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Methane potential and degradation kinetics of fresh and excavated municipal solid waste from a tropical landfill in Colombia

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Abstract

The optimization of degradation processes and the management of leachate and biogas produced in landfills are key aspects for the establishment of more sustainable municipal solid waste (MSW) disposal in developing countries. In this study, biochemical methane potential (BMP) tests were used to evaluate CH_4 production potential and degradation kinetics of fresh waste (FW) and five-year aged excavated waste (EW) samples from a tropical controlled landfill with compositional characteristics of developing countries. BMP tests with reconstituted samples of the biodegradable fraction of both MSW types were performed at three substrate/inoculum (S/I) ratios (0.3, 0.5 and 1.0 g VS substrate g^{-1} VS inoculum), and CH_4 generation parameters were determined using the first-order and modified Gompertz kinetic models. After 30-d, the best BMP results were reached at S/I ratios of 0.5 and 1.0, with cumulative CH_4 productions of 528 and 433 mL CH_4 g^{-1} VS for FW, respectively; and 151 and 135 mL CH_4 g^{-1} VS for EW, respectively. The first-order kinetic model provided a good fit to BMP results for FW, whereas the modified Gompertz model showed a better adjustment to the BMP data for EW. Calculated first-order CH_4 generation rates for FW and EW were in the range 0.19–0.36 and 0.23–0.25 d^{-1}, respectively. These results evidence the high biodegradability and CH_4 potential of FW disposed of in a tropical landfill in Colombia and the reduced BMP of EW despite a relatively short period after disposal under conventional landfill operation conditions.

Keywords: Biochemical methane potential, Municipal solid waste, Biogas, Tropical landfill, Sustainable development goals

Introduction

Although about 80% of municipal solid waste (MSW) produced globally ends up in final disposal sites, it is estimated that only 20% of these are sanitary landfills [1]. It is possible that the production of MSW in low- and middle-income economies will change over time, however, the amount of waste sent to landfills will not decrease in the short to medium term. In low-income countries, over two-thirds of wastes are openly dumped; in contrast, in low- and upper-middle countries 18 and 54% of the waste produced are disposed of in landfills, respectively [2].

The continuous growth in waste generation and the lack of integrated waste management systems put constant pressure on the available space for landfilling in developing countries [3]. In Colombia, by 2016, about 38% of landfills had less than 3 years lifespan and the estimated deficit in installed capacity for the final disposal of solid waste is 95.4 Mt by 2030 [4]. This is not a rare situation for other developing and emerging economies and is one of the reasons why, as countries improve economically, the construction and improvement of landfills are seen as a first step towards the establishment of more sustainable waste management systems [2].

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The MSW generated in low- and middle-income countries have characteristics that facilitate its degradation in landfills, such as the high organic fraction (OFMSW) of readily biodegradable wastes, mainly composed of food and green waste [5, 6]. These characteristics influence leachate and gas emissions from landfills, resulting in potentially higher but less prolonged biogas production rates [7].

Determining the degree of stability of MSW allows: (1) to establish the management criteria, treatment or use of MSW before its final disposal [8], which it is associated with the biodegradability of the materials, and (2) to estimate the biogas production potential of MSW. These are key elements when considering more sustainable landfill methods for developing countries, mainly in terms of their capability to mitigate greenhouse gas emissions and enhance the feasibility of landfill gas (LFG) utilization projects [6]. In this context, the United Nations established Objective 7 of the Sustainable Development Goals, which seeks to ensure access to affordable, reliable, sustainable and clean modern energy for all. The Colombian government embraced this initiative and agreed to reduce greenhouse gas emissions by 20% by the year 2030, through the development of an agenda that integrates the energy from biomass and biowastes to the national energy system, including LFG utilization projects [4].

The basic principle used to evaluate the stability of MSW is to determine how much and how fast the carbon (biodegradable fraction) can be mineralized [9]. Anaerobic tests, such as the biochemical methane potential (BMP), are among the most widely used experimental methods used to determine the degree of biological stabilization of MSW [10, 11]. Other measurements used to evaluate landfill stabilization and leachate quality include parameters such as pH, chemical oxygen demand (COD), biochemical oxygen demand (BOD) and the BOD/COD ratio [8].

The BMP methodologies may change due to different experimental conditions (temperature and pressure, incubation time, gas measurement method), the wide variability in MSW characteristics and its conditioning for the essays (moisture content, particle size and sample size), and the substrate-to-inoculum (S/I) ratios employed, among others [12–14].

BMP studies for landfills had been used to estimate the CH_4 production potential and evaluate the biological stability of the biodegradable fraction of MSW by adjusting the test parameters to simulate conditions similar to those of landfills [15, 16]. Although the S/I ratio is one of the main factors in BMP tests [17], its influence on the quality of the results for landfill MSW is rarely assessed [18]. Also, most of the BMP studies with landfill MSW reported in the literature have been carried out in developed countries [9–11].

Given the compositional characteristics of MSW, as well as the particular environmental and operational conditions of landfills in tropical developing countries like Colombia, it is very likely that BMP results differ from those reported in the literature. Therefore, a proper evaluation of its measurement is necessary. While some studies have pointed out these differences for wet landfill wastes with high OFMSW [19, 20], little information is available about BMP characterisation for fresh waste (FW) and excavated waste (EW) from landfills in tropical developing countries.

Knowledge of methane production potential and biodegradation kinetics for landfill waste of different age can help in predicting gas production and landfill performance over time [15]. First-order decay models are commonly used to describe waste decomposition in landfills, and its use together with BMP measurements has proven to be an effective alternative approach to determine appropriate gas generation parameters for landfills [20, 21].

In this way, kinetic analysis of BMP data for FW can aid in selecting appropriate modelling parameters to predict CH_4 generation for landfills in low- and middle-income countries with potentially gas production, associated to their highly biodegradable MSW compositional characteristics. In addition, measuring the remaining CH_4 potential of EW can be used to characterize the extent of stabilization achieved under the specific environmental and operational conditions of landfills in tropical developing countries [6].

The novelty of this research work is to characterize, through the combined used of BMP tests and kinetic models, the methane potential and anaerobic biodegradability of MSW disposed of in a tropical landfill in Colombia. This type of work has been scarcely conducted for landfills in developing countries and is particularly relevant for an adequate assessment of their biogas utilization potential and its relation to the compositional characteristics and biodegradation dynamics of landfill wastes in tropical climates. Samples of FW and EW obtained from a tropical landfill serving 20 municipalities in the south-west part of Colombia were employed in the study. Additionally, the extent of degradation and stability characteristics of both waste samples was characterized through the determination of parameters suggested as indicators of the stabilization in landfills.

Materials and methods

Source and composition of the MSW

The MSW samples were collected from a regional landfill in Colombia western province of Valle del Cauca, which receives approximately 0.832 kt d^{-1} of MSW [22]. The landfill comprised of approximately 75 ha, began accepting waste in 1998 and since then more than 2 Mt of MSW have been disposed of in the site. The controlled landfill has a passive LFG structure in place consisting of venting wells, however, LFG is neither collected, controlled or treated. The region has an average annual precipitation of 1597 mm (± 224 mm) and an average temperature of 21.3 °C (± 0.5); however, due to the presence of a bi-modal period of precipitation in Colombia, the monthly rainfall in the region can increase up to 800 mm during the rainy seasons [23].

The FW was taken directly from an active (operational) cell receiving fresh MSW no more than 24 h after disposal and without daily covering material. Because MSW comes in plastic bags, it was necessary to open the bags to empty and characterize their contents. The EW had an age of 5 years since its disposal, as it was extracted at depths between 3 and 4 m from a closed cell covered with soil and vegetation.

Using a quartering method, 150-kg samples of FW and EW were obtained. The physical composition of the waste was characterized manually on site and included the categories commonly found in MSW such as food waste, yard waste, plastics, paper and cardboard, glass, textiles, sanitary waste, metals, wood and other materials [2, 24]. For the EW, a category commonly found in aged waste from landfills and hereafter termed as non-identifiable waste was also categorised, which consisted of a mixture of soil-like fines and degraded organic materials [20, 25].

Conditioning of samples

For the conditioning of waste samples, the biodegradable fractions (food and yard waste, paper and cardboard, non-identifiable and sanitary waste) were dried and processed in order to reduce their size for the BMP tests [18, 26]. First, yard waste, paper and cardboard, non-identifiable and sanitary materials were dried (70 °C), then cut and shredded employing a forage mill (TRF 300, Trapp, Jaraguá do Sul, Brazil). Food waste was processed using an industrial blender (CB15, Waring Commercial, Connecticut, USA).

In this way, the biodegradable waste fractions were reduced to particle sizes (< 30 mm) more suitable for evaluating the BMP of MSW [11] and to approximate physical characteristics of wastes affecting flow and the distribution of solutes and microorganisms in landfills [27]. Subsamples of each of the biodegradable fractions were milled (LAB MILL-8000, Gardco, Florida, USA) to a particle size < 1.4 mm and used to measure total solids (TS) and volatile solids (VS) according to the 2540-G method [28].

BMP tests

The BMP tests were performed by the manometric method using 500-mL amber coloured glass bottles that were hermetically sealed with a metallic cap and a septum, as shown in Fig. 1 [18, 29]. The working volume in each test was 400 mL, which left 100 mL for the accumulation of biogas. To guarantee that the manometric measurement of biogas corresponded mainly to methane, each reactor was equipped with a trap in the head space filled with NaOH pellets to capture CO_2.

To record the biogas pressure in the head space of the reactors, a CPG500-type WIKA manometer was used. The quantification of the produced CH_4 volume is

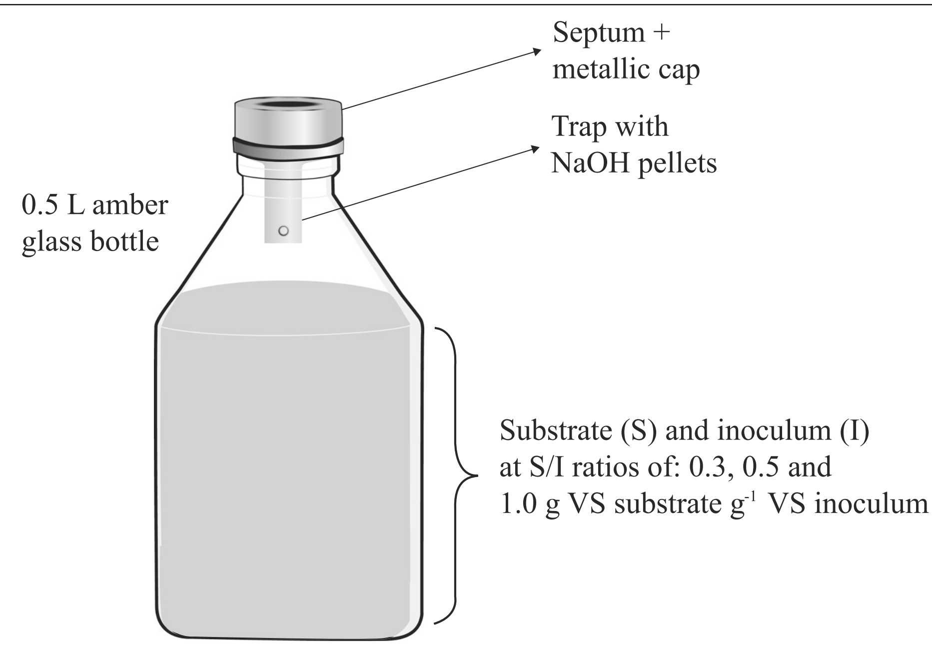

Fig. 1 Illustration of the experimental unit used in BMP tests

reported at standard temperature and pressure (T = 273 K, $P = 101.3$ kPa) and considers the dissolved CH_4 [13]. CH_4 composition was determined using a chromatograph (GC-2014, Shimadzu) equipped with a flame ionization detector and an electron capture detector using nitrogen as a carrier gas in a 3-m long HayeSep column. Granular sludge from an anaerobic digester receiving wastewater from a cattle and pig slaughterhouse in Valle del Cauca (Colombia) was used as inoculum, which was kept at 35 °C in containers that were periodically opened to allow for degassing. The inoculum characteristics are shown in Table 1 and included pH, TS, VS measurements [28] and determination of the specific methanogenic activity (SMA) following the method recommended by Torres and Perez [30].

The pH of the inoculum was in the range recommended for its use in BMP tests [17] and its VS/TS ratio indicates a significant proportion of organic matter and active biomass. Also, the SMA of the inoculum indicated a moderate biological activity under anaerobic conditions according to the values suggested by Angelidaki et al. [12] for granular inoculum. To enhance conditions for substrate biodegradation, a solution of macro-nutrients (NH_4CL, $NaHCO_3$, KH_2PO_4, $MgSO_4$, $CaCl_2$) and micronutrients ($FeCl_3$, $ZnCl_2$, $CuCl_2$, $MnCl_2$, $(NH_4)_6Mo_7O_{24}$, $AlCl_3$, $CoCl_2$, $NiCl_2$, H_3BO_3, Na_2SeO_3) used in studies with OFMSW was added [31]. The mixture was completed with distilled water and the pH was adjusted to neutrality using a $NaHCO_3$ solution at 8% (v/v).

The reactors were fed with a reconstituted sample of the biodegradable fraction of the MSW, which was prepared by separating the readily and moderately biodegradable components (food, yard waste, paper and cardboard, toilet paper and non-identifiable waste) and mixing them keeping their original proportions in the landfill. Keeping the substrate concentration constant at 18 g $VS_{substrate}$ L^{-1}, the quantity of inoculum was varied to assess three S/I ratios (0.3, 0.5 and 1.0 g $VS_{substrate}$ g^{-1} $VS_{inoculum}$), which are within the range recommended for the analysis of readily degradable substrates like FW as well as substrates with reduced biodegradable fractions such as EW [14].

Tests under each S/I condition were carried out in triplicate, and blank reactors (only inoculum) were run to determine the endogenous CH_4 generation in order to discount its contribution to the total CH_4 production. Before being sealed, the reactors were purged with N_2 gas to guarantee anaerobic conditions; subsequently, they were placed in an incubator (WTW TS 606-G 2-I, Giessen, Germany) at 35 ± 0.5 °C without agitation. The duration of the tests (30 d) was defined considering previous studies with FW and EW and the recommendation given by Holliger et al. [14] that BMP tests should end once the daily production of CH_4 is less than 1% of the total CH_4 volume that has accumulated for three consecutive days.

Table 1 Inoculum characteristics

Parameter	Value
pH (units)	7.96
TS (g L^{-1})	89.83
VS (g L^{-1})	68.10
VS/TS	0.76
SMA (g COD_{CH_4} g^{-1} VS d^{-1})	0.17

Methane production modelling

BMP test results were analyzed using growth models that allow determination of kinetic parameters such as the maximum CH_4 potential, CH_4 generation rate and the duration of the lag phase. The cumulative methane generation data obtained from the BMP tests were fitted to a first-order decay model used to calculate gas produced by landfills [32] and the modified Gompertz model [33], as given by Eqs. (1) and (2), respectively.

$$B = B_0 \times \left(1 - e^{-kt}\right) \qquad (1)$$

$$B = B_0 \times e\left\{-e\left[\frac{R_m e}{B_0}(\lambda - t) + 1\right]\right\} \qquad (2)$$

where B is the cumulative CH_4 generation (mL CH_4 g^{-1} VS) at time t, B_0 is the maximum CH_4 potential (mL CH_4 g^{-1} VS), e is the mathematical constant (2.718), k is the first-order decay rate (d^{-1}), R_m is the maximum CH_4 rate (mL CH_4 g^{-1} VS d^{-1}) and λ is the lag phase (d). The software Matlab 2018a® was used to conduct a non-linear least square regression analysis to determine B_0, k, R_m and λ. The coefficient of determination (R^2) and the scale-dependent root mean square error (RMSE) were used as a measure of the goodness of fit [34]. The significance differences in the BMP due to the S/I ratio were calculated through a single factor analysis of variance using Excel® and Tukey's tests ($p < 0.05$).

Waste stability characterization

Once the BMP tests were completed, the reactors were sampled destructively and physicochemical parameters used to evaluate waste stabilization and leachate quality in landfills were analysed. Thus, reactors were opened, centrifugation was immediately performed at 10000 rpm for 10 min and representative samples of the liquid waste fraction were filtered using a 0.45-μm nitrocellulose filter. Total COD and filtered COD (COD_f), pH, BOD, total alkalinity (TA) and bicarbonate alkalinity (BA) were determined according to APHA [28].

Results and discussion

MSW composition

The physical characterisation results for fresh and excavated MSW samples taken from the regional landfill are shown in Table 2. Here, previous compositional data measured at the landfill site are compared against average MSW composition reported for main urban centres in Colombia.

In FW, the organics (mainly food and smaller amounts of yard waste) were the predominant fraction (> 51%), which is a common characteristic of MSW in low- and middle-income countries [2]. Plastics (e.g., plastic bags, packaging material, bottles and containers) constituted the second largest category in terms of mass, whereas the percentages of paper and cardboard, metal and glass were within the range reported for fresh MSW from developing countries [2, 35].

In contrast, the greatest proportion of EW corresponded to non-identifiable waste (61%), similar to that reported for EW in other studies [20, 25]. This fraction was characterized by a high percentage of fines (due to soil used as daily cover material) mixed with highly degraded organic matter. Plastics was the second largest category in EW, a consequence of both its high proportion in household solid wastes produced in developing countries with low biodegradability [27].

Significant amounts of sanitary waste were found in the FW and EW, mostly toilet paper, as it has also been observed for MSW generated in emerging economies such as China [35]. Zheng et al. [26] evaluated the biodegradability of toilet paper and found it to be similar to that of most food waste types but higher than that of moderate biodegradable materials like yard waste or office paper. Thus, it is likely that food waste, and to a lesser extent, less degradable materials such as yard waste and toilet paper, are responsible for the greater proportion of CH_4 generated by MSW disposed of in landfills in Colombia.

The organic matter content can be related to the state of degradation of MSW [36] and the VS content has been identified as a suitable parameter to evaluate the effectiveness of stabilization strategies for landfills [37]. Fig. 2 shows a VS content profile indicating the contribution of each waste material to the biodegradable fraction of FW and EW, as a percentage of dry mass (DM) (g VS g^{-1} DM). The VS content for FW was comparable to that of OFMSW generated in several cities in both developed and developing countries [24]. The easily biodegradable waste materials (food and yard waste) represents 57% of the VS of FW (mainly from food waste: 46%), whereas the remainder was made up of moderately degradable materials, such as paper and cardboard and toilet paper; the contribution of the latter is even greater than that of paper and cardboard because of its greater proportion and possibly higher biodegradability [35].

The VS content for EW was low, even when compared to that reported for older wastes from landfills with ages over 8 [20], 10 [38] and 30 yr [36]. In the EW, the non-identifiable fraction composed of degraded organic materials contributes to 67% of the VS, which is mostly because of its high proportion rather than its organic matter content. Toilet paper and yard waste, both with moderate biodegradability, contributed with 17 and 14%, respectively. VS contents below 25% DM had been suggested as a stability indicator for the biodegradable

Table 2 Physical Compositions of FW and EW from the landfill (% by wet mass)

Waste category	FW	EW	Landfill records [a]	Average Colombia [b]
Food	45.9	–	26.7–40.6	61.5[c]
Yard waste	5.9	7.4	6.1–14.5	
Paper and cardboard	5.6	1.4	1.9–16.3	6.6
Plastics	22.3	26.2	10.8–19.2	10.8
Sanitary	8.8	2.4	2.4–6.3	–
Textiles	5.0	1.4	1.3–6.2	2.7
Metals	0.3	–	0.2–6.9	1.0
Wood	1.2	–	0.1–5.7	0.5
Glass	2.4	–	0.8–5.0	2.4
Ceramic	0.3	–	0.0–11.3	–
Rubber and leather	1.3	–	0.0–1.8	–
Others	0.9	–	0.0–14.0	14.4
Non-identifiable	–	61.1	–	–
Total	100	100	100	100

a: Fresh MSW received between 2010 and 2016; b: Fresh MSW produced in major cities (Banco Interamericano de Desarrollo (Inter-American Development Bank), cited by [4]); c: Organics, mainly consisting of food and yard waste

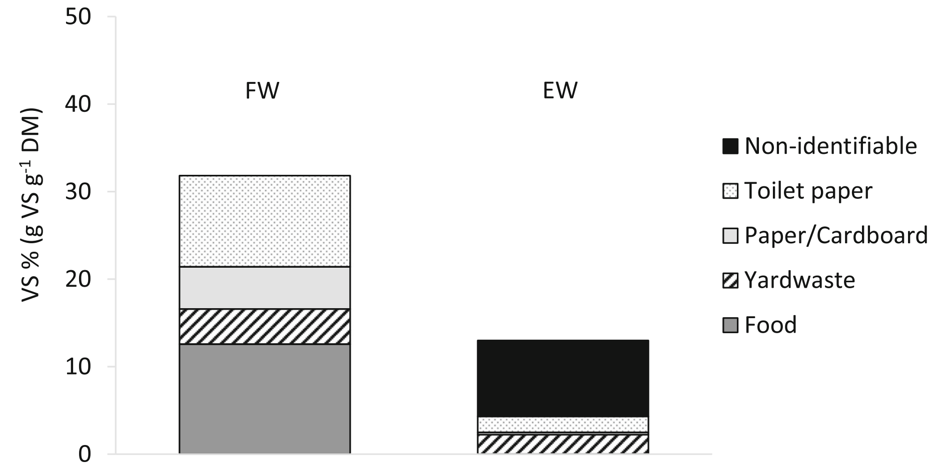

Fig. 2 VS content profile for fresh and excavated waste from landfill

fraction of MSW [25, 37]. However, since VS measurement can be influenced by lignin and non-biodegradable organic compounds, its use as stabilization criteria must be taken cautiously [38]. In this way, the readily biodegradable fraction of FW, especially food waste, has the greatest potential for biogas generation, whereas, for EW, the remaining CH_4 potential can be attributed to partially degraded materials in the non-identifiable fraction.

BMP tests

Table 3 shows the composition (% dry mass) of the reconstituted samples of FW and EW used in the BMP tests and Fig. 3 shows the CH_4 yield obtained at the three S/I ratios evaluated. The accumulated production of CH_4 for the FW varied between 433 and 528 mL CH_4 g^{-1} VS, with no significant statistical differences ($p <$ 0.05) between the three S/I ratios. These CH_4 yields are similar or higher than those reported for fresh waste from landfills with similar compositional characteristics [15, 16] and are even close to the highest values reported for OFMSW [10]. Noticeably, the S/I = 0.5 gave the highest production of CH_4, similar to what was found by Boulanger et al. [18] for BMP tests with MSW at different S/I ratios; however, they used waste samples with lower content (< 16%) of readily degradable materials characteristic of developed countries.

Table 3 Composition of FW and EW reconstituted samples (% by dry mass)

Waste category	FW	EW
Food	51.8	–
Yard waste	12.9	8.8
Paper and cardboard	10.3	1.3
Sanitary	25.0	5.7
Non-identifiable	–	84.3

In the EW tests, the ratios of 0.5 and 1.0 yielded BMPs of 151 and 135 mL CH_4 g^{-1} VS, respectively. These values are within the range reported for waste excavated from landfills with similar ages [20, 21, 38]. The S/I ratio of 0.3 resulted in a lower BMP of 54 mL CH_4 g^{-1} VS, statistically significantly different ($p < 0.05$) than the other S/I ratios, which can be associated with limitations related to the bioavailability of the EW conforming materials, rather than to the concentration of biomass, as observed by Boulanger et al. [18].

The potential effect of endogenous CH_4 production during BMP tests must be properly assessed and, as a quality standard, is recommended that the production of CH_4 by the inoculum does not exceed 20% of the total measured production (inoculum + substrate) [14]. In this study, the average CH_4 production by the inoculum in FW tests was 7, 15 and 16% of the total CH_4 at S/I ratios of 0.3, 0.5 and 1.0, respectively. For EW, CH_4 production by the inoculum accounted for 53, 19 and 18% of the total CH_4 at S/I ratios of 0.3, 0.5 and 1.0, respectively. For the EW tests at S/I of 0.3, the endogenous CH_4 production due to the inoculum was higher than the recommended value; incidentally, this S/I proportion resulted in the lowest CH_4 yield. This result indicates that higher S/I ratios (> 0.3) must be used for BMP tests with EW. Also, by the end of the tests, the daily production of CH_4 for all tests was less than 1% of the total cumulative CH_4 produced for three consecutive days, indicating that the production of CH_4 had stabilized [14].

Methane production modelling

Figures 4 and 5 show the cumulative CH_4 production for FW and EW, respectively, and the fitting curves obtained using the first-order kinetic model and the modified

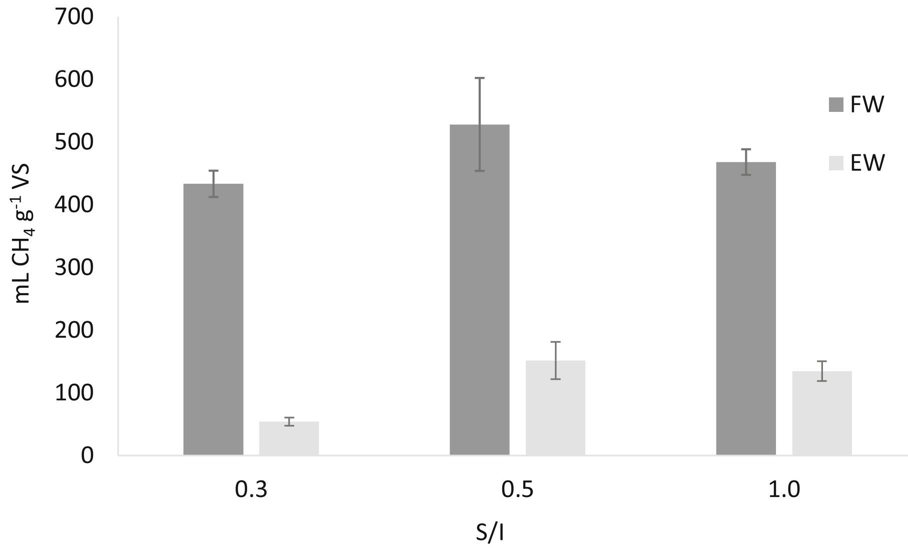

Fig. 3 BMP for FW and EW at each S/I ratio

Gompertz model. In Table 4, kinetic parameters determined for each model using Matlab 2018a® are presented.

Figures 4 and 5, and Table 4 show that for FW both models produced a similar fit to the experimental results ($R^2 \geq 0.98$; RMSE: 4.3–15.0), whereas, for EW, the modified Gompertz model had a better fit ($R^2 \geq 0.98$; RMSE: 2.4–5.2) than the first-order kinetic model, which produced lower R^2 and larger RMSE. Similar fitting performance of the first-order kinetic model to BMP experimental data had been reported in studies with food waste and other organic substrates [34, 39]. Noticeably, calculated first-order kinetic parameters for FW were higher to those reported by Bilgili et al. [15] who employed BMP results for the organic fraction of fresh waste samples taken from a sanitary landfill in Turkey and determined maximum CH_4 potential (B_0) and CH_4 generation rates (k) of 425 mL CH_4 g^{-1} VS and 0.13 d^{-1}, respectively. FW kinetic parameters were also higher to those obtained by Parra-Orobio et al. [31] (B_0 = 149 mL CH_4 g^{-1} VS, k = 0.19 d^{-1}) and Cardenas-Cleves et al. [39] (B_0 = 71 mL CH_4 g^{-1} VS, k = 0.06 d^{-1}) employing Eq. (1) and BMP results for food waste.

As shown in Fig. 4, CH_4 production for FW begins almost immediately (λ ~ 0), which suggests the rapid establishment of adequate conditions for anaerobic digestion. Schirmer et al. [16] conducted BMP tests on fresh and one-year-old OFMSW samples from a landfill in Brazil, obtaining also latency periods below 1 day due to the rapid transformation of the readily biodegradable matter. Although the latency phase for the EW was

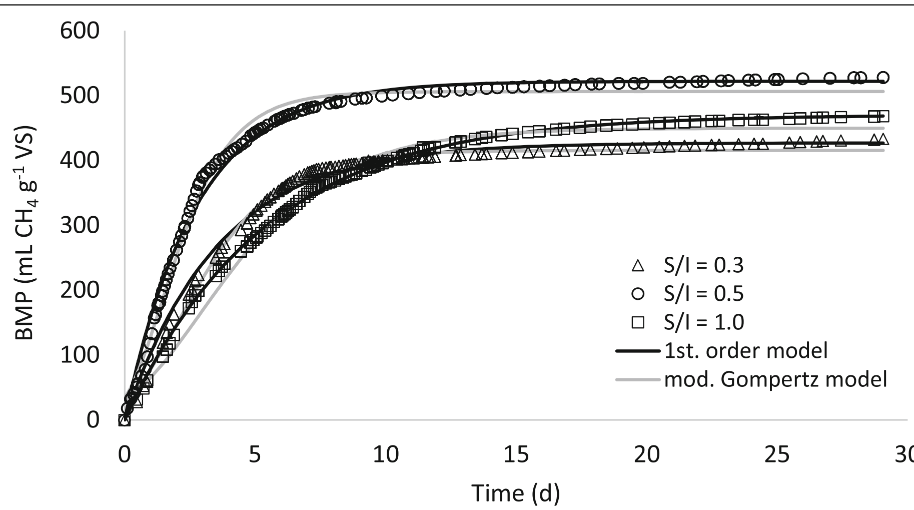

Fig. 4 FW BMP at three S/I ratios and best-fit curves using first-order and modified Gompertz models

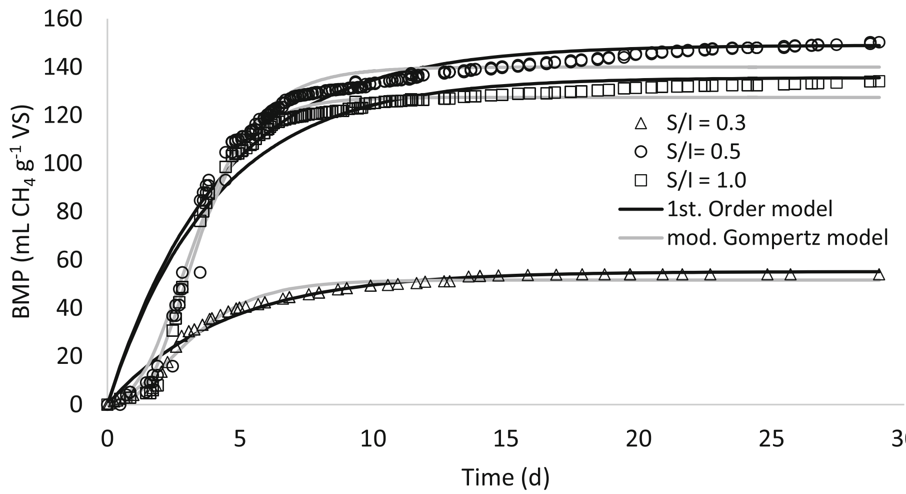

Fig. 5 EW BMP at three S/I ratios and best-fit curves using first-order and modified Gompertz models

slightly longer (0.7–1.5 d), Fig. 5 shows that the CH_4 production had a relatively early onset, most likely associated to the remaining organic content in the non-identifiable waste fraction (Fig. 2), which thus constituted a substrate of rapid assimilation.

The BMP value and CH_4 generation rates for FW show the potential for biogas utilization from waste with a high content of easily biodegradable materials, such as that disposed of in landfills in developing countries. In contrast, the degradation rates of EW are lower, being the BMP values approximately one quarter of the CH_4 potential measured for FW. This means that under technically adequate disposal conditions and enhanced management strategies waste degradation can be accelerated and landfills should be expected to have increased gas production [6]. Landfill management strategies such as those used in modern bioreactor landfills (i.e., leachate recirculation, liquid addition or aeration) have proven to be effective in accelerating stabilization and CH_4 production of landfills in tropical countries [19, 40]. This is particularly relevant for the establishment of more sustainable waste disposal methods in developing countries like Colombia where improved waste stabilization processes have the potential to enhance the environmental performance of landfills, contributing to mitigate CH_4 emissions and reduce both their long-term environmental impacts and post-closure management costs.

Stability characteristics

Table 5 summarizes the results of the characterization performed on the liquid waste fractions at the end of the BMP tests. The pH values for FW and EW at all S/I ratios were within the range 7–8, recommended for the adequate performance of the anaerobic process [10]. Furthermore, TA for FW and EW was in the range 3.6–7.8 and 2.5–6.3 g L^{-1}, respectively, with BA/TA ratios > 0.9, indicating favourable conditions for methanogenesis

Table 4 Parameters of the first-order and modified Gompertz models

S/I	First-order kinetics model				Modified Gompertz model				
	B_0 [a]	k [a]	R^2	RMSE	B_0 [a]	R_m [a]	λ [a]	R^2	RMSE
	(mL CH_4 g^{-1} VS)	(d^{-1})	(–)	(–)	(mL CH_4 g^{-1} VS)	(mL CH_4 g^{-1} VS d^{-1})	(d)	(–)	(–)
FW									
0.3	427 ± 2	0.28 ± 0.006	0.987	9.6	417 ± 2	69.9 ± 1.5	0.00 ± 0.08	0.993	7.2
0.5	522 ± 3	0.36 ± 0.008	0.991	14.9	506 ± 3	127.4 ± 3.8	0.00 ± 0.06	0.991	15.0
1.0	470 ± 1	0.19 ± 0.002	0.998	4.3	457 ± 2	48.5 ± 1.0	0.00 ± 0.12	0.992	8.9
EW									
0.3	55 ± 2	0.23 ± 0.020	0.965	3.3	52 ± 1	11.0 ± 0.9	0.66 ± 0.21	0.982	2.4
0.5	149 ± 3	0.23 ± 0.014	0.921	9.9	140 ± 1	31.9 ± 1.4	1.16 ± 0.12	0.978	5.2
1.0	136 ± 3	0.25 ± 0.018	0.893	10.8	127 ± 1	35.5 ± 1.3	1.51 ± 0.08	0.988	3.6

[a] Calculated at 95% confidence interval

Table 5 Comparison of degradation and stability indicators for FW and EW

	pH	BA[a]	TA[a]	COD[a]	CODf[a]	BOD[a]	BOD/DQO
S/I	(units)	(mg $CaCO_3$ L^{-1})	(mg $CaCO_3$ L^{-1})	(mg L^{-1})	(mg L^{-1})	(mg L^{-1})	(–)
FW							
0.3	7.7	6951 ± 25	7756 ± 17	5093 ± 529	2179 ± 27	450 ± 30	0.09
0.5	7.6	4729 ± 21	4800 ± 13	4018 ± 36	1491 ± 9	400 ± 25	0.10
1.0	7.5	3545 ± 13	3624 ± 8	1591 ± 110	1083 ± 36	140 ± 20	0.09
EW							
0.3	7.9	6155 ± 29	6313 ± 21	4876 ± 294	3058 ± 187	350 ± 30	0.07
0.5	7.5	4032 ± 8	4099 ± 4	2654 ± 35	1444 ± 10	270 ± 30	0.10
1.0	7.2	2435 ± 4	2489 ± 8	1032 ± 30	661 ± 20	140 ± 20	0.14

[a]Average values ± SD (standard deviation)

and the stabilization of MSW [40]. On the other hand, COD values for FW and EW were within the range 500–4500 mg L^{-1} reported for mature landfills [41] and distributed between its particulate and soluble form (CODf/COD = 0.5), indicating degradation of the readily and moderately biodegradable fraction of the organic matter present in the waste samples [42]. BOD and COD concentrations depend on the waste degradation level, and they decrease as they stabilize, therefore BOD/COD ratios < 0.1 have been suggested as indicators of stabilization for MSW in landfills [8]. The BOD/COD ratios of FW and EW liquid fractions were below 0.1 and 0.14, respectively, suggesting an advanced grade of degradation. Nevertheless, BOD/COD ratios have been observed to decrease faster than other waste stabilization parameters and as such, they alone must not be taken to represent the stabilization of the solid waste [37].

Studies in developed countries have led several authors to suggest BMP target values less than 10 mL CH_4 g^{-1} DM as termination indicators for landfills [43]. The average BMP of EW was 113 mL CH_4 g^{-1} VS (14.6 mL CH_4 g^{-1} DM), close to the aforementioned target values and significantly low considering the relatively short time since its disposal (5 yr) under the conventional operation conditions of the landfill.

In this way, the use of BMP tests together with kinetic models can help in determining appropriate parameters to predict CH_4 generation rates for landfill waste of different ages, and in particular for landfills in tropical developing countries characterised by both receiving wet and highly organic wastes and experiencing dramatic climate changes between dry and wet seasons [19, 20]. This type of analysis can be particularly useful in developing countries where waste degradation characteristics are different, most sites do not have LFG collection systems, and, therefore the customary determination of CH_4 generation parameters based on LFG collection data is not viable.

Nevertheless, although kinetic parameters B_0 *and* k, respectively, are related to the CH_4 production potential and CH_4 generation rate constants used in first-order decay landfill models, their application to predict LFG production from landfills must take care of the differences in the way parameters are derived. For instance, *Bo* cannot be taken as equal to the CH_4 production potential at the landfill, as the latter takes into account physical and environmental factors affecting final disposal sites (e.g., particle size, moisture distribution and temperature) that cannot be fully reproduced at the laboratory scale [44]. In the same way, parameter k would be different to the first-order rate constant used in landfill models, since in the field CH_4 generation rate is affected by the waste age and composition, and operational factors such as waste depth, density and water content, as well as climatic conditions at the landfill site [20].

Due to the significant proportion of food waste and other moderately biodegradable materials sent to landfills in tropical developing countries like Colombia, the CH_4 potential and other stabilization indicators may be different to those reported for developed countries. Likewise, the termination criteria for landfills in developing countries may vary from those found in the literature, which have been mostly investigated for landfill waste with less content of readily biodegradable materials. The BOD/COD and BMP results and the biodegradation kinetic analysis for FW show the favourable biodegradability characteristics of wastes disposed of in the regional landfill at Valle del Cauca. On the other hand, characterisation of the CH_4 remaining potential and the extent of degradation achieved by EW is important, as it helps in establishing adequate completion criteria for MSW and to identify appropriate stabilization strategies for landfills in tropical developing countries. Finally, besides evaluating the biodegradability and CH_4 potential of landfill wastes with varying aged and composition, it is recommendable to conduct experiments at larger scales in order to asses aspects related to the particular operational and environmental conditions of final disposal sites in developing countries.

Conclusions

The BMP results, along with CH_4 generation rates determined, confirm the high biodegradability and biogas potential of MSW disposed of in a tropical landfill in Colombia, characterized by high contents of both readily and moderately degradable materials typical for developing countries. The BMP of the FW was relatively high in comparison to that reported for fresh MSW and even OFMSW. In contrast, the BMP for EW was nearly one-quarter of that measured for FW but falls within the range reported for landfilled wastes of similar age and even older.

The first-order and modified Gompertz kinetic models gave similar fit to BMP data for FW ($R^2 \geq 0.99$), whereas the latter gave a better fit for EW ($R^2 \geq 0.98$). First-order CH_4 generation rates (k) for FW and EW were in the range 0.19–0.36 d^{-1} and 0.23–0.25 d^{-1}, respectively, whereas latency values for both types of MSW indicated a rapid establishment of methanogenic degradation conditions ($\lambda < 1.5$ d). Furthermore, the analysis of stability indicators showed the favourable biodegradability characteristics of the landfill wastes evaluated. In particular, BMP and BOD_5/COD results for EW were close to target values suggested as indicators of stabilization for landfills despite its relative short disposal period under conventional landfill conditions.

These results also indicate that, given the MSW characteristics and the environmental conditions of landfills in tropical developing countries, the application of enhanced landfill management strategies has the potential to accelerate waste degradation, a key aspect towards improving biogas utilization and the lifespan of final disposal sites in developing countries.

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Authors' contributions
J. J. Sandoval-Cobo (JSC), L. F. Marmolejo-Rebellón (LM) and P. Torres-Lozada (PT) were responsible for the conceptualization and design of the study. SC, M. R. Casallas-Ojeda (MC), Lina Carabalí-Orejuela (LC), A. Muñoz-Chávez (AM) and D. M. Caicedo-Concha (DC) worked in the acquisition and interpretation of data through field and laboratory work. JSC drafted the article and LM, DC and PT revised it critically. All authors read and approved the final manuscript.

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Availability of data and materials
All data generated or analysed during this study are included within the article.

Competing interests
The authors declare they have no competing interests.

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