METHANE PRODUCTION IN ANAEROBIC DIGESTION OF ORGANIC WASTE FROM RECIFE (BRAZIL) LANDFILL: EVALUATION IN REFUSE OF DIFERENT AGES

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Abstract - This work focuses on monitoring the generation of biogas by biochemical methane potential (BMP) assays, commonly used to assess anaerobic biodegradability of solid and liquid wastes under controlled conditions. The experiment employed 5 g of substrate of both refuses (fresh and one-year-old wastes), digested with 250 mL of inoculum in 1 L flasks as bioreactors (all of them in triplicate, operating under batch conditions at ± 35 ºC). Despite the difference of age of both refuses evaluated, there was no significant differences in volume (near 1800 mL) and composition (55% methane) of biogas generated in 80 days of incubation under mesophilic conditions. The important parameters of both refuses (such as moisture content, volatile solids and chemical oxygen demand) also showed very similar initial values.
Keywords: Biochemical methane potential (BMP); Hydrogen sulfide; Methane; Odor; Municipal solid waste (MSW).

INTRODUCTION

In Brazil, landfill is the main destination of urban refuse, due to operational factors as well as cost (Alcantara, 2007). According to data from the Brazilian Geography and Statistics Institute (IBGE, 2008, in the Brazilian abbreviation), 50.2% of the refuse is disposed of in landfills. In developing countries such as Brazil, about 50% of the municipal solid waste is composed of organic matter (Alves, 2008; Bidone and Povinelli, 1999). This points to the importance of studying the behavior of such refuse in

the landfill, its degradation kinetics and the parameters that influence the stabilization process of the refuse organic fraction the most, particularly in an anaerobic environment.

A landfill is a complex ecosystem, in which physical, chemical and biological processes interact with each other in the degradation of organic matter, resulting in the generation of liquid refuse (leachate) and gaseous refuse (organic, inorganic, odorant) (Alcantara, 2007). The gas generation in landfills is influenced by factors such as the environmental humidity, the refuse nature, its physical state, pH,

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temperature, buffering capability, nutrient availability and oxygenation rate (Castilhos Jr. *et al.*, 2003). Anaerobic digestion is a process in which a combination of bacteria acts to degrade the refuse through different mechanisms and biodegradation phases. The efficiency of the anaerobic digestion process depends directly on the environment, the operation and the start up conditions of the process. In this case, the bacteria must find an oxygen-free environment, with pH close to neutral, suitable temperature, and enough humidity, nutrients and alkalinity, among other parameters relevant to the process (Rajeshwari *et al.*, 2000; Tchobanoglous *et al.*, 1993).

Under anaerobic conditions, the biodegradable refuse fraction is biologically converted into a gas, in which the main constituents are methane, carbon dioxide, nitrogen, oxygen, ammonia, hydrogen, sulphur compounds, and carbon monoxide. Other gases in trace level concentration, usually below 1% in volume, might present a risk to human health, due to the toxicity that many of the compounds present (Allen *et al.*, 1997; Castilhos Jr. *et al.*, 2003; Pagé *et al.*, 2007; Rasi *et al.*, 2011; Tchobanoglous *et al.*, 1993).

According to Capelli *et al.* (2007), another important aspect regarding the environmental impact of landfills is the emission of odor associated with its management operations and final deposition of refuse under anaerobic conditions. Landfills are among the main odor sources and are responsible for the emission of a variety of odorant gases, most of them present in low concentrations (Bowly, 2003; Pagé *et al.*, 2007; Sironi *et al.*, 2005). Although the landfill odor is the result of a complex mixture of several compounds (Stretch *et al.*, 2001), the most representative among them in terms of odor is hydrogen sulfide (H_2S) (Kim *et al.*, 2005; Kim, 2006), together with other organosulphur compounds, aldehydes and carboxylic acids. The combination of the individual odors of these compounds (all with different limits of detection) gives the characteristic odor of the landfill gas (Karnik *et al.*, 2003; Odorizzi *et al.*, 2003). USEPA (1991) observed that the landfill odor originates both from the refuse degradation process (decomposition anaerobic phases) and from the previously disposed refuse in the landfill (painting products, solvents, pesticides, adhesives, etc.). This odor results mainly from chemical groups such as organosulphur compounds, esters, alkylbenzenes, limonene, among other hydrocarbons responsible for the characteristic landfill odor. For Senante *et al.* (2003), the odor of landfills has as main sources the leachate, fresh refuse and biogas. In this case, the odorant compounds can belong to the following chemical groups: sulphur compounds, nitrogen compounds, aldehydes, acids, ketones, alcohols, aromatic compounds, esters,

and chlorinated compounds. Still, although hydrogen sulfide is the main odorant present in landfill gas, due to its very low limit of odorant perception, other compounds are also responsible for the characteristic landfill odor (Haarstad *et al.*, 2003). Odorizzi *et al.* (2003) point to two techniques to determine odor: analytical methods, which determine the chemical composition of odorant gases; and olfactometry, a sensorial method which measures the human perception of odor. The analytical methods include, for example, portable instruments and gas chromatography (Karnik *et al.*, 2003; Pagé *et al.*, 2007; Schirmer, 2004). Regarding olfactometry, the detector for odor evaluation is the olfaction system, in charge of discriminating and identifying the odorant compounds (Belli Filho and Lisboa, 1998).

In accordance with Rasi *et al.* (2011), the production and composition of the generated biogas might vary temporally and spatially in the landfill, due to the different ways the landfill is filled or even the diversity of materials used to fill it. The biogas composition will depend on other properties of these residues. These properties can comprise the kind of refuse (composition) and age, humidity, pH, temperature, density, etc. (USEPA, 1991).

Important parameters to determine the organic matter stabilization are the ratio cellulose/lignin (C/L), the volatile solid content (VS) of the residual mass (broadly employed due to its low cost; besides, it is easy to obtain), and biochemical methane potential (BMP) analysis (Hansen *et al.*, 2004; Kelly *et al.*, 2006). The biochemical methane potential (BMP) assay can measure a small fraction of refuse, usually incubated with inoculums and in an anaerobic environment, that can be effectively converted into biogas. Besides those, complementary parameters might be the chemical oxygen demand (COD), alkalinity, and the sample humidity content. The rate at which the substrates will degrade is highly dependent on these properties (Labatut *et al.*, 2011).

Many authors employed the BMP method (or similar methods) in order to verify the methane generation potential from a certain amount of refuse on a small scale. Speed, simplicity and low cost are some of the advantages which make BMP a suitable method used to estimate the generation of biogas from organic refuse (Alves, 2008; Angelidaki *et al.*, 2009; Hansen *et al.*, 2004; Kelly *et al.*, 2006; Labatut *et al.*, 2011; Maciel, 2009; Maciel and Jucá, 2011). Despite de number of studies available in the literature, the comparison of biodegradability data between them is a hard task, due to the diversity of experimental conditions, such as substrate and inoculums amounts, inoculum nature, the flask headspace volume, environmental parameters, etc., besides the

different units in which results are presented (Angelidaki *et al*., 2009).

This study monitored the generation of biogas (generation rate and composition) from the degradation of the organic fraction of municipal solid waste of two different ages (fresh and 1 year old) from Recife (Brazil), in batch reactors using the BMP method. Besides the evaluation of the biogas generation potential of this refuse, the study monitored methane, carbon dioxide and hydrogen sulfide gases (the latter as odorant) throughout the biodigestion period, in order to follow the evolution of gas formation in the different phases of refuse degradation.

MATERIALS AND METHODS

Refuse and Inoculum Characteristics

The refuse was collected at the Jaboatão dos Guararapes municipal landfill, which serves the metropolitan region of Recife, Brazil. This region has, nowadays, about 3.3 million inhabitants, 43% of these correspond to the city of Recife (Recife, 2012). Only the organic fraction was chosen to be worked with, and plastic, textile, metal, paper, and wood (the last two with high lignin content) artifacts were removed, as well as others with difficult or prolonged degradation time. The procedures of sampling (dug up with a backhoe) followed Method NBR 10.007 (ABNT, 2004).

Organic refuse of two different ages were evaluated (1 day, before burial, and 1 year) in order to assess the biogas generation potential of each one, as well as the hydrogen sulfide (H_2S) emissions resulting from the biodigestion of each one. These two ages was chosen according to ease of access as well as the short time of landfill operation. In order to guarantee homogeneous samples, young refuse was collected in three different waste piles and the old refuse at three points of the one year old cell (three subsamples of each refuse); these samples were homogenized, as described in Method NBR 10.007. The amount of refuse necessary for all the characterizations of the sample (assays and analysis) was 1 kg of each refuse.

Haarstad *et al*. (2003) claim that different kinds of refuse yield different kinds of odor. Besides that, the biogas composition is highly dependent on the refuse composition and its decomposition phases (Allen *et al*., 1997). The concentration of trace compounds tends to decrease with the refuse age (Knox *et al*., 2005), and that is why it is important to evaluate refuses of different ages and, therefore, different decomposition stages.

The refuse was collected on the same day at the municipal landfill in Recife and was preserved in plastic bags. The refuse was dried in an oven at 60 ºC up to the point where no mass variation was observed. The refuse was then ground, presenting approximately the following granulometric ranges, in % of retained mass measured in 5 sieves: 22% Mesh/ Tyler 65 (0.212 mm); 28% Mesh/Tyler 48 (0.297 mm); 34% Mesh/Tyler 28 (0.590 mm); 12% Mesh/Tyler 14 (1.18 mm); 4% Mesh/Tyler 8 (2.36 mm). The grinding aims to guarantee the homogeneity, besides increasing the refuse superficial area, because the size of the substrate particles is an important parameter in the biogas production rate (process reactivity) (Angelidaki *et al*., 2009; Bidone and Povinelli, 1999; Labatut *et al*., 2011).

The inoculums relative volume used in the experiment can vary a lot, depending on its characteristics (Angelidaki *et al*., 2009). In this study, the substrate/inoculum ratio kept the same proportion as that in the studies of Alves (2008) and Maciel (2009), that is, 1:50. Anaerobic digestion sludge was used as inoculum, from the wastewater treatment plant in Recife, the same plant which supplied the sludge used in the Alves (2008) and Maciel (2009) studies.

BMP Assays: Sample Preparation

The biodigesters consisted of 1 liter borosilicate flasks, sealed with lids with manometer and valves for the discharge and biogas monitoring. Thus, in each flask, the equivalent of 5 grams of substrate (dry matter) and 250 mL of inoculum were deposited. Each assay was performed in triplicate, so that the reproducibility of assays was guaranteed. Blank assays were also employed, that is, flasks (also in triplicate) containing only 250 mL inoculum without any substrate. The average methane produced by the blanks, due to the presence of inoculum only, was subtracted from the methane production in flasks containing substrate + inoculum. Table 1 summarizes the sample conditions.

Table 1: Characteristics of refuse used in the experiment.

Assay (sample)	Waste age	Observations
NW[1]	New waste (same day)	Flask with fresh refuse, dryed in incubator and ground.
OW[2]	One-year-old waste	Flask with one year refuse, dryed in incubator and ground.
INOC[3]	-	Flask containing inoculum only, substrate free. (blank)

(1) NW: new waste; (2) OW: one year waste; (3) INOC: inoculum (blank)

The parameters monitored of each refuse were: humidity, total organic carbon (TOC), total Kjeldahl nitrogen (TKN), pH, alkalinity, chemical oxygen demand (COD) and volatile solids (VS), all verified prior to and at the end of the digestion, regarding the characteristics of a batch process. Parameters were evaluated according to the Standard Methods for the Examination of Water and Wastewater (APHA, 1998; 2005).

Before sealing, the BMP bottles were gassed with nitrogen (N_2) for 5 minutes so that the anaerobic environment conditions were guaranteed (headspace reactor) (Mshandete *et al*., 2004). Once sealed, the BMP flasks were placed in an incubator with constant temperature (35 ± 2 ºC), appropriate to the mesophilic bacteria and, according to Khalid *et al*. (2011), suitable for the production of methane. During the incubation period, the batches were shaken at least 3 times a week, in order to homogenize the sample.

In Labatut *et al*. (2011, p. 2256), the BMP "test was ended when the cumulative biogas curve reached the plateau phase, usually after 30 days". In this work, the incubation time was 80 days (from 24/march to 13/june), 20 days longer than suggested by Alves (2008), for similar refuses, inoculum and environmental conditions.

Gas Monitoring

Biogas Monitoring

The gas accumulated in the flask's headspace was constantly monitored, in order to follow the gas generation (verified through the pressure in the manometers) and its composition. The frequency of biogas collection depended on the accumulation of generated gas, since all the analyses required a minimum amount of sampled gas. Gases were collected in Tedlar bags (1 L capacity, SKC, USA) with two valves (one of them with a rubber stopper for collection with a micro-syringe). Before each sampling, bags were cleaned with N_2 and entirely emptied, ensuring the same condition for all the samples.

The analyses of the generated biogas composition (methane and carbon dioxide) were carried out in a gas chromatograph with thermal conductivity detector (GC/TCD, Appa Gold). The packed column was Porapak N, 80/100 mesh, with a length of 3.0 m. The injector, detector and furnace temperatures were 120 ºC, 150 ºC and 60 ºC, respectively. The hydrogen gas flow was 30 mL.min^{-1}. The samples were collected from Tedlar bags and injected onto the chromatograph using a gas-tight syringe.

Hydrogen Sulfide Gas Monitoring

In this study, the H_2S concentrations were measured with portable equipment Dräger model X-AM 7000, with electrochemical sensor and measuring range from 0 to 1000 ppm. The hydrogen sulfide was monitored on the same occasions that the biogas was measured, also from the Tedlar bags.

RESULTS AND DISCUSSION

Refuse Stabilization

Table 2 presents the total Kjeldahl nitrogen (TKN) values, moisture content, volatile solids (VS)*,* chemical oxygen demand (COD), pH and alkalinity of fresh refuse (assay NW), old refuse (OW), and inoculums (IN), prior to and post 80 days of biodigestion.

According to USEPA (1991) and Andreoli *et al*. (2003), refuse with high humidity content (60 to 90%) might increase the gas generation rate. In fact, Alves (2008) verified that the higher the humidity percentage in the environment, the higher the biogas generation rate. The humidity values observed in this study for fresh and old refuse at the time of collection were 68.1 and 67.3% (on a humid base), respectively. After the preparation of these samples (inoculum addition to the ground refuse at the ratio 1:50), the humidity values were close to 90%; therefore, highly suitable for the generation of biogas (Table 2).

The pH for methane formation is neutral and slightly alkaline (USEPA, 1991). Volatile fatty acids (VFA) formed during the acid phase of the anaerobic digestion tend to reduce the environmental pH, making the methanogenic bacteria, which are sensitive to low pH values, reduce their activity (Zhang *et al*., 2008). Thus, a balance between the production and consumption of acid during the refuse biodigestion is essential for the stability of the anaerobic process. The stability of the pH values (always close to neutrality) and alkalinity observed in this study highlight the buffering capability of biodigesters and suggest that there was no souring of the process. The reestablishment of alkalinity values, which stayed close to the initial values, is probably due to the presence of CO_2 (a soluble gas) in the headspace biogas, which partitions to the liquid environment (inoculum) of the biodigester, increasing the concentration of bicarbonate. Another probable reason for the reestablishment of alkalinity is the presence of

Table 2: Degradation parameters of fresh refuse (NW) and old refuse (OW) verified before and after the biodigestion process (with standard deviation).

	NW		
Parameter	**Pre-assay**	**Post-assay**	**Reduction**
Moisture content (%)	86.8 ± 2.16	89.3 ± 3.17	-
pH	7.09 ± 0.11	7.12 ± 0.14	-
Alkalinity (mg_{CaCO_3} L^{-1})	7.534 ± 301.2	7.933 ± 265.7	-
VS (%)	81 ± 0.34	46 ± 1.25	43.2
COD (mg L^{-1})	23.698 ± 989.5	2.768 ± 198.2	88.3
TKN (mg L^{-1})	1.164	233	79.9
	OW		
Parameter	**Pre-assay**	**Post-assay**	**Reduction**
Moisture content (%)	89.8 ± 1.98	90.1 ± 2.56	-
pH	6.98 ± 0.09	7.02 ± 0.12	-
Alkalinity (mg_{CaCO_3} L^{-1})	7.528 ± 413.1	7.196 ± 321.6	-
VS (%)	76 ± 0.86	40 ± 0.05	47.4
COD (mg L^{-1})	21.136 ± 715.6	1.723 ± 132.6	91.8
TKN (mg L^{-1})	998	162	83.7

- Values presented in the table are the average of triplicates, except TKN (only one measure).

ammonia (ammonia buffer acids formed in the acid phase) (Cho *et al.*, 1995; Georgacakis *et al.*, 1982; Raposo, 2006) which, in an anaerobic process, results from the degradation of nitrogenous compounds.

The determination of volatile solids is a good parameter to follow the biodegradable organic matter degradation (Redon *et al.*, 2005) and its analysis is commonly applied to the biological stability measurement in sludge from liquid effluents (Metcalf and Eddy, 1991). In Table 2, it can be seen that the initial and final values of volatile solids for the 1 year refuse were lower than those for the fresh refuse, indicating a more advanced degree of degradation (for higher ageing). According to Decottignies *et al.* (2005), a refuse can be considered to be stabilized in the VS band from 10 to 17.4%, considerably below the final values observed in this study after 80 days of digestion. Throughout the 80 days of biodigestion, a percent reduction from 43.2 and 47.4% was observed for the fresh refuse and for the 1 year refuse (NW and OW), respectively. Although this percentage is above that obtained by Maciel (2009), who verified a reduction of around 40% in the VS content in 200 days of digestion in an experimental cell with refuse from the Muribeca landfill (also in Jaboatão dos Guararapes), it can be seen that the final VS values reported here for the two refuses are still relatively high (46 and 40% for NW and OW, respectively). This indicates a remaining potential of solids that can be degraded, although the real capability of the environmental microorganisms to act is not known, since the more easily degradable organic fraction has already been consumed (Maciel, 2009).

The anaerobic stabilization process starts when the volatile suspended solids of the system are hydrolyzed (initial phase of the anaerobic digestion process), resulting in soluble COD (Leite *et al.*, 2003). The soluble COD represents the soluble organic matter of the environment, which in turn, is substrate for the methanogenesis, being converted into CH_4 and CO_2 (Zhang *et al.*, 2008). Because it was a batch system, the reduction of 88.3 and 91.8% in the COD values for the fresh refuse and 1 year refuse, respectively, is due to the conversion of organic matter into biogas.

Carbon is among the main nutrients for the microorganisms, as it is a source of energy for the microbial population; nitrogen is crucial for the microbial population growth (Igoni *et al.*, 2008; Richard, 1992). Despite the volatile solid values being still relatively high at the end of the process, the final carbon values reveal that the biogas production develops to the end in the biodigesters, as 88.3 and 91.8% of COD and 79.9 and 83.7% of TKN (from NW and NO refuses, respectively) were consumed within the 80 days of biodigestion.

Gas Monitoring: Biogas

Biogas Yield

Figure 1 presents the daily production of biogas obtained throughout the 80 days of biodigestion in the six monitored bioreactors (fresh and old refuse, in triplicate), after subtracting from each the average volume of biogas generated in the blank assays.

The initially established anaerobiosis of the

process, with the complete elimination of oxygen by the nitrogen circulation, enabled the process to initiate with high production of biogas since the first day of the assay. The initial peak observed in the first five days of biodigestion is probably due to easily degradable organic substance hydrolyses and the great volume of inoculum used (Parawira *et al*., 2004) in relation to the amount of refuse (ratio of 50:1). This high initial production of biogas was observed in all assays. Still, in all biodigesters evaluated, the majority of biogas produced (80%) was in the first 50 days of assay, staying constant after this period (biogas generation curve reached a constant pattern), when the slower degradation of the refuse started to govern the process. In Hansen *et al*. (2004), the incubation time was 50 days (with reactors kept at 55 ºC) and the majority of the biogas volume accumulation also occurred in the first ten days of the experiment, regardless of the age of the refuse evaluated.
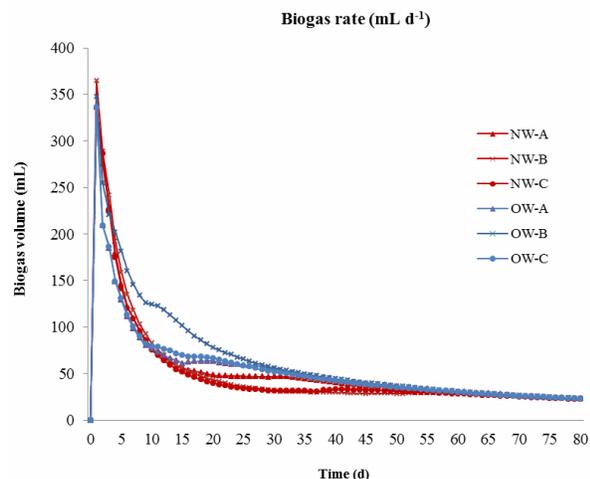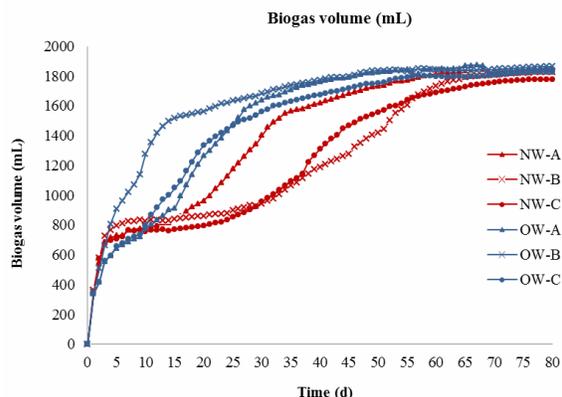

Letters A, B and C indicate the triplicate. All reported values are in STP conditions.

Figure 1: Daily biogas production during the experiment (mL d^{-1}).

Biogas production curves in a BMP assay might present various forms. This happens because, according to Labatut *et al*. (2011), the biodigestion mechanisms of each substrate, as well as the formation of inhibiting substances, act on the kinetics of degradation of such refuse, resulting in different curves for the process. Even when it comes to different age refuse degradation, the pattern of the degradation curves presented in this study was very similar, differing only in the daily generation of biogas. Besides, the deviation between the triplicates was small. Similar biogas production curve patterns were verified by Alves (2008) and Maciel (2009), in

their BMP assays with refuse from the Municipal Solid Waste Landfill in Recife, and in Parawira *et al*. (2004), who investigated the anaerobic biodegradation of potato waste alone and co-digested with sugar beet leaves.

The total biogas accumulated in the bioreactors was obtained by summing the daily production of biogas throughout the whole experimental period. Figure 2 presents the biogas accumulation throughout the 80 days of biodigestion in the six reactors monitored (fresh and old refuse in triplicate), with the average biogas volume generated in the blank assays already subtracted.

Letters A, B and C indicate the triplicates. All reported values are in STP conditions.

Figure 2: Total volume of biogas produced during the experiment (mL).

Again, the pattern of the biogas accumulation curves was very similar, regardless of the age of the refuse. Similar curve patterns for biogas accumulation were also verified by Alves (2008) and Maciel (2009). According to Parawira *et al*. (2004), comparisons between the methane production curves found in the literature are rather complicated due to the differences between experiments, such as type of refuse, inoculums and process conditions.

Figure 2 shows that, although the volume of biogas generated in all assays is very similar to the final experiment (close to 1800 mL, regardless of the age of the refuse), the assays with 1 year refuse (represented by curves OW-A, OW-B and OW-C) presented a more accelerated state of degradation in relation to the fresh refuse (curves NW-A, NW-B and NW-C) since the first days of the assay, probably due to its more advanced degradation stage at the moment of the collection in relation to the fresh refuse.

According to Hansen *et al*. (2004, p. 396), "the methane potential is defined as the maximum of produced methane during" the experiment. In this

case, the measurement results for biogas generated throughout the biodigestion period were 1816 NmL for the fresh refuse and 1846 NmL for the old one (average total value generated in each case) or, 75 NmL g_{vs}^{-1} (biogas volume per volatile solid mass) for the fresh waste and 105 NmL g_{vs}^{-1} for the one year waste. It can be seen that, in spite of the age difference between wastes, both yielded very similar biogas volumes, although OW generated a slightly superior volume.

As previously observed, the VS and COD parameters can be used to measure the biodegradable organic matter degradation. According to Table 2 and, furthermore, considering the principle that the pH and alkalinity values measured at the beginning and at the end of the assays remained constant, the slight superiority of the initial humidity values (3%) of the OW refuse in relation to the NW, together with the small superiority of VS, COD and TKN reduction (addition of organic and ammoniac nitrogen) for the OW refuse in relation to the NW might explain the (also slight) 1.7% greater biogas generation by the 1 year refuse. Unlike the literature findings, the old refuse, in this case, yielded more biogas than the fresh refuse. Alves (2008), for instance, obtained 162.0 NmL g_{vs}^{-1} for the fresh refuse and only 12.5 NmL g_{vs}^{-1} for the 1 year refuse in terms of biogas accumulated in the BMP reactors. This same author found that the volatile solid values were 49.2 and 40.9% for fresh refuse and 1 year refuse, respectively, much lower than the initial values of refuse in this study (81 and 76%, respectively). Maciel (2009) obtained, for fresh refuse ($\cong$20 days) and refuse aged between 7 and 14 months, the maximum values of 462.4 and 145.7 NmL g_{vs}^{-1} of biogas generated, respectively; in this case, the VS values varied between 46.9 and 56.9% for both age refuses.

Therefore, there is a great disparity between the biogas yield and the process parameters, even when it comes to similar studies. Maciel (2009) claims that establishing a direct relation between the physical-chemical characteristics of samples with the BMP results might be a complicated task, due to the complexity of other factors which interfere in the process and that were not monitored such as, for instance, microbial population characteristics, and concentration of all nutrients present both in the refuse evaluated and in the inoculums used.
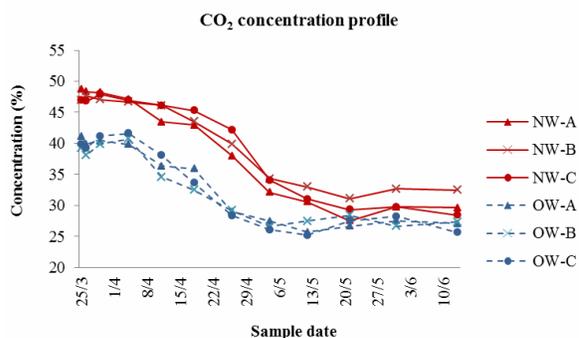
Methane Concentration

Altogether, 12 biogas samples were collected for analysis, since the frequency of sampling depended

on the accumulation of the gas generated. As was previously shown, the majority of biogas was generated in the first half of the experiment and, thus, the majority of biogas analyses were concentrated in this period. Figures 3 and 4 present, respectively, the profile of methane and carbon dioxide concentrations, observed during the biodigester monitoring (12 samples along 80 days of biodigestion).
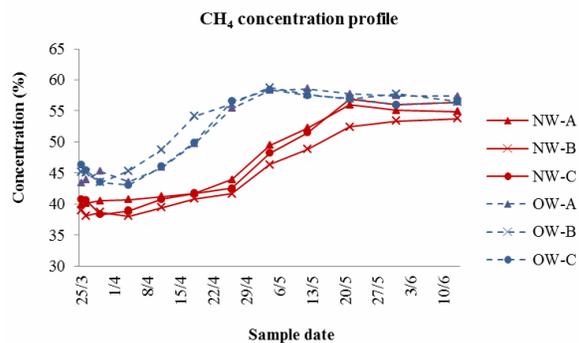
Letters A, B and C indicate the triplicates.

**Figure 3:** Profile of methane concentration throughout the monitoring period.

Letters A, B and C indicate the triplicates.

Figure 4: Profile of carbon dioxide concentration throughout the monitoring period.

The methanogenic phase, after the acid phase in the biodigestion process, is characterized by presenting methane concentration at a 50 to 60% level, with a decrease in the concentration of carboxylic acids and consequent increase in pH of the environment (Barlaz *et al*., 1989). Through Figures 3 and 4, it can be seen that, as the methanogenic phase advances, the methane concentration increases, while the carbon dioxide decreases, basically in the same proportion. It is also observed that, in the case of the 1 year refuse, the biogas reaches 50% in the methane concentration in the 6th measurement (4th week of biodigestion, approximately) whereas, for the fresh refuse, the biogas reaches the 50% methane concentration only in the 9th measurement (two weeks later).

According to Reinhart and Towsend (1998), the landfill gas composition is affected by the refuse composition. In fact, Figure 3 shows that the 1 year refuse (curves OW-A, OW-B, and OW-C) started the experiment with a methane concentration around 5% higher than the fresh refuse (curves NW-A, NW-B, and NW-C). The difference between average concentrations of methane between NW and NO residues is even bigger from the 5th measurement (3rd week of biodigestion), converging to similar values (close to 55%) at the end of the experiment. It can also be seen that the tendency for the methane concentration to stabilize for both refuses is exactly around 55%. From there, there is a decrease when the process starts the maturation phase. A comparison with the methane concentrations in the Alves (2008) and Maciel (2009) studies would not be valid, as these authors used portable equipment instead of the chromatograph.

Figure 3 indicates that the biodigestion started with a relatively high methane percentage; 5% more methane in the OW refuse confirms the more accelerated degradation state of this refuse in relation to the NW refuse. With the average methane percentage (given in Figure 3) and the average biogas volumes generated (given in Figure 2), it was possible to determine the methane volume that was really generated in the biodigesters of NW and OW refuses (Figure 5).
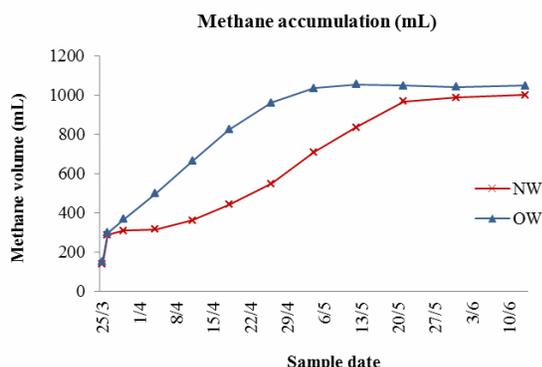
Figure 5: Volume of methane accumulated in the biodigesters during the experiment.

Results reveal that the average generated methane volumes (for the period under monitoring), for the NW and OW refuses were, respectively, 1000 and 1048 mL, which correspond to 54.2 and 57.7% of the total biogas generated. According to Sponza and Ağdağ (2004), the amount of methane produced per mass of biodigested organic material can be used as an indicator of the stabilization degree of the refuse evaluated.

Gas Monitoring: Hydrogen Sulfide (H₂S)

In accord with Tchobanoglous *et al.* (1993), the formation of odorant gases results from the anaerobic decomposition of easily degradable organic compounds present in the municipal solid waste, being even more representative in hot climate regions, which is the case of Jaboatão dos Guararapes, with an average temperature of 28 ºC (Jaboatão, 2012). Sulfate, for example, during the methanogenic phase (in anaerobic conditions), is reduced to sulfide (Reinhart and Townsend, 1998), which subsequently combines with hydrogen in the environment to form hydrogen sulfide (H_2S) (Tchobanoglous *et al.*, 1993). In the acid phase, a phase prior to the methanogenic, the microbiological activity accelerates the production of organic acids, generating hydrogen gas in low concentrations. When the methanogenesis takes place in the biodigestion process, these acids, as well as the H_2 (H_2S precursor), are gradually converted into CH_4 and CO_2. This reduction in acids and hydrogen concentrations raises the pH in the environment, leading it to neutrality (range of 6.8 to 8.0) (Tchobanoglous *et al.*, 1993).

It is relevant to highlight that the H_2S is an odorant in its molecular form, while under basic conditions H_2S formation is inhibited (the ionized forms of sulfide are prevalent), controlling the formation of odor due to sulphur compounds (Gostelow and Parsons, 2001). Figure 6 shows the profile of concentration of H_2S gas throughout the biodigestion process (12 samples) for all the refuse evaluated, including the blank assays.

It can be seen from Figure 6 that there was a decrease in the concentration of H_2S during the biodigestion process in all reactors (NW, OW and INOC refuse) in contrast to the evolution in the methane concentration verified in Figure 3, as claimed by Tchobanoglous *et al.* (1993).

According to Figure 6, there was no significant difference between the H_2S gas emissions from the two refuses and the inoculum. Thus, it is believed that the H_2S gas emission in the biodigesters was mainly due to the inoculum, probably because of its high proportion in relation to the substrate (50:1).

Because the process in the biodigesters was anaerobic since the beginning of the experiment, high concentrations of H_2S (a reduced compound) were simultaneously verified; this fact was confirmed by the strong rotten egg smell, characteristic of this gas (Gostelow *et al.*, 2003; Mbuligwe, 2005), observed in all samplings. Even with the reduction in H_2S gas concentrations along the biodigestion, the values observed remained far above the olfaction
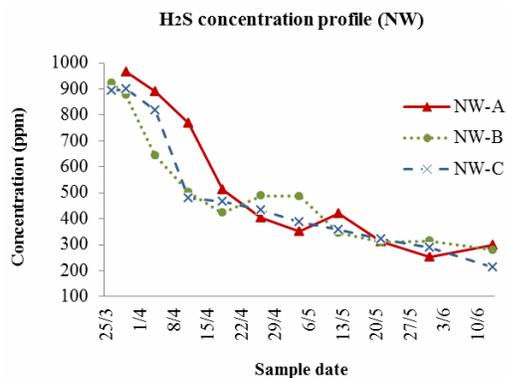
(a) Concentration (in ppm) of hydrogen sulfide gas (H_2S) in the NW refuse.
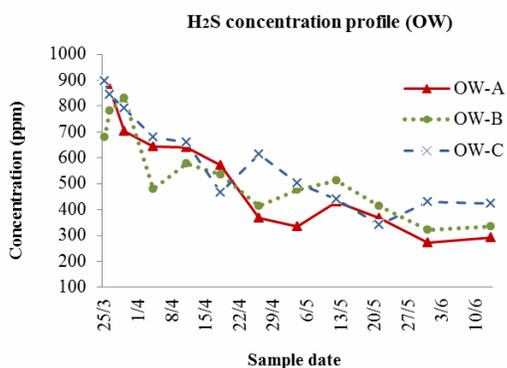
(b) Concentration (in ppm) of hydrogen sulfide gas (H_2S) in the OW refuse.
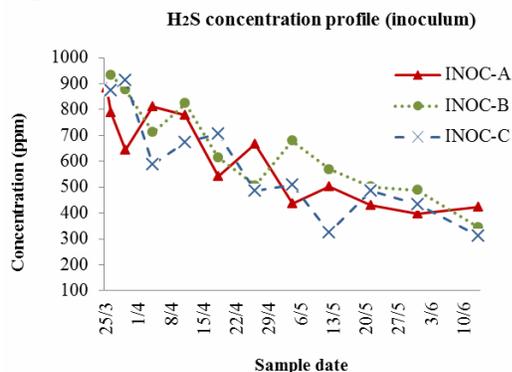
(c) Concentration (in ppm) of hydrogen sulfide gas (H_2S) in the inoculum.

- Letters A, B and C indicate the triplicates.
- The first points of some biodigesters could not be determined because they were above the Dräger sensor detection limit (1000 ppm).

Figure 6: Concentration profile of the hydrogen sulfide gas (H_2S) in the biodigesters evaluated: a) fresh refuse (NW); b) 1 year refuse (OW); c) inoculums (INOC).

perception limit (0.0011 ppm, according to Summer, 1971) and toxicity for this compound (10 ppm – time

weighted average, according to OSHA, 2012). As the human olfaction system is able to detect extremely low concentrations of odorant gases, many times below the detection limits of analytical instruments (Senante *et al.*, 2003), considering the H_2S concentration values observed here, one can see that the olfactometric analysis in this study (if this option was made as a complement to the analytical instrumental determination) would be unnecessary, given that the concentration values are hundreds of times superior to the threshold odor. The permanent strong intensity odor could even be dangerous to the health of the olfactometric jury because the concentration values were tens of times above the toxicity limit in all phases of the biodigestion evaluated.

Besides the odor issue, it is important to emphasize that elements such as sulfide act as inhibitory agents in the anaerobic digestion process (Chen *et al.*, 2008). Under anaerobic conditions, sulfate is reduced to sulfide through the action of sulfate-reducing bacteria (SRB), which will compete for the substrate with the methane-producing bacteria (MPB), resulting in lower methane production during the methanogenic phase (Harada *et al.*, 1994; Isa and Anderson, 2005; Karhadkar *et al.*, 1987).

CONCLUSIONS

Due to the number of variables (pH, humidity, temperature, etc.) involved in the evaluation of large scale refuse stabilization (landfill), as well as the difficulty of control *in loco,* studies on a pilot scale have been more and more frequent and important to optimize the biodegradation parameters. In this sense, the BMP represents a simple alternative with low operational cost, standardizing the refuse degradation conditions, variable control and monitoring of the process.

The study of biodigestion of organic refuse of different ages (fresh and 1 year old) from a Recife landfill revealed a very similar pattern of degradation curves. Thus, the production of biogas in BMP flasks for both refuses evaluated was also similar: 1816 NmL of accumulated biogas for the fresh refuse and 1846 NmL for 1 year old refuse, or, 75 NmL g_{vs}^{-1} for the fresh waste and 105 NmL g_{vs}^{-1} for the one year waste. In this case, despite the difference in age of 1 year between the refuses, the volume of biogas accumulated in the reactors presented a difference below 2%. Even the methane composition for both showed similar values – stabilization around 55% at the end of the experiment.

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