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The Effect of Different Pretreatment Applications on Biogas Production from Plant and Animal Wastes

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Abstract: In the study, horse manure, apple pulp, and sugar beet pulp were used as raw materials to produce biogas. Biogas production efficiency was examined under anaerobic conditions by applying pretreatments to mixtures obtained from raw materials. In the first phase of the experiments, the optimum mixing ratio was determined in the mixtures prepared at various ratios, and the reactor with the highest biogas production was identified as the optimum reactor. The mixing ratio of this reactor by mass was determined as 2:1:3 for horse manure, apple pulp and sugar beet pulp, respectively, and biogas production was found to be 189.7 ml/g TS. In the second phase, the reactor determined as optimum was administered thermal, alkali, and acid pretreatments, respectively, and biogas production efficiencies were examined. As a result of the thermal pretreatments, the highest biogas production efficiency was found as 329.4 ml/g TS in the reactor which was pretreated at 150°C for 60 minutes. As a result of alkaline pretreatments, the highest biogas production efficiency was determined as 300.9 ml/g TS in the pretreatment reactor which was added NaOH as much as 20% of the solid matter. As a result of acid pretreatments, the highest biogas production efficiency was determined as 310.4 ml/g TS in the pretreatment reactor which was added HNO_3 as much as 20% of the solid matter.

In conclusion, it was determined that there was an increase in biogas production efficiency in all reactors as a result of thermal, alkali, and acid pretreatments administered to the optimum mass mixing ratio of horse manure, apple pulp, and sugar beet pulp. Also, the pretreatment that increased the biogas production efficiency the most was the thermal pretreatment.

Keywords: Horse manure, Biogas, Apple pulp, Pretreatment, Sugar beet pulp

Farklı Önişlem Uygulamalarının Bitkisel ve Hayvansal Atıklardan Biyogaz Üretimine Etkisi

Öz: Bu çalışmada; biyogaz üretimi için hammadde olarak at gübresi, elma posası ve şeker pancarı küspesi kullanılmıştır. Hammaddelerden elde edilen karışımlara önişlemlerin uygulanmasıyla, anaerobik koşullarda biyogaz üretim verimi incelenmiştir. Deneylerin ilk aşamasında farklı oranlarda hazırlanan karışımlar içerisinde, optimum karışım oranı belirlenmiş ve en yüksek biyogaz üretiminin olduğu reaktör optimum reaktör olarak saptanmıştır. Bu reaktörün kütlece karışım oranı sırasıyla at gübresi, elma posası ve şeker pancar küspesi için 2:1:3 olarak belirlenmiş ve biyogaz üretimi 189.7 ml/g KM olarak bulunmuştur. İkinci aşamada ise belirlenen optimum reaktöre sırasıyla termal, alkali ve asit önişlemler uygulanıp biyogaz üretim verimleri incelenmiştir. Termal önişlemler sonucunda en yüksek biyogaz üretim verimi, 150 °C'de 60 dakika önişlem uygulanan reaktörde 329,4 ml/g KM değerinde bulunmuştur. Alkali önişlemler sonucunda en yüksek biyogaz üretim verimi, katı maddenin %20'si kadar NaOH ilavesi ile yapılan önişlem reaktöründe 300,9 ml/g KM değerinde saptanmıştır. Asit önişlemler sonucunda ise en yüksek biyogaz üretim verimi, katı maddenin %20'si kadar HNO_3 ilavesi ile yapılan önişlem reaktöründe 310,4 ml/g KM değerinde belirlenmiştir.

Sonuç olarak at gübresi, elma posası ve şeker pancarı küspesinin, optimum kütlece karışım oranına uygulanan termal, alkali ve asit önişlemleri sonucunda, bütün reaktörlerde biyogaz üretim veriminde artış olduğu görülmüştür. Biyogaz üretim verimini en fazla artıran önişlemin ise termal önişlem olduğu belirlenmiştir.

Anahtar Kelimeler: At gübresi, Biyogaz, Elma posası, Önişlem, Şeker pancarı küspesi

1. Introduction

Today, the need for energy is increasing every other day. Energy comes from three main resources: fossil, nuclear energy, and renewable energy resources (Wikimedia Commons 2020). A large part of the energy needed in today's world is met by fossil resources, such as coal, oil, and natural gas (Delborne et al. 2020; Höök 2020;

IEA 2013). The high consumption of fossil energy around the world leads to a rapid decline in these energy resources, which has made it necessary to turn to new and renewable energy resources. On the other hand, renewable energy resources consist of solar energy, wind energy, geothermal energy, hydraulic energy, hydrogen energy, marine power, and biomass energy, which are available in nature, do not run out, are clean, and do not cause environmental pollution (Güneş 1999; Oktit 2000). Several fuel types, such as bioethanol, biogas, biodiesel, briquettes, pellets, are produced from biomass (Kapluhan 2014). Biogas is a type of biofuel that can be in the form of liquid or gas, and it is preferred since it is more useful, eco-friendly, and energy efficient compared to other fuels produced from biomass (Wilkie 2019).

Biogas is a mixture of various gases forming as a result of microbial activities in organic substances found in many types of waste, including agricultural, industrial, and municipal wastes (Ezeonu et al. 2005). Biogas contains 50 to 80% CH_4 and low rates of CO_2, H_2, N_2, and O_2 (Kalia et al. 2000). The mixture is flammable when the methane content is above 50%. Anaerobic digestion is a biotechnology utilized worldwide for the production of biogas through the processing of organic waste. Production of biogas from biomass such as manure through anaerobic digestion contributes to creating a renewable energy resource and solving ecological and agrochemical problems (Budiyono et al. 2014). Anaerobic fermentation of animal manure used in biogas production does not decrease the quality of the fertilizer source. Essential nitrogenous and other compounds remain in the processed manure, also making it usable for plants (Alvarez and Liden 2008). Various studies are carried out throughout the world to increase biogas production via anaerobic digestion. Biogas technology is widely used for heat and power generation in developing countries (Boe and Angelidaki 2009).

While some of the organic wastes are easily broken down and fermented, some of them are not easily broken down by methanogenic bacteria due to their chemical content. In such cases, some pretreatments are applied to facilitate the decomposition of materials that are difficult to decompose such as cellulose and lignin, which are present in some of the materials obtained from agricultural activities. Pretreatments used to increase biogas production can be divided into four groups: physical pretreatments, thermal pretreatments, chemical pretreatments, and biological pretreatments.

In the studies carried out, one or more of these processes are applied to organic wastes and the decomposition process is tried to be facilitated. The important thing here is how much the applied preprocessing increases the biogas production (Sözer et al. 2016).

In recent years, it has become very important to evaluate organic wastes together and to make pretreatment applications in anaerobic fermentation (Peker and Çelik 2019; Garan 2016; Taherdanak and Zilouei 2014; Monlau et al. 2012; Varinli 2010). In this study, vegetable and animal wastes were used as raw materials in different mixing ratios, and the results were examined by applying various pretreatments to increase biogas production.

Horse manure, apple pulp, and sugar beet pulp were used as raw materials in the study. Apple pulp and sugar beet pulp were preferred because of the availability of these raw materials in abundance in the region where we are located and their high organic matter content.

Also, horse manure was preferred in the study since it produces more biogas than other animal wastes. Mandal and Mandal (1997) investigated biogas production by mixing different animal manures at certain ratios for 90 days at 37°C, by mixing them with a magnetic stirrer for 2-3 minutes twice a day. As a result, they found that the biogas production capacity of horse manure was higher than other animal manures.

2. Material and Methods

2.1. Raw materials and analyses

The raw materials used in the study included horse manure, apple pulp, and sugar beet pulp. Horse manure and apple pulp were obtained from Emirseyit town of Tokat province, and sugar beet pulp from Çamlıbel town of Tokat province. Dry matter and organic matter analyses of the raw materials used in the study were done.

2.2. Pretreatments applied to the raw materials used in the study

The samples were administered thermal, alkali, and acidic pretreatment technologies. Thermal pretreatments included holding the aqueous mixtures containing solids as much as 10% of the organic sample at 100, 120, and 150°C for 10, 30, and 60 minutes. Alkaline pretreatments were applied by adding solutions of 50% aqueous NaOH by mass and 50% aqueous KOH by mass, as much as 10%, 20%, 30% of the solid mass in the aqueous mixture, at room temperature. Acidic pretreatments were applied by adding 98% concentrated H_2SO_4 and 65% HNO_3 solutions, as much as 10%, 20%, 30% of the solid mass in the aqueous mixture, to the aqueous mixture at room temperature.

2.3. Determination of water solubility as a result of applied pretreatments

In the process of determination of water solubility was performed according to Bayrak (2014), a necessary quantity of glass cotton was weighed on a precision scale, which was set to a fixed weight beforehand. The pretreated samples were filtrated through this glass cotton. The solid matter remaining in the glass cotton as a result of the filtration process was dried in an oven at 70-80°C until it was brought to a constant weight, and the weights were recorded to find the percentage of water solubility.

2.4. Anaerobic fermentation procedures

First of all, the optimum mixing ratios were determined to process the wastes together. At this stage, the mixing ratios of horse manure, apple pulp, and sugar beet pulp by mass were determined as 1:1:1, 2:1:1, 1:2:1, 1:1:2, 2:1:3, 2:3:1, and 3:2:1, respectively, which made up seven reactors. Pretreatment was applied to reactors exhibiting best digestion performance according to mixing ratio. In the experiments, aqueous phases containing 10% solids by mass were used. Nuche Erlenmeyer flasks were used as bioreactors. Aluminum gas collection bags were attached to the outlet pipe with the help of a tube. Reactors were wrapped in foil to prevent light permeability to prevent phototrophic growth and they were filled with certain volumes of substrate and inoculum mixture. pH was adjusted to 7 by NaOH or H_2SO_4. The reactors were placed on a heather and mixed manually. Produced biogas was measured using gas collection bags of known volume until the end of gas production.

3. Results

3.1. The raw materials

Before the anaerobic fermentation characterization of the raw materials were determined. The results are given in Table 1.

Table 1. Analysis results of the raw materials
Çizelge 1. *Hammaddelerin analiz sonuçları*

Parameters	Horse manure	Apple pulp	Sugar beet pulp
Dry matter (%)	28.30	81.52	82.06
Organic Matter (Dry matter (%))	74.95	83.60	84.25
C % (by mass %)	43.47	54.18	50.33
N % (by mass %)	1.85	0.76	1.76
C/N	23.50	71.30	28.60
pH	8.32	4.11	4.17

3.2. Determination of the optimum mixing ratio

The anaerobic processes of 7 reactors set to determine the optimum mixing ratio are given in Figure 1. The highest biogas formation was found as 189.7 ml/g TS in reactor 5 with a mixing ratio of 2:1:3 by mass and pretreatment experiments were conducted with this reactor. During the process, the ratio of water solubility ranged from 14.7 to 36.5%. Highest biogas production was observed in reactor with 36.5% water solubility.

As seen in Figure 1, biogas production showed an increasing trend in all reactors.

3.3. Thermal pretreatment results

Figure 2 shows the anaerobic process as a result of the thermal pretreatment applied at different temperatures (100, 120, 150°C) and various time intervals (10, 30, 60 minutes).

After the thermal pretreatment was applied, the water solubility and biogas production of the samples varied by the application time and quantity of the pretreatment. Generally, water solubility was increased with increasing temperature and time. The biogas production rate, on the other hand, increased in direct proportion to the water solubility, and the water solubility was found as 45.6% in the reactor in which the highest biogas production was achieved. Water solubility in the reactors varied between 11.3 and 45.6%. It was observed that the anaerobic fermentation process shortened after thermal pretreatment. Biogas production showed an increasing trend in general. According to Figure 2, the highest biogas production was determined as 329.4 ml/g TS in reactor 16 at a thermal pretreatment temperature of 150°C for 60 minutes.

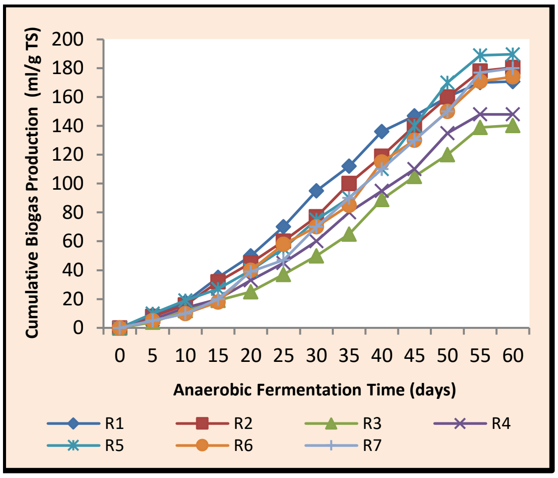

Figure 1. Anaerobic process of 7 reactors in the study

Şekil 1. *Çalışmadaki 7 adet reaktörün anaerobik süreci*

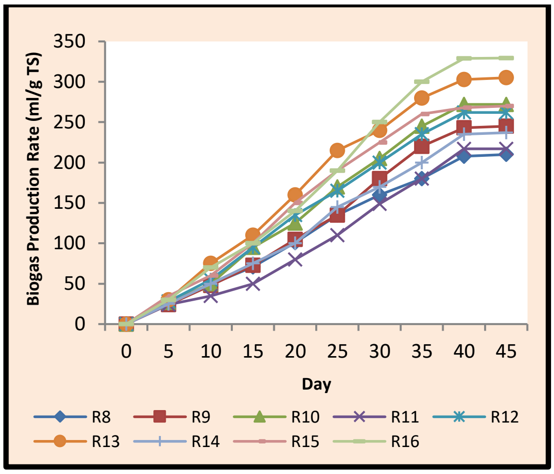

Figure 2. The anaerobic process of thermally-pretreated organic waste

Şekil 2. *Termal önişlem uygulanan organik atığın anaerobik süreci*

3.4. The results of alkaline pretreatment

Figure 3 shows the anaerobic process as a result of the alkali pretreatment applied with different solutions (KOH, NaOH) and varying ratios of solid mass in the reactor (10%, 20%, 30%).

After alkaline pretreatment, the water solubility of the samples varied by the quantity of pretreatment. In general, as the quantity of chemicals used increased, the water solubility increased, as well. While the ratio of water solubility by reactor ranged between 14.8 and 40.1%, the water solubility in the reactor that yielded the highest biogas production was determined as 40.1%. The biogas production rate indicated an increasing trend in direct proportion to the rations of water solubility. The highest biogas production was determined as 300.9 ml/g TS in the reactor 21 a result of pretreatment with the addition of NaOH as much as 20% of the solid matter.

3.5. Results of acid pretreatment

Figure 4 presents the anaerobic process occurring as a result of the addition of H_2SO_4 and HNO_3 solutions at different ratios.

The water solubility of the samples after acid pretreatment varied by the quantity of pretreatment. In general, as the amount of acidic substance used increased, water solubility increased, as well. The rate of water solubility between reactors ranged between 7.3 - 42.4% and highest biogas production was observed with 42.4% water solubility. The rate of biogas production generally showed an increasing trend. The highest biogas production was determined as 310.4 ml/g TS in the reactor 24 with the addition of HNO_3 as much as 20% of the solid matter.

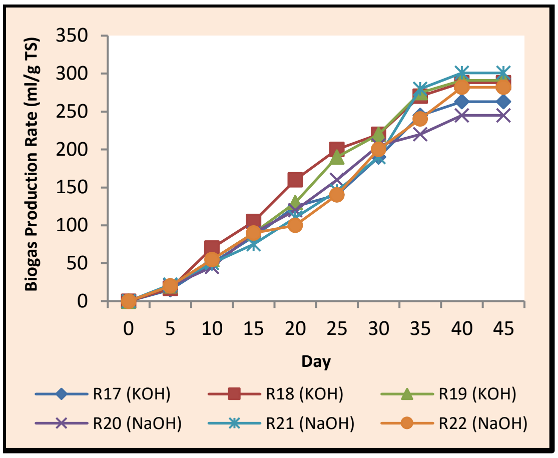

Figure 3. The anaerobic process of alkaline-pretreated organic waste

Şekil 3. *Alkali önişlem uygulanan organik atığın anaerobik süreci*

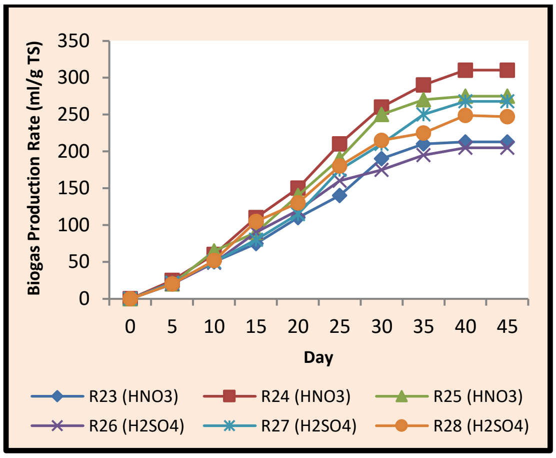

Figure 4. The anaerobic process of acid-pretreated organic waste

Şekil 4. *Asit önişlem uygulanan organik atığın anaerobik süreci*

4. Conclusions

This study was conducted to evaluate the effects of pretreatment applied to horse manure, apple pulp, and sugar beet pulp mixtures with high organic matter content on water solubility and biogas production.

While the ratio of water solubility of the mixtures without pretreatment ranged from 14.7 to 36.5%, the ratios obtained as a result of thermal, alkali, and acid pretreatments were 45.6%, 40.1%, and 42.4%, respectively. As a result, the pretreatments applied in the study increased the ratio of water solubility.

The highest biogas yield was determined as 329.4 ml/g TS in the reactor, which was pretreated at 150°C for 60 minutes.

Alkaline pretreatments were carried out with KOH and NaOH solutions. The highest biogas formation was found as 300.9 ml/g TS in the reactor that was pretreated with the addition of 20% NaOH.

Acid pretreatments were carried out with HNO_3 and H_2SO_4 solutions. The highest biogas formation was determined 310.4 ml/g TS in the reactor that was pretreated with 20% HNO_3.

In conclusion, pretreatments were found to increase the proportion of water solubility and biogas production efficiency. The results of the current study indicate that horse manure, apple pulp, and sugar beet pulp mixture can be used in biogas production by subjecting them to different pretreatments. Thus, raw materials, which are considered as waste, can be used efficiently in the energy sector.

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