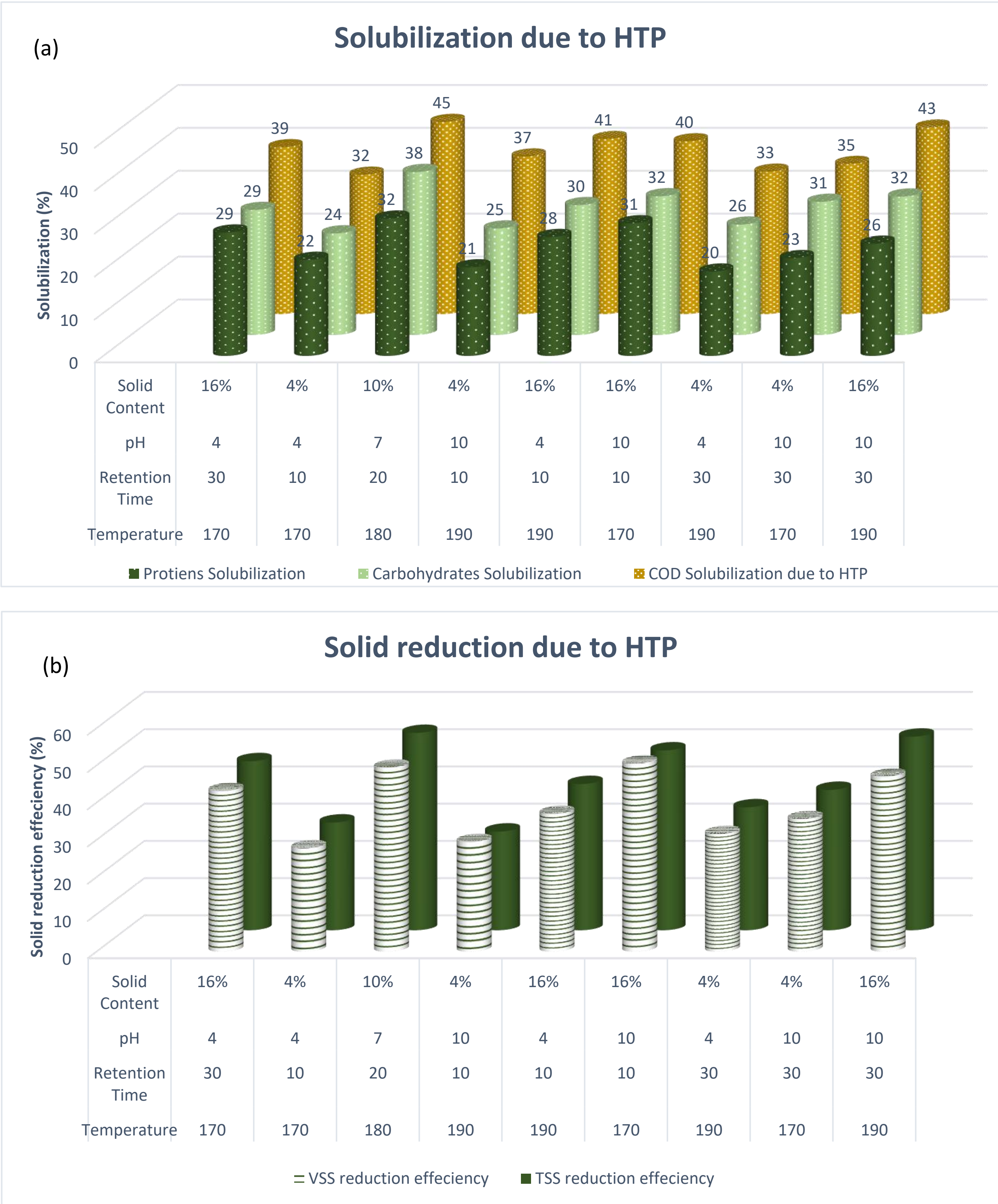


Figure 1. (**a**) Solubilization due to HTP, (**b**) Solid reduction efficiency due to hydrothermal pretreatment.

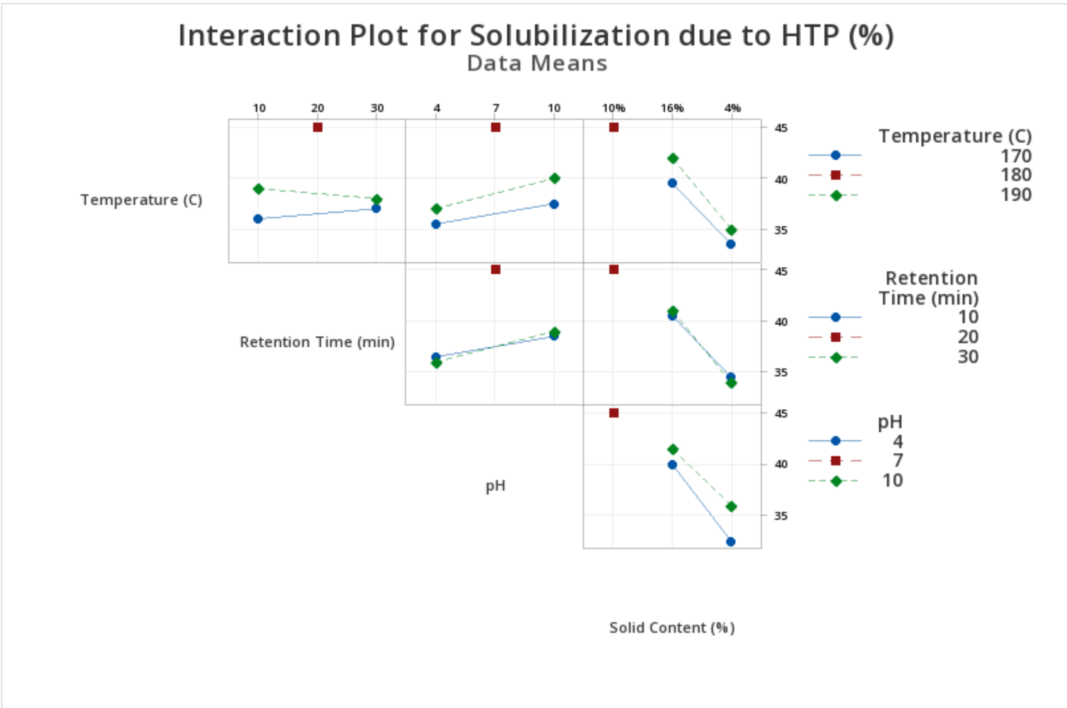
The pH of the sludge also impacted the COD solubilization of the TWAS when pretreated. Superior results were found for pH 10 in all samples compared to a similar condition with pH 4. For example, for the samples with the same SC of 4% and were pretreated with the same conditions of 190 °C for 30, when the pH increased from 4 to 10, the COD solubilization increased from 33% to 37%. The literature also reported that the COD solubilization for the thermo-alkaline pretreatment is higher than that of the thermo-acid pretreatment [24]. Other scholars have also broadly investigated the privilege of alkaline addition when using HTP [14,15,33–36].

Since SC, temperature, and pH were substantial factors, the impact of retention time in a small range of 10–30 min was negligible. However, a higher retention time was associated with slightly higher COD solubilization. This observation agrees with the literature as it has been reported that the COD solubilization increased when the retention increased from 10 min to 30 min [37].

Carbohydrates and proteins followed the same trend as COD solubilization for all the samples demonstrating similar responses to HTP parameters. Nevertheless, the carbohydrate solubilization percentage was slightly higher than the protein solubilization for most of the samples. Carbohydrate solubilization ranged between 24% and 38%, whereas protein solubilization ranged between 22% and 32%.

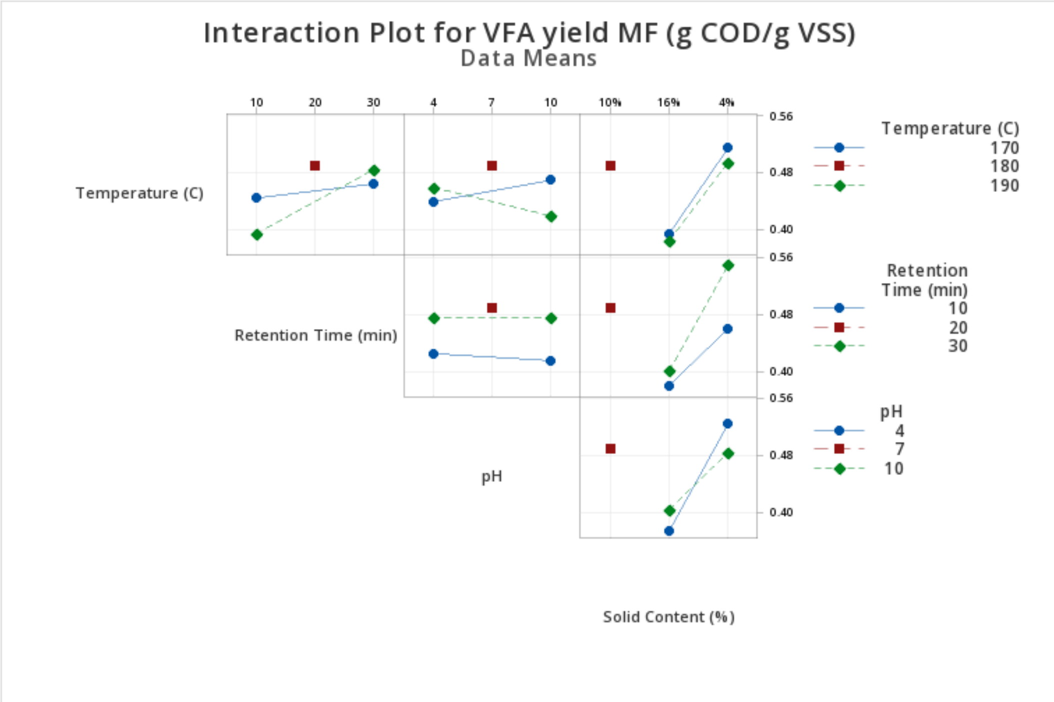
The solid reduction outcomes confirm the COD, carbohydrates, and protein solubilization results followed the same trend and responded similarly for the four parameters. Figure 1b reports the reduction in TSS and VSS of the samples after HTP for all nine scenarios compared to the raw TWAS. As illustrated, the highest TSS and VSS removal efficiencies of 53% and 49%, respectively, were achieved for the sample with SC of 10% and pH 7 that was pretreated at 180 °C for 20 min.

An interaction plot of the parameters was generated to study the correlation between HTP parameters and their impact on COD solubilization. Figure 2a shows the interaction between HTP parameters for COD solubilization. As seen in the figure, for most of the scenarios, evaluating the interaction between two parameters combination revealed that higher levels of the parameters resulted in higher COD solubilization except for the retention time.



(**a**)

Figure 2. *Cont.*



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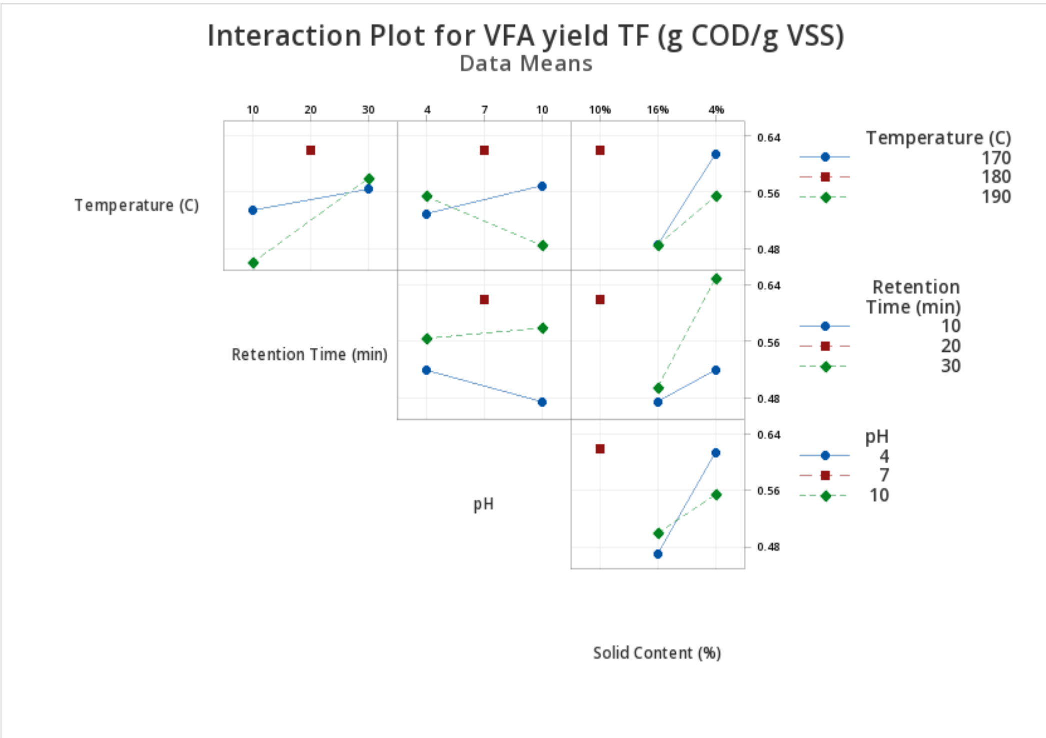

(**c**)

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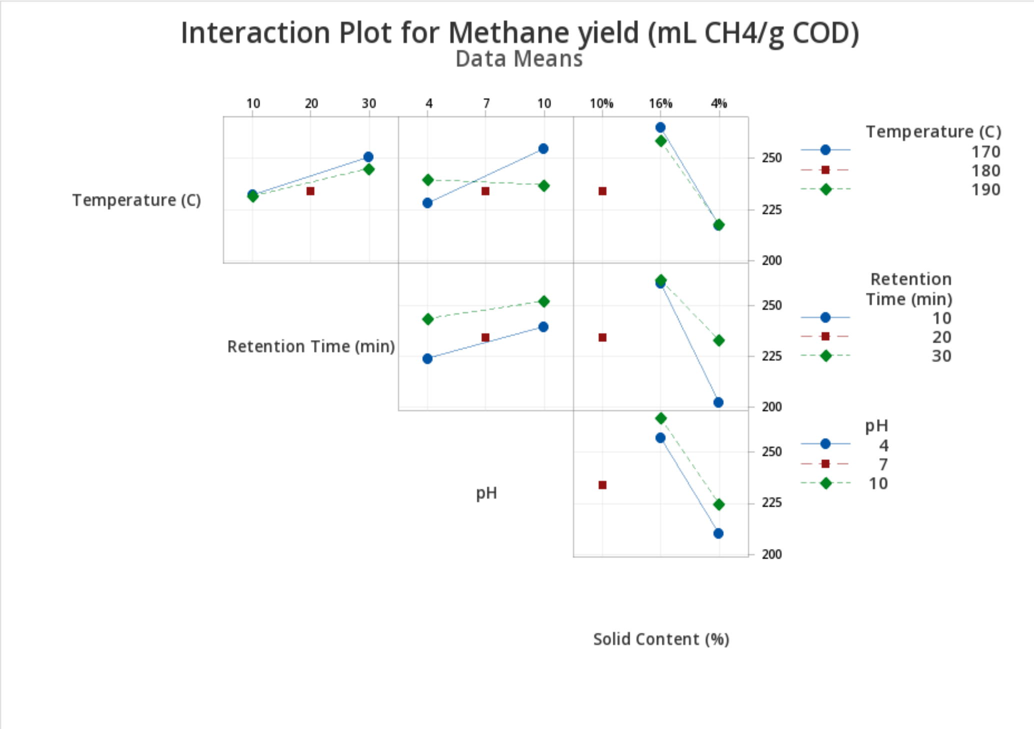


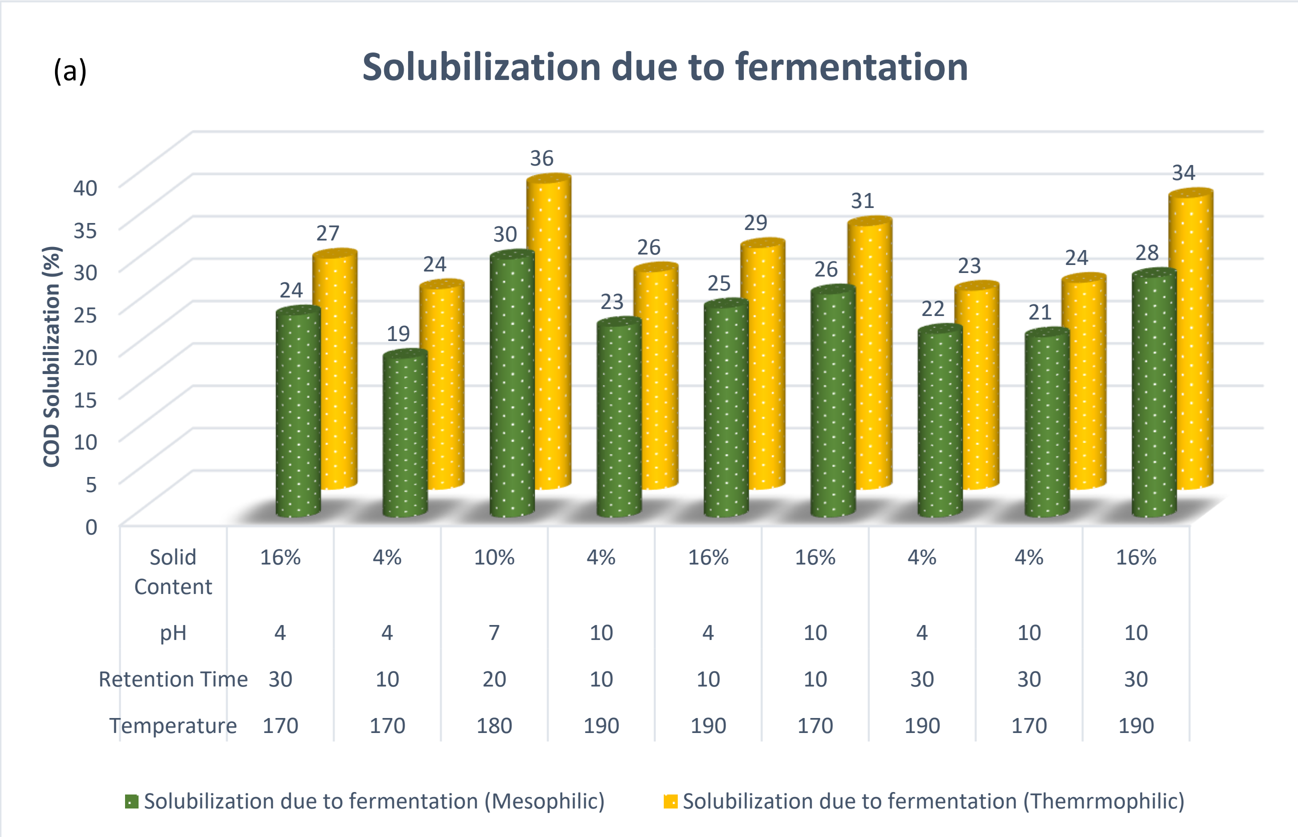
(**d**)

Figure 2. Statistical analysis (**a**) interaction plot for COD solubilization, (**b**) interaction plot for mesophilic fermentation, (**c**) interaction plot for thermophilic fermentation, (**d**) interaction plot for methane production.

3.1.2. Solubilization Due to Fermentation

Figure 3a reports the COD solubilization percentage for mesophilic and thermophilic fermentation. As seen in the figure, the thermophilic fermentation demonstrated higher solubilization potential than the mesophilic. The COD solubilization percentage for thermophilic fermentation ranged from 23% to 36%, whereas it ranged from 19% to 30% for mesophilic fermentation. One of the reasons behind the release of the higher SCOD during the thermophilic fermentation of pretreated TWAS compared to mesophilic could presumably be the accelerated growth rate [15,31,37–45]. Zhang et al. [37] have reported a higher hydrolysis rate for WAS during thermophilic fermentation than the mesophilic for all different pH values of sludge (4, 5, 6, 7, 8, 9, 10, and 11) that they have studied during HTP application.

The results revealed that samples with alkaline conditions such as "190-30-pH10-16%" demonstrated higher solubilization of 34% during fermentation compared to 29% for acidic conditions "190-10-pH4-16%". This difference might be due to the different solubilization of the proteins and carbohydrates for the two samples due to HTP. The alkaline pretreatment resulted in higher carbohydrate solubilization (32%) than the acidic pretreatment (30). The repulsions between the negatively charged EPS, thus carbohydrates and proteins (the main component of the EPS), were quickly released during the alkaline pH [40]. The highest COD solubilization due to fermentation was observed for the control sample conditions "180-20-pH7-10%" for both mesophilic and thermophilic conditions. The COD solubilization in the thermophilic fermentation was 20% higher than that in the mesophilic fermentation, 30% versus 36%.



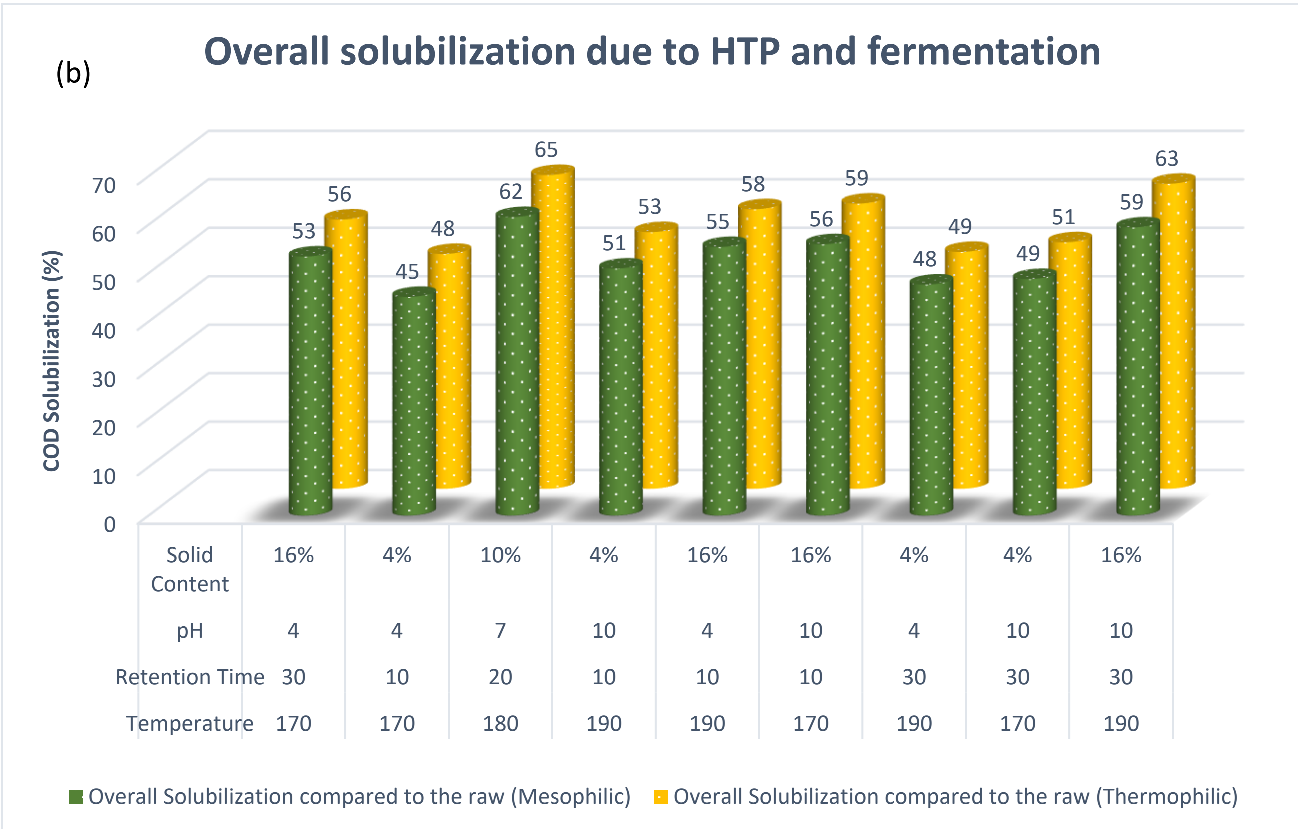


Figure 3. (**a**) solubilization due to mesophilic and thermophilic fermentation, (**b**) overall solubilization. All values in these graphs had less than 10% error.

Moreover, the overall solubilizations of the organic matters (i.e., solubilization due to both HTP and fermentation) were calculated for both thermophilic and mesophilic fermentation and are shown in Figure 3b. All the samples for both fermentation types responded the same way as the solubilization due to the individual process of HTP or fermentation. Except for retention time, higher levels of three other parameters (SC, temperature, and pH) led to higher sludge disintegration. The highest overall COD solubilization percentages were observed for the control sample "180-20-pH7-10%", counting 62% for HTP and mesophilic fermentation and 65% for HTP and thermophilic fermentation. The results revealed that applying the HTP reduces the fermentation temperature's significant effect. The overall SCOD solubilization of thermophilic fermentation was only 5–10% higher than the overall solubilization of mesophilic fermentation.

3.2. Volatile Fatty Acid Production

The impact of HTP factors on VFA production during mesophilic and thermophilic fermentation was investigated. The results revealed that the four HTP parameters were determined to be significant ($p < 0.005$). The VFA yield from both fermentations revealed that thermophilic fermentation is associated with a higher VFA recovery potential than mesophilic fermentation. The VFA yields for both mesophilic and thermophilic fermentation are shown in Figure 4a,b, respectively. As seen in the figure, thermophilic fermentation showed about 15–20% improvement in VFA yield compared to mesophilic fermentation. The VFA yields during the thermophilic fermentation ranged from 0.36 to 0.56 g COD VFA/g VSS, whereas for the mesophilic fermentation, VFA yields ranged from 0.43 to 0.65 g COD VFA/g VSS. This improvement was expected as fermentative bacteria react and grow faster in higher temperatures, producing higher VFA [41].

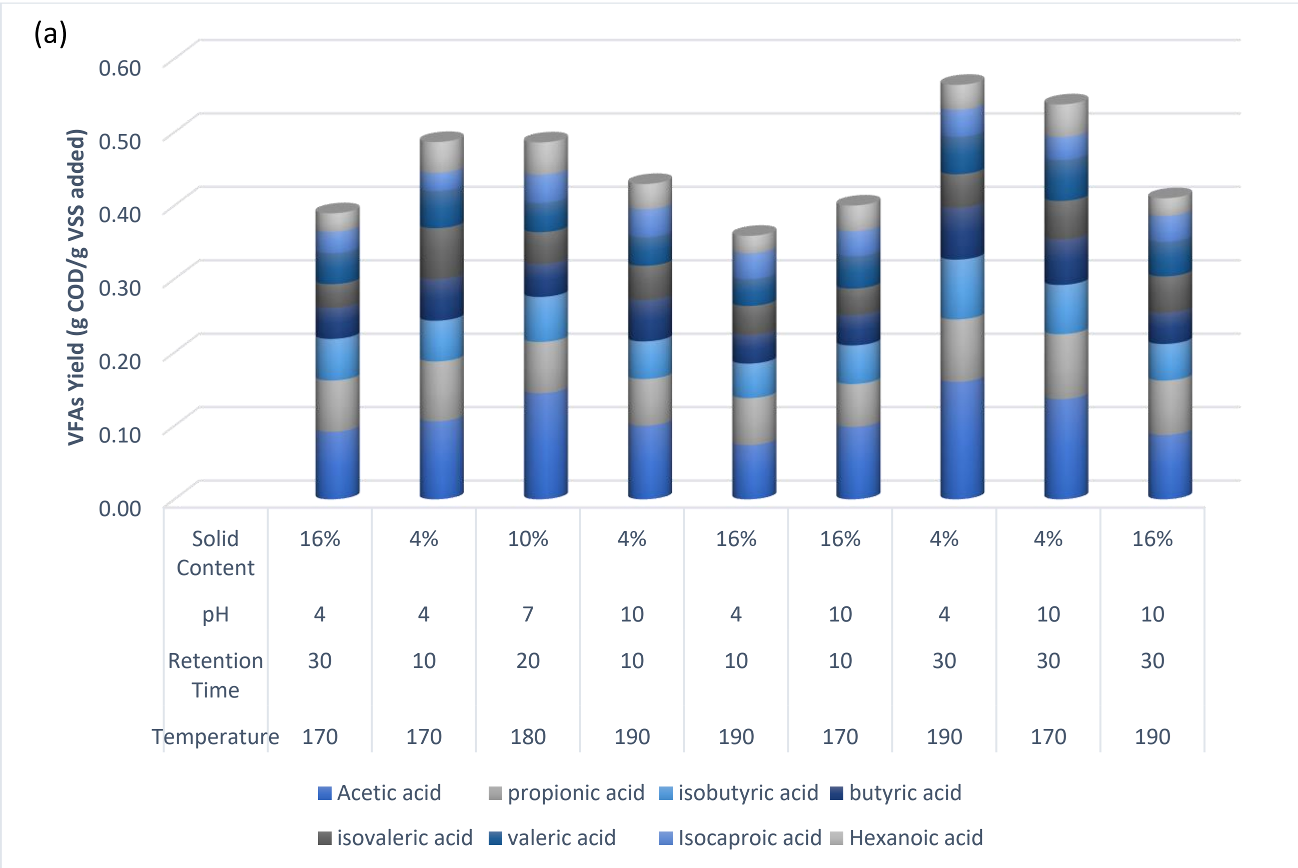


Figure 4. *Cont.*

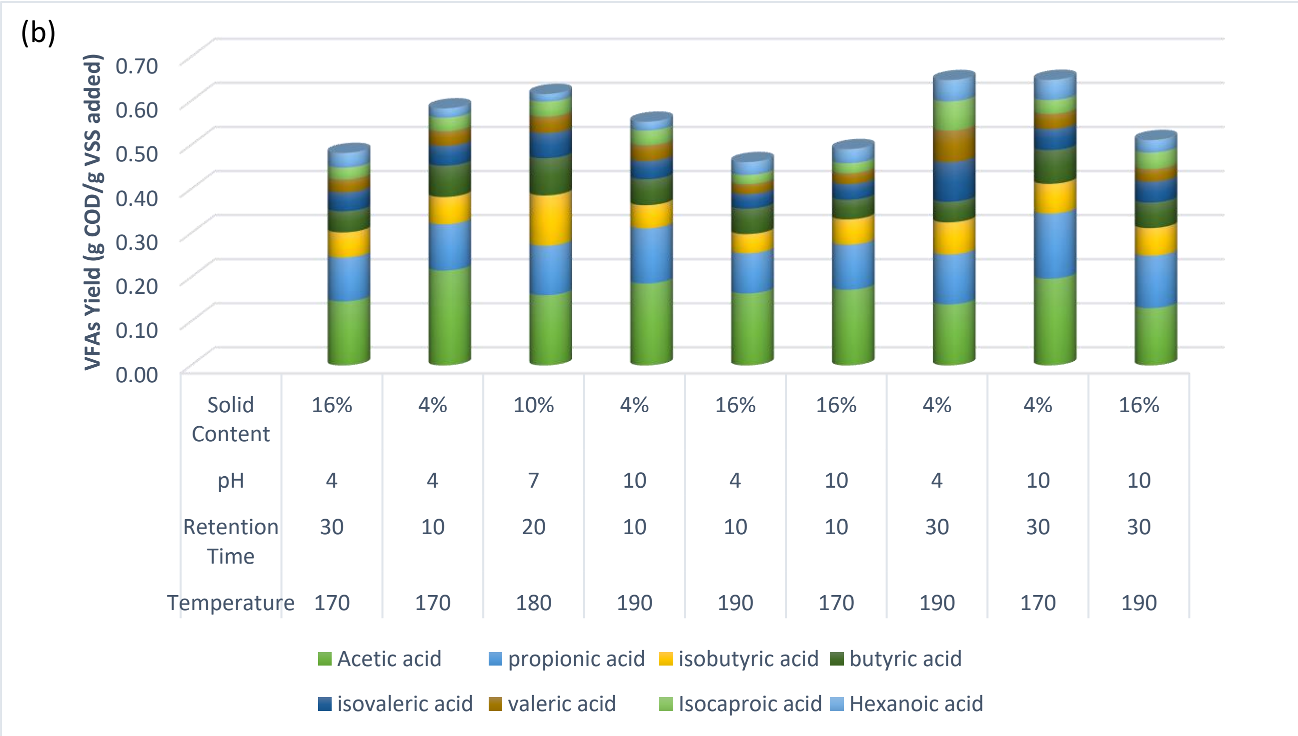


Figure 4. VFAs yield (**a**) mesophilic fermentation, (**b**) thermophilic fermentation.

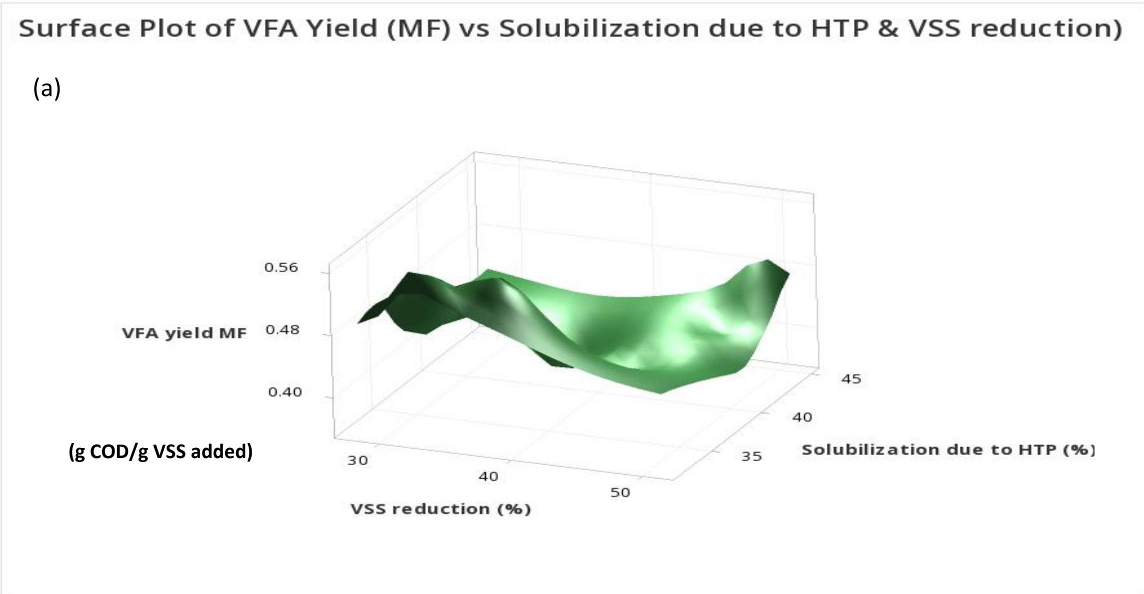
The lower SC and pH levels and at higher temperature and retention time levels were associated with higher VFA yield during both fermentation processes when analyzing the impact of each of the four parameters individually. "190-30-pH4-4%" samples fermentation produced VFA yields of 0.56 and 0.65 g COD VFA/g VSS added for mesophilic and thermophilic fermentation, respectively, whereas "170-30-pH10-4%" samples demonstrated higher VFA yields production potential of 0.54 and 0.64 g COD VFA/g VSS added compared to the sample mentioned above for mesophilic and thermophilic fermentation, respectively. Hence, it was observed that higher temperature and lower pH led to slightly better results between the two samples with similar SC and RT. However, higher pH conditions with higher solid contents resulted in higher VFA production.

The interaction between the four parameters and their influence on VFA production is reported in Figure 2b,c for mesophilic and thermophilic fermentation, respectively. As shown in the figure, there is an interaction between all these parameters, and there were no significant differences in both fermentation processes in terms of parameters interaction.

In contrast to the COD solubilization results, VFA production was enhanced at the lower SC. Better performance is likely due to the availability of readily biodegradable materials, lower viscosity, and changes in the nature of organics. Gameiro et al. [27] also spotted a 15–20% decrease in VFA content when the TS of the OMSW was increased from 5% to 8% and 10% during mesophilic fermentation. Gameiro et al. [27] reported a 50% increase in VFA production potential when the alkaline dosage was increased from 10 to 50 g $CaCO_3$/L. These observations also agreed with our findings where samples with higher solid content and pH 10 showed higher VFA yield than the lower pH. Higher VFA production for alkaline conditions could be due to the increase in buffer capacity of the waste during acidification, preventing sudden pH drop, maintaining the pH range favorable to the acidogenic and acetogenesis bacteria, and preventing inhibition problems [27].

The correlation between the VFA yield with COD solubilization and VSS destruction efficiency during both mesophilic and thermophilic fermentation is essential to evaluate the impact of sludge disintegration on the performance of VFA production. Figure 5a,b illustrate these correlations through surface plots for mesophilic and thermophilic fermentation, respectively. The figure shows that both fermentation types responded similarly to the COD solubilization and VSS reduction efficiency. Two peaks were observed in this graph, where the highest VFA was produced when higher solubilization was achieved for the TWAS.

The variation in VFA for mesophilic and thermophilic fermentation is indicated in Figure 4a,b, respectively. For both fermentation processes, the most abundant VFA detected was acetic acid but with a different ratio compared to TVFA. The concentrations of acetic acid in the TVFA were about 25% and 35% for mesophilic and thermophilic fermentation, respectively. The next most abundant VFA for both fermentations were propionic acid and isobutyric acid, followed by iso-valeric acid, valeric acid, isocaproic acid, and hexanoic acid.



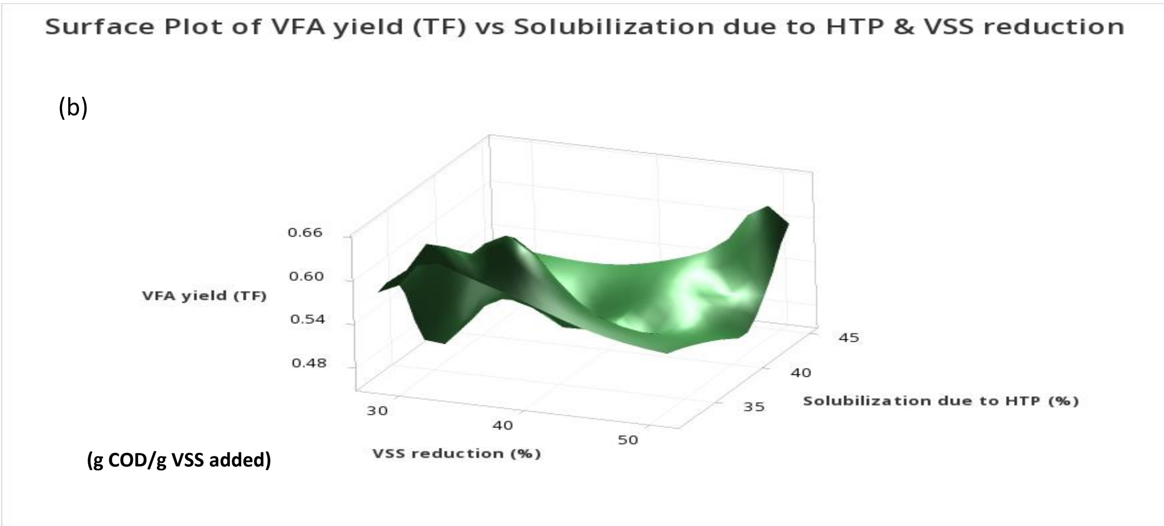


Figure 5. *Cont.*

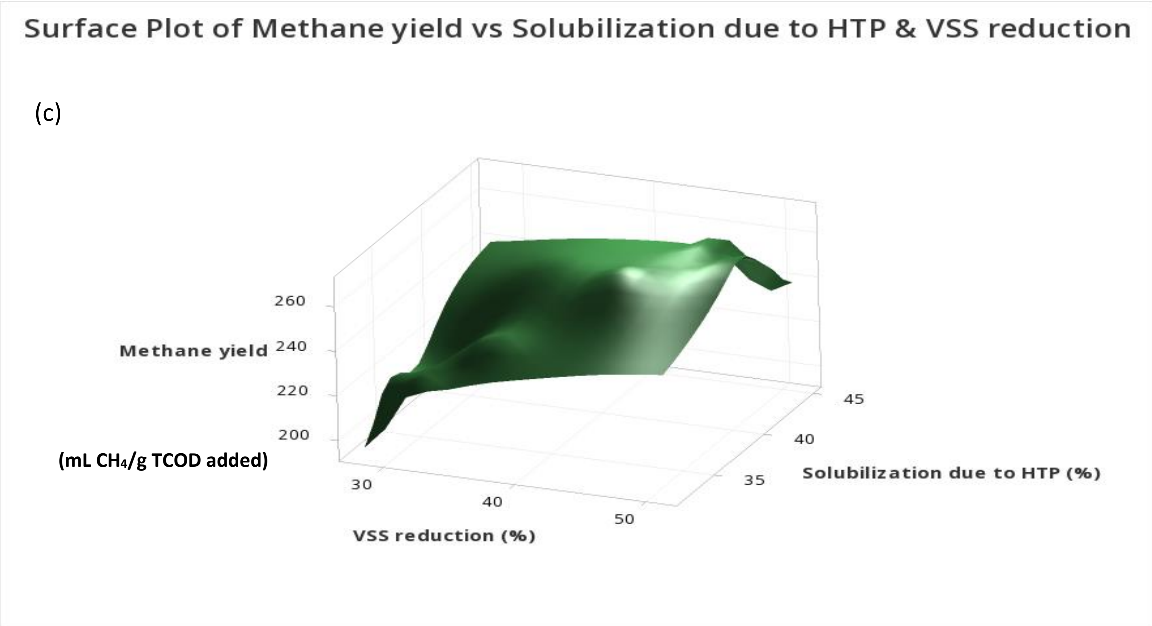


Figure 5. Statistical analysis (**a**) Surface plot for mesophilic fermentation (**b**) Surface plot for thermophilic fermentation (**c**) Surface plot for Methane production.

3.3. Methane Production

3.3.1. Methane Yield

Batch BMP tests were carried out for all nine samples, and the methane yields are shown in Figure 6a. As shown in the figure, most methane was produced during the first 15 days for all the samples. It has been observed that feeding the same pretreated samples to anaerobic digestion and fermentation has a different impact on the bi-product yield. Higher methane yields were observed for the higher level of the SC and pH and lower temperature and retention time levels. The highest methane yield of 269 mL CH_4/g TCOD added was observed for the "170-10-pH10-16%" sample, which counted for a 13% improvement compared to the control"180-20-pH7-10%".

In general, sludge with a higher level of SC (16%) produces higher methane than the lower levels (4%), studying the impact of each parameter individually. These observations might be due to the higher solubilization for the sample with 16% SC compared to the sample with an SC of 4%. Contrary to our results, Gong et al. [16] reported higher methane yield for samples with lower solid content than those with higher ones. Gong et al. [16] pretreated WAS with a different solid content of 5%, 8%, 10%, 12%, and 15% under 160 °C for 60 min and then used them as a substrate for batch BMP. They reported cumulative biogas yields of 389, 425, 238, 233, and 211 N mL/g VS, for solid-liquid ratios (SLR) of 5%, 8%, 10%, 12%, and 15%, respectively. Whereas in our study, the cumulative methane yields were 412–543, 373, and 393–417 mL CH_4/g VSS added for the samples with SC of 4%, 10%, and 16%, respectively. The difference in our results and Gong's results could be due to the nature of the substrate used, the HTP temperature (lower temperature was used in Gong et al.'s study), or the retention time (longer retention time was used in Gong et al.'s study). As seen in Figure 2d, an obvious interaction was established between the HTP temperature and SC.

The pH level is the second factor significantly impacting the methane production yield ($p < 0.005$). It has been reported that the pH pretreatment (alkaline or acid) interrupts the microbial cell walls and consequently improves methane production [33,35,40–43]. In our study, the alkaline pH (10) was shown to positively influence the methane production yield compared to the neutral and acidic pH. Therefore, the highest methane production yield of 269 mL/g COD added was observed for the sample with pH 10 and a lower level of temperature and RT. The pH, temperature, and RT interaction are shown in Figure 2d.

Other studies have reported found alkaline pH to be more effective than acidic pH in enhancing methane production [14,33,42–44].

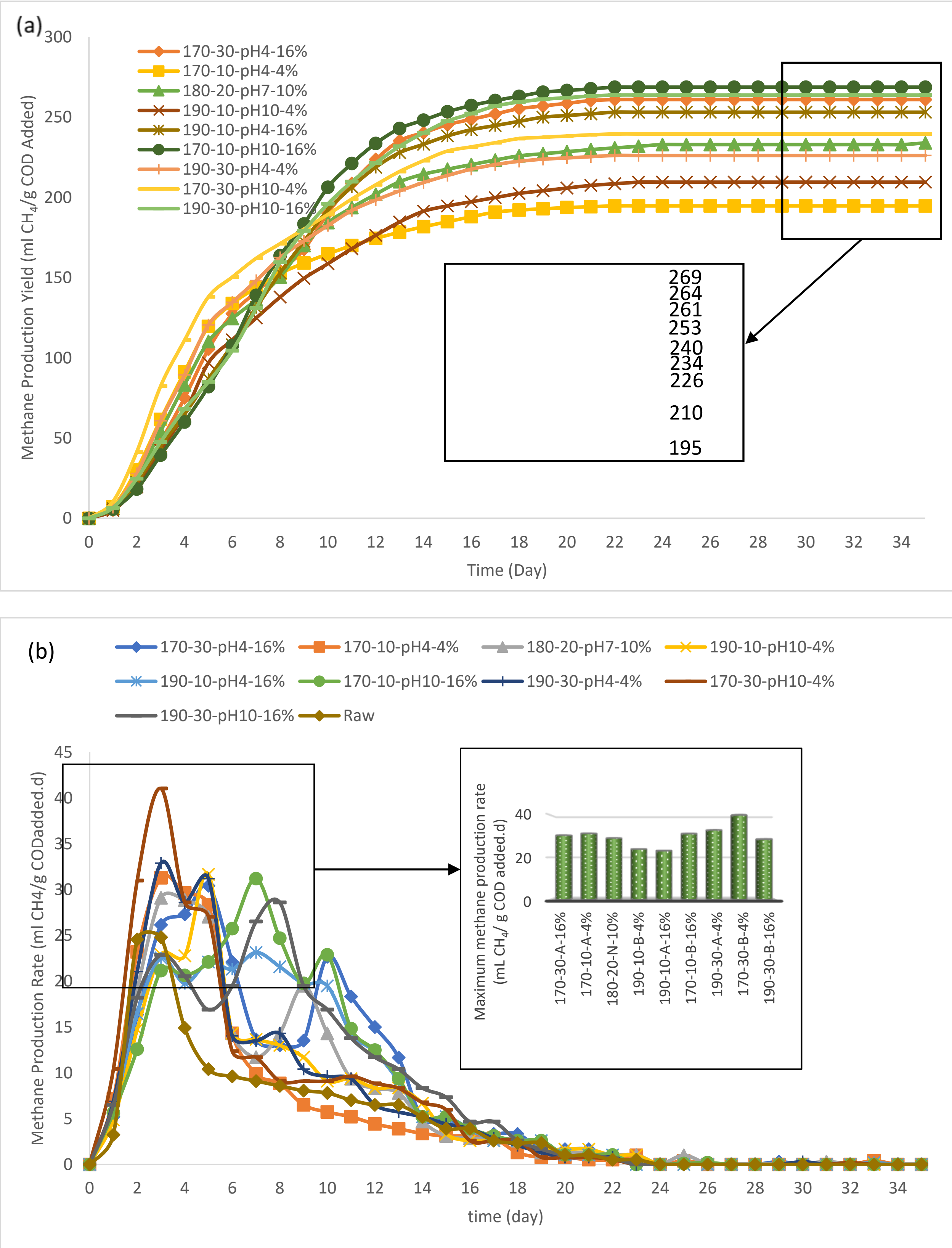


Figure 6. (**a**) Methane production yield and (**b**) methane production rate.

The results revealed that temperature impacted sludge disintegration, fermentation, and BMP in different ways. Similar to fermentation, lower temperature levels resulted in higher methane yields. Notably, the highest methane yield was achieved for the lowest temperature of 170 °C. The negative impact of the high-temperature level could be due to the formation of toxic compounds such as melanoidins during HTP [29,31,45], inhibiting the methanogenesis activities [46]. The retention time reacted differently.

In some cases, a longer time was more efficient, and, in other cases, a shorter time was more efficient. This variation led to an ambiguity in the temperature's impact, denoting that other parameters were the dominant factors. The interaction between all the factors based on the methane yield is plotted in Figure 2d.

The correlation between methane production and COD solubilization and VSS reduction is illustrated in Figure 5c. The results confirmed a positive correlation between sludge disintegration and methane production. As seen in the figure, COD solubilization and VSS removal improved the methane enhancement. The highest methane yield of 269 mL CH_4/g TCOD added was achieved at 40% COD solubilization and 50% VSS removal efficiency. Our observations agree with Gong et al. [17], who found a linear relationship between the increase in SCOD during HTP and methane production.

3.3.2. Methane Production Rate

Figure 6b shows the methane production rate throughout the BMP process in 35 days. As shown in the figure, all the samples had two main peaks. The results revealed that solid content was a significant factor in the delay in methane production. Peaks of methane production for the samples with higher SC were observed later than those with lower SC. As seen in the figure, samples with lower SC started producing methane immediately. In these conditions (lower SC), methane was produced mainly during days 2–5 with the highest methane production rates of 41, 33, 31, and 24 mL CH_4/g COD_{added}.d for samples "170-30-pH10-4%", "190-30-pH4-4%", "170-10-pH4-4%", "190-10-pH10-4%", respectively. Whereas for the samples with higher SC, most of the methane was produced mainly during days 5–9 and 9–13 with the highest methane production rates of 32, 30, 29, and 23 mL CH_4/g COD_{added}.d for samples "170-10-pH10-16%", "170-30-pH4-16%", "190-30-pH10-16%", "190-10-pH4-16%", respectively. In a similar study using different solid content ranging from 5% to 15%, Gong et al. [17] also observed higher and earlier methane production rates for lower SC. They found that the maximum methane production rates of 43, 55 22, 20, and 19 N mL/gVS were observed for SLR 5%, 8%, 10%, 12%, and 15%, respectively.

3.3.3. Modeling

The BMP data was fitted to the modified Gompertz model. Table 1 contains estimated methane production yields, maximum methane production rates, and lag phase times of all nine samples. The highest ultimate methane production yields of 272 $mLCH_4$/g COD added and the highest max methane production rate of 28 $mLCH_4$/g COD_{added}.d was observed for the "170-10-pH10-16%" sample.

Nonetheless, the model established a perfect linear relation with the experimental data, considering the R^2 value of 0.897–0.985 and the 10% difference between the experimental data and the predicted values. Other scholars have used the Gompertz model to evaluate the biomethane production potential of the sludge, and generally, high R^2 values have been reported. Gong et al. [17] have compared their experimental data with the modified Gompertz model and reported a similar and slightly higher range of R^2 values of 0.975–0.995.

The Gompertz model predicted a more extended lag phase for the samples with higher SC than those with lower SC. The reason might be the nature of the actual feed at the wastewater treatment plant, where it also has 4% solid content and bacteria are familiar to them. Gong et al. [17] have also reported a slightly higher lagging time for the samples with higher SC. In their study, as the SC was increased from 5% to 10%, the slow time was delayed from 1.79×10^{-16} to 0.0073 days. Whereas in our study, the average lag times for 4% and 16% were 0.5 and 1.5 days, respectively.

Compared to the Gompertz model, the first-order kinetics data fit better with the experimental data. The R^2 value for the first-order kinetic ranged between 0.962 and 0.994. The hydrolysis coefficient of all samples calculated by first-order kinetic ranged from 0.11 to 0.22 days. The hydrolysis coefficient demonstrated a linear relationship between solid content and retention time, where higher levels resulted in a higher hydrolysis rate.

4. Conclusions

This study revealed the importance of HTP parameters on COD solubilization, VFA, and methane recovery and the interactions between them. Acidogenic fermentation responded favorably to lower levels of SC (<10%) and pH (4.5). In contrast, the opposite was observed for anaerobic digestion, where increases in methanogenesis were observed at the higher levels of SC (>10%) and pH (10.0). Further, the highest COD solubilization due to HTP (45%) and overall COD solubilization due to the HTP and fermentation (65% for thermophilic, 62% for mesophilic) was found for the control sample "180-20-pH7-10%". Also, the mesophilic and thermophilic fermentation processes fed with the same samples were compared, while the highest VFA yield was associated with thermophilic fermentation ranging between 0.43 and 0.65 g COD VFA/g VSS. Moreover, the highest methane yield of 269 mL CH_4/g TCOD added was recorded for the sample with high SC (16%) and pH (10) and low temperature (170 °C) and RT (10). In contrast, the highest methane production rate was for the lower SC (4%) and temperature (170 °C) and higher RT (30 min) and pH (10).

Author Contributions: F.L.K.: Conducting the experiments, data curation, formal analysis, writing—original draft, conceptualization, methodology. H.A.: Data curation, writing—review and editing. S.N.L.: Conceptualization, methodology, writing—review and editing, supervision, funding acquisition. E.E.: Conceptualization, methodology, writing—review and editing, supervision, funding acquisition. All authors have read and agreed to the published version of the manuscript.

Funding: This work was funded by the Natural Sciences and Engineering Research Council of Canada (NSERC), grant number [RGPIN-2022-03825, RGPIN/07224-2020 and RPGIN/054222-2014].

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: All the data are reported in this article.

Acknowledgments: The authors would like to acknowledge the research funding awarded to SNL and EE from the Natural Sciences and Engineering Research Council of Canada (NSERC) and the award of the Vanier Canada Graduate Scholarship by the Government of Canada to FLK.

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

List of Abbreviations

AD	anaerobic digestion
WWTP	wastewater treatment plant
TWAS	thickened waste-activated sludge
WAS	waste activated sludge
HTP	hydrothermal pretreatment
SC	solid content
RT	retention time
COD	chemical oxygen demand
TCOD	total chemical oxygen demand
SCOD	soluble chemical oxygen demand
TSS	total suspended solids
VSS	volatile suspended solids
VFA	volatile fatty acid
BMP	biochemical methane production
ANOVA	analysis of variance

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