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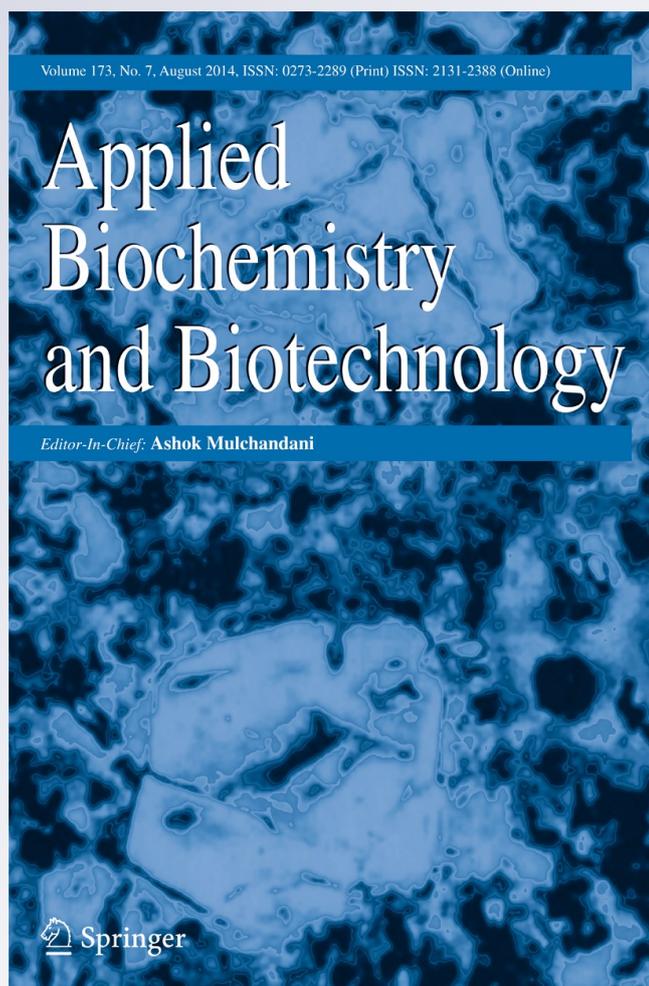
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Abstract Anaerobic digestion (AD) process is a well-established method to generate energy from the organic wastes both from the environmental and economical perspectives. The purpose of present study is to evaluate energy production from potato wastes by incorporating cow manure into the process. Firstly, a laboratory pilot of one-stage biogas production was designed and built according to continuously stirred tank reactor (CSTR) system. The setup was able to automatically control the environmental conditions of the process including temperature, duration, and rate of stirring. AD experiment was exclusively performed on co-digestion of potato peel (PP) and cow manure (CM) in three levels of mixing ratio including 20:80, 50:50, 80:20 (PP:CM), and 0:100 as control treatment based on the volatile solid (VS) weight without adding initial inoculums. After hydraulic retention time (HRT) of 50 days on average 193, 256, 348, and 149 norm liter (L_N) (kg VS^{-1}), methane was produced for different mixing ratios, respectively. Statistical analysis shows that these gas productions are significantly different. The average energy was determined based on the produced methane which was about $2.8 \text{ kWh } (\text{kg VS}^{-1})^{-1}$, implying a significant energy production potential. The average chemical oxygen demand (COD) removal of treatments was about 61 %, showing that it can be leached significantly with high organic matter by the employed pilot. The energy efficiency of 92 % of the process also showed the optimum control of the process by the pilot.

Keywords Anaerobic digestion · Renewable energy · Biogas · Potato peel · CSTR system · Biowaste · Food industry waste

A. Sanaei-Moghadam (✉) · J. Abedini-Torghabeh
Laboratory of Waste Management Organization of Mashhad Municipality, Mashhad, Iran
e-mail: aksanaei@gmail.com

A. Sanaei-Moghadam · M. H. Abbaspour-Fard · H. Aghel · M. H. Aghkhani
Bio-System Engineering Department, Ferdowsi University of Mashhad, Mashhad 9177948978, Iran

Introduction

Security of energy supply along with environment protection is vital for attaining sustainable development in many countries. Much of the world's energy currently comes from conventional sources, and the overuse of fossil fuels has been caused ecological-environmental irreversible threats, such as global warming, climate change, and acid rains. The weather and global warming may be stabilized by reducing 70 % in carbon dioxide emissions by 2050 [1]. Hence, due to the environmental damage caused by a single system of energy supply based on fossil fuel, diversification of energy sources and its localization can provide good strategy for energy production and distribution to the consumer [2].

Anaerobic digestion process is one of the biochemical technologies known to be as one of the major options in commercial generation of renewable energy from high moisture content organic wastes. Its energy can be directly used in producing heat or combined generation of heat and electricity (CHP). Additionally, the usage of biogas reduces greenhouse gases, and the semi-solid sludge of the process can be used as a high-grade and environment-friendly fertilizer for the agriculture soils. In fact, the technology improves the standard of living and can directly contribute to the economic and social development of a country [3]. The rate and performance of process are dependent on factors such as pH, temperature, stirring, amount of organic materials, and moisture content of materials. Yadvika et al. [4] reported the optimum range of relevant parameters to enhance biogas production process. The well-known technology for digestion of very wet biomaterials, such as animal residues and biowastes of the food processing industry, is continuously stirred tank reactor (CSTR), with regular agitator and continuous control of the process parameters [5–7].

Co-digestion of the organic matters generally can improve the performance of anaerobic digestion process [4]. The main concern for the co-digestion process is balancing several factors in the mixture including macro- and micronutrients, C:N ratio, pH, inhibitors, toxic compounds, biodegradable organic matter, and dry matter [8, 9]. Sharma [10] observed a rise of 40 to 80 % in biogas production by adding 1 % onion storage wastes to cattle dung. In co-digestion of tomato wastes and cow manure with different mixing ratios of cow manure to tomato, the biogas production rate increased by an increase in the amount of tomato and reached to $0.22 \text{ L (kg volatile solid (VS))}^{-1}$ [11]. El-Mashad and Zhang [12] examined the co-digestion of screened cow manure and food wastes for producing biogas in a batch digester under mesophilic conditions. After 30 days of digestion, the produced methane in two compounds of 68:32 and 52:48 obtained 282 and 311 L (kg VS)⁻¹, respectively. Callaghan et al. [13] reported that methane yield increased from 230 to 450 L (kg VS)⁻¹ by increasing the content of fruit and vegetable wastes (FVWs) from 20 to 50 % in co-digestion with cow manure, at 35 °C. Misi and Forster [14] found that batch co-digestion of cattle manure with molasses (50 % on dry weight basis) at 35 °C increased the biogas yield from 60 to 230 L (kg VS)⁻¹. Some studies have also been conducted for producing biogas from organic wastes in Iran. However, the results indicate the low productivity of biogas production or lack of their production, mainly due to inappropriate control of parameters at the optimum range, especially in the first day of process.

Mashhad plain is one of the major regions of agriculture, food industry, and livestock productions in Iran. Consequently, it has a significant potential in producing organic wastes from this sector. Recent studies showed that about 2,100 Mm³(10⁶ × m³) biomethane can be obtained annually from these organic wastes in this origin [15], which can provide the natural gas demand for about 2.5 million population of this area. Improvement of rural conditions and improvement of employment are other outcomes of using the technology for the area. However, no long-term investment has been performed for producing methane from these

resources in the area yet. Since three of the biggest by-product units of potato are located in Mashhad region and potato is one of the main staple foods of people (70–80 kg per capita consumption), so, the purpose of the present study is to examine the production of biomethane from co-digestion of potato wastes and cow manure using a one-stage digestion system without adding inoculums. Due to a lack of an appropriate laboratory setup, a pilot for data acquisition was constructed to provide necessary information for an industrial scale unit. The pilot can perform an automatic control of process conditions of biogas production such as temperature, pH, speed, and time interval of agitator.

Methods and Materials

Laboratory Pilot

Based on the literature, there was no laboratory pilot of biogas production in this area which could control temperature, pH, rate, and duration of stirred time of the digester. Therefore, a laboratory pilot batch digester was designed and built in the laboratory of Waste Management Organization of Mashhad Municipality. The reactor of the pilot was considered as a double-wall glass cylinder with working volume of 5 L (Fig. 1). Its lid was made from a steel plate of 14 mm thickness and was screwed to the reactor by six bolts along with a suitable gasket (sealing) between contact surfaces of the reactor and the lid for secure gas and liquid tightening. Five holes for inserting thermocouple and pH meter probes, gas outlet port, agitator shaft, and sampling tap were drilled on the lid and airtight by a threaded steel adapter. The stirring system was equipped with an AC variable speed electromotor (100 W, 0.5 A, Model 79-4DY-100; Y.K.K., Japan). The motor speed and duration of its running time were adjusted by means of a dimmer circuit and a digital timer (SDT-8 M, made by Shiva Amvaj Corporation, Iran), respectively. The stirring speed varied between 60 and 600 rpm. The stirring shaft was equipped with a suitable impeller and installed on the lid through two ball bearings, and two seals were used for preventing gas leakage from the gap of the shaft and the lid. The temperature controller of system was equipped with a thermocouple (TK900, 0–900 °C) connected to a digital temperature controller (TR-900 K, made by Shiva Amvaj Corporation, Iran), centrifuge pump (220 V, 0.5 A, 2900 rpm, type SH200; Moto Gen Co., Tabriz, Iran), and Ben Mary. The pump circulated warm water (42 °C) to the space between the walls of the reactor to warm up the temperature inside of the digester to reach a stabilized mesophilic condition (35–37 °C). The produced biogas was gathered in a gas volume meter, which its schematic is shown in Fig. 2. It consists of two cylindrical bells: fixed and floating (which is inverted and centimeter graded), and the volume of the produced gas was equal to the displaced volume of the inverted bell above the water surface. A digital pressure transmitter with 0.5 % accuracy (Sensys, model M5156, Korea) placed on the pipe (between digester and gas tank) and connected to a panel meter (Autonics, model MT4W-DA-4 N, Korea) and AC to DC adaptor for power supply.

Substrates

Potato Peel (PP)

The PP was collected during January 2013 from potato chips factory (BehAra Co, under license of Lorenz Co., Germany) located in industrial estate of Toos (Mashhad, Iran). In addition, there are three other big potato by-product factories in this area with about total



Fig. 1 The employed digester pilot of this study

potato by-products of 20–30 ton per week. The PP was obtained from potatoes in the cleaning unit with an average size between 1 and 2 cm. The samples were stored separately in two sealed plastics (each 15 to 20 kg), were transported to the laboratory of waste management

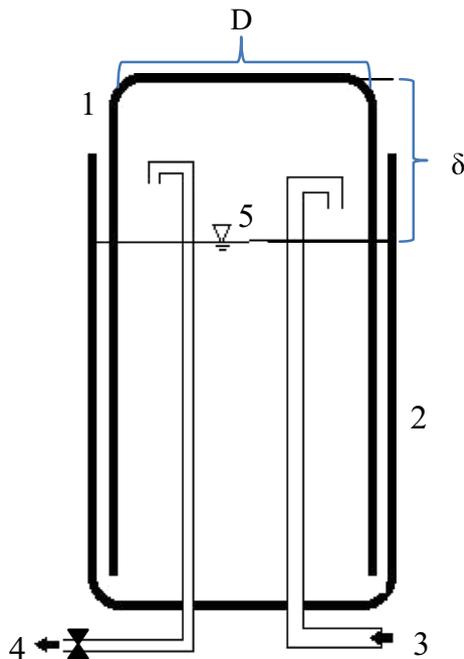


Fig. 2 The schematic of the gas volume meter: 1 floating bell, 2 fixed bell, 3 inlet biogas (connect to digester), 4 biogas discharge (to gas analyzer), 5 water level (constant), D diameter of cylinder (constant), δ displacement of floating bell to water level (variable)

organization of mashhad, and then were cut into smaller pieces of 0.3 to 0.5 cm, suitable for anaerobic digestion (AD) feeding, and were stored in a refrigerator at 4 °C.

Cow Manure (CM)

The CM samples were collected freshly from a dairy farm of Agriculture Faculty, Ferdowsi University of Mashhad, during January 2013. The samples were transported to the laboratory and were kept the same conditions. Annually, about 22,000 ton CM is a product in Mashhad area [15]. Currently, the CM is used directly as a fertilizer in agriculture. Because there was no biogas plant in the area, the CM was used as an inoculum in tests of this study.

Prior to AD, chemical characteristics of CM and PP were analyzed based on American Public Health Association (APHA) standard methods [16], and organic carbon of the substrate was measured in accordance to ISO 14235 [17]. Results of these measurements are shown in Table 1.

Experimental Method

Experimental Design

The AD processes performed with the combination of potato peel and cow manure with three mixing ratios (PP:CM): 80:20, 50:50, and 20:80 based on VS, in duplicates, and the control treatment was considered without PP content, ratio of 0:100. To obtain the best performance of biogas production at each mixing ratio, the effective operational parameters (pH, temperature, water content, stirring) were kept within the optimum range and were invariant for all ratios. The co-substrate concentrations (C:N ratio) were merely the variable parameter. For all of the treatments, firstly, PP and CM were mixed together in accordance to their fractions, and then, tap water was added so that the water content in the digester reached the desirable content, 93 %. In Table 1, the wet weight, C:N ratio, and the added water of the mixtures are shown. The C:N ratio between 12.5 and 24.4 is suitable for AD conditions [18]. The pH value for all of the treatments was reached to a desirable amount (7.6), at the beginning of the process, by adding sodium bicarbonate solution (10 % concentration) [19]. The substrates were charged into the reactor, and the lid was tightly closed. To assure anaerobic conditions, the head space of the reactor was purged with helium gas for about 5 min prior to starting the digestion tests. During the

Table 1 The composition of potato pulp and cow manure and the mixtures

	Substrates		Co-substrate PP:CM			
	PP	CM	80:20	50:50	20:80	0:100
%TS (%water content)	15.3	16.7	(93)	(93)	(93)	(93)
%VS	90.9	81.3	88.5	87.1	85	81.3
Wet weight (g:g)	–	–	1,629:429	1,025:1,054	418:1,685	0:2,105
%W (added water (ml))	84.7	83.3	(2,057)	(2,080)	(2,038)	(2,039)
pH	4.32	7.13	5.78	6.23	6.86	7.13
%C	38.92	29.6	–	–	–	–
%N	1.44	2.52	–	–	–	–
C:N	27.03	11.75	24.4	19.4	15.5	11.75

AD, digester temperature was in mesophilic condition (35–37 °C), and its content was stirred for 10 min every 30 min. To control the quality and stability of the AD, the pH level of each treatment was measured every 3 days by a pH meter (Lutron, Taiwan; pH-201 model, accuracy 0.1 %). The produced biogas was collected in the biogas collection tank, and the volume was measured daily. The specific biogas yield was calculated on the basis of norm conditions, 0 °C and 1,013 mbar, and is given in norm liter per kilogram of volatile solid (L_N (kg VS)⁻¹) [20]. The composition of the produced biogas such as methane, carbon dioxide, hydrogen sulfide, oxygen, and carbon monoxide was measured every day using a gas analyzer GA2000 (Geo Tech Incorporation, England). Before each measurement, the analyzer was calibrated with CH₄ calibration gas containing 60 % CH₄ and 40 % CO₂. Chemical oxygen demand (COD) of the substrates was measured twice: in the beginning and in the end of process. The COD was measured using a spectrometer DR5000 (Hach Co., Germany) in accordance to method 8000. Energy efficiency of the AD process and for the tests was calculated by the following relation [20]:

$$\eta = \frac{PHV_{CH_4}}{GE_{substrat}} \times 100 \quad (1)$$

where η is the process efficiency (%), PHV_{CH_4} (kWh (kg VS)⁻¹) is the heating value of the produced methane (9.93 kWh/m³_{CH₄}) during the process, and $GE_{substrat}$ (kWh (kg VS)⁻¹) is the gross energy of the materials and was measured with a calorimeter. The energy content of cow manure and potato has been reported in the literature based on the energy of agricultural products [21–23].

Statistical Data Analysis

Statistical data analysis was carried out using the software package JMP (version 4, SAS Institute, Inc.). In the first step, the descriptive statistics were performed, determining means, standard deviations, and frequency distributions of the data. Differences in the specific biogas and methane yields were tested with a pairwise comparison by the Tukey's honestly significant difference (HSD) test and *t* test. The level of significance was set to 0.05. Excel 2007 was used for showing diagrams and tables.

Results and Discussion

Produced Biogas and Its Components

Figures 3 and 4 represent the daily variation curves of specific biogas production and CH₄ and CO₂ contents, for all mixing ratios of PP:CM during batch digestion without adding inoculums. It can be seen that biogas production procedures were similar at all treatments which contain PP, but these went on at a lower rate until day 17. It is seen that CO₂ is the major content of the produced biogas, due to the low concentration of bacteria, and afterward, biogas production rate (BPR) and CH₄ content were enhanced with bacteria concentration and their metabolism, so the pick points of BPR for PP:CM treatments were observed between days 25 and 35. Also, the highest methane content in the biogas was detected in range (duration). However, the procedure shifted back approximately 10 days for the control treatment ratio of 0:100. Among all treatments, the considerable methane content of 75–82 % showed a stable

process for a ratio of 20:80. In general, as CM contains a high concentration of bacteria, therefore, the increase of this material has an optimistic effect on the digestion conditions. For that reason, the degradation rate of substrates and the methane production rate in a ratio of 80:20 were slower than those of the other treatments, and hence, with an increase of CM proportion in the treatments, better performance was observed with improved and maximized BPR.

The gentle slopes of the curves in Fig. 5 show that the degradation of the substrates completely occurred in all treatments. Since the system was discontinuous, by fading the substrates in the digester, BPR gradually declined (until it became constant and close to zero), indicating that the process is terminated. The BPR variation is comparable with the biogas production method reported by Parawira et al. [24], using potato waste in an acidogenic reactor. Kryvoruchko et al. [20] observed a maximum higher biogas production point from sugar beet and potato wastes in the first 10 days, by adding the inoculums into 20 % of the working volume of the digester, but the duration of digestion and total produced biomethane is comparable with the results of this study (Table 2). According to Table 2, the total specific produced biogas for 80:20, 50:50, 20:80, and 0:100 ratios were 375, 521, 565, and 256 L_N (kg VS) $^{-1}$ $_{added}$, respectively. There was no significant difference ($\alpha=5$ %, HSD) between 50:50 and 20:80 ratios. However, the yielded methane was significantly different in all treatments. In this table, the other components of the produced biogas such as H_2S and CO_2 for each treatment are also presented.

The cumulative curves (Fig. 5) show the highest methane production of 348 L_N (kg VS) $^{-1}$, for a ratio of 20:80 with 62.1 % methane content on average. The produced methane at 80:20 and 50:50 ratios was higher than that at 0:100 ratio, but the methane content of the latter with 58.8 % was higher than that of the first two mixing ratios. By increasing the CM proportion in the ratios, the amount of the produced methane progressed to 30, 32.5, and 36 %, respectively. On the other hand, it is obvious that the produced methane is enhanced by combining PP and CM compared to digestion of CM only. So, the increased percent of methane yielded in ratios 80:20, 50:50, and 20:80 is 31.5, 74.2, and 136.8 %, respectively. It can be concluded that the best condition for digestion of PP and CM was obtained with a ratio of 20:80 having C:N=15.5. This result is comparable with the findings in the literature in the positive synergism of digestion of more than one substrate [13, 14].

The equivalent energy of produced methane in ratios 80:20, 50:50, and 20:80 is 2.05, 2.72, and 3.7 kWh (kg VS) $^{-1}$, respectively. Parawira et al. [25] reported that the equivalent energy

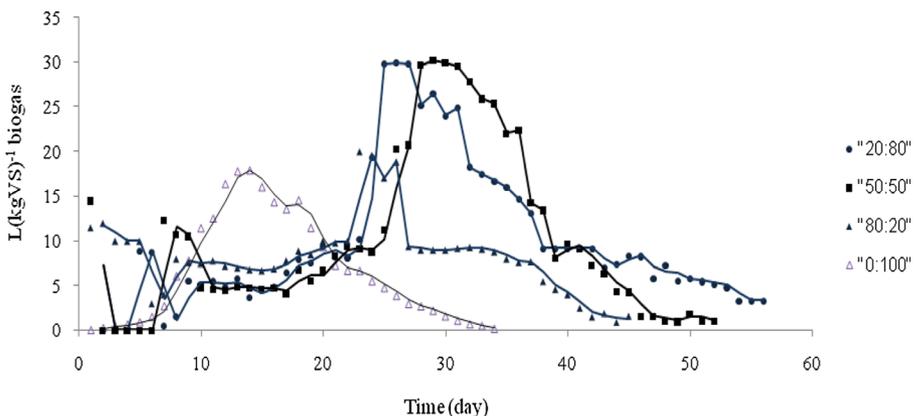


Fig. 3 Specific biogas production in various mixing ratios without adding initial inoculums

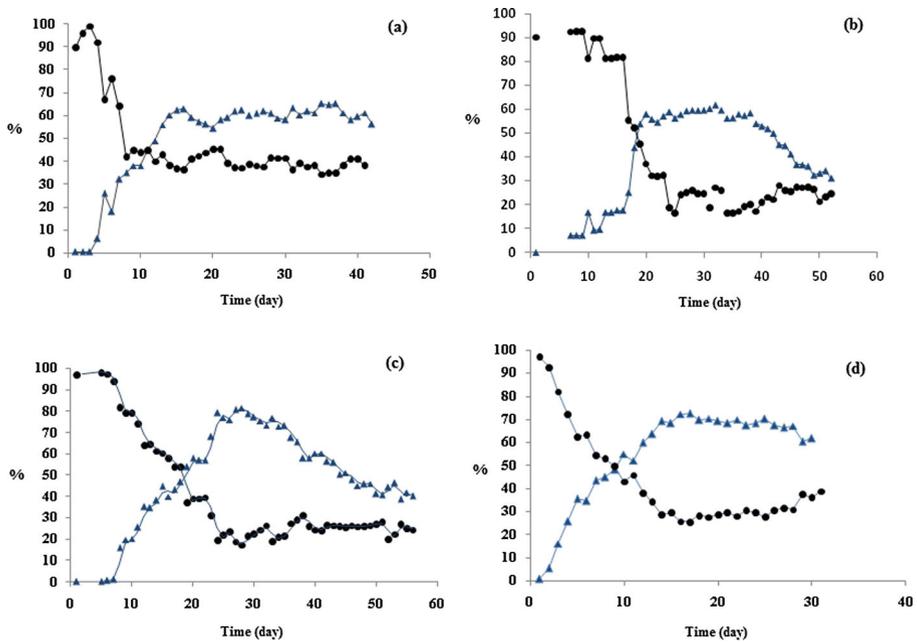


Fig. 4 CH₄ (blue triangle) and CO₂ (black circle) contents during digestion of treatments: **a** ratio of 80:20, **b** ratio of 50:50, **c** ratio of 20:80, **d** ratio of 0:100

from anaerobic digestion of sugar beet and potato wastes was in the range of 2.1 to 3.4 kWh (kg VS)⁻¹ in a two-stage system. The best energy efficiency was observed in a ratio of 20:80 with 92 % (Table 2). This efficiency is comparable with that of Kryvoruchko et al. [20]. However, the efficiency of the other mixing ratios was much lower than this efficiency value. The reason for the lower efficiency of the first two treatments may be related to the shortage of

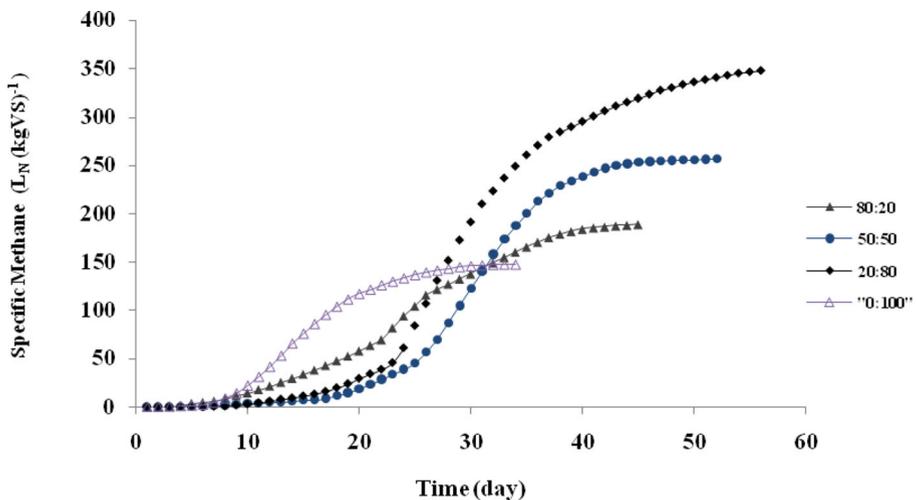


Fig. 5 Cumulative specific methane yields of co-digestion of PP and CM

Table 2 Specific biogas yield and its components and energetic efficiency (η) obtained for the experiments. All data are on average duplicates

PP:CM	Yielded biogas (L_N (kg VS) $^{-1}$)	Yielded CH ₄		CO ₂ content (%)	H ₂ S ^a (ppm)	Increasing percent of CH ₄ production compared to control treatment	Obtained energy (kWh (kg VS) $^{-1}$)	η
		Content (%)	L_N (kg VS) $^{-1}$					
80:20	375.4 a	51	193 e	46.5	1820	31.5	2.05	17.2
50:50	520.9 b	50.2	256 f	45.04	1434	74.2	2.72	34
20:80	565.2 b	62.1	348 g	29.7	677	136.8	3.7	91.7
0:100	256.5 d	58.8	147 h	39.15	547	–	1.56	86.3

Mean values within a column with different lower case letters are significantly different ($P < 0.05$; Tukey's HSD test)

^a Total produced H₂S in during the process

methanogenesis. Because of their low tendency of methane making, the obtained amount of energy from the process decreases too.

pH Variations

The role of pH in the stability of the process, as evidenced by the concentration of volatile fatty acids, is one of the most important parameters in anaerobic digesters [26]. As illustrated in Fig. 6, for a ratio of 0:100, the pH value remained stable within the optimal range (7.5–7.6) during digestion. However, in all of the treatments that contained PP, it reduced to 5.5–6.3 in the first 5 days of the process, and the maximum reduction befell for a ratio of 80:20, while the pH variation in a ratio of 20:80 was closer to the optimal condition. Each data point is the average of duplicate measurements for each treatment. To provide suitable environmental conditions for microorganisms and to prevent rapid change in pH, the substrates' pH was adjusted to the optimum range (6.8–7.2) by adding NaHCO₃ (solution 10 %). Afterward, pH values with a growing trend reached to 7.75, 7.66, and 7.36 at the end of digestion for ratios 20:80, 50:50, and 80:20, respectively. Parawira et al. [24], in their investigation on biogas production from potato wastes, reported a similar procedure in pH variations of the first stage reactor, but there was less pH variations in the second reactor which included more methanogenesis. According to the AD theory, the concentration of volatile fatty acids increases in the first days due to the beginning of acidification phase, and the process has not yet reached its steady state after startup [27]. The increasing trend of pH within the range of 6.7–7.4 during days 25–35 (Fig. 6) indicates that the process was placed in steady state. This time is coincident with the highest rate of methane production in the treatments (Figs. 4 and 5). According to the procedure, to change this system into two-stage, it is suggested that the HRT of the acidification stage be considered as 4–5 days.

COD and VS Removal

To measure the efficiency of the reactor, VS and COD were determined at the beginning and at the end of AD tests. According to Fig. 7, the amounts of COD elimination varied between 54.2 and 67.3 % and with an average of about 60.3 %. The COD removal was

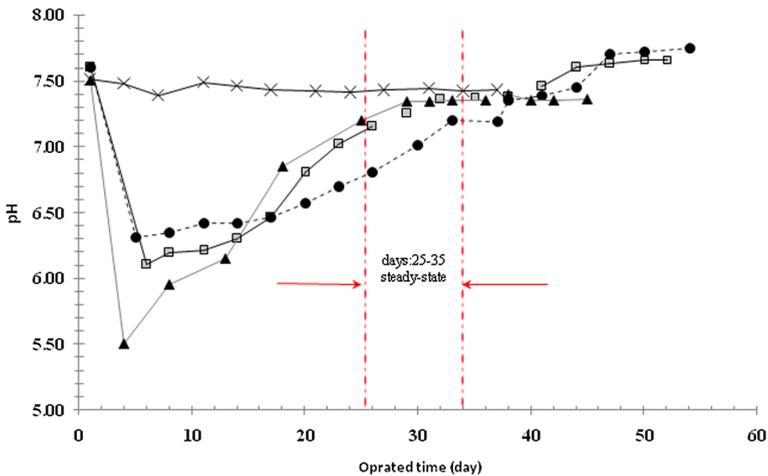


Fig. 6 Profiles of pH in the reactor. *Filled triangle* indicates ratio of 80:20, *filled circle* ratio of 50:50, *empty square* ratio of 20:80, and *multiplication sign* ratio of 0:100

increased with the reduction of PP content, and maximum amount was observed in a ratio of 20:80. The maximum methane production was also obtained in this mixing ratio; therefore, the best efficiency of the experiments is related to this experimental run. Nayono et al. [27] reported that in co-digestion of press water and food waste, the COD elimination at all of the organic loading rates (OLRs) ranged between 53 and 70 %. Also, Shokuh et al. [28], in their study on MSW leachate treatment by anaerobic digestion, observed the COD removal percents of 32, 34, 89, and 96 in mesophilic condition. They stated that the low percent level of COD removal can be related to the relatively low loading of the organic matters.

In Fig. 8, the relationship of biogas production and VS removal was plotted. Based on the obtained data in this study, a linear regression equation was established. The high correlation coefficient (R^2) indicated that there was positive and significant correlation between BPR and

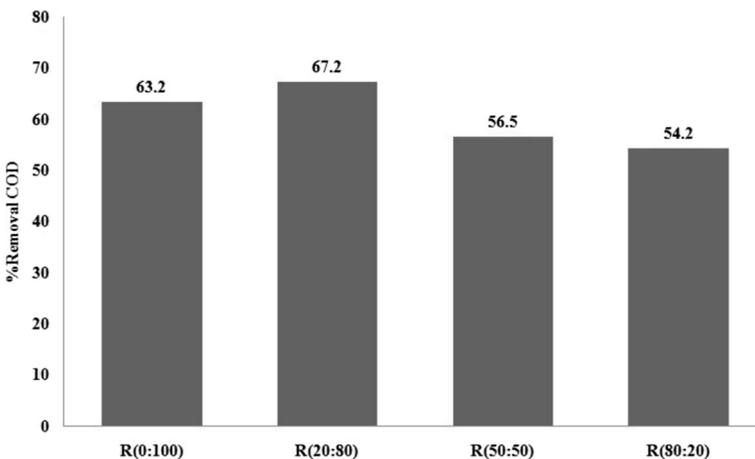


Fig. 7 Removal rates of COD affected by the mixing ratios of potato pulp and cow manure

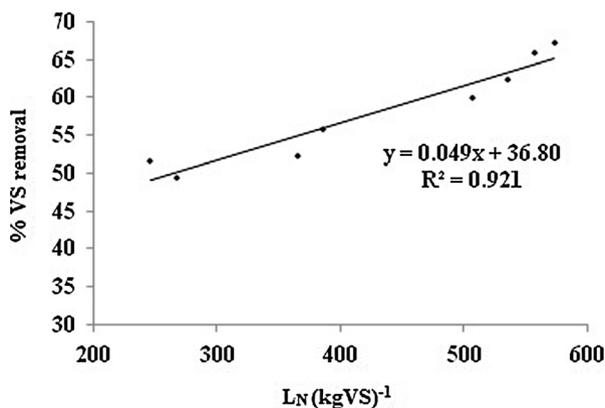


Fig. 8 Correlation of biogas production rate (BPR) and VS removal rate

VS elimination rate. In other words, more BPR implies more organic matter conversation rate and more VS removal, accordingly. Li et al. [29] obtained a linear regression equation between BPR and VS and TS removal rate.

Conclusion

Anaerobic digestion is an applied biotechnology to convert potato wastes to energy that can be produced in potato chips manufactures as by-products. In this study, a single-stage batch digester with continues stirring was built in a laboratory scale to evaluate the performance and efficiency of biogas production from the co-digestion of potato peel (PP) and cow manure (CM) in mesophilic condition, without initial inoculums. Based on the experimental results, it can be concluded that increasing the percent of cow manure in potato peel improves the efficiency of the biogas production. Incorporating PP to CM provides a positive synergism in methane production with the best result of 375 L_N (kg VS)⁻¹ and 92 % energy performance by a mixing ratio of 20:80. The best percent of COD removal was also observed in the co-digestion treatment as 67.2 %.

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