Ciência e Tecnologia de Alimentos
Print version ISSN 0101-2061

Ciênc. Tecnol. Aliment. vol.20 no.2 Campinas May/Aug. 2000

doi: 10.1590/S0101-20612000000200010

CASSAVA WASTEWATER (MANIPUEIRA) TREATMENT USING A TWO-PHASE ANAEROBIC BIODIGESTOR[1]

Ana Cláudia BARANA[2,*], Marney Pascoli CEREDA[3]

SUMMARY

A two-phase anaerobic biodigestor was employed in order to analyze methane production with different *manipueira* organic loading rates. The acidogenic phase was carried out in a batch process whereas the methanogenic in an up-flow anaerobic fixed bed reactor with continuous feeding. The organic loading rates varied from 0.33 up to 8.48g of Chemical Demand Oxygen (COD)/L.day. The highest content of methane, 80.9%, was obtained with organic loading rate of 0.33g and the lowest, 56.8%, with 8.48gCOD/L.d. The highest reduction of COD, 88.89%, was obtained with organic loading rate of 2.25g and the lowest, 54.95%, with 8.48gCOD/L.d. From these data it was possible to realize that anaerobic biodigestion can be managed in at least two ways, *i.e.,* for energy production (methane) or for organic loading reduction. The organic loading rate should be calculated as part of the purpose of the treatment to be accomplished.

Keywords: anaerobic biodigestion; biogas; wastewater; cassava; methane.

RESUMO

TRATAMENTO DE ÁGUA RESIDUAL DO PROCESSAMENTO DE MANDIOCA (MANIPUEIRA) UTILIZANDO BIODIGESTOR ANAERÓBIO DE DUAS FASES. Um biodigestor anaeróbio de duas fases foi utilizado para se analisar a produção de metano com diferentes cargas de entrada de *manipueira*. A fase acidogênica foi realizada em processo de batelada e a metanogênica em biodigestor anaeróbio de fluxo ascendente e leito fixo com alimentação contínua. As cargas orgânicas de entrada variaram de 0,33 a 8,48 gDQO (Demanda Química de Oxigênio)/L.dia. A maior porcentagem de metano encontrada foi de 80,9%, com carga orgânica de 0,33g e a menor, 56,8%, obtida com 8,49gDQO/L.d. A maior taxa de redução de DQO foi de 88,89%, obtida com carga orgânica de 2,25g e a menor, 54,95%, com 8,48gDQO/L.d. Analisando-se os dados apresentados verificou-se que a biodigestão anaeróbia pode ser conduzida, pelo menos, de duas maneiras, ou seja, para produção de energia (metano) ou para redução de carga orgânica. A carga orgânica de entrada deve ser calculada em função do objetivo a ser alcançado com a biodigestão anaeróbia.

Palavras-chave: biodigestão anaeróbia; biogás; resíduo; mandioca; metano.

1 — INTRODUCTION

Cassava flour mills produce solid and liquid residues. Concerning liquid residues, there are the wash water and the water extracted from the roots by squeezing (*manipueira*) [7]. The latter is toxic due to the presence of Lynamarin, a cyanogenic glycoside that is enzymatically hydrolyzed to cyanide and is a polluting source with high content of organic matter, COD 40-100 gO_2/L [1, 6, 7, 12, 16].

Cassava flour mills are generally concentrated in specific areas, commonly close to streams and brooks causing great environmental pollution. Even nowadays there are discharges into rivers or on soil without any kind of treatment. Another problem faced by cassava flour producers is related to firewood, the fuel employed by them to dry flour, something that is becoming very scarce these days. An alternative solution to satisfy both ecological and energy problems is the use of anaerobic biodigestion and the utilization of biogas produced (methane gas) as fuel for drying flour. Biogas technology could contribute to improve environmental protection in the food production sector in most developing countries [22].

Anaerobic microorganisms can grow on substrates containing cyanide [4]. On the other hand, aerobic microorganisms are sensitive to cyanide because it affects ATP formation, acting on the oxidative phosphorilation by combining with the cytochrome oxidase, inhibiting electron transport [4].

Manipueira treatment in one phase reactor with agitation is not feasible due to excessive medium acidification, what drives the biodigestor to an unstable state [11]. Wastewater with high starch levels, when treated in one-phase anaerobic biodigestor, has a rapid conversion to organic acids that can acidify the column and inhibit methanogenic bacteria [6].

For anaerobic digestion of hydrolyzable carbohydrates, two-phase process is more stable when compared with one-phase process [5, 6, 8]. Therefore it may be advantageous to apply a two-stage process when treating wastewater with large particulate organic fractions [23].

Studies showed that *manipueira* treatment is technically viable in up-flow anaerobic reactors with separation of acidogenic and methanogenic phases [1, 12, 16]. In those conditions, good treatment efficiency was obtained with HRT (Hydraulic Retention Time) of one day in the acidogenic and three days in methanogenic phase.

BARANA [1], studying methanogenic phase in an up-flow anaerobic fixed bed reactor for *manipueira* treatment, concluded that methanogenic phase was stable with organic loading rates between 0.33 and 5.24gCOD/L.d.

The objective of this work was to asses *manipueira* treatment and quantify the methane production by methanogenic phase in an upflow fixed bed reactor with different organic loading rates.

2 — MATERIALS AND METHODS

2.1 – Substrate

Manipueira was collected in December 1994 in a cassava flour factory in São Paulo State (**Plaza Industry**, of Santa Maria da Serra city), just below the press. After that *manipueira* was kept at rest for 30 minutes at 4ºC so that starch could be removed by sedimentation process.

2.2 – Acidogenic fermentation

A plastic container with a 60 litter capacity was filled with 50 litters of manipueira. Fermentation occurred at room temperature, around $25^{o}C$ and the fermentation agents were microrganisms spontaneously present in the substrate and capable of converting carbohydrates to organic acids [5]. The pH was measured daily and corrected when necessary with an alkaline solution (50% NaOH, w/v) so that it was maintained between 5.5 and 6.0, a feasible interval for acidogenic fermentation and amylolytic enzyme activity [5]. At the end of acidogenic fermentation (14 days), detected by pH stabilization, the following factors were characterized in *manipueira:* COD, total and volatile solids and organic acids, total cyanide and minerals. It was then frozen at $-20^{o}C$ and stored.

2.3 – Methanogenic fermentation

The reactor, an up-flow anaerobic fixed-bed reactor, was built with two PVC (polivinil cloride) pipes arranged vertically one inside the other (*Figure 1*). The smaller pipe was filled with PVC rigid rings, with 3 cm length and 2.5 cm diameter and used as fixed bed. Between the two pipes, water was kept in constant temperature ($32 \pm 1^{o}C$) with the use of three fishbowl type heaters, arranged in different heights and connected to a thermostat. The useful volume of the reactor, internal column, was 9.33 litters. In order to have a 3-day- HRT [17], a constant flow rate of 3.11L/d was considered. Methanogenic phase was divided into 5 periods (from A to E) differentiated by organic loading rates administered daily. Besides, each period was studied for 4 HRT (12 days).

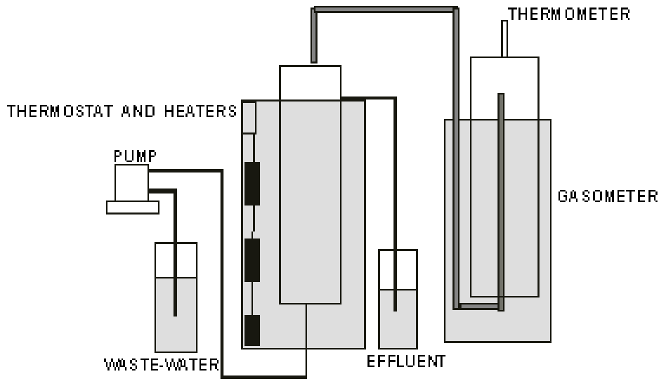

FIGURE 1. Schematic diagram of methanogenic reactor and gasometer.

Organic loading rates were 0.33, 1.10, 2.25, 5.24 and 8.48gCOD/L.d. Data were not collected in the first HRT of each period so as to obtain only steady-state information. The influent of methanogenic biodigestor was neutralized to pH between 6.5 and 7.0 by addition of an alkaline solution (50% NaOH, w/v).

Wastewater was fed to the bottom of the column using a variable speed pump (Masterflex). The treated liquid flowed through the top of the reactor and the gas so produced was released through its proper exit, located on the top of the reactor, being collected through a telescope type gasometer.

2.4 – Gasometer

The gasometer was formed by two PVC pipes: one of 10cm and another of 15cm diameter, both of them with 100cm length. The larger tube was filled with an acidified saline solution (25% sodium chloride and 5% concentrated sulfuric acid) [12], and the smaller one, closed on top, was left floating on that solution. Through a U-form PVC pipe of 2cm diameter, the gas was conducted through a 10cm diameter tube that was proportionally elevated for gas production. The volume of gas produced was calculated multiplying the area of the tube ($39.27cm^2$) by the moved height (measured). Gas volume correction was made considering its moisture and temperature according to [12].

2.5 – Analyses

In order to assess the treatment efficiency, pH, COD, and total and volatile solids were carried out every day according to [13], alkalinity and volatile acidity were also carried out every day according to [20], organic acids were done in the end of each period by HPLC according to [3], total cyanide, once in the last day of each period according to [9], biogas volume was measured daily and qualified in the last three days of each period according to [12]. Macro and micro nutrients were determinate only in the substrate, carbon and nitrogen according to [13], sulfur and boron according to [2], phosphorous according to [19] , calcium, magnesium, copper, potassium, iron, manganese and zinc by atomic absorption spectrophotometry according to Handbook Perkin-Elmer Corp. [18].

3 — RESULTS AND DISCUSSION

The results of physical and chemical characteristics of *manipueira* utilized in this study are shown in Table 1.

TABLE 1. Chemical composition of *manipueira*.

Parameters	1	2
Moisture (%) (w/v)	97.28	94.08
Total solids (%) (w/v)	2.72	5.92
Volatile solids(%) (w/v)	0.98	3.01
COD (gO_2/L)	20.93	42.80
PH	6.92	7.95
Alkalinity (mg $CaCO_3/L$)	5.80	10.77
Acidity (mg CH_3COOH/L)	7.10	18.50
Acidity/Alkalinity	1.22	1.72
Carbon (%) (w/v)	2.10	2.36
Nitrogen (%) (w/v)	0.67	0.38
Relation C/N	3.13	6.21
Phosphorous (%) (w/v)	367	171
Potassium (%) (w/v)	1.98	11.20
Calcium (%) (w/v)	160	236
Magnesium (%) (w/v)	360	340
Sulfur (%) (w/v)	72	178
Iron (%) (w/v)	3.7	5.5
Zinc (%) (w/v)	1.7	N. D.
Copper (%) (w/v)	0.7	0.9
Manganese (%) (w/v)	1.4	3.0
Boron (%) (w/v)	N. D.	traces
Cyanide (ppm)	33.59	16.60

N. D. - Not detected
1 - *manipueira* utilized in this experiment
2 - *manipueira* utilized by LACERDA [17]

As shown in *Table 1*, the two samples of *manipueira* are divergent. *Manipueira* quality depends on harvest time, age of the roots, type of equipment used for the production of flour and cassava variety [10]. The *Manipueira* used in this experiment was collected in December, out of harvest time, at Plaza Industry that processes some varieties of cassava, while the *manipueira* studied by LACERDA [17] was collected in June, harvest time, in the Model Plant of Cassava Flour Production of the State University of São Paulo where only *Branca de Santa Catarina* cassava variety was made use of.

In this kind of wastewater treatment, bacteria can survive at cyanide levels between 20 and 40ppm [21]. The utilized *manipueira* presents total cyanide level of 33.59ppm.

In anaerobic digestion, the ratio of carbon and minerals, C:K:Ca:Mg, should be respectively, 30 : 0.1 : 0.04 : 0.025 [14]. *Manipueira* utilized presented the ratio 30 : 2.81 : 0.23 : 0.52, much higher than recommended by GHOSH [14]. SOUZA [21] refers to C/N and C/P ratio of about 25 and 150, respectively. The *Manipueira* utilized presented 3.12 and 0.006 for C/N and C/P ratios, respectively. Even with these values, the biodigestor worked well. LACERDA [17] and FERNANDES JR. [12], working with an anaerobic two-phase biodigestor, also utilized *manipueira* with C/N and C/P ratio smaller than suggested by SOUZA [21]. In spite of it, the methanogenic biodigestor ran properly.

During the whole experiment the reactor worked in stable conditions. From *Table 2*, variations of organic matter in influent and effluent can be accompanied with corresponding degree of the treatment of the system.

TABLE 2. Daily average values of influent and effluent organic loading.

Period	Organic loads (g COD/L.d)	COD concentration (g O_2/L)		COD reduction (%)
		Influent	Effluent	
A	0.33	1.00	0.33	67.00
B	1.10	3.30	0.40	87.87
C	2.25	6.75	0.75	88.89
D	5.24	15.72	2.25	85.68
E	8.48	25.44	11.46	54.96

It can be observed in *Table 2* that periods with highest COD reduction, B, C and D, had organic load rate between 1.10 to 5.24g. With organic load of 5.24gCOD/L.d, COD reduction in effluent began to drop. This demonstrates that the highest reduction of COD in effluent occured with organic load rate between 2.25 and 5.24g.

Values of alkalinity and volatile acidity are shown in Table 3.

TABLE 3. Daily average values of alkalinity and volatile acidity of the effluent.

Period	Volatile Acidity ($mgCH_3COOH/L$)	Alkalinity ($mgCaCO_3/L$)	AV/AL Ratio
A	244	726	0.34
B	200	1,146	0.17
C	252	2,380	0.10
D	792	3,070	0.25
E	4,520	6,706	0.67

VA – Volatile acidity
AL – Alkalinity

8g/L do not cause instability in the biodigestor if pH is maintained in an optimum range to methanogenic bacteria [21]. In stable conditions, reactors have values of volatile acidity between 100 and 300mg/L [15]. *Table 3* indicates that volatile acidity values obtained in this experiment would be limiting with influent organic loadings of 5.24 and 8.48gCOD/L.d [15], but it did not pose any problems considering that pH was maintained in a safety range to methanogenic bacteria (6.5 and 7.0) [21].

The relation acidity/alkalinity is an important indicator to denote the instability of the process. The reactor is stable for values ranging from 0.1 to 0.3, whereas around 0.4, it shows instability, and for values above 0.8, it collapses [21]. In this experiment the relation was stable for loadings between 0.33 and 5.24gCOD/L.d.

The analysis of the *manipueira* after acidogenic step detected tartaric, succinic, lactic, acetic, propionic, iso-butyric, butyric and iso-valeric acids. The acids present at higher concentrations were lactic (82%), butyric (6%) and acetic (5%). FERNANDES JR. [12] also detected predominance of lactic acid production in *manipueira* fermented in an acidogenic reactor. The methanogenic effluent analysis has not detected organic acids that were probably completely consumed in this phase.

From *Table 4* it is possible to realize that there is higher methane production with higher loads, despite its content on biogas that decreases with increasing load. It can be observed in *Table 5* that biogas calorific power is calculated in agreement with its methane content.

TABLE 4. Production of methane in relation to the consumed organic load.

Period	COD (g O_2/L)		Methane	
	Influent	Consumed	L/gCOD_c.day^{-1}	% in biogas
A	1.00	0.66	0.88	80.85
B	3.30	2.88	0.53	69.08
C	6.75	6.00	0.69	69.20
D	15.72	13.47	0.52	67.93
E	25.44	13.98	1.04	56.80

COD_c - consumed COD

TABLE 5. Calorific power of the biogas obtained in the present experiment.

Period	CH_4 (%)	Calorific power (kcal $N^{-1}m^3$)
A	80.85	6,41
B	69.08	5,33
C	69.20	5,34
D	67.93	5,22
E	56.80	4,20

4 — CONCLUSIONS

As mentioned previously, when devising an anaerobic digestion system, the objectives must be adequately established, whether for energy production or for organic loading reduction. The incoming organic load defines the final quality both of biogas and the remaining residues.

5 — REFERENCES

[1] BARANA, A.C. Estudo de carga de manipueira na fase metanogênica de reator anaeróbio de fluxo ascendente e leito fixo. Botucatu, 1996. 82p. Dissertação de Mestrado - Faculdade de Ciências Agronômicas, Universidade Estadual Paulista (UNESP). [Links]

[2] BATAGLIA, O.C., FURLANI, A.M.C., TEIXEIRA, J.P.F, GALLO, J.R. Métodos de análises química de plantas. **Bol. Técn. Inst. Agron. Campinas**, n. 78, p. 1-48, 1983. [Links]

[3] BRABET, C.; DUFOUR, D. El almidón agrio de yuca. Producción y estudio de las propriedades fisicoquímicas. **Simposio en carbohidratos***,* Escuela Politécnica Nacional de Quito, Quito, 4-6 de octubre de 1993. [Links]

[4] CEREDA, M.P. *et al*. Atividade respiratória em microrganismos isolados de líquido residual de fecularias. **XI Congresso Brasileiro de Microbiologia**. Florianópolis, 1981. [Links]

[5] CEREDA, M.P. *et al*. Tratamiento anaeróbio en dos fases de suspensiones amiláceas I-Fase acidogênica. **Rev. Agroquim. Tecnol. Aliment**., v. 26, p. 101-108, 1986. [Links]

[6] CEREDA, M.P. *et. al*. Tratamento anaeróbio em duas fases de suspensões amiláceas II. fase metanogênica. Influência da adição de CN^-. **Revista de Microbiologia**, v. 21, n. 1, p. 73-78, 1990. [Links]

[7] CEREDA, M.P. Caracterização dos resíduos da industrialização da mandioca. In: CEREDA, M.P. (Ed). **Resíduos da industrialização da mandioca**. São Paulo: Paulicéia, 1994, p. 11-50. [Links]

[8] COHEN, A. *et al.* Influence of phase separation on the anaerobic digestion of glucose-II. Stability and kinetic responses to shock loading. **Water Research**, v. 15, p. 449-455, 1982. [Links]

[9] COOKE, R.D. An enzymatic assay for total cyanide content of cassava (*Manihot esculenta,* Crantz). **J. Sci. Food Agric**., v. 29, p. 345-52, 1978. [Links]

[10] DEL BIANCHI, V.L. Balanços de massa e energia do processamento de farinha de mandioca em uma empresa de médio porte do Estado de São Paulo. Botucatu, 1998. 107p. Tese de Doutorado - Faculdade de Ciências Agronômicas, Universidade Estadual Paulista

(UNESP). [Links]

[11] FERNANDES JR., A. Ocorrência de instabilidade e forma de seu controle na digestão anaeróbia de manipueira, em reator de bancada de mistura completa. Botucatu, 1989. 118p. Dissertação de Mestrado - Faculdade de Ciências Agronômicas, Universidade Estadual Paulista (UNESP). [Links]

[12] FERNANDES JR., A. Digestão anaeróbia de manipueira em separação de fases: cinética da fase acidogênica. Botucatu, 1995. 139p. Tese de Doutorado - Faculdade de Ciências Agronômicas, Universidade Estadual Paulista (UNESP). [Links]

[13] GREENBERG, A.E., CLESCERI, L.S., EATON, A.D. (Ed) 1992. **Standard Methods for the examination of water and wastewater**. American Public Health Association, Washington. [Links]

[14] GHOSH, S.; KLASS, D.L. Two phase anaerobic digestion. **Process Biochem**., v. 13, p. 15-25, 1978. [Links]

[15] HENZE, M., HARREMOES, P. Anaerobic Treatment of wastewater in fixed bed film-reactors. A literature review. **Wat. Sci. Technol**, v. 15, p. 1-101, 1983. [Links]

[16] HIEN, P.G., OANH, L.T.K., VIET, N.T., LETTINGA, G. Closed wastewater system in the tapioca industry in Vietnam. **Wat. Sci. Tech.**, v. 39, n. 5, p. 89-96, 1999. [Links]

[17] LACERDA, T.H.M. Estudo cinético da fase metanogênica de substrato de manipueira. Botucatu, 1991. Tese de Doutorado - Faculdade de Ciências Agronômicas, Universidade Estadual Paulista (UNESP). [Links]

[18] PERKIN-ELMER CORP. 1966. **Analytical method for absorption spectrophotometry**. Perkin-Elmer, Connecticut. [Links]

[19] RODELLA, A.A. Métodos de análises quantitativa inorgânica em caldo de cana, vinhaça e melaço. II – Nova marcha analítica para determinação de cálcio, magnésio, potássio, enxofre e fósforo em um mesmo extrato. **Bras. Açucareiro**, v. 1, p. 43-50, 1976. [Links]

[20] SILVA, M.O.S.A. 1977. **Análises físico-químicas para controle das estações de tratamento de esgotos**. Companhia de Tecnologia e Saneamento Ambiental, São Paulo. [Links]

[21] SOUZA, M.E. Fatores que influenciam a digestão anaeróbia. **Rev. DAE**, v. 44, p. 88-94, 1984. [Links]

[22] TENTSCHER, W.A.K. Biogas technology as a component of food processing systems. **Food Technology**, jan, p. 80-85, 1995. [Links]

[23] VAN HAANDEL, A.C., LETTINGA, G. (1994) **Anaerobic sewage treatment**: A practical guide for regions with a hot climate. John Wiley and Sons, Chichester. [Links]

[1] *Recebido para publicação em 26/08/99. Aceito para publicação em 17/07/00.*

[2] *Departamento de Zootecnia e Tecnologia de Alimentos, Univer-sidade Estadual de Ponta Grossa, Praça Santos Andrade s/n, Ponta Grossa-PR, CEP 84010-330.*

[3] *Centro de Amidos e Raízes Tropicais, Universidade Estadual Paulista, C.P. 237, Botucatu-SP, CEP 18603-970.*

[*] *A quem a correspondência deve ser enviada.*

SBCTA

Av. Brasil, 2880
Caixa Postal 271
13001-970 Campinas SP - Brazil
Tel.: +55 19 3241.5793
Tel./Fax.: +55 19 3241.0527

e-Mail
revista@sbcta.org.br