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Research Article

Biogas production from the co-digestion of urban solid waste and cattle manure

Halil Şenol[1*], Mehtap Erşan[2], Emre Görgün[3]

[1] Giresun University, Department of Genetic and Bioengineering, Engineering FacuJty, Giresun, Turkey, (ORCID: 0000-0003-3056-5013)
[2] Sivas Cumhuriyet University, Department of Chemical Engineering, Engineering Faculty, Sivas, Turkey, (ORCID: 0000-0002-5429-4468)
[3] Sivas Cumhuriyet University, Department of Railway Systems, Sivas, Turkey (Orcid: 0000 0002 1971 456X)

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Abstract

In recent years, the need for alternative energy sources has become an urgent concern due to the decline in fossil fuel input and also the disruption of fossil fuels to cause global warming and waste management, which is a human problem. Biogas, an example of alternative energy, can be used to eliminate these problems related to fossil fuels and biodegradable waste management. Since ancient times, biodegradable waste has been the subject of the discovery of environmentally friendly fuel products such as biogas. Animal manure and urban solid wastes produced by humans are the leading ones among these wastes. In this study, anaerobic digestion of different ratios of cattle manure (CM) and municipal solid waste (MSW) was investigated. Anaerobic digestion studies untreated were carried out in mesophilic conditions. In the reactor where CM: MSW mixture ratio is 2: 1, the highest biogas production (222.5 ± 15.7 mL/g $_{\text{solid matter}}$) was realized compared to other mixture ratios. NaOH pretreatments were applied to this mixing ratio with concentrations of 0.1, 0.5, 1 and 2 N in order to increase biogas yield. After NaOH 1N pretreatment, biogas production increased by 47.46% compared to the untreated reactor. As a result of the application of NaOH pretreatment with 2N value, due to possible rapid resolution, biogas production was decreased compared to 1N NaOH pretreated reactor. As a result of the study, it has been understood that CM and MSW can be a good mixture in anaerobic digestion and biogas production can be increased successfully with NaOH pretreatments.

Keywords: Biogas, Cattle manure, Urban solid wastes, NaOH pretreatment.

Kentsel katı atık ve sığır gübresinin ko-sindiriminden biyogaz üretiminin incelenmesi

Öz

Son yıllarda alternatif enerji kaynağına duyulan ihtiyaç, fosil yakıt girdisinin azalması ve ayrıca fosil yakıtların çevreyi bozarak küresel ısınmaya neden olması ve insan sorunu olan atık yönetimi nedeniyle acil bir endişe kaynağı olmuştur. Alternatif enerji örneklerinden biri olan biyogaz, fosil yakıtlar ve biyolojik olarak parçalanabilir atık yönetimi ile ilgili bu sorunları ortadan kaldırmak için kullanılabilir. Çok eski zamanlardan beri, biyolojik olarak parçalanabilen atıklar, biyogaz gibi çevre dostu olan yakıt ürünlerinin keşfinin konusu olmuştur. Bu atıkların başında çoğunlukla hayvan gübreleri ve insanların ürettiği kentsel katı atıklar gelmektedir. Bu çalışmada sığır gübresi (SG) ve kentsel katı atıkların (KKA) farklı oranlardaki karışımlarının anaerobik sindirimi incelenmiştir. Ön işlemsiz anaerobik sindirim çalışmaları mezofilik koşullarda yürütülmüştür. SG: KKA karışım oranının 2:1 olduğu reaktörde diğer karışım oranlarına kıyasla en yüksek biyogaz üretimi (222.5 ± 15.7 mL/g $_{\text{katı madde}}$) gerçekleşmiştir. Bu karışım oranına biyogaz verimini artırmak amacıyla NaOH ön işlemler 0,1, 0,5, 1 ve 2 N konsantrasyonlarda uygulanmıştır. 1N NaOH ön işlem sonucunda biyogaz üretimi ön işlemsiz reaktöre kıyasla % 47,46 oranında artmıştır. NaOH ön işlem konsantrasyonun 2N olması muhtemel hızlı çözünürlük nedeniyle 1N NaOH ön işlemli reaktöre kıyasla biyogaz üretimi azalmıştır. Çalışma sonucunda SG ve KKA' nın anaerobik fermantasyonda iyi bir karışım olabileceği ve NaOH ön işlemler ile biyogaz veriminin başarıyla artırılabileceği anlaşılmıştır.

Anahtar Kelimeler: Biyogaz, Sığır gübresi, Kentsel katı atıklar, NaOH ön işlem.

[*] Corresponding Author: Giresun University, Department of Genetic and Bioengineering, Engineering FacuJty, Giresun, Turkey, ORCID: 0000-0003-3056-5013, halil.senol@giresun.edu.tr

1. Introduction

The Earth has generally benefited from natural energy sources up to the 21st century. However, from the beginning of the 21st Century it has been noticed that these energy sources are the depleting and that the reserves remain in limited quantities. For this reason, demand for renewable energy sources has begun [1]. Biogas is among the renewable energies and it is a flammable gas obtained as a result of decomposition of biomass in the anaerobic environment. Biogas differs from other combustible gases in that it is obtained only from animal or vegetable, i.e. organic raw materials. Biological wastes, organic waste from food industry sources, organic kitchen wastes, energy plants such as corn or sugar beet and animal feces that are formed in animal fatigue can be used in biogas plants. Biogas content is approximately 50-80 % methane (CH_4), 20-50 % carbon dioxide (CO_2), 0.01-0.2 % oxygen (O_2), 0.1-1 % nitrogen, depending on the type of organic material used (N_2) and hydrogen sulphide (H_2S) in the range of 10-4000 ppm [2]. The biogas flammability feature is due to CH_4 gas, which is a natural gas similar [3]. The raw materials and properties used in the biogas production have a significant effect on the energy efficiency produced. Biogas production from organic materials is dependent on substances that can decompose into CH_4 and CO_2. For this reason, the components of animal manure and energy plants and their decomposability are important parameters for methane production [4]. Crude protein, crude oil, fiber, cellulose, hemicellulose, starch and sugar are effective in the formation of methane. Feeding animals also affects methane production and biogas production positively, as the majority of the substances that convert to carbon in the cattle are digested in the rumen and intestines. For this reason, cattle grazing, pigs and poultry have lower potential for biogas production compared to fertilizer. The CH_4 concentration in the biogas produced from cattle manure (CM) can be lower. It has been reported that higher protein levels of substrates during anaerobic fermentation have higher methane yield [5]. Anaerobic digestion and biogas production depend on many important parameters. These parameters are temperature, organic matter ratio, C/N ratio, pH, dry matter rate, hydraulic retention time and organic loading rate [6].

The lignocellulosic components in the structure of organic substances used for anaerobic digestion limit the production of biogas. The dissolution of lignocellulosic materials in water is very limited [7]. Hydrolysis of cellulose and hemicelluloses takes time. Lignin has no hydrolysis under anaerobic conditions [8]. For this reason, pretreatment technologies have been developed to provide biogas production from these lignocellulosic materials [9]. These pretreatments are; thermal, chemical, biological and solvent addition pretreatments [7, 10].

In the literature, anaerobic digestions of urban solid wastes have previously been studied on a large scale. Forster et al. [11] investigated the effect of anaerobic decomposition of urban solid wastes under thermophilic conditions on the inoculum source. To measure the performance of laboratory scale reactor with a capacity of 1.1 liters; different organic substances such as pig manure and sewage sludge was used. As a result, 44% COD removal and 43% volatile solid removal were observed. Lopes et al. [12] investigated the effect of animal liquid rumen on the organic part of urban solid wastes, a liquid inoculum during the anaerobic process of decay. Highest methane concentrations were 42.6%. The data obtained confirmed that the process significantly improved the performance of reactors with an inoculum. Rasopoor et al. [13] applied ultrasound wave pretreatment for the production of biogas from urban solid wastes. The maximum yield was found to be 478.1 mL/g volatile solid. It has been stated that cattle manure can be a co-substrate that helps other organic components [10]. Ahmadi-Pirlou et al. [14] examined different mixture ratios and alkali pretreatment effect of urban solid wastes and sewage sludge in mesophilic conditions. In literature, the anaerobic digestion of urban solid wastes has been examined in detail and it has been explained that there may be co-digestion with different organic wastes. However, there are no studies in the literature investigating the application of different NaOH pretreatments to the optimum mixing ratio of urban solid wastes and cattle manure. In order to use multiple organic substances in anaerobic digestion, it may be necessary to find the optimum mixing ratio first. Applying pretreatments to the optimal mixing ratio can maximize final biogas production.

In this study, biogas production was carried out under mesophilic conditions (35^{o}C) from mixtures of CM and MSW in order to achieve higher yields in anaerobic digestion. The aim of this study was to find the optimum mixing ratio of MSW and CM for anaerobic digestion under untreated conditions. In order to evaluate two different organic wastes in anaerobic digestion, different mixture ratios were prepared and the most suitable mixture ratio was selected according to the highest biogas yield. Alkaline pretreatments were applied to the most suitable mixture ratio and biogas yield was examined gradually. In the literature, there are no studies examining anaerobic digestion after alkaline pre-treatment on the optimum mixture of MSW and CM.

2. Material and Method

Fresh CM was obtained from Boztekke village in the center of Giresun city. MSW was taken from 3 different regions of the central solid waste facility of Giresun city. Organic parts of were separated from non-organic parts.

C and N values of organic wastes were measured using a Costest Elemental Analyzer and C/N ratios were calculated. The dry matter content was determined by drying for 24 h at 105 °C. The volatile solids content was obtained by burning the dried material in an ash furnace at 550 °C for 2 h [15]. The burnt ash was found by subtracting the starting mass from the known mass. Likewise, cellulose, lignin and hemicellulose determinations were determined by standard methods according to chemical methods [16].

In Table 1, the C/N ratio for CM is 18.78 while the C/N ratio of MSW is 13.02.

Table 1. Physical and chemical parameters of organic wastes

Parameters	CM	MSW
C% (%w)	31.75 ± 0.2	23.68 ± 0.2
N% (%w)	1.69 ± 0.1	1.82 ± 0.1
C/N (%w)	18.78	13.02
% solid matter (% w)	18.20 ± 0.2	15.30 ± 0.2
% Volatile solid matter (TS %)	83.05 ± 0.3	85.01 ± 0.3
moisture% (% w)	81.80 ± 0.3	84.70 ± 0.3
pH	7.21 ± 0.05	7.28 ± 0.05
Cellulose (% w)	27.20 ± 0.25	31.46 ± 0.29
Hemicellulose (% w)	13.80 ± 0.27	15.28 ± 0.35
Lignin (% w)	11.01 ± 0.52	10.97 ± 0.85

In table 2, MSW are collected at random from 3 different regions of Giresun urban solid waste landfill and divided into categories. In this way, the organic part that has been separated from the other waste types such as food waste, vegetable waste and paper. This organic part constituted 50 % of urban solid waste. Anaerobic digestion was continued with this part.

Table 2. MSW composition

MSW composition	weight % (w)
Food leftovers	29
Vegetable wastes	7
Paper waste	14
Glass material waste	6
Plastic wastes	12
Metal wastes	6
Other non-organic parts	26

2.1. Anaerobic Digestion Process methods

In order to examine the biogas production process from organic wastes, firstly, the optimum mixing ratio determination studies were performed to evaluate waste together. The mixture ratio of SG:MSW was prepared as 5:1, 1:1, 1:2, 0:1, 1:0 w/w, respectively. These reactors were designated as R1, R2, R3, R4 and R5 respectively. Each reactor was run of triples. Then, alkaline pretreatments were applied to the reactor which had the optimum mix ratio in the anaerobic process. In all experiments, the solids content was determined as 9 % by mass. As a bioreactor, filtering flask (500 mL) was used. To the outlet pipe of the reactor, an appropriate silicone hose was added, and 1-0.5 liters of gas collecting bags were installed at the end of this hose. All reactors were then covered with aluminum foil. In all experiments, 80 % of the volume used as bioreactors was filled with the slurry. The inlet and outlet of the hoses are taped to prevent gas leakage in the system. The pH of each reactor was measured for anaerobic digestion. In this process, if the pH value is not 6.6-7.4 which is necessary for the production of methane bacteria, it was adjusted with 5 N NaOH and 5 N H_2SO_4 buffers prepared up to the values in this range. The heating temperature was chosen as 35 °C for all experiments. The heating was done by means of a flat plate from below. After the start of the experiments, it was ensured that the reactors were manually mixed for 3-4 min on average within 12 hours. The amount of gas produced was measured by means of biogas gas collection bags of 0.3-0.5 liters and continued until gas formation stopped. The biogas production ratio of each reactor was determined as mL biogas/g $_{\text{solid matters}}$. CH_4, CO_2 and H_2S analyzes were performed by a portable biogas meter (IRCD4 Multi-Gas Detecting Alarm Manual Instruction.)

2.2. NaOH Pretreatment Studies

In each bottle, 45 g total solid (TS) of MSW-CM mixture was mixed with 500 mL NaOH solution. NaOH concentrations applied to the optimum reactor were 0.1, 0.5, 1 and 2 N. The bottles were sealed in incubator at approximately 25 °C for 48 h. A bottle without a NaOH solution but containing only 25 g of HH and 250 mL of deionized water was used as the control. NaOH pretreatment [17] experiments were performed in triples. After NaOH pretreatment, the pretreated MSW-CM mixture was cooled to room temperature and taken from the bottles. The pretreated slurry was filtered to vacuum until maximum liquid removal, and dried in an oven at 40 °C for 72 h. The soluble chemical oxygen demand (sCOD) and pH of the liquid were analyzed at the beginning and end of the NaOH pretreatment. Every pretreated MSW-CM mixture was stored in a refrigerator for anaerobic digestion. In the final step, the pH of the slurry prepared for anaerobic digestion from pretreated solid MSW-CM mixture was adjusted to 7.0 with 1 M HCl.

2.3. Soluble Chemical Oxygen Demand Analyzes

SCOD is one of the most important parameters used to determine the amount of pollution in domestic or industrial wastewater. It represents the oxidation capacity of all organic materials irrespective of the rate of biodegradation of the material by chemical oxidation. It is the most commonly used parameter in environmental pollution. A method is obtained by determining the amount of organic substances in the wastewater in terms of the amount of oxygen required for chemical oxidation. The method is based on the principle that all organic materials can be oxidized in acidic environments with strong oxidizers [18]. SCOD values are a measure of the rate at which organic materials are consumed in the anaerobic process. For this reason, it gains importance in anaerobic processes [19]. All SCOD determinations in anaerobic digestion were made according to standard closed reflux method [15].

3. Results and Discussion

The reactors with mass ratios 2: 1, 1: 1, 1: 2, 0: 1, 1: 0 of CM: MSW are named R1, R2, R3, R4 and R5 respectively. In Table 3, biogas production and SCOD removal after anaerobic digestion of reactors formed according to different C / N ratios are given. The anaerobic digestion temperature was 35 ^{o}C and the anaerobic period lasted approximately 35-40 days. After this process the anaerobic digestion was stopped because there was no gas production. Accordingly, the highest biogas production was occurred in the R1 reactor. Similarly, the highest COD removal rate was 41 % at the R1 reactor. For this reason, alkaline pretreatments was applied to R1 reactor (CM: MSW; 2:1) in order to obtain maximum yield from organic waste in anaerobic processes.

Table 3 C/N values and biogas production rates of wastes mixed at certain ratios.

CM:MSW mixture ratios	C/N ratio	Biogas production (mL/g $_{\text{solid matter}}$)	SCOD% removal
R1	**16.76**	**222.5 ± 15.7**	**41.0 ± 2.7**
R2	15.82	205.4 ± 12.7	38.9 ± 3.8
R3	14.88	187.9 ± 19.1	37.6 ± 2.5
R4	13.01	149.5 ± 17.7	35.1 ± 4.7
R5	18.63	174.8 ± 12.9	36.6 ± 3.5

In Figure 1, cumulative biogas production rates are given for the reactors R1, R2, R3, R4 and R5, which are measured every 5 days according to gas volumes. According to this, the anaerobic digestion process of all reactors varied between about 35-40 days and the gas production stopped. Biogas production in all reactors has been accomplished successfully (cumulatively) over time. This may be due to the growth of anaerobic bacteria in reactors over time, their resistance to volatile fatty acids and the ideal mixture in reactors.

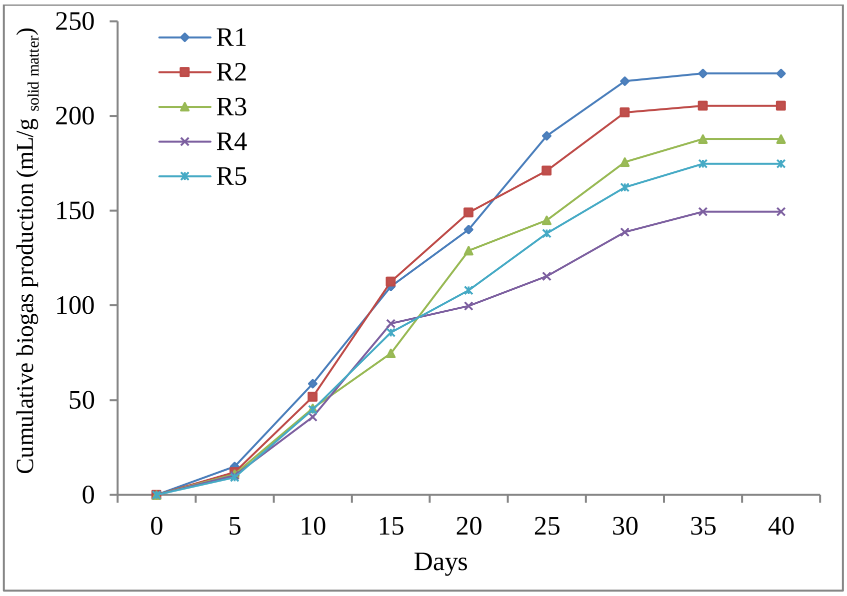

Figure 1. Anaerobic process in optimization studies

In Table 4 are given the gas contents of the gases produced by the reactors prepared at different mixing ratios. The highest methane content was 62.4 % v/v in R1. The lowest methane content was 57.9 % in R4. H_2S contents varied between 309-628 ppm.

Table 4 Gas content of wastes mixed at certain ratios.

Reactors	CH_4 %	CO_2 %	H_2S ratio (ppm)
R1	62.4 ± 1.2	37.3 ± 1.5	399 ± 220
R2	60.2 ± 2.5	39.3 ± 2.5	408 ± 180
R3	58.5 ± 1.4	41.1 ± 3.1	459 ± 252
R4	57.9 ± 0.9	41.8 ± 2.7	628 ± 320
R5	58.4 ± 1.9	41.2 ± 1.8	309 ± 241

In Figure 2, the anaerobic digestion process was checked every 5 days for the determination of SCOD and the anaerobic process was controlled. Thus, the rate of SCOD removal of all reactors increased in parallel with the gas production rate. This gives the anaerobic system's determination. SCOD removals continued to be cumulative over time. After the 40th day, SCOD removal stopped at all reactors.

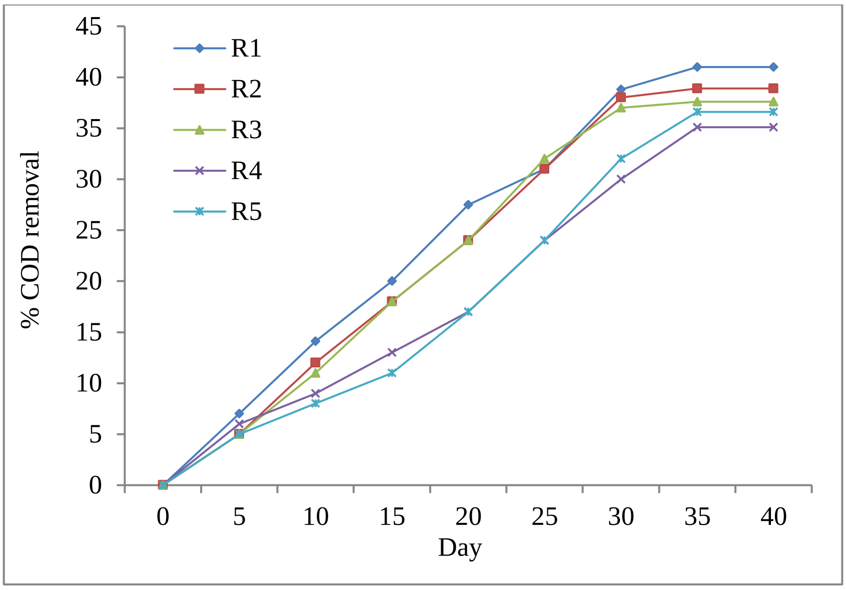

Figure 2. COD removals process at 35 °C

The biogas production rates and SCOD% removals produced by the 0.1, 0.5, 1, 2N NaOH pretreatments applied to the R1 reactor are given in Table 5. The highest increase in biogas yield occurred as a result of 1 N NaOH pretreatment. A total of 328.1 mL/g $_{\text{solid matter}}$ biogas production was achieved in this reactor. Thus, biogas efficiency was increased by 47.4 % by NaOH pretreatment. Similarly, the highest increase in % COD removal occurred due to 1 N alkaline pretreatment. SCOD removal in this reactor increased from 41% to 66.5 %. The increase in biogas production showed a close correlation to the linear correlation with the efficiency of SCOD removals. The lowest biogas yield occurred as a result of 0.1 N alkali pretreatment. In this reactor, 280.4 mL/g $_{\text{solid matter}}$ produced biogas and the lowest increase was 26.0 %.

Table 5 Results of alkali pretreatment applied to reactor R1.

NaOH concentrations	Biogas production (mL/g $_{\text{solid matter}}$)	Incremental biogas yield (%)	sCOD% removal	Incremental sCOD % removal
0.1 N	280.4 ± 11.4	26.0	52.8 ± 1.5	28.7
0.5 N	300.2 ± 18.7	34.9	61.2 ± 1.9	49.2
1 N	328.1 ± 12.5	47.4	66.5 ± 2.4	62.2
2 N	305.2 ± 15.1	37.1	58.0 ± 2.8	41.4

Figure 3 shows the anaerobic process of the alkali pretreated reactors. Biogas production began to increase faster than in Figure 2. The anaerobic digestion period lasted about 35-40 days. The reason for this is that some of the lignocellulosic molecules was converted into water-soluble small monomer molecules. Thus, biogas production was faster.

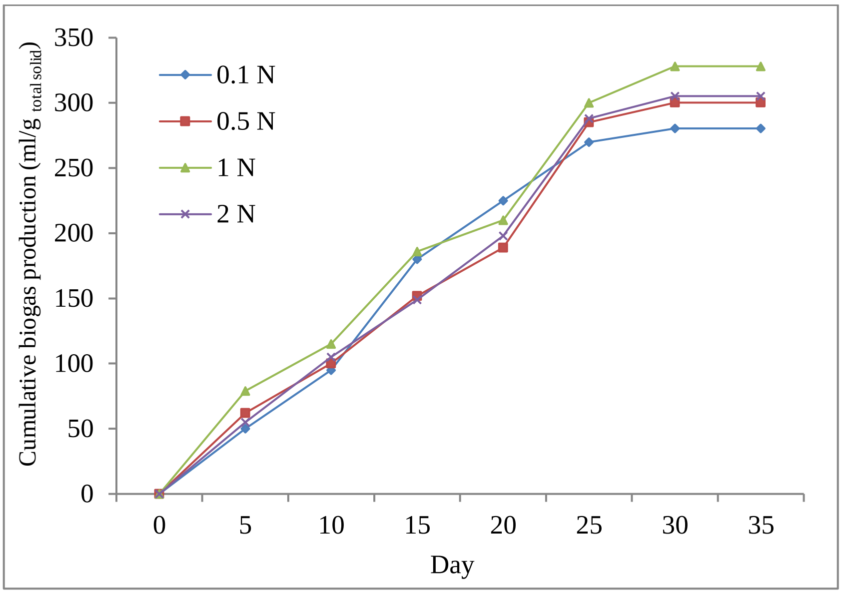

Figure 3. Cumulative biogas production of different concentrations of alkaline pretreatments

In Figure 4, the COD removal stage in the anaerobic process of the reactors pretreated is given. Accordingly, in the reactor (1.0 N pretreated) with the highest biogas production, the highest sCOD removal occurred.

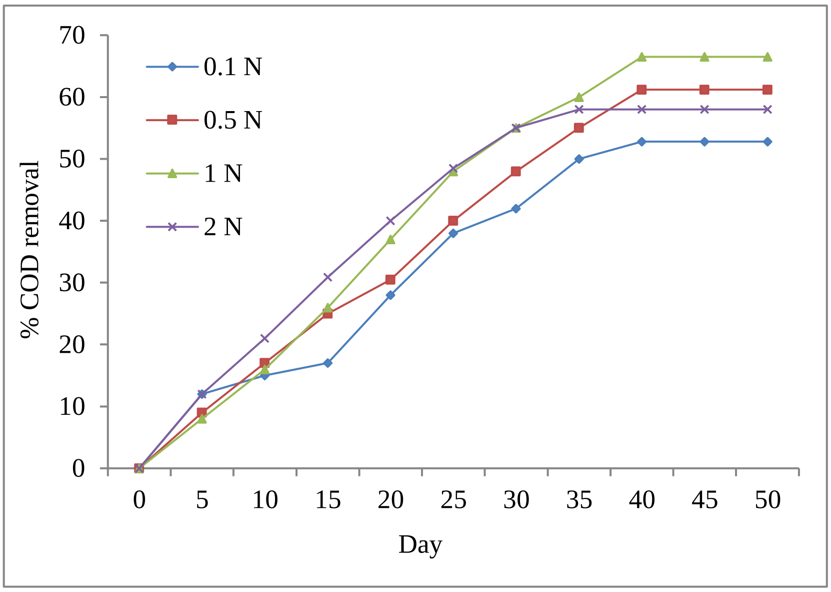

Figure 5. SCOD removals of different concentrations of alkaline pretreatments

Table 6 gives the results of different preliminary techniques applied as a result of different studies. Accordingly, it is understood that biogas production varies according to the type of pretreatment applied and the concentration value. In a study by Salehian et al.[20] alkaline pretreatment was applied to pine tree waste between 10, 30 and 60 min. As a result of this pretreatment, the highest biogas production increased by 118.6% as a result of the pretreatment applied for 60 minutes compared to the pretreatment reactor. In the literature, NaOH pretreatment results at different concentrations increased biogas yields at a different rate. Application of NaOH pretreatment at low concentrations had different effects on biogas yield. When the related literature is examined in general, NaOH pretreatment concentration value of 4% increased the biogas efficiency compared to lower concentration values. In a study, for corn stover, the optimum NaOH pretreatment concentration was found to be 5% w/v [21].

Table 6 Comparison of results with literature.

Type of organic sample	Pretreatment conditions	Anaerobic digestion results	References
CM and MSW mixture	1 N NaOH	47.4% incremental biogas production	This study
Rice straw	NaOH % 1 w/w	% 36.7 incremental biogas production	[22]
Rice straw	NaOH % 1.6 w/w	% 21.4 incremental methane production	[23]
Rice straw	NaOH % 2 w/w	% 23.2 incremental biogas production	[22]
Rice straw	NaOH % 3 w/w	% 18.9 incremental biogas production	[22]
Paddy straw	NaOH % 4 w/w	% 54.7 incremental biogas production	[24]
Pine tree	NaOH 8% w/w	118.6% incremental biogas production	[20]

4. Conclusions and Recommendations

There is a potential to benefit from all organic wastes in biogas production. However, due to the presence of lignocellulosic components in the structure of some organic wastes, the hydrolysis stage takes a long time and the production yield is very low. For this reason, the development of various pretreatment technologies increases production efficiency and shortens the hydrolysis step.

Studies were performed to determine the optimum mixing rates of CM and MSW in anaerobic digestion. The best mixing ratio of CM and M in anaerobic digestion was determined as 2: 1 w/w. The pretreatments were applied for increase of biogas production since it was achieved the lignocellulosic components soluble in water. Then NaOH pretreatments were applied to determine the optimum mixing ratio. Biogas production of the 1N pretreated reactor increased by 47.4% compared to the untreated reactor.

In order to evaluate different organic substances together in anaerobic digestion, firstly, finding the most suitable mixture ratio may reveal higher biogas yield. Applying NaOH pretreatments to the optimal mixing ratio of waste can significantly increase biogas production compared to untreated reactors. The cost of pretreatment technologies may require small volumes of optimization experiments. Thus, besides achieving the highest biogas efficiency, the cost of pretreatments can be minimized.

Contribution of the Authors

In designing the study, making and interpreting the experiments belongs to the author himself.

Conflict of Interest Statement

There is no conflict of interest among the authors.

Research and Publication Ethics Statement

In the study, research and publication ethics were followed.

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