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CO-FERMENTATION OF PROCESSED ORANGE WASTES WITH CATTLE MANURE

PORTAKAL İŞLEME ATIKLARININ BÜYÜKBAŞ HAYVAN GÜBRESİ İLE KO-FERMANTASYONU

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ÖZET

Bu çalışmada, büyükbaş hayvan gübresine portakal işleme atıklarının (kabuk ve posa) farklı oranlarda (%25, %50, %75) eklenmesinin biyogaz verimine etkisi, HBT (Hohenheim Batch Yield Test) yöntemi ile belirlenmiştir. Bu kapsamda, büyükbaş hayvan gübresi çiftlikten, portakal işleme atıkları ise meyve suyu işleme tesislerinden alınarak laboratuar ortamında kurutulup öğütülmüş ve beş materyal (%100 portakal işleme atıkları, %100 büyükbaş hayvan gübresi, %25 portakal işleme atıkları + %75 büyükbaş hayvan gübresi, %50 portakal işleme atıkları + %50 büyükbaş hayvan gübresi, %75 portakal işleme atıkları + %25 büyükbaş hayvan gübresi) meydana getirilmiştir. Yapılan araştırma sonucunda en yüksek, ham protein oranı (%12.06) ve ham yağ oranı (%2.30) %100 portakal işleme atıkları materyalinden, kuru madde oranı (%90.75) %100 büyükbaş hayvan gübresi materyalinden, organik kuru madde oranı (%95.56) %100 portakal işleme atıkları materyalinden, ADF oranı (%60.20) %100 büyükbaş hayvan gübresi materyalinden ve NDF oranı (%26.50) %25 portakal işleme atıkları + %75 büyükbaş hayvan gübresi materyalinden elde edilmiştir. Ele alınan materyallerde en yüksek metan üretimi 25 ile 35 günler arasında gerçekleşmiştir. Karışım materyallerinde en yüksek biyogaz (0.70 Nm^3/kg OKM) ve metan (0.37 Nm^3/kg OKM) üretim değerleri, %75 portakal işleme atıkları + %25 büyükbaş hayvan gübresi materyalinden oluşmuştur. Biyogazdaki metan oranı, en yüksek (%53.77) %50 portakal işleme atıkları + %50 büyükbaş hayvan gübresi materyalinden elde edilmiştir. Çalışmada portakal işleme atıklarının büyükbaş hayvan gübresi ile ko-fermantasyonu, metan ve biyogaz üretimini istatiksel olarak önemli düzeyde ($P \leq 0.05$) arttırmıştır.

Anahtar Kelimeler: Portakal işleme atıkları, Büyükbaş hayvan gübresi, Ko-fermantasyon, Biyogaz, HBT

ABSTRACT

In this study, the biogas production using the co-fermentation of processed orange wastes and cattle manure at different ratios (25%, 50%, 75%) was analyzed by been analyzed by Hohenheim Batch Yield Test. Cattle manure collected from the farms and processed orange waste was collected from the fruit base juice companies then dried and ground in the standard laboratory conditions. Five mixtures (100% processed orange waste, 100% cattle manure; 25% processed orange waste+ 75% cattle manure; 50% processed orange waste+50% cattle manure; 75% processed orange waste+ 25% cattle manure) were prepared. As a result of this study, the highest percentage of raw protein (12.06%) and percentage of raw fat (or raw oil) (2.30%) were obtained from from 100% processed orange waste mixture, the highest dry material percentage (90.75%) was obtained from 100% cattle manure mixture, the highest organic dry material percentage (95.56%) was obtained from 100% processed orange waste mixture, the highest ADF percentage (60.20%) was obtained from 100% cattle manure mixture and the highest NDF percentage (26.20%) was obtained from 25% processed orange waste+75% cattle manure mixture. The highest amount of biogas (0.70 Nm^3/kg ODM) and methane (0.37 Nm^3/kg ODM) was produced from the mixture of 75% processed orange waste+ 25% cattle manure. The highest amount of methane (53.77%) in biogas was produced from the mixture of 50% processed orange waste+50% cattle manure. Based on this study, co-fermentation of processed orange waste with cattle manure statistically increased the production of methane and biogas in higher amount ($P \leq 0.05$).

Keywords: Processed orange waste, Cattle manure, Co-fermentation, Biogas, HBT

INTRODUCTION

Energy and energy resources are the decisive indicator values of development of countries (Acaroğlu, 2007; Aybek and Üçok, 2017) are of great importance for the survival of societies (Onurbaş Avcıoğlu et al., 2011). Today, the interest in renewable energy sources is increasing due to the decrease in fossil fuel sources and negative environmental effects (Mansourpoor and Shariati, 2012). Renewable energy sources have been naturally extracted from the energy-flow available in our natural environment (Deublein and Steinhauser, 2008). Biomass (63%) has an important place among the renewable energy sources (Demirbaş and Demirbaş, 2007). Biomass refers to the biological material that can be used for industrial production or fuel in general (Haggerty, 2010). In broader terms, biomass are non-fossilized organic material sources (Klass, 1998). Plant (corn, wheat, barley straw), animal, urban wastes, and food industry wastes constitute an important potential for biomass (Brown, 2003; McGowan, 2009; Üçgül & Akgül, 2010).

Biomass and wastes depending on their properties can be converted to energy or fuel together with other fuels through combustion, gasification, anaerobic digestion (Manyi-Loh et al., 2013). Anaerobic digestion converts biological materials or biomass materials (organic matter) into biogas with hydrolysis, acidogenesis, acetogenesis and methanogenesis stages (Tiehm et al., 2001; Cassidy et al., 2008; Xiao et al., 2010; Ogunleye et al., 2010). Biogas occurs as the result of decomposition in the anaerobic fermentation of organic origin wastes. It is a colorless, odorless, lighter than air, burning with a bright blue flame, and it preserves 40-75% CH_4, 15-60% CO_2, 0-3% hydrogen sulfide (H_2S) with very little ammonia (NH_3), hydrogen (H_2) and nitrogen (N_2) depending on the content of organic matter in the composition (Ryckebosch et al., 2011; Ozturk, 2011; Abbasi et al., 2012; Matuszewska et al., 2016). Anaerobic digestion of animal waste is the most common biogas application in worldwide. At the same time, rich organic fertilizers as useful as biogas is produced. Today, because organic industrial wastes are added to animal waste, it increases gas production and economic inputs of the system. Disposal in biogas plants of organic solids emerging from industries is gradually increasing. Although some of the substances are difficult to digest, they have not any problems by mixing with animal wastes or wastewater sludge. In this way, the fermentation of different wastes at the same time is called co-fermentation (URL, 2017). Biogas potential of fruit pulp (500-660 m^3/ton organic dry matter (ODM), vegetable and fruit waste (400-600 m^3/ton ODM) is about twice as much as organic materials like cattle manure (200-500 m^3/ton ODM) and chicken manure (250-500 m^3/ton ODM) (Calli, 2012). Pulp from fruit juice production is very rich in chemical composition. Evaluating the potential of fruit pulp and wastes in biogas production can make an important contribution to energy production and also prevent environmental pollution. Fruit pulp and wastes, which have more biogas content than organic materials such as cattle manure and chicken waste which have a significant potential in our country are not utilized sufficiently. To eliminate these problems in the evaluation of fruit pulp and wastes as single, some organic residues can be mixed with these wastes and biogas production efficiency can be increased. This will make more attractive the use of fruit pulp and waste.

In this study, it is aimed to obtain biogas and organic fertilizer by adding orange wastes (OW) to cattle manure (CM) in different ratios and to provide data source for environmental protection and to ensure efficiency. In this study, biogas and methane production efficiencies of blends obtained by mixing in different proportions (25%, 50%, 75%) of orange processing wastes (husk and pulp) collected from fruit juice plants with cattle manure were determined by HBT (Hohenheim Batch Yield) Test) method.

MATERIALS AND METHODS

CM (Figure 1a) and OW (Figure 1b) were used as materials. CM was collected from a farm in Gaziantep and OW were obtained from a fruit juice processing plant in Adana. CM was left in the open air until it dries completely and OW were dried in natural drying environment at room temperature for 3 weeks.

The dried materials were milled by an industrial grinder until the standard size (VDI 4630. 2006) of 1 mm. Bacterial culture, which is a mixture of solid + liquid phase was taken from Gaziantep Water and Sewerage Administration (GWSA) waste water treatment plant. Inoculum (Figure 2) was prepared by mixing with a 1:2 buffer solution and filtered through four layers of cheesecloth in order to keep the bacterial culture in a better environment. 500 mL of distilled purified water, 0.1 mL of solution A, 200 mL of solution B, 200 mL of solution C, 1 mL of resazurine (0.1%, w/v) solution C and 40 mL of solution were used for the buffer solution. Solution A; 13.2 g CuCl22H2O, 10.0 g MnCl24H2O, 1.0 g CoCl26H2O, and 8.0 g $FeCl_26H_2O$ were prepared in 100 mL with purified water. Solution B; 35 g of $NaHCO_3$ and 4 g of NH_4HCO_3 were dissolved in distilled water and prepared in 100 mL. Solution C; 5.7 g

Na_2HPO_4, 6.2 g KH_2PO_4 were prepared in 1000 mL by dissolving 0.6 g $MgSO_47H_2O$ in purified water. Solution D; 0.5 g of resazurine were dissolved in distilled water and prepared in 100 ml. Solution E was prepared from 95 mL of purified water, 4 mL of 1 N-NaOH and 625 mg of Na_2S9H_2O.

a) Cattle manure b) Orange processing wastes

Figure 1. Cattle manure (CM) and orange processing wastes (OW)

Figure 2. Inoculum

Before starting the experiment, chemical analyzes of milled waste materials were carried out. These chemical analyzes consist of dry matter content (DM), crude ash (CA) and organic matter content (OM), crude protein content (CC), crude fat content (CF) (AOAC, 1990) and ADF and NDF (Van Soest et al., 1991).

Materials (100% OW, 100% CM, 25% OW+ 75% CM, 50% OW + 50% CM, 75% OW + 25% CM) were prepared for the experiment. Three samples were taken and weighed to 0.2 g in the microbalance and placed in 100 ml glass syringes (Figure 3a). The syringes were placed to the hole in the incubator (Figure 3b). For the comparison group samples, 3 inoculum syringes prepared by using burette to receive 30 mL were also placed to the hole in the incubator. According to the standard (VDI 4630 2006), the syringe plunger was removed before the materials were put into syringes and plastic clips were attached to the silicone hoses at the end of the injectors and used for gas transfer. Vaseline was applied to the pistons of the injectors in order to prevent gas leakage during the experiment. Then, the syringe pistons were inserted and the clips were closed and made ready for use. After placing the inoculum into the syringes, it was placed in the incubator at a temperature of 37 ºC. The methane measuring device (methane-sensor "Advanced Gasmitter" D-AGM Plus 1010), which was used to determine the methane content in the incubator was calibrated with a calibration tube (60.5% CH_4). The purpose of the calibration is to verify that the measured gas is at standard conditions (0 °C and 1013 hPa). Measurements (Figure 3c) were performed for 35 days. The measurements were made every 6 hours for the first 2 days, 8 and 12 hours in the following days to determine the methane yield in each sample.

a) Glass syringe b) Incubator c) Methane measurement

Figure 3. Glass syringe, incubator and methane measurement

RESULTS AND DISCUSSION

The chemical properties (CP, CO, DM, ODM, ADF, and NDF), biogas and methane production values of the materials were discussed. The data obtained are presented below.

The chemical properties of the materials obtained from the analysis are given in Table 1.

Table 1. Chemical properties of materials

Materials	CP (%)	CO (%)	DM (%)	ODM (%)	ADF (%)	NDF (%)
% 100 OW	7.78	2.30	88.67	95.56	14.76	20.12
% 100 CM	12.06	1.77	90.75	90.79	60.20	23.30
%25 OW + %75 CM	11.07	2.11	90.12	90.58	52.96	26.50
%50 OW + %50 CM	9.89	2.03	89.70	91.82	39.14	20.92
%75 OW + %25 CM	8.76	2.14	89.26	94.48	37.42	22.19

Materials; CP values were 7.78-12.06%, CO values were 1.77-2.30%, DM values were 88.67-90.75%, ODM values were 90.58%, ADF and NDF values were between 14.76% and 60.20%, respectively. The highest crude protein value was obtained in 100% CM (12.06%), lowest in 100% OW (7.78%). The highest crude oil value was obtained in 100% OW (2.30%), the lowest in 100% CM (1.77%). The highest DM was obtained in 100% CM (90.79%), lowest in 100% OW and the highest ODM was obtained in 100% OW (95.56), the lowest in 25% OW + 75% CM. The highest ADF value was occurred in 100% CM (60.20%), the lowest in 100% OW (14.76%). The highest NDF value was occurred in 25% OW + 75% CM (26.50%), the lowest in 100% OW (20.12%).

Average cumulative specific methane production over time are given in Figure 4 for all the mixture. Average cumulative specific methane, biogas values and methane ratios of biogas materials are given in Table 2. The changes of average cumulative specific methane and biogas production are given in Figure 5. The variance analysis of biogas, methane production and methane ratios of biogas are presented in Table 3.

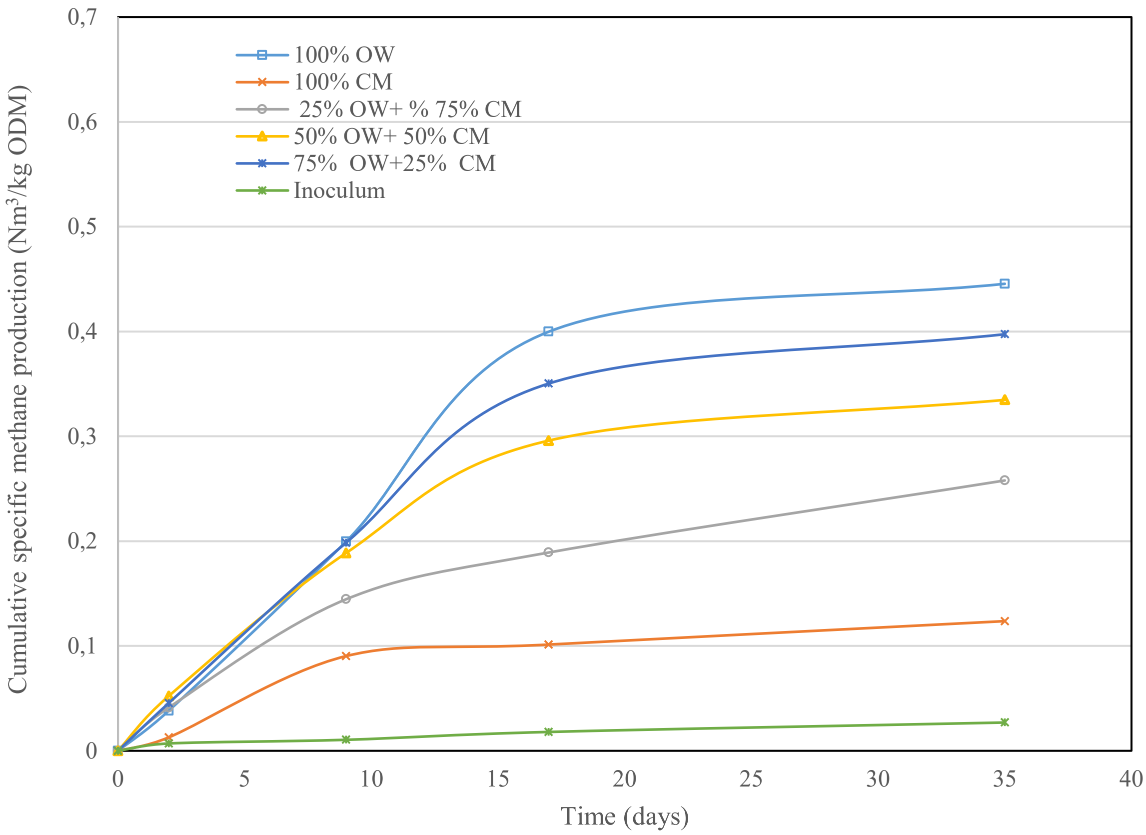

Figure 4. Average cumulative methane production over time of all materials

Table 2. Average cumulative specific methane, biogas values and methane ratios of biogas materials

Materials	Cumulative specific biogas production (Nm^3/kg OKM)				Cumulative specific methane production (Nm^3/kg OKM)				Methane ration in biogas
	Measurements			Avr.±Std. error	Measurements			Avr.±Std. error	(%)
	1.	2.	3.		1.	2.	3.		
% 100 OW	0.82	0.87	0.86	0.85±0.016a	0.41	0.39	0.42	0.41±0.008a	48.42 b
% 100 CM	0.25	0.31	0.24	0.27±0.023d	0.10	0.14	0.10	0.12±0.013d	44.01 c
%25 OW+%75 CM	0.47	0.48	0.49	0.48±0.006c	0.24	0.24	0.25	0.25±0.004c	51.66 ab
%50 OW+ %50 CM	0.63	0.69	0.59	0.64±0.029b	0.35	0.36	0.31	0.34±0.015b	53.77 a
%75 OW + %25 CM	0.75	0.70	0.66	0.70±0.027b	0.39	0.36	0.33	0.37±0.017ab	51.74 ab

$p \leq 0.05$; a, b, c, d,: differences between cumulative specific methane, biogas production and methane ratio averages in biogas indicated by different letters in the same column are important.

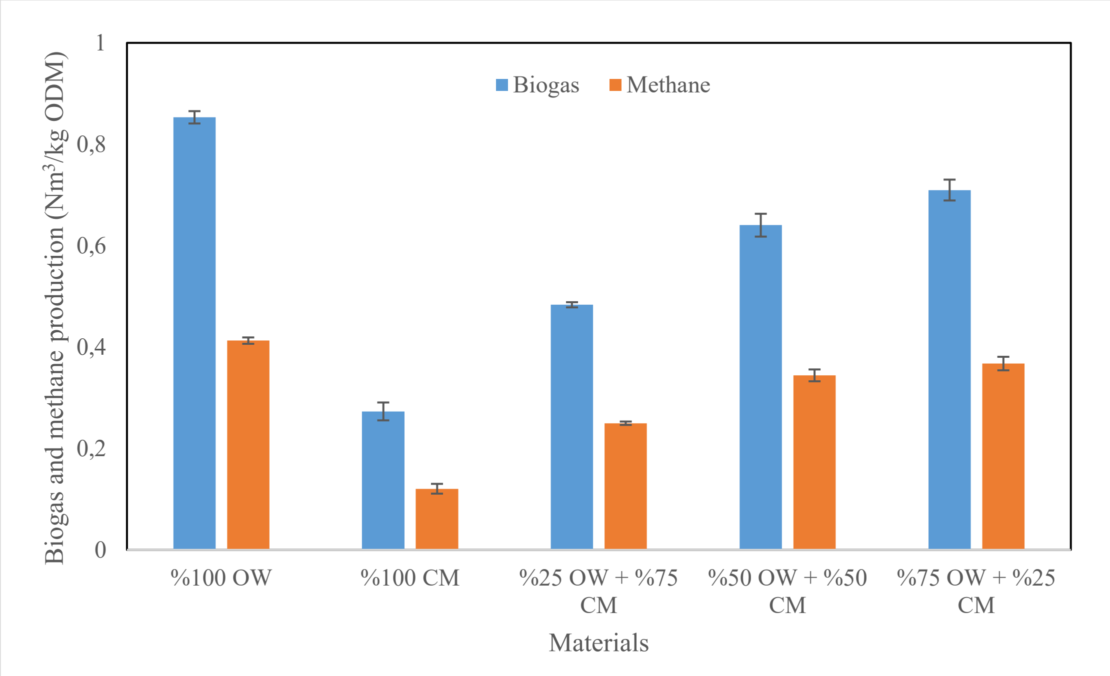

Figure 5. Variation of average cumulative specific methane and biogas production of materials

Table 3. Analysis of variance of biogas, methane production and methane ratios

	Variation source	**DF**	**SS**	**MS**	**F value**	**SEM**	**P value**
Biogas production (m^3/kg ODM)	Between groups	4	0.594	0.148	104.719	0.3074	0.000***
	In Groups	10	0.014	0.001		0.3074	
	Total	14	0.608			0.3074	
Methane production (m^3/kg ODM)	Between groups	4	0.162	0.040	88.146	0.1749	0.000***
	In Groups	10	0.005	0.000		0.1749	
	Total	14	0.166			0.1749	
Methane ratio (%)	Between groups	4	175.152	43.788	17.450	1.2933	0.000***
	In Groups	10	25.093	2.509		1.2933	
	Total	14	200.245			1.2933	

Methane production in all materials starts on the first day and increased rapidly until the 17th day, the rate of increase gradually decreased between 17-35 days and reached maximum value on 35th day (Figure 4). Biogas and methane values in co-fermentation increased, as the proportion of OW in the materials increased. The highest average cumulative biogas values were in 100% OW (0.85 Nm^3 / kg ODM). Biogas values of other materials were determined as 75% OW + 25% CM (0.70 Nm^3 / kg ODM), 50% OW+ 50% CM (0.64 Nm^3 / kg ODM), 25% OW + 75% CM (0.48 Nm^3 / kg ODM), 100% CM (0.27 Nm^3 / kg ODM), respectively (Table 2, Figure 5).

Average cumulative methane production of the materials from the highest to the lowest were determined as 100% OW (0.41 Nm^3 /kg ODM), 75% OW + 25% CM (0.37 Nm^3/kg ODM), 50% OW + 50% CM (0.34 Nm^3/kg ODM), 25% OW+ 75% CM (0.25 Nm^3/kg ODM), 100% CM (0.12 Nm^3/kg ODM), respectively (Table 2, Figure 5).
The methane content of biogas produced by 100% CM, 100% OW and 75% CM+ 25% OW are 44.01%, 48.42 and 51.66-53.77%, respectively. As a result of the statistical comparison, the methane, biogas and methane ratios were found to be significant stage ($P \leq 0.05$) (Table 3).

While Amon et al. (2007) determined methane production of corn silage with animal manure waste as 0.31-0.36 Nm^3/kg ODM- 0.26 Nm^3/kg ODM) in their study, Martin et al. (2010) determined the methane production orange peel as 0.27-0.29 Nm^3/kg ODM). In this study, methane production obtained was found to be different from other studies. These differences may be due to the chemical structure in the material (fat, protein, carbohydrate, C/N ratio, cellulose content, etc.) and initial pH, mixing ratios, electrical conductivity (EC) and animal feed.

The correlation and the main chemical biomasses between biogas and methane production, the fiber particles contained in the biomass confirmed that their chemical composition is essential to predict biogas potential (Angelidaki et al., 1999). Pearson coefficient is used to correlate hemicellulose content in a significant and positive way. Another negative and statistically significant relationship is the biogas production and ADF parameter, especially the degree of fiber lignification with biogas production. Cases that a linear relationship between methane production and cellulose mass content cannot be evaluated, it can be partly explained by the fact that the biomasses tested have different chemical properties (Jimenez et al., 1990). Even if cellulose is digestible by active microorganisms in anaerobic environment, by connecting to the lignin becomes unsuitable for digestion (Dinuccio et al., 2010). In this study, as a result of chemical analysis of materials used, the lowest ADF (14.76) was determined in 100% OW. The highest cumulative specific biogas production was also observed in 100% OW. There was a negative correlation between ADF content and biogas production.

CONCLUSIONS AND RECOMMENDATIONS

The aim of this study was to determine the biogas and methane production efficiencies of the mixtures obtained by mixing OW (husk and pulp) in different ratios (25%, 50%, and 75%) with CM that has an important potential in our country.

The results and recommendations are summarized below.

- While the highest (2.30%) CO values was obtained in 100% OW, the lowest in (1.77%) was obtained in100% CM.
- DM values ranged from 88.67% to 90.75% and ODM values are within the range of 90.58% to 95.56%.
- ADF value was found the highest (60.20%) in 100% CM and the lowest (14.76%) in 100% OW.
- NDF value was found the highest (26.50%) 25% OW + 75% CM, the lowest (20.12%) in 100% OW
- Highest methane production of materials between days 25-35 occurred.
- As the ratio of OW in the mixture materials increased, biogas produced by co-fermentation and methane values in biogas increased.
- Cumulative biogas values was found the highest (0.85 Nm^3 / kg OKM) in 100% OW, the lowest (0.27 Nm^3/kg ODM) in 100% CM
- The highest biogas (0.85 Nm^3/kg OKM) and methane (0.37 Nm^3/kg OKM) values occurred in the mixture of 75% OW + 25% CM.
- Methane content in biogas was obtained from the highest (53.77%) in 50% OW+ 50% CM.
- Methane, biogas and methane content of all materials were statistically significant ($P \leq 0.05$).

Recommendations for this study can be listed as follows.

- Biogas and methane production efficiencies can be increased as a result of co-fermentation of OW with CM.
- As a result of co-fermentation of OW with CM, environmental and natural resources can be protected by eliminating wastes.
- OW are important materials for biogas plants.
- Greenhouse gases (methane and carbon dioxide) to be released to the atmosphere due to the uncontrolled storage of OW and CM will be prevented by the introduction of the biogas process.
- The significant potential of the fruit processing waste and cattle manure waste in Turkey can be utilized based on anaerobic digestion process to acquire the energy.

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