



Investigation and Modeling of Biogas Production Potential from Urban and Fruit Juice Wastewater Treatment Plant Sludge through Pretreatment

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ABSTRACT

In this study, the effect of pretreatments applied to the sewage sludge of the Tokat Municipality wastewater treatment plant (WTP), the sewage sludge of the packaged wastewater treatment plant (PWTP) of a fruit juice production plant, and the aqueous phases of their mixtures on biogas production was investigated. Chemical, thermal (microwave (MW) and hot plate (HP)) and chemical-thermal pretreatments were applied to these sludge samples. Considering the results in all samples, the highest biogas production amount and efficiency were found in the pre-biogas-unit aqueous phase of the sewage sludge of the Tokat WTP, which was applied 20% H₂SO₄+10-minute (min) thermal MW pretreatment, with 667.51 ml and 396.34 ml biogas/g water dissolved SM value, respectively. Statistical analyses included the Duncan comparison test for cumulative biogas production efficiencies at the end of 65 days and the maximum exponential increase function and Gompertz equations for cumulative biogas amounts. Accordingly, the most appropriate model was tried to be determined. The electricity generated at the end of the 22-day incubation period at the facility meets 36% of the electricity needed by the Tokat WTP. At the end of the experimental studies (20% H₂SO₄+10 min thermal MW pretreatment), it can be said according to the 22-day biogas data that the biogas production efficiency increased by 3.41 times, this would meet all the electricity needed by the facility, and that there would be an extra 23% electricity generation of the total generation. Mixing and using fruit juice PWTP and WTP treatment sludge in the production of biogas will enable both the utilization of this waste in biogas production and the weakening and reduction of high parameter values, which sometimes cause problems in the sludge discharged from the Tokat WTP due to urban wastewater treatment, to acceptable limits.

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Introduction

Treatment sludge, which is produced as a result of the treatment of wastewater, is a major economic and environmental concern. In recent years, the increase in environmental awareness and the development of environmental behavior have led to the investigation and application of new methods to reduce its amount. The methods of sludge disposal include stabilization, minimization, recycling, incineration, landfilling, composting, and agricultural use. To eliminate the treatment sludge without further environmental problems, it is necessary to dispose of it with appropriate methods (Yalçın et al., 2010).

Most of the energy needs are met by using fossil fuels and it is one of the main causes of environmental problems. For this reason, renewable energy produced from waste is considered as one of the future alternative energy sources. One of the biomasses that can be used as a renewable energy source is the sludge left after treatment in wastewater treatment plants. Since the organic load of the treatment sludge is high, high biogas efficiency can be obtained by digesting it in anaerobic processes. Anaerobic biological

treatment systems are one of the methods to convert biomass into energy. This method can also be applied to many industrial and agricultural wastes (Speece, 1996).

All pathogenic organisms and pollutants in wastewater, and chemicals used in the processes to reach the discharge limits of the effluent in wastewater treatment plants turn into sludge. For this reason, there may be harmful substances in treatment sludge. This sludge, which threatens human health and cause negativities for the environment, is quite good in terms of calorific value (<https://inevaturkiye.com.tr>). For this reason, treatment sludge can be used to obtain energy.

Some studies on the subject have shown very good results of biogas production from treatment sludge samples by using an anaerobic system. In addition, many studies have indicated that pretreatment applications give positive results of biogas production from both treatment sludge and different raw materials (Wang et al., 2022; Hämäläinen et al., 2022; Akçakaya et al., 2022; Gülşen Akbay et al., 2022; Zeng et al., 2022; Gülşen Akbay et al., 2021; Zhao et al., 2021; Mainardis et al., 2021).

In this study, the effect of pretreatments applied to the sewage sludge of two different facilities in our city and to their mixtures on biogas production was investigated. The results were evaluated statistically on the SPSS software, and the most appropriate model for biogas production was determined by applying various mathematical models (maximum exponential increase and Gompertz). It was seen that using the resulting biogas as an energy source could provide both environmental and economic benefits.

Materials and Methods

Raw Materials Used in the Study and Their Preparation for Analysis

The samples given in Table 1 were studied separately in the laboratory. After the treatment sludge samples were taken from the facilities, they were brought to the laboratory without delay, and moisture, total solids, ash, and volatile matter analyses were carried out in the laboratory according to standard methods (APHA, 2005). The remaining parts of the sludge samples were dried in an oven at 70°C for one day until they were completely dry. These dry samples were ground in a grinder, and the samples remaining under the sieve were used in the study for pretreatment applications. The HO-1000 model ring grinder of Yerli Unal Engineering and Machine Industry was used for grinding raw materials. The pure water to be used during analyses was produced by using the MES brand MP MINIPURE device. A Yuksel Kaya Machine brand shaking incubator was used for mixing samples. For the weighing processes of the samples, a Denver Instrument brand precision balance with ±0.1mg sensitivity was used.

Drying processes and moisture analyses were conducted in a Nuve Dry Heat Sterilizer FN-055 brand oven according to standard methods.

Ash and volatile matter values were determined in a Lentom brand muffle furnace that can be adjusted up to 1200°C. A BEKO MD 1500 Model 5 microwave oven (70-700 W) and the four-burner jacket heater of Thermal Laboratory Instruments Company model N11742, which is adjustable up to 400°C, were used for the microwave and hot plate thermal pretreatments applied to the raw materials. A Hach brand Sension1 model pH meter was used for pH measurements of the samples.

Pretreatments Applied to Raw Materials

The pretreatments applied to the samples were administered to the aqueous mixtures of the treatment sludge containing 10% solids by mass.

HP thermal pretreatments were carried out in a four-flask balloon heater at the normal boiling point of water (100°C) under reflux, which is a part of the process, and MW thermal pretreatments were performed in a microwave oven under reflux with 700W power.

Pretreatments performed by adding acid and base to sludge samples containing 10% solids were as follows: 50% diluted 98% concentrated H₂SO₄ (with 1.86 kg/L density) or 25% aqueous NaOH solutions by mass were added to 10%, 15%, and 20% of the solid matter in the sludge, and they were cooked for 10, 20, and 30 min. Additionally, the flow chart of the pretreatments applied to the samples and their combinations is given in Figure 1.

Table 1. Raw materials used in the study

The sources of the treatment sludge	The names of the samples
Fruit juice PWTP treatment sludge	Sample 1
Tokat WTP sludge before the biogas unit	Sample 2
Tokat WTP sludge after the biogas unit	Sample 3
Dimes fruit juice company PWTP sludge and treatment sludge mixture from Tokat WTP (both 50% by weight) before the biogas unit	Sample 4

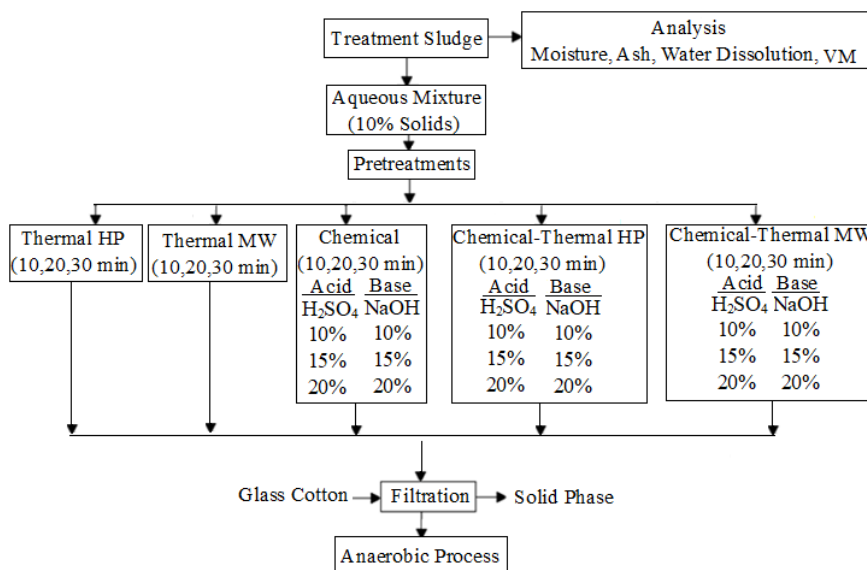


Figure 1. Flow chart of the procedures applied to the treatment sludge

Determination of Solubility in Water and Preparation of Materials for Analysis

Aqueous mixtures containing 10% solids by mass, which were left without pretreatment at room temperature or were subjected to chemical, thermal HP, thermal MW, chemical-thermal HP, and chemical-thermal MW, underwent a total of 588 water dissolution processes as 3 replications. After the water dissolution experiments, 24 samples with the highest water solubility values were selected for analysis. H₂SO₄ and NaOH solutions were used to adjust the pH of the selected 24 aqueous phases to 7, which is the necessary pH level for the biogas-producing bacteria to live.

The bottles in which the 10% of aqueous phases obtained from samples with and without pretreatment would be put into were wrapped with aluminum foil to allow anaerobic degradation and prevent light transmission. Bottles of 100 ml were used for biogas measurements. The samples obtained from the pretreatments were filled in these bottles in volumes of 3/4. All aqueous phases were inoculated to produce methane. The inoculated solution was obtained from the aqueous solution formed by filtration of fresh cow manure containing 5% solids through glass cotton. The samples were put in bottles of 100 ml in certain volumes, the bottles were capped, and then nitrogen gas was filled in them for approximately 45 seconds to remove the oxygen completely from the bottles. While nitrogen gas was filled in the bottles, a second serum needle was used for gas evacuation.

Determination of Biogas Amounts Forming during Anaerobic Process

The bottles, which were provided with anaerobic conditions, were left for anaerobic biodegradation in an incubator, whose temperature was set to 35°C to create optimum conditions. The volume of biogas and methane forming in 100 ml serum bottles placed in the incubator for biogas formation was measured in a setup similar to that of the Orsat gas analyzer.

First, the biogas volume in the device was determined. Then, all of the biogas was taken to the absorption column on the device, which contained 33% of KOH solution that absorbs CO₂, and the gas was washed with this solution several times to ensure that all CO₂ was absorbed. Afterward, the remaining gas was transferred to the burette, which is the other gas level measurement point on the device, and the methane volume was read from there.

Statistical Analysis Applied to Biogas Production Efficiencies

The biogas data obtained in the study were also evaluated statistically. To do this, the anaerobic treatment results were based on a statistical method. In this context, the analyses were conducted on the SPSS 17 statistical software package. The study was designed in accordance with the "Random Plots Trial Plan". First of all, the test to be applied was decided depending on the number of samples. In cases where there are two samples, T or Z test should be employed, while in cases where there are more than two samples, variance analysis should be conducted and the variances should be homogeneous in this case.

Therefore, the Levene variance homogeneity test was applied.

When the variances are homogeneous (P>0.05), the variance analysis stage is started. When the analysis of variance is homogeneous (P<0.001), the Duncan test is used. Duncan test (P<0.05) is performed to find the difference between the methods. In the Duncan test, letters are used to show which means are equal and which are different.

Modeling

A modeling study was carried out to show that biogas production amounts could be estimated with several mathematical equations without using tables. Following this objective, maximum exponential increase and Gompertz modeling were applied by evaluating the cumulative biogas production amounts of four sludge samples after 65 days.

Maximum exponential increase equation;

$$f = a \times (1 - \exp(-b \times X))$$

where;

f: total amount of biogas forming in x time

X: time during decomposition period

a: biogas production potential

b: first order kinetic constant

Another equation used in comparison was the Gompertz equation. The equation of this model was as follows (Lo et al., 2010);

$$f = a \times \exp(-\exp(-(X - X_0) / b))$$

where;

f: total amount of biogas forming in x time

X: time during decomposition period

X₀: maximum time at the biogas production rate

a: biogas production potential

b: first order kinetic constant

Findings and Discussion

Characteristics of Raw Materials

The moisture, ash, solid matter, and volatile matter measurements of the samples taken from the treatment sludge of both plants are given in Table 2.

Table 2. Analysis results of the treatment sludge samples

	Sample 1	Sample 2	Sample 3
Solid content%*	14.72	5.08	3.25
Moisture%*	85.28	94.92	96.75
Ash content%**	34.37	33.00	51.00
Volatile matter%**	65.63	67.00	49.00

*In the original sample **In the dry solid

Findings of Water Dissolubility in Samples with and without Pretreatment

The water dissolution percentages of four treatment sludge samples with and without pretreatment are given in Table 3.

Table 3. The water solubility percentages of raw materials with and without pretreatment

	Pretreatment	WS	Pretreatment	WS
S1	Without pretreatment	49.56	Without pretreatment	49.40
	Chemical (20% H ₂ SO ₄)	73.08	Chemical (20% H ₂ SO ₄)	59.16
	Thermal HP (10 min)	55.62	Thermal HP (30 min)	53.54
	Thermal MW (10 min)	60.87	Thermal MW (10 min)	54.22
	Chemical-Thermal HP (20% H ₂ SO ₄ , 20 min)	73.06	Chemical-Thermal HP (20% NaOH, 30 min)	70.01
	Chemical-Thermal MW (15% NaOH, 10 min)	89.85	Chemical-Thermal MW (20% H ₂ SO ₄ , 30 min)	60.05
S2	Without pretreatment	51.96	Without pretreatment	49.38
	Chemical (10% H ₂ SO ₄)	64.49	Chemical (15% NaOH)	61.37
	Thermal HP (30 min)	64.03	Thermal HP (30 min)	58.67
	Thermal MW (10 min)	55.45	Thermal MW (30 min)	79.31
	Chemical-Thermal HP (20% NaOH, 10 min)	79.04	Chemical-Thermal HP (20% H ₂ SO ₄ , 30 min)	83.01
	Chemical-Thermal MW (20% H ₂ SO ₄ , 10 min)	84.21	Chemical-Thermal MW (20% H ₂ SO ₄ , 20 min)	80.26

WS: Water solubility (%); S1: Sample 1; S2: Sample 2; S3: Sample 3; S4: Sample 4

Table 4. Cumulative biogas production amounts

	Pretreatment	CB	Pretreatment	CB
S1	Without pretreatment	146.7	Without pretreatment	98.55
	Chemical (20% H ₂ SO ₄)	231.9	Chemical (20% H ₂ SO ₄)	139.74
	Thermal HP (10 min)	209.26	Thermal HP (30 min)	190.55
	Thermal MW (10 min)	232.48	Thermal MW (10 min)	166.54
	Chemical-Thermal HP (20% H ₂ SO ₄ , 20 min)	295.32	Chemical-Thermal HP (20% NaOH, 30 min)	208.43
	Chemical-Thermal MW (15% NaOH, 10 min)	278.02	Chemical-Thermal MW (20% H ₂ SO ₄ , 30 min)	215.31
S2	Without pretreatment	195.37	Without pretreatment	176.71
	Chemical (10% H ₂ SO ₄)	366.85	Chemical (15% NaOH)	293.14
	Thermal HP (30 min)	425.71	Thermal HP (30 min)	331.71
	Thermal MW (10 min)	398.66	Thermal MW (30 min)	419.25
	Chemical-Thermal HP (20% NaOH, 10 min)	566.87	Chemical-Thermal HP (20% H ₂ SO ₄ , 30 min)	472.72
	Chemical-Thermal MW (20% H ₂ SO ₄ , 10 min)	667.51	Chemical-Thermal MW (20% H ₂ SO ₄ , 20 min)	471.96

CB: Cumulative Biogas (ml); S1: Sample 1; S2: Sample 2; S3: Sample 3; S4: Sample 4

It is seen in Table 3 that all chemical (acid/base addition) and thermal (HP/MW) and chemical (acid/base) + thermal (HP/MW) pretreatments increased the solubility of solid matter in water. In a similar study, it was concluded that thermal, chemical, and chemical-thermal treatments applied to increase the biological decomposition efficiency of treatment sludge disrupted the flock structure of the sludge and increased its solubility and that the treatments administered increased the rate and efficiency of biodegradation (Genç, 2008). In other studies on the subject, it was observed that pretreatments applied to samples increased the water solubility levels (Ardıç and Taner, 2004; Halisdemir, 2009; Ardıç, 2009; Bayrak Işık and Polat, 2017; Şenol, 2019).

When the water solubility percentages of the pretreatments applied to four sewage sludge samples were compared, it was seen that the highest water solubility was obtained as 89.85% from the chemical-thermal MW (15% NaOH+10 min MW) pretreatment applied to the sewage sludge of the fruit juice PWTP.

Biogas Production in Aqueous Phases Obtained From Unpretreated and Pretreated Sludge Samples

Anaerobic degradation of the aqueous phases in the bottles took 65 days. During these 65 days, biogas production amounts of the samples kept in the incubator at 35°C were measured every five days (Table 4). Since a decrease was observed in the biogas production as a result of the measurements, no measurements were made after the 65th day and the study was terminated.

Biogas production amounts were measured in ml. Then, they were calculated as biogas/ml per gram of solids dissolved in water, and biogas production efficiency assessments were made. Figure 2 shows the biogas production efficiency obtained from unpretreated and pretreated samples of sewage sludge.

When the biogas production efficiencies obtained from the four different treatment sludge samples were compared, the results obtained from all pretreatments were found to be higher than those obtained from samples without pretreatment. There are various studies showing that pretreatment increases the amount of biogas production (Arıkan, 2008; Varinli, 2010; Martin, 2017; Çilingir, 2018; Şenol et al., 2020).

It can also be said that thermal HP and thermal MW pretreatments provided more biogas production efficiency than only chemical pretreatment applications. As seen in Figure 2b, it was determined that the highest biogas production efficiency in the samples was obtained on the 20th day from the 10 min thermal MW pretreatment with 69.69 ml biogas/g SM dissolved in water.

In the thermal pretreatments, it was observed that the gel structure was broken down, the substances in the cell passed into the aqueous phase, and that these substances were broken down anaerobically, causing an increase in water solubility and biogas production. These findings are supported by findings obtained by Murto et al. (2004) and Crawford et al. (1982).

Cumulative biogas production efficiencies obtained for 65 days are given in Figure 3 as ml biogas/g SM dissolved in water.

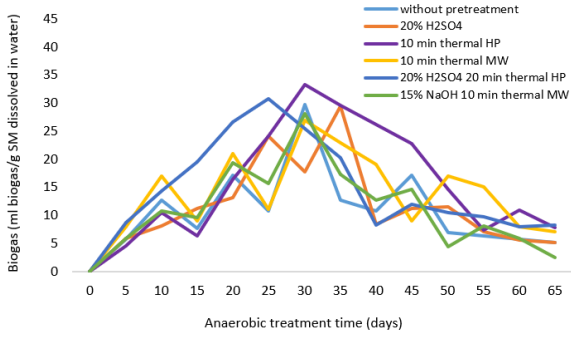


Figure 2a. Biogas production efficiency of the 1st sample

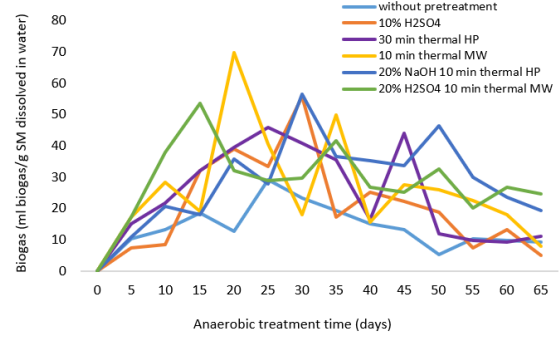


Figure 2b. Biogas production efficiency of the 2nd sample

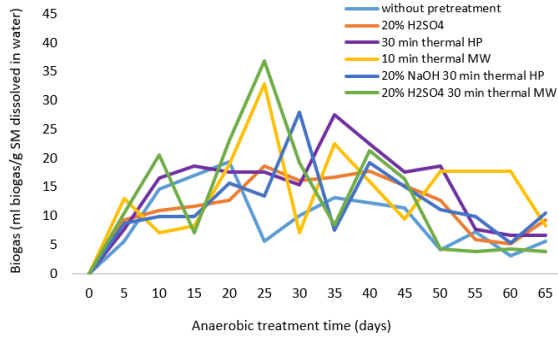


Figure 2c. Biogas production efficiency of the 3rd sample

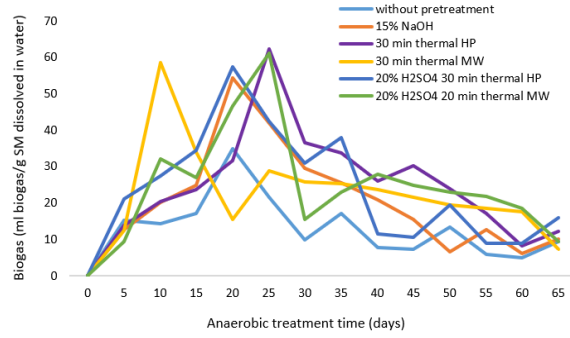


Figure 2d. Biogas production efficiency of the 4th sample

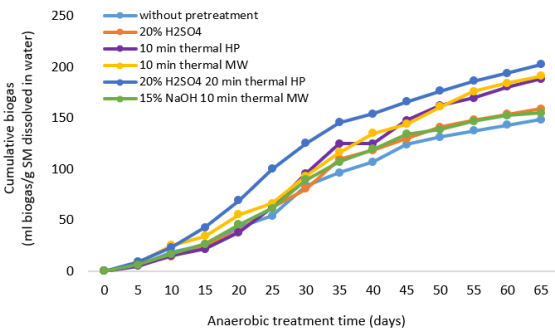


Figure 3a. Cumulative biogas production efficiencies of the 1st sample

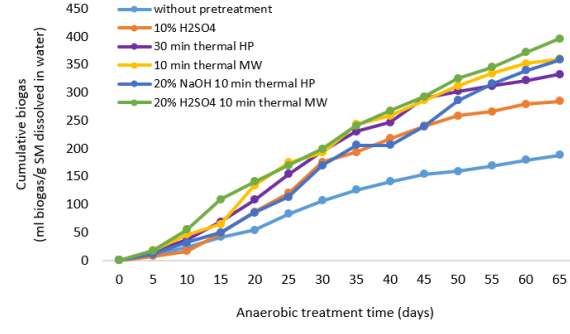


Figure 3b. Cumulative biogas production efficiencies of the 2nd sample

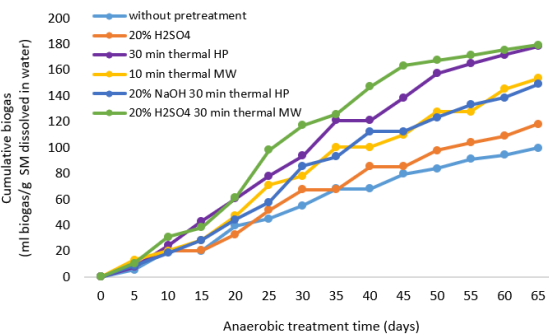


Figure 3c. Cumulative biogas production efficiencies of the 3rd sample

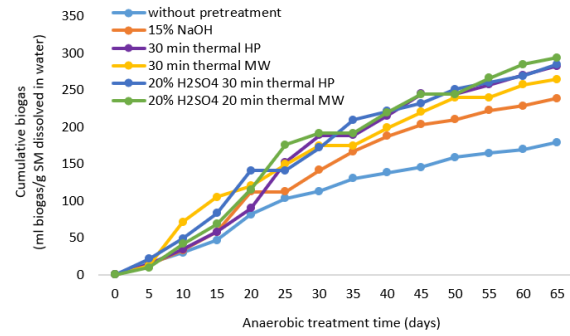


Figure 3d. Cumulative biogas production efficiencies of the 4th sample

The highest cumulative biogas production efficiency (396.34 ml biogas/g SM dissolved in water) was obtained from the aqueous mixture of the 2nd sample (Figure 3b), which was followed by the aqueous mixture of the 4th sample (294.02 ml biogas/g SM dissolved in water), the aqueous mixture of the 1st sample (202.11 ml biogas/g SM dissolved in water), and the aqueous mixture of the 3rd sample (179.28 ml biogas/g SM dissolved in water).

During the anaerobic process, the methane percentage of biogas obtained from raw materials was found to range between 42.66 and 58.90%. In addition, pH evaluation, which is effective in biogas and methane production stages, was also performed in the study. Figure 4 shows the pH changes. The anaerobic process consists of three steps, namely hydrolysis, acid formation, and conversion to methane. As seen in Figure 4b, there was an acid formation phase on the 10th day in the aqueous phase of the 2nd sample,

which was added 20% H₂SO₄ and subjected to 10 min thermal MW pretreatment. During the acid formation phase, pH increased and then continued with small changes until biogas production ended. The day of the acid formation phase changed in untreated and pretreated aqueous sludge samples, but the processes took place in the same way.

Since methane-forming bacteria live in a neutral or slightly alkaline environment, the pH of the environment

normally varies between 7 and 7.5 while the fermentation process continues stable under anaerobic conditions (Öztürk, 2005). Our study results were similar to the information provided in the literature. The examination of the time-dependent change in pH concentration in the aqueous phases obtained from sludge samples with and without pretreatment indicated that neutral and slightly alkaline values were determined.

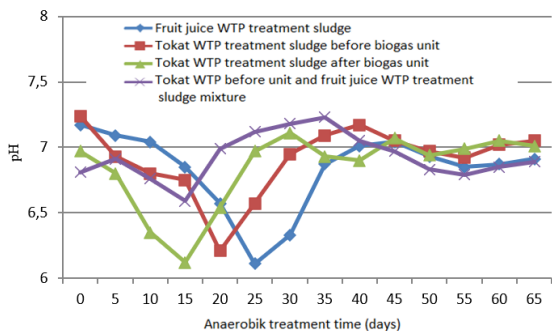


Figure 4a. Time-dependent pH change in untreated sludge samples for four different sludge samples

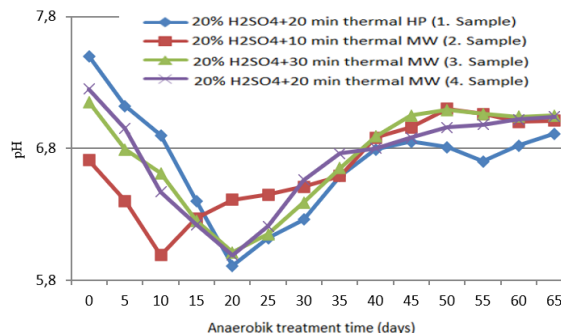


Figure 4b. Time-dependent pH change in sludge samples under pretreatment conditions where the highest biogas per solid matter was obtained for four different sludge samples

Table 5. Duncan test results applied to cumulative biogas production efficiencies of sewage sludge samples

	Pretreatment	MS		Pretreatment	MS
S1	Without pretreatment	148.00 ± 1.743 ^d	S3	Without pretreatment	99.75 ± 2.100 ^e
	Chemical (20% H ₂ SO ₄)	158.66 ± 2.170 ^c		Chemical (20% H ₂ SO ₄)	118.10 ± 1.196 ^d
	Thermal HP (10 min)	188.12 ± 3.356 ^b		Thermal HP (30 min)	177.95 ± 1.483 ^a
	Thermal MW (10 min)	190.96 ± 1.182 ^b		Thermal MW (10 min)	153.58 ± 2.435 ^b
	Chemical-Thermal HP ¹	202.11 ± 2.290 ^a		Chemical-Thermal HP ⁵	148.86 ± 1.204 ^c
	Chemical-Thermal MW ²	154.71 ± 1.878 ^{cd}		Chemical-Thermal MW ⁶	179.28 ± 1.478 ^a
	S2	Without pretreatment		188.00 ± 2.108 ^e	S4
Chemical (10% H ₂ SO ₄)		284.42 ± 1.408 ^d	Chemical (15% NaOH)	238.83 ± 1.207 ^d	
Thermal HP (30 min)		332.43 ± 0.764 ^c	Thermal HP (30 min)	282.69 ± 1.438 ^b	
Thermal MW (10 min)		359.48 ± 1.909 ^b	Thermal MW (30 min)	264.31 ± 0.609 ^c	
Chemical-Thermal HP ³		358.60 ± 1.444 ^b	Chemical-Thermal HP ⁷	284.74 ± 0.613 ^b	
Chemical-Thermal MW ⁴		396.34 ± 2.859 ^a	Chemical-Thermal MW ⁸	294.02 ± 1.298 ^a	

MS: Mean ± Standard deviation; S1: Sample 1; S2: Sample 2; S3: Sample 3; S4: Sample 4; 1: (20% H₂SO₄, 20 min); 2: (15% NaOH, 10 min), 3: (20% NaOH, 10 min); 4: (20% H₂SO₄, 10 min); 5: (20% NaOH, 30 min); 6: (20% H₂SO₄, 30 min); 7: (20% H₂SO₄, 30 min); 8: (20% H₂SO₄, 20 min); ^{a-b-c-d-e}: Values with the same letters indicate that there is no significant difference at P<0.05

Statistical Evaluation of Biogas Production Efficiency Obtained from Aqueous Phases of Treatment Sludge

The cumulative biogas production efficiencies of the aqueous mixtures of the treatment sludge after 65 days were statistically compared.

Accordingly, the variance homogeneity test was applied to the biogas production efficiencies per gram of solid material formed as a result of anaerobic decomposition in the treatment sludge samples with and without pretreatment. Since the level of significance was p>0.05 in the results of the variance homogeneity test, variance analysis was applied afterward. Then, Duncan's multiple comparison test was administered because the results of the analysis of variance were found to be significant (P<0.001) (Table 5).

The Duncan's multiple comparison test results indicated that there was no difference between the biogas production efficiencies obtained from the 10 min thermal HP and 10 min thermal MW pretreatments in the 1st sample, between 10 min thermal MW and 20% NaOH+10 min thermal HP pretreatments in the 2nd sample, between

30 min thermal HP and 20% H₂SO₄+30 min thermal MW in the 3rd sample, and between 30 min thermal HP and 20% H₂SO₄+30 min thermal HP pretreatments in the 4th sample at P<0.05 significance level.

There are similar studies showing that the biogas production efficiencies obtained from different raw materials are compatible with the Duncan test results (Adelekan and Bamgboye, 2009; Abimbola and Olumide, 2014; Adeniran et al., 2014; Mustafa et al., 2018; Oporum et al., 2019).

Modeling

Maximum exponential increase and Gompertz models were employed for the cumulative amounts of biogas forming after 65 days by applying pretreatments to sewage sludge samples. The maximum exponential increase curve of cumulative biogas amounts is given in Figure 5, and the representation of the curve formed by subjecting the data to Gompertz models is given in Figure 6. The range values obtained as a result of applying cumulative biogas amounts to the models are given in Table 6.

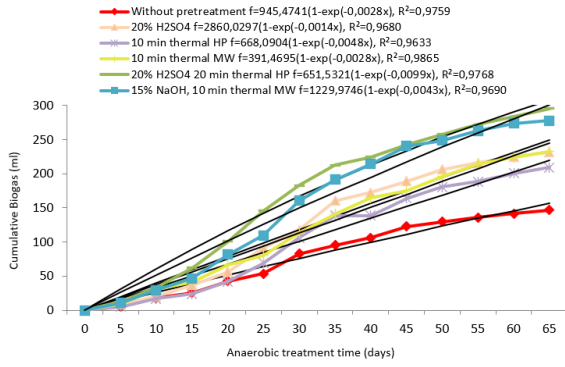


Figure 5a. Maximum exponential increase curve applied to the cumulative biogas in the aqueous phase of the 1st sample

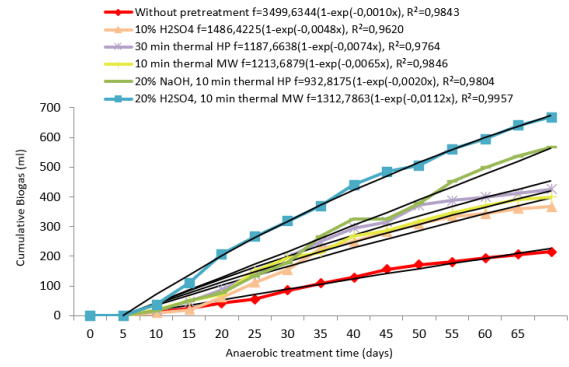


Figure 5b. Maximum exponential increase curve applied to the cumulative biogas in the aqueous phase of the 2nd sample

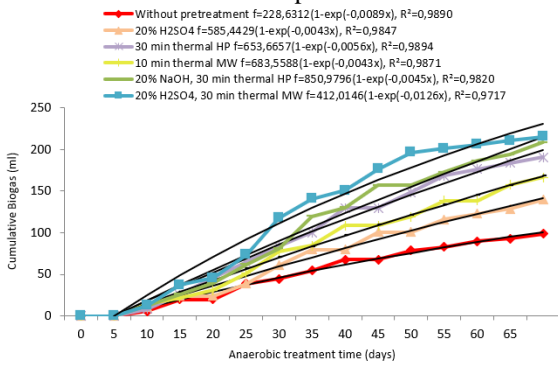


Figure 5c. Maximum exponential increase curve applied to the cumulative biogas in the aqueous phase of the 3rd sample

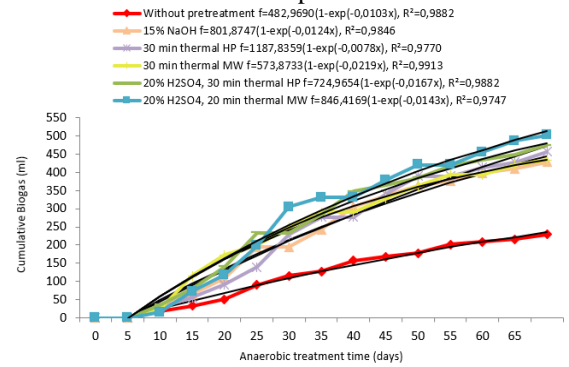


Figure 5d. Maximum exponential increase curve applied to the cumulative biogas in the aqueous phase of the 4th sample

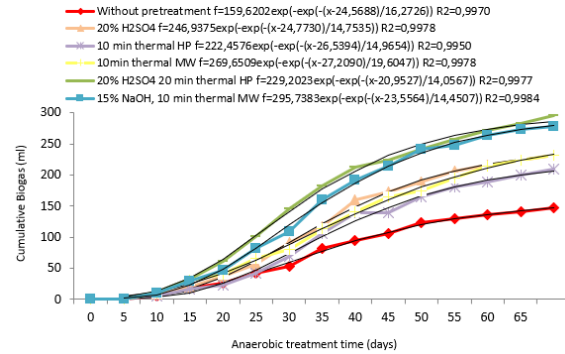


Figure 6a. Gompertz curve applied to the cumulative biogas in the aqueous phase of the 1st sample

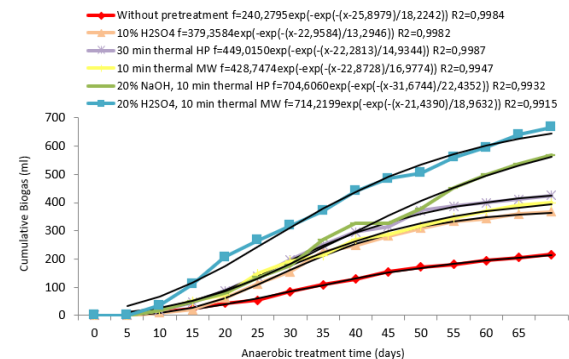


Figure 6b. Gompertz curve applied to the cumulative biogas in the aqueous phase of the 2nd sample

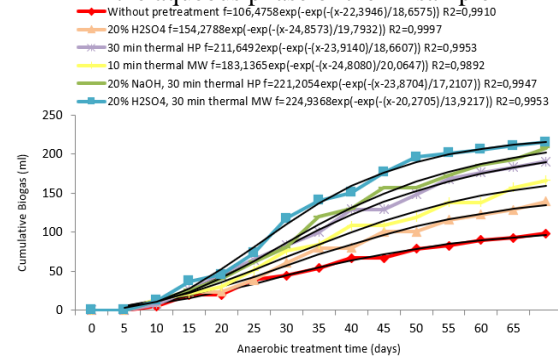


Figure 6c. Gompertz curve applied to the cumulative biogas in the aqueous phase of the 3rd sample

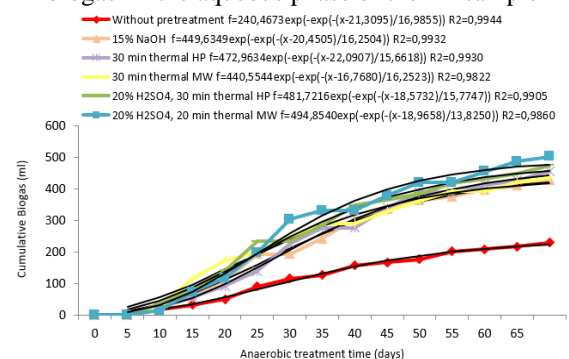


Figure 6d. Gompertz curve applied to the cumulative biogas in the aqueous phase of the 4th sample

Table 6. Models where cumulative biogas amounts were applied and R² value ranges from the graphs

Models	Sample 1 (R ²)	Sample 2 (R ²)	Sample 3 (R ²)	Sample 4 (R ²)
Maximum Exponential Increase	0.9633-0.9865	0.9620-0.9957	0.9717-0.9894	0.9747-0.9913
Gompertz	0.9950-0.9984	0.9915-0.9987	0.9892-0.9997	0.9822-0.9944

When the R² (correlation coefficient) values in the graphs emerging in the maximum exponential increase and Gompertz models applied concerning cumulative biogas were compared, it can be said that the cumulative biogas curve in the four samples was more compatible with the Gompertz model. The equations describing the graphics created in previous studies were found consistent with the modified Gompertz model (Öz Eldem and Öztürk, 2006; Genç, 2010; Zorlugenç and Evliya, 2011; Patil et al., 2012, Yılmaz et al., 2018, Bayrakdar, 2020; Özarslan et al., 2021).

Conclusions

As a result of this study, in which the effect of pretreatments applied to sewage sludge samples on biogas production potential was investigated, it was found that pretreatments (chemical, thermal HP, thermal MW, chemical-thermal HP, and chemical-thermal MW) applied to four different sewage sludge samples increased the solubility in water. The increase in water solubility was between 62.07 and 81.29% compared to the untreated sample.

When the biogas production efficiency of the samples with the highest water solubility was examined, it was determined that the pretreatment application increased the efficiency. Of all the samples, the highest biogas production amount (667.51 ml) and the highest biogas production efficiency (396.34 ml biogas/g SM dissolved in water) were found in the pre-biogas-unit aqueous phase of the sewage sludge of Tokat WTP.

The statistical results showed that pretreatment had a significant effect on biogas production efficiency. The comparison of R² results obtained by applying the cumulative biogas amounts forming at the end of 65 days to the maximum exponential increase and Gompertz models indicated that the Gompertz model was more compatible.

In conclusion, it is thought that the electrical energy generated by using the biogas produced by pretreating the sewage sludge in anaerobic digesters will provide a significant saving in operating costs.

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References

Abimbola, O. and Olumide, O. (2014). Evaluation of biogas production from food waste. The International Journal of Engineering and Science (IJES). Vol: 3, Issue: 01, pp.01-07 ISSN (p): 2319-1805.

- Adelekan, BA. and Bamgboye, AI. (2009). Comparison of biogas productivity of cassava peels mixed in selected ratios with major livestock waste types. African Journal of Agricultural Research, Vol: 4(7), pp.571-577.
- Adeniran, KA., Yusuf, KO., Iyanda, MO. and Alo, OA. (2014). Relative effectiveness of biogas production using poultry droppings and swine dung. Ethiopian Journal of Environmental Studies & Management, 7(4): 371-378. <https://doi.org/10.4314/ejesm.v7i4.4>
- Akçakaya, M., Tuncay, S. and İçgen, B. (2022). Two-stage anaerobic digestion of ozonated sewage sludge predominantly took over by acetotrophic methanogens with increased biogas and methane production. Fuel, Volume 317. <https://doi.org/10.1016/j.fuel.2022.123434>
- APHA (American Public Assoc), (2005). Standard methods for the examination of water and wastewater, 21st Edition, Washington DC.
- Ardıç, İ. (2009). Investigation of the effects of thermal, chemical and thermochemical pretreatments on the biogas production yield of cattle manure (Publication No. 258979) [PhD Thesis, Mersin University].
- Ardıç, İ. and Taner, F. (2004). Effects of acidic pretreatment on water solubility of solid matter in chicken manure. Journal of Ecology, 14, 53, pp.39-43.
- Arıkan, B. (2008). Investigation of the efficiency of biogas production from organic solid wastes by anaerobic treatment (Publication No. 178079) [Master Thesis, Çukurova University].
- Bayrak Işık, EH. and Polat, F. (2017). Effects of pre-processes on production of biogas from cow manure. International Advanced Researches & Engineering Congress-2017.
- Bayrakdar, A. (2020). Anaerobic co-digestion of tannery solid waste: Optimum leather fleshing waste loading. Pamukkale University Journal of Engineering Sciences, 26(6), 1133-1137. <https://doi.org/10.5505/pajes.2020.22465>
- Crawford, GV., Alkema, T., Yue, M. and Thorne, M. (1982). Anaerobic treatment of thermal conditioning liquors. Journal (Water Pollution Control Federation), 54(11). <https://www.jstor.org/stable/25041737>
- Çilingir, EÇ. (2018). Effect of microwave assisted acid&alkali pretreatment on biogas production from poultry manure (Publication No. 521451) [Master Thesis, Hacettepe University].
- Genç, N. (2008). The importance of pretreatment in the improvement of the biodegradability of wastewater and treatment sludge. Trakya University Journal Science, 9(1), pp.15-24.
- Genç, N. (2010). Modeling of fermentative hydrogen production process. Sakarya University Journal of the Institute of Science, 14(2), pp.87-97.
- Gülşen Akbay, HE., Dizge, N. and Kumbur, H. (2021). Enhancing biogas production of anaerobic co-digestion of industrial waste and municipal sewage sludge with mechanical, chemical, thermal, and hybrid pretreatment. Bioresource Technology, Volume 340. <https://doi.org/10.1016/j.biortech.2021.125688>
- Gülşen Akbay, HE., Dizge, N. and Kumbur, H. (2022). Evaluation of electro-oxidation and Fenton pretreatments on industrial fruit waste and municipal sewage sludge to enhance biogas production by anaerobic co-digestion. Journal of Environmental Management, Volume 319. <https://doi.org/10.1016/j.jenvman.2022.115711>

- Halisdemir, B. (2009). Biogas production yield of activated sludge and orange pulp and investigation of some pretreatments biogas production yield (Publication No. 259966) [PhD Thesis, Mersin University].
- Hämäläinen, A., Kokko, M., Chatterjee, P., Kinnunen, V. and Rintala, J. (2022). The effects of digestate pyrolysis liquid on the thermophilic anaerobic digestion of sewage sludge - Perspective for a centralized biogas plant using thermal hydrolysis pretreatment. *Waste Management*, Volume 147, pp.73-82. <https://doi.org/10.1016/j.wasman.2022.05.013>
<https://inevaturkiye.com.tr/at%C4%B1ktan-enerji-%C3%BCretim-sistemi>
- Lo, HM., Kurniawan, TA., Sillanpää, MET., Pai, TY., Chiang, CF., Chao, KP., Liu, MH., Chuang, SH., Banks, CJ., Wang, SC., Lin, KC., Lin, CY., Liu, WF., Cheng, PH., Chen, CK., Chiu, HY. and Wu, HY. (2010). Modeling biogas production from organic fraction of MSW co-digested with MSWI ashes in anaerobic bioreactors. *Bioresource Technology*, Vol. 101, Issue 16, pp.6329-6335. <https://doi.org/10.1016/j.biortech.2010.03.048>
- Mainardis, M., Buttazzoni, M., Gievers, F., Vance, C., Magnolo, F., Murphy, F. and Goi, D. (2021). Life cycle assessment of sewage sludge pretreatment for biogas production: From laboratory tests to full-scale applicability. *Journal of Cleaner Production*, Volume 322. <https://doi.org/10.1016/j.jclepro.2021.129056>
- Martin, K. (2017). Investigation of biochemical methane potential of banana waste treated with different pretreatment process in biogas production (Publication No. 476719) [Master Thesis, Necmettin Erbakan University].
- Murto, M., Björnsson, L. and Mattiasson, B. (2004). Impact of food industrial waste on anaerobic co-digestion of sewage sludge and pig manure. *Journal of Environmental Management*, Volume 70, Issue 2, pp.101-107. <https://doi.org/10.1016/j.jenvman.2003.11.001>
- Mustafa, AM., Li, H., Radwan, AA., Sheng, K. and Chen, X. (2018). Effect of hydrothermal and Ca(OH)₂ pretreatments on anaerobic digestion of sugarcane bagasse for biogas production. *Bioresource Technology*. Vol: 259, pp.54-60. <https://doi.org/10.1016/j.biortech.2018.03.028>
- Oporum, CC., Nweke, CO., Nwanyanwu, CE. and Nwachukwu, IN. (2019). Kinetic study of anaerobic digestion of goat manure with poultry dropping and plantain peels for biogas production. *International Journal of Engineering and Applied Sciences (IJEAS)* ISSN: 2394-3661, Volume 6, Issue 8.
- Özarıslan, S., Abut, S., Atelge, MR., Kaya, M. and Unalan, S. (2021). Modeling and simulation of co-digestion performance with artificial neural network for prediction of methane production from tea factory waste with co-substrate of spent tea waste. *Fuel*, Volume 306. <https://doi.org/10.1016/j.fuel.2021.121715>
- Öz Eldem, N. and Öztürk, İ. (2006). pH and ammonia inhibition in anaerobic treatment. *Journal of ITU*, Volume 5, Issue 1, pp.3-14.
- Öztürk, M. (2005). Biogas production from animal manure. Ministry of Environment and Forestry, Ankara.
- Patil, JH., Malourdu Antony Raji., Muralidhara, PL., Desai, SM. and Mahadeva Raju, GK. (2012). Kinetics of anaerobic digestion of water hyacinth using poultry litter as inoculum. *International Journal of Environmental Science and Development*, Vol. 3, No. 2, pp.94-98.
- Speece, RE. (1996). *Anaerobic biotechnology for industrial wastewaters*. Archae Press, Tennessee, p394.
- Şenol, H. (2019). Investigation of biogas production by applying thermal, chemical and physical pretreatments from cattle manure, corn silage and sugar beet pulp (Publication No. 557776) [PhD Thesis, Sivas Cumhuriyet University].
- Şenol, H., Açikel, Ü., Demir, S. and Oda, V. (2020). Anaerobic digestion of cattle manure, corn silage and sugar beet pulp mixtures after thermal pretreatment and kinetic modeling study. *Fuel*, Volume 263. <https://doi.org/10.1016/j.fuel.2019.116651>
- Varinli, F. (2010). The effect of the thermal pre-treatment on biogas and methane production from apple pulp (Publication No. 274989) [Master Thesis, Erciyes University].
- Wang, Y., Li, W., Wang, Y., Turap, Y., Wang, Z., Zhang, Z., Xia, Z. and Wang, W. (2022). Anaerobic co-digestion of food waste and sewage sludge in anaerobic sequencing batch reactors with application of co-hydrothermal pretreatment of sewage sludge and biogas residue. *Bioresource Technology*, Volume 364. <https://doi.org/10.1016/j.biortech.2022.128006>
- Yalçın, G., Yavuz, R., Taşpınar, K., Yılmaz, M. and Ateş, Ö. (2010). Use of sludge from Eskişehir wastewater treatment plants in different alternation systems. T.R. Ministry of Agriculture and Rural Affairs, General Directorate of Agricultural Research, Eskişehir, 2010. <https://kutuphane.tarimorman.gov.tr/vufind/Record/1210691>
- Yılmaz, F., Kökdemir Ünşar, E., Akman, HE., Altınay Perendeci, N. and Yıldız, O. (2018). Biogas production from cattle manure together with greenhouse harvesting wastes and modelling of anaerobic co-digestion. *Yüzüncü Yıl University Journal of Agricultural Sciences*, 28(1): 62-69. <https://doi.org/10.29133/yyutbd.346849>
- Zeng, Q., Zan, F., Hao, T., Khanal, SK. and Chen, G. (2022). Sewage sludge digestion beyond biogas: Electrochemical pretreatment for biochemicals. *Water Research*, Volume 208. <https://doi.org/10.1016/j.watres.2021.117839>
- Zhao, J., Hou, T., Lei, Z., Shimizu, K. and Zhang, Z. (2021). Performance and stability of biogas recirculation-driven anaerobic digestion system coupling with alkali addition strategy for sewage sludge treatment. *Science of The Total Environment*, Volume 783. <https://doi.org/10.1016/j.scitotenv.2021.146966>
- Zorlugenç, B. and Evliya, İB. (2011). Degradation of Aflatoxin B1 in Various Foods by *Nocardia corynebacterioides* (*Flavobacterium aurantiacum*) NRRL B-184. *Çukurova University Journal of Science and Engineering Sciences*, 26(2):193-203.