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Anaerobic co-digestion of tannery solid waste: Optimum leather fleshing waste loading

Tabakhane katı atıklarının anaerobik birlikte çürütülmesi: Optimum etleme atığı yükü

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Abstract

In this study, loading of optimum leather fleshings was investigated with four identical batch reactors with different fleshings and treatment sludge ratios (0:1, 0.25:1, 0.35:1, 0.50:1) to contribute to the state of art of the biogas production from tannery solid wastes. Results showed that lipids-containing leather fleshings boosted the methane production potential. However, H2S inhibition and volatile fatty acids accumulation were the main concern in the anaerobic digestion of these wastes. The modified Gompertz model was applied to the batch tests data to determine the kinetic constants of anaerobic digestion of tannery solid wastes. It was calculated with the model outputs that the ultimate methane production potential and maximum methane production rate in reactors having mixing ratio of 0.35:1 and 0.5:1 (dry basis) were highly similar. 0.35 was found to be an optimum leather fleshing and treatment sludge ratio with a 54% more methane production potential than that of control reactor in this study.

Keywords: Anaerobic digestion, Leather fleshings, Biogas, Lipids, Hydrogen sulfide.

Öz

Tabakhane katı atıklarından biyogaz üretimi üzerine literatüre katkı sağlamak amacıyla yürütülen bu çalışmada deri etleme atığı yükünün anaerobik biyogaz üretimine etkisi ve optimum deri etleme atığı yükü, farklı etleme atığı ve arıtma çamuru karışım oranlarıyla (0:1, 0.25:1, 0.35:1, 0.50:1) kesikli olarak işletilen dört eşdeğer anaerobik reaktör ile incelenmiştir. Elde edilen sonuçlar, lipit içeren atıkların metan üretim potansiyelini arttırdığını göstermiştir. Ancak, H2S inhibisyonu ve uçucu yağ asitlerinin birikimi bu atıkların anaerobik olarak çürütülmesinde dikkat edilmesi gereken önemli hususlar olarak görülmüştür. Kesikli deneyler ile elde edilen verilere Gompertz modeli uygulanarak bu atıkların anaerobik olarak çürütülmesinde kinetik katsayılar belirlenmiştir. 0.35: 1 ve 0.5: 1 (kuru bazda) karışım oranı ile işletilen reaktörlerin nihai metan üretim potansiyelleri ve metan üretim hızı değerlerinin oldukça benzer olduğu model çıktıları ile hesaplanmıştır. Çalışmada, 0.35:1 karışım oranı ile işletilen reaktörün hiç etleme atığı ilave edilmemiş kontrol reaktörüne göre %54 daha fazla metan üretim potansiyeline sahip olduğu ve bu karışım oranının optimum etleme atığı ve arıtma çamuru oranı olduğu gözlenmiştir.

Anahtar kelimeler: Anaerobik çürütme, Etleme atığı, Biyogaz, Lipit, Hidrojen sulfur.

1 Introduction

Tanning industry is one of the oldest sectors in the history of human beings. Because of the severe environmental problems related to leather production process and the increasing labor prices, the production sector has been declining in developed regions and become widespread mostly in the far east countries such as China, Vietnam, Endonesia [1],[2].

Leather making process is basically divided into three steps: pre-tanning including soaking, unhairing and liming, fleshing, splitting, deliming, bating and pickling; tanning process; and the finishing process [1]. Substantial amount of solid waste is generated during pre-tanning operations such as skin trimmings, keratin wastes and fleshings, which consist of mainly protein and lipids [3]. The fleshing operation is performed in order to remove flesh and fats from the skin so that the rapid skin degradation can be prevented and chemicals used in the subsequent steps can easily penetrate to the raw skin [4]. Hence, fleshing wastes are the major portion of the solid waste caused by tanning industry [5]. Besides, high amount of treatment sludge is revealed due to treatment of leather industry's wastewater. As a result of the production of one ton of raw hide, up to 250 kg of fleshings and 200 kg of treatment sludge are generated [4],[6].

Because of the high organic and inorganic content, tanning industry solid wastes may cause severe environmental problems unless managed properly [7]. Substantial amount of research has been carried out to develop methods for the recovery and utilization of fleshings such as proteolic enzymes [8] and biodiesel [9] production, fat and protein recovery and glue production [10]. However, they are generally complex processes requiring high amount of energy, chemical and time [10]. Landfilling is the most widely used way for the management of leather industry solid wastes since recovery opportunities are very limited and not feasible [5],[10],[11]. Nevertheless, it is well known that landfilling of those wastes is not a good option from the environmental point of view [12],[13].

In response to increasing energy demand and new strict environmental regulations and policies, anaerobic digestion has become an attractive solution in the management of tannery solid wastes [7],[14]. In addition to energy recovery and production of lower amount of sludge, which has to be managed, biologically stabilized nutrient-rich digestate can be

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used as an organic fertilizer in the agricultural activities [11],[15].

Several studies regarding anaerobic digestion of leather solid wastes agree on process feasibility. However, possible operational problems such as unbalanced C/N ratio, inhibition of ammonia, long chain fatty acid and sulfide have also been reported [6],[14],[16].

The present work is aimed to increase knowledge on the application of anaerobic co-digestion of fleshings, and treatment sludge, which is caused by tannery wastewater treatment activities, by investigating optimum treatment sludge and fleshings mixing ratio with batch bio-methane potential tests.

2 Material and methods

2.1 Substrates and Inoculum

Tannery fleshings and dewatered treatment sludge (primary and secondary sludge) were taken from the leather industrial zone located in Turkey. Fleshings had been ground to 5 mm-diameter using a meat mincer and homogenized before being characterized. Inoculum (active methanogenic sludge) used in the batch tests was collected from the existing anaerobic digester of leather industrial zone operated with treatment sludge of leather industry wastewater. Characterization of leather fleshings, treatment sludge and inoculum were performed just after arriving at our laboratory.

2.2 Experimental set-up and operational conditions

Bio-methane potential (BMP) experiments were carried out to determine the optimum fleshings and treatment sludge mixing ratio for anaerobic digestion process. Four identical glass 1100 ml-total and 800 ml-active volume of batch reactors (R1-R4) were operated for 72 days. BMP tests were performed under mesophilic conditions (36±1ºC) using temperature-controlled cabinet (WTW, TS606/4-i). Reactors were placed onto an orbital shaker (Biosan, PSU-20i) and continuously stirred during the study. Total solid (TS) concentration of each reactor was adjusted to 8%, which is the same with the existing digester solid content (dissolved solid was excluded). R1 was operated as a control reactor in which no fleshings were added. Fleshings to sludge ratio of R2, R3 and R4 were adjusted to 0.25:1, 0.35:1 and 0.5:1 on TS basis, respectively (Table 1).

Table 1. Operational conditions.

	Reactor #			
Parameters	R1	R2	R3	R4
Fleshings, gr	-	63	82	105
Sludge, gr	256	200	190	107
Inoculum, gr	90			
TS[a] , %	8			
VS, %	5.08	5.25	5.47	5.55
Fleshings: Sludge Ratio (TS basis)	0	0.25	0.35	0.50

*: Control reactor, TS: Total solid/Dry matter, [a]: dissolved solid values were excluded, VS: volatile solid

After adding required amount of fleshings and sludge, pH of R2, R3 and R4 were adjusted to 7.6-7.8 with 1N HCl and reactors were flushed with nitrogen gas for 10 min to maintain the anaerobic conditions before initializing the experiments. Aluminum foil gas bags were connected to reactors to collect biogas produced (Figure 1).

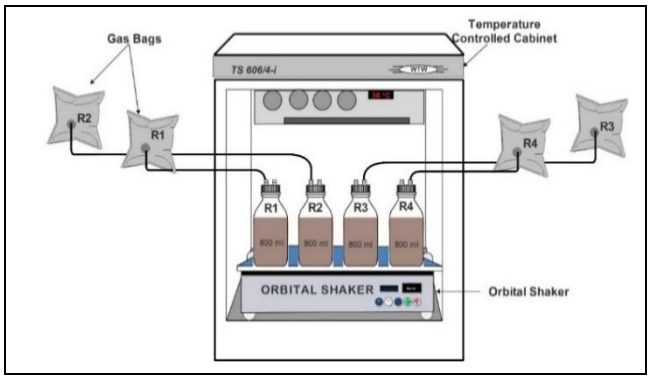

Figure 1. Experimental set-up

2.3 Analytical techniques

Total solid (TS, APHA-2540B), volatile solid (VS, APHA-2540E), chemical oxygen demand (COD, APHA-5220D) and total kjeldahl nitrogen (TKN, APHA-4500N_{org}-C) analyses were performed according to standard methods [17]. Dissolved solid was determined by using a conductivity meter (Eutech cyberscan PCD 6500, Singapore). Total ammonia nitrogen (TAN) was measured with the nesslerization method (HACH-8038) by using a spectrophotometer (WTW photoLab 6100, Germany). Volatile fatty acids were determined by using a gas chromatograph (GC) (Shimadzu GC-2014, Japan) according to method described by Bayrakdar et al. [18]. pH was analyzed using a pH meter (WTW 3310, Germany). Total sulfide was analyzed according to a spectrophotometric method described by Cord-Ruwisch [19] using WTW photoLab 6100 (Germany) spectrophotometer. Daily biogas production was measured with weight-type gasometer and biogas composition (CH_4, CO_2 and H_2S) was determined using GC equipped with thermal conductivity detector according to method reported by Reddy et al. [20].

2.4 Data analyses

The kinetic constants which are maximum methane production rate (Rm: L/kgVS/d), lag-phase time (λ: day) and methane production potential (P: L/kgVS) were estimated for each BMP test with modified Gompertz model (Equation 1) using Microsoft Excel 2016 Solver tool.

$$M = P \times \exp\left\{-exp\left[\frac{R_m \times e}{P}(\lambda - t) + 1\right]\right\} \quad (1)$$

Where M is the cumulative methane production (L) at time t (day) and e is the Euler's number (2.718).

3 Results and discussions

3.1 Characterization of waste and inoculum

The characterization of leather fleshings, treatment sludge and inoculum were given in Table 2. In addition to lipids and protein, tannery solid wastes contain residual chemicals such as lime and sulfide, which are used in beam house operations for the purpose of hair removal [16]. Hence, the pH of fleshings was more than 12 like reported also by Thangamani et al. [16].

Since this pH value will adversely affect the biogas production, pH of the fleshings-added reactors was decreased with 1N HCl before initializing the study.

Table 2. Characteristics of Fleshings, Treatment Sludge and Inoculum.

Parameters	Fleshings	Treatment Sludge	Inoculum
pH	12.5±0.5	7.91±0.2	7.8±1
TS, %	20.6±0.9	23.63±0.38	5±0.5
VS, %	16.1±0.65	15.35±0.22	2.5±0.3
TSS, %	18.7±0.91	23.17±0.40	2.86±0.01
Total COD, g/kg	221±6.5	252±21	42±2
TKN, g/kg	13.61±1	11.14±0.51	1.05±0.02
Total Sulfide, mg/kg	305±8.8	120±20	93.3±5.34

TS: Total solid, VS: Volatile solid, TSS: Total suspended solid, COD: Chemical oxygen demand, TKN: Total kjeldahl nitrogen.

3.2 Effect of mixing ratio on bio-methane potential

Bio-methane potential tests lasted for 72 days. Biogas amount and the compositions were analyzed and recorded daily. The methane yield profiles of batch experiments were given in Figure 2.

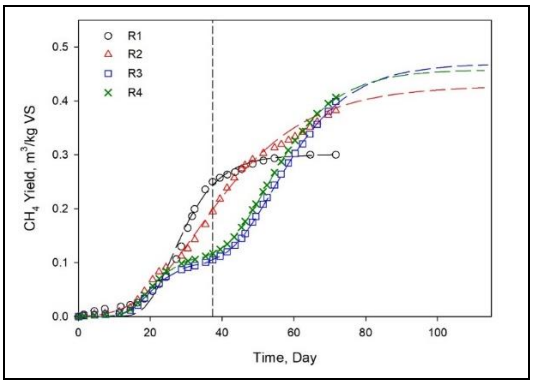

Figure 2. Methane yield profiles of BMP tests

It can clearly be seen from Figure 2 that no significant methane production was observed for almost 15 days of operation for all BPM tests because of likely high concentration of H_2S (Figure 3). Methane production rate increased when H_2S concentration in biogas decreased below 2% (Fig.3). The sulfide is one of the inhibitory compounds for anaerobic digesters and causes an inhibition at a wide-range of 100-800 mg/L total sulfide depending on pH, temperature and existence of other inhibitory compounds like ammonia. [21,22]. Bayrakdar et al. [18] reported that VFA accumulation was observed when the H_2S concentration exceeded 1% in biogas and a similar result was also reported by Sürmeli et al. [22].

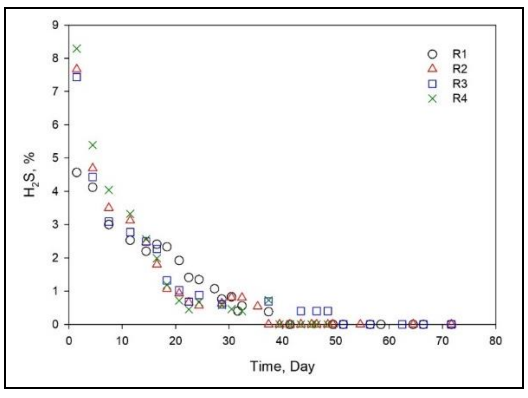

Figure 3. H_2S concentrations in biogas.

Total methane productions were 11.7 L, 15.6 L, 16.7 L and 17.2 L and methane yields were 0.3, 0.38, 0.39 and 0.40 m^3CH_4/kgVS for R1, R2, R3 and R4, respectively, in 72 days. However, methane production rates of R3 and R4 were decreased seriously compare to R1 and R2, after day 28 (Fig.2 and 4). To find out the reason of declining methane production rate, samples were taken from the supernatant of all reactors on day 30 and pH, TAN and VFAs analyses were performed. Results were given in Table 3.

Table 3. Results of analyses performed on day 30.

Reactor #	pH	TAN, mg/L	Total VFAs, mgCOD/L
R1	7.55	1330	3.73
R2	7.45	2100	7.21
R3	7.6	2593	9.14
R4	7.7	2700	9.83

According to results, TAN and pH of R3 and R4 were not at the inhibitory levels but a serious VFAs accumulation were observed in both reactors. During the anaerobic digestion, lipids are first hydrolyzed to long chain fatty acids and glycerol, then long chain fatty acids are further degraded to volatile fatty acids and may cause a VFAs accumulation [23,24]. It is known that increasing VFA concentrations results in system inhibition [25]. Over 9 g/L of total VFA in COD equivalent caused very likely an inhibition for methanogens. Besides, the shock load of long-chain fatty acids can stop methanogenic activity for longer periods was reported by Angelidaki et al. [23]. It was also reported in the same study that this problem could be overcome after a long adaptation period. To rebuild the methanogenic activity, 90 gr of active inoculum was added to R3 and R4 on day 37 shown with dashed line in Figure 2 and Figure 4. With the addition of inoculum, an obvious increase in methane production rates of R3 and R4 was observed (Figure 4).

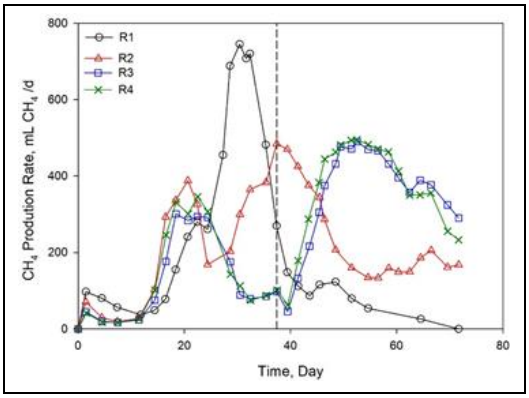

Figure 4. Daily methane production rates.

At the end of the study, 33%, 42% and 46% more methane gas were generated in R2, R3 and R4, respectively, than that of R1. Even though the biogas production in R1 in which no fleshings were added was completed on day 55, fleshings-added reactors continued to produce methane because biogas production potential of lipids higher than that of carbohydrates and proteins [26]. In addition to biogas production potential, methane content of the lipids is higher than those [11].

In the present study, the average methane content of fleshings-added reactors was 75±1% and this shows that the fleshings is a potential substrate for anaerobic digesters in terms of energy generation. The study was stopped on day 72 although

fleshings-added reactors were still producing methane. Residual total VFA, which are over 3000 mgCOD/L, at the end of the experiment also promote this (Table 5). To determine the ultimate methane production potential and the maximum methane production rate Gompertz model was applied. The model was perfectly fit to the actual data with a correlation of over 99%. The model outputs were summarized in Table 4.

Table 4. Gompertz model outputs.

Reactor #	λ, day	P, L/kgVS	Rm, L/kgVS/d
R1	14	306	13.92
R2	15	418.5	9.09
R3	13	470	11.34
R4	13	463	11.66

λ: Lag phase, P: Methane production potential, Rm: maximum methane production rate.

Methane production completed in R1 in a shorter time with a maximum methane production rate of 13.92 L/kgVS, compared to fleshings-added rectors, due to likely the slow hydrolysis rate of lipids [27]. However, methane production potential of R3 was 1.5 times higher than R1. According to model outputs, there is no significant difference between R3 and R4 in terms of methane production potential and maximum methane production rate (Table 4). Hence, it can be proposed that fleshing to sludge ratio of 0.35 is an optimum ratio for the anaerobic co-digestion of fleshings and treatment sludge.

pH, TS, VS and VFAs analyses were performed from samples taken at the end of the study. Results were given in Table 5. According to the results of the final analyses, TS and VS removal efficiency of R1, R2, R3 and R4 were 35%, 42%, 43%, 40 and 42%, 43%, 48%, 43%, respectively. Similar results were also reported by Basak et al. [28]. According to results, 0.35 was determined to be an optimum Fleshings/Sludge mixing ratio for the anaerobic co-digestion of tannery solid wastes. With an almost 50% of organic matter degradation efficiency and 470 L/kgVS methane potential, anaerobic co-digestion of tannery solid wastes is observed to be an environmentally friendly and energy-generating alternative for the management of these type of wastes.

Table 5. Characterization after Anaerobic Digestion

Reactor #	pH	TS, %	VS, %	Total VFA, mgCOD/L
R1	7.55	5.17	2.94	500
R2	7.67	4.65	3.03	3201
R3	7.76	4.56	2.89	3099
R4	7.84	4.83	3.10	3647

4 Conclusions

In this study, different treatment sludge and leather fleshings ratios were investigated to determine the optimum fleshings amount to be loaded to an anaerobic digester. Results showed that lipids containing leather fleshings boosted the methane production. Additionally, its methane content makes the anaerobic digestion process feasible. However, to prevent long-chain fatty acid and VFAs accumulation, shock loads must be avoided. Besides, some pretreatments like rinsing of leather fleshings might be needed to eliminate H_2S inhibition problem. 47% more methane gas was produced than that of control reactor in 72 days when the fleshings to sludge ratio of feed mixture was 0.35:1 on TS basis. According to Gompertz model, the ultimate methane production potential and maximum methane production rate of R3 and R4 were highly similar and methane potential of R3 was 54% more than that of control reactor (R1). It is concluded that optimum leather fleshing to treatment sludge ratio is 0.35:1.

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