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Anaerobic Co-digestion of Pig Manure, Organic Fraction of Municipal Solid Waste, Fruit Residues of Drinks Industry and Cocoa Residues

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In Colombia, large amounts of residual biomass are generated from different productive sectors that are susceptible to be valorized in the shape of biogas, through anaerobic digestion and co-digestion processes. The present article tries the evaluation of the potential to value in the shape of biogas, four residues that are produced in the country: pig manure, cocoa industry residues, residues of the industry of bottled fruit drinks and organic fraction of municipal solid waste. In an initial stage, a non-agitated test was performed to measure the methane production potential of individual residues (anaerobic digestion) and different mixtures of three residues (anaerobic co-digestion), where the carbon nitrogen ratio (C/N) and the number of grams of volatile solids (gSv) were varied. The evaluated mixtures were constituted with two C/N levels, taking as values 25 and 35. Also, three levels of gSv were considered in the mixtures: 0.5, 1 and 2. The mixtures that obtained better results in the non-agitated tests were then evaluated in agitated experimentation to observe how this variable affects the production of biogas. Mixtures with 0.5 gSv and C/N equal to 35 were found to have the greatest potential for methanization in non-agitated tests. Agitated tests were performed with mixtures of pig manure and fruit residues. For the third component, municipal solid wastes and cocoa industry residues were used. In all the agitated tests, the potential of biogas production was higher than in the non-agitated test.

1. Introduction

The treatment of solid residues turned into a basic topic for governmental policies worldwide, because of the environmental deterioration that the planet suffers. As the uncontrolled increase in solid waste and its lack of management contributes to the emission of greenhouse gases and the generation of volatile organic compounds, among others (Toro et al., 2017). Likewise, it is important to bear in mind that the increase of the population turns out to be a critical factor now of evaluating the pollutant indices generated by the residues; as there is no culture of "reduce, reuse and recycle", that allows to diminish the impact to the environment caused by the human activities (Lett, 2014). To solve this problem, the application of appropriate technologies for the final disposal of residues and wastes has been relied upon, which will allow a rational control of the impact produced. One of the technologies applied for these waste recovery processes is anaerobic co-digestion; which can be defined as the digestion of two or more substrates involving the transformation of organic matter into biogas (methane, 60-70% and carbon dioxide, 30-40%), the production of methane in anaerobic treatment uses a microbiological process for the degradation of organic matter (Mohd et., al 2017). The main factors that determine the behavior of the microorganisms are the environmental conditions (temperature) and the type of organic waste or mixture under study (María González, 2015). The present study focuses on the evaluation of waste generated in Colombia, which represent approximately 65% of the 11.6 million tons generated per year. The study is centered on the evaluation of municipal solid waste (MSW), bottled beverage industry waste (BBIW), pig manure (PM) and cocoa industry waste (CIW), under the effect of

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the agitation in discontinuous reactors and thus to find sources of use of them and as a contribution to the knowledge in subjects of anaerobic co-digestion (Toro et al., 2017).

2. Materials and Methods

Inoculum: The inoculum that was used for all tests was a sludge from a biodigestor located at the sewage plant of Alpina S.A., in Sopo, Cundinamarca (Colombia). This sludge was selected because it comes from a stabilized running system which gives the guarantee of obtaining biogas production.

Substrates and co-substrates: The substrates used for testing were the cocoa industry waste (CIW), pig manure (PM), organic fraction of municipal solid waste (MSW) and bottled beverage industry waste (BBIW). The substrates were previously placed in a freezer at -4ºC, to avoid the change in the physiochemical characteristics. The cocoa industry residues were simulated in the laboratory based on different references found of this industry (Federación Nacional de Cacaoteros, 2013). Cocoa shells and pods were used and obtained from a private farm located in the department of Santander – Colombia. The cocoa species worked for the trial was Trinitarian; this species is caused by the crossing of other two cocoas (Federación Nacional de Cacaoteros, 2013) and is characterized by a wide variability of shapes, sizes, and behavior, being nowadays the cocoa type that prevails in Colombia (Federación Nacional de Cacaoteros, 2013). Pig manure was obtained in Marengo Agricultural Research Center (C.A.M) belonging to the National University located in the municipality of Mosquera (Cundinamarca). The residues come from animals fed on commercial concentrate. The sample of urban solid waste used for the experimentation came from two typical homes in the city of Bogotá; of this only the organic fraction composed of vegetables, fruits and processed foods was taken. Residues of fruit drinks were simulated based on the fruit consumption of a bottled fruit beverage factory in Colombia, the percentage was used in weight of residues that are generated by fruit. In this way, it was determined that the residues that were produced in greater proportion were mango, banana, passion fruit, blackberry and lulo. For the banana, the shell was mainly taken and for the other shells, seeds and bran were used. All residues, except pig manure, went through a process of downsizing and liquefied. To determine the amount of substrate to be used in each of the mixtures, the main physicochemical characteristics of the residues studied were evaluated per the protocols of Cabeza et al. (2016). The values obtained are detailed in Table 1. The volatile solids and total solids allow to determine the amount of organic matter (OM) in the substrate since this is greater than 70%, it is possible to infer that there will be a good biological digestion in the initial stage of each test. Regarding nitrogen, it can be observed that most substrates have a low content of this, which in principle will benefit the system, since not having high concentrations of nitrogen this will not allow the process to be inhibited in the beginning due to the generation of free ammonia derived from the degradation of proteins (Fierro et al., 2014). The lowest concentration of this parameter is presented by the residues of the cocoa industry, and it could be thought that this would affect the balance and requirements of microorganisms during the digestion.

Table 1: Physicochemical characteristics of substrates

SUSTRATES	PARAMETERS				
	TS (%)[b]	VS (%)[b]	DQO (g/L)[a]	NTK (%)[a]	OM (%)[a]
Pig manure	31,47	24,31	25,71	1,88	77,24
Cocoa industry waste	15,94	14,96	10,46	0,99	93,85
Municipal solid waste	22,76	21,24	13,73	1,56	93,32
Bottled beverage industry waste	16,57	15,52	15,25	1,92	93,66

a. Sample on dry base/ b. Sample on wet base

The BMP methodology used in this study is based on the principles described by Owen et al. (1979) and Angelidaki et al. (2009). The tests were carried out in 250 mL bottles by triplicate, with a working volume of 80%. The mixing ratio of the volatile solids of the substrate and inoculum in the individual tests (S/X) was of 1.728 to minimize the inhibition by acidification or ammonium toxicity. The total volume of work mentioned above was completed with distilled water. Then the bottles were closed with plastic lids and sealed with silicone, but not before having measured the corresponding pH of the contents of each one of them, which should be in a range of 6,3-7,8, with an ideal pH of 7 (Kondusamy et al., 2014). Once sealed, the bottles were placed in a thermostatic bath with an automatic controller without agitation at a temperature mesophilic constant of 32°C for 20 days (during the period of the test none of the reactors was fed). Also, some of the mixtures were placed in a plate with continuous agitation of 120 rpm and a constant temperature of 32°C. Methane production was monitored daily by volume displacement, wherein the carbon dioxide present in the biogas was retained by the bubbling of the biogas in a solution of NaOH with alkaline pH, pH>9 (Cendales Ladino, 2011). The anaerobic co-digestion test in discontinuous regime was carried out monitoring eighteen mixtures, each composed of three substrates where PM was always used as co-substrate. The possible combinations of the co-substrates under study were defined, which are detailed in Table 2. Also for each possible combination the C/N was changed in two levels (25 and 35) and the amount of gSv in three different levels (0.5, 1 and 2), with the objective of studying its influence on the production of biogas. The relation of substrates was established in such a way that the C/N relation was reached and the amount of gSv were fixed considering the physicochemical characterization of the substrates used.

Table 2: Description of mixtures used in co-digestion tests

COMBINATION	SUBSTRATES	MIXTURE	C/N	gSv
1	PM, BBIW & MSW	1	25	0.5
		2	25	1
		3	25	2
		4	35	0.5
		5	35	1
		6	35	2
2	PM, BBIW & CIR	7	25	0.5
		8	25	1
		9	25	2
		10	35	0.5
		11	35	1
		12	35	2
3	PM, MSW & CIR	13	25	0.5
		14	25	1
		15	25	2
		16	35	0.5
		17	35	1
		18	35	2

The parameters analyzed for the substrates were the following: Total Solids (ST) per 2540B from the Standard Methods (APHA), Volatile Solids (SV) per D3174 from the American Society for Testing and Materials (ASTM), Chemical Oxygen Demand (COD) per D1252 - 06 from the American Society for Testing and Materials (ASTM), And Kjeldahl Nitrogen (NTK) per D1426-15 from the American Society for Testing and Materials (ASTM).

3. Results and Analysis of Results

The BMP obtained in each substrate is shown in Table 3, where the pig manure has the highest production of methane with 479.25 mL CH_4/gSv, and the bottled beverage industry waste presents the lowest production with 126.33 mL CH_4/gSv. The residues possess different relations C/N being the highest one the CIW with 55, what implies that this one is rich in carbon and poor in nitrogen, which causes that the decomposition of materials occurs more slowly and therefore the multiplication and the development of bacteria is low by the lack of nitrogen, and this would prevent a rapid fermentation of the organic material and in turn, can present losses of carbon in the form of carbon dioxide (CO_2), for anaerobic digestion the bacteria use 25 to 35 times more carbon than nitrogen and the ratio of carbon to nitrogen should be 25-30:1 (Kondusamy et al., 2014), according to the above the substrate that has the closest proximity to this optimal relation is the Pig manure with a C/N of 23.8. Table 4 shows the results of the methane production of the mixtures indicated in Table 2.

Table 3: Methane production of the substrates used in the test

SUBSTRATES	mL CH_4/gSv	C/N
Pig manure	479,25	23,83
Municipal solid waste	329,08	34,69
Cocoa industry waste	251,17	54,98
Bottled beverage industry waste	126,33	49,64

Table 4: Methane production of the mixtures

MIXTURE	mL CH_4/gSv	MIXTURE	mL CH_4/gSv
1	325,33	**10**	349,33
2	219,83	**11**	244,50
3	121,00	**12**	165,17
4	348,67	**13**	340,67
5	271,33	**14**	226,83
6	144,33	**15**	151,83
7	327,33	**16**	364,33
8	237,50	**17**	256,83
9	134,00	**18**	163,33

In Table 5, it is possible to show the mixtures that present a higher production of methane which are: mix 10 with 384 mL CH_4/gSv and C/N 35, mix 16 with 376 mL CH_4/gSv and C/N 35, mix 13 with 360 mL CH_4/gSv and C/N 35 and the mix 1 with 347 mL CH_4/gSv and C/N 25; being subjected under the effect of agitation generates a yield of 18.99% in comparison with the non-agitated mixtures. This performance is due to the constant movement of the substrates; allowing the bacterial population to remain fresh, avoiding crust formation inside the digester, being uniform the bacterial density and mitigating the "dead" spaces that can reduce the volume and sedimentation of the reactor. It is important to emphasize two reasons that allow the increase of biogas production under effects of agitation, which basically are due to the greater contact between the substrate and the bacteria and to avoid the accumulation of foam in the upper part of the digester (Moreno, 2011).

Table 5: Methane production of the mixtures

MIXTURE	mL CH_4/gSv (Without agitation)	mL CH_4/gSv (With agitation)
1	325,33	347
2	219,83	303,80
4	327,33	334,30
9	151,83	275,20
10	348,67	384
13	349,33	360
15	165,17	305,20
16	364,33	376
18	163,33	295,80

Figure 1 compares the results of the BMP produced by each of the mixtures subjected under agitation and without agitation with a C/N 25. It is evident that the mix 1 presents the highest methane production with 347 mL CH_4/gSv as opposed to the non-agitated one that generates 325,33 mL CH_4/gSv implying a 6.24% increase in biogas production. These mixtures are composed of residues PM, BBIW and MSW with 0.5 gSv. On the other hand, in Figure 2, one can observe the results of each of the mixtures with a C/N 35, where it is evident that the mix 10 is the one that presents a greater production of methane with 384 mL CH_4/gSv in comparison with the non-agitated of 348,67 mL CH_4/gSv implying an increase of 9.20% of biogas. These mixtures are composed of residues PM, BBIW and CIW with 0.5 gSv

The relation of the C/N in function of the production of biomethane in anaerobic digestion is irrelevant as investigated by the Department of Engineering and Industrial Information and of Biological and Pharmaceutical Environmental Sciences and Technologies of the University of Naples (Giovanna Guarino, 2016), while the results obtained in the present study show a significant influence of C/N at the time of biogas production. Also, in Figure 3 it can be identified that mixtures that contain 0.5 gSv are the ones that generate a higher production of biogas, since when the load is higher, there is a risk of inhibiting the process, making it unstable; generating a more frequent observation and analysis (Bosch Martí, 2011).

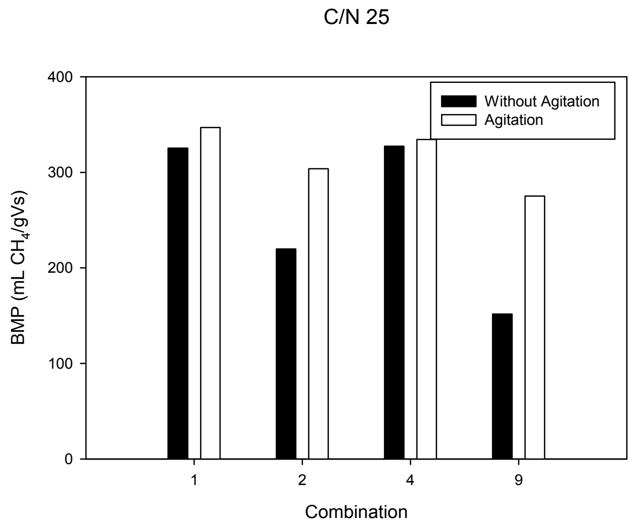

Figure 1: Potential of methane production of mixtures with C/N 25

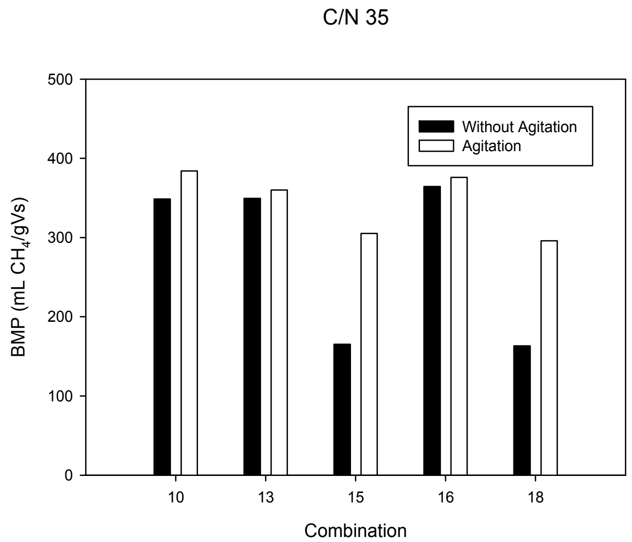

Figure 2: Potential of methane production of mixtures with C/N 35

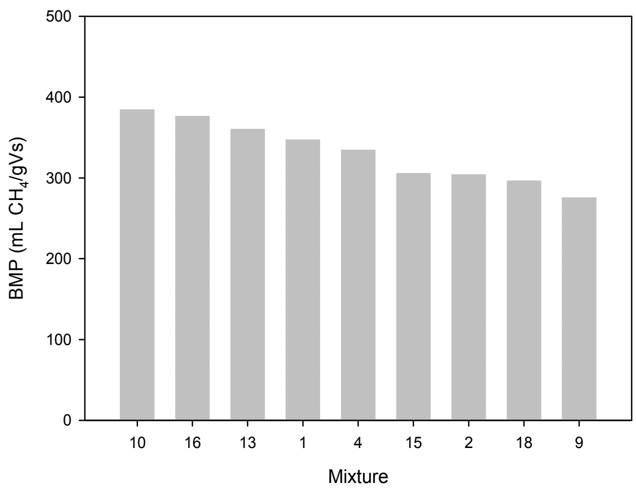

Figure 3: gSv index of the mixtures

4. Conclusions

According to the four residues evaluated (pig manure, municipal solid waste, cocoa industry waste and bottled beverage industry waste), it is observed that the mixtures that generated higher methane are those who contain pig manure (PM) and bottled beverage industry waste (BBIW). However, individual BMP tests show that pig manure was the largest producer with 479.25 mL CH_4/gSv, followed by municipal solid waste whose production was 329.08 mL CH_4/gSv. In addition, the experimental results indicate that the anaerobic co-digestion of the combinations in mixtures containing C/N 35 and a gSv of 0.5 generate a better efficiency of 5.14% in the yield of the low biogas production the agitation effect, as compared to all mixtures and combinations which were not subjected to this factor. In the methodology of waste recovery, the use of factors such as agitation, generates an important contribution to the moment of the production of BMP, since it favors the transfer of substrate to each population of bacteria, establishing a balance and a good homogenization, giving a greater efficiency to the treatment applied to the residues worked in the present project.

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