



A fractal-like kinetics equation to calculate landfill methane production[☆]

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Abstract

Landfill appears as a convenient choice to get rid of municipal solid waste while providing energy, due to methane generated through anaerobic fermentation. However, without capture and treatment landfill gas is considered an important source of atmospheric methane. The control and use of this gas require knowledge of both, current yield and long-term accumulative production. These values are usually calculated with mathematical expressions that consider 100% of conversion, and homogeneous chemical reactivity inside the fill. Nevertheless, fermentation in landfills is erratic and spatially heterogeneous. This work introduces a fractal-like chemical kinetics equation to calculate methane generation rate from landfill, Q_{CH_4} (m^3/year), in the way: $Q_{\text{CH}_4} = L_0 \sum_j \sum_i M_{ij} C_{ij}^0 k_i (t_j)^{-d_s/2} \exp[-k_i t_j]$, where fermentable wastes are partitioned in readily, moderately and slowly biodegradable categories, L_0 is the potential of methane yield of refuse (m^3/tonne under standard conditions), d_s is the solid-phase fracton dimension, k_i is the reaction kinetics constant of waste category i (year^{-1}), and t_j is the time from the year of burying j (year), C_{ij}^0 (kg/tonne) and M_{ij} (kg) are the initial concentration and the mass of waste category i landfilled in year j , respectively. The idea behind this equation is that methane production kinetics is limited by the diffusion of hydrolyzed substrate into a heterogeneous solid-phase towards discrete areas, where methanogenesis occurs. A virtual study for a hypothetical case is developed. The predictions from this fractal approach are contrasted with those coming from two equations broadly used in the industrial work. The fractal-like kinetics equation represents better the heterogeneous nature of the fermentation in landfills.

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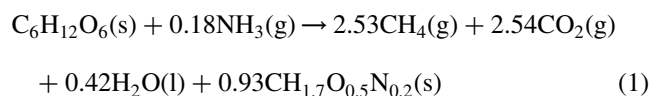
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1. Introduction

The most common disposal method for municipal solid waste (MSW) disposal is burial in landfills [1]. There, atmospheric oxygen is early excluded from the MSW, and aerobic digestion of the organic matter filled is bounded by the little amount of air caught during MSW-burying. When initial aerobic MSW degradation exhausts oxygen reserves, anaerobic conditions are established. Observations made at various landfill sites have shown that the end of aerobic respiration (due to the lack of oxygen) occurs few weeks after MSW were buried, while gas production goes on for more than 30 years after landfill completion [2]. Then, MSW degradation in landfill essentially means the digestion of its organic content by anaerobic bacteria.

Typically 90% of the organic mass in MSW is identified as glucose polymers: cellulose and hemi-cellulose [3].

Then, glucose composition can be assumed as representative of all organic matter contained in MSW. With this idea and assuming NH_3 as the nitrogen source, the following global material balance was proposed elsewhere [4]



A reaction such as (1) represents the overall process taking place when anaerobic bacteria consume the biodegradable organic matter ($\text{C}_6\text{H}_{12}\text{O}_6$) contained in MSW to produce the bacterial cell mass ($\text{CH}_{1.7}\text{O}_{0.5}\text{N}_{0.2}$) and the by-products of bacterial metabolism (CO_2 , CH_4 and H_2O). In particular, reaction (1) evidences the generation of a gas mixture with a significant energetic value because of its methane content (~50% on volume). In absence of collection and treatment, methane landfills emissions represent both, a potential explosion hazard [1] and a strong environmental threat because CH_4 is a powerful greenhouse gas [5]. In consequence, assessing landfills potential, as methane

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Nomenclature

γ	Dimensionless value.
A	Constant value, $\text{year}^{-1} \text{m}^{d_s/2}$.
β	Dimensionless value.
B	Constant value, $\text{year}(1 - d_s/2)$.
b	Time from the initial MSW placement, year.
c	Time from site closure, year.
C^0	Initial organic reactant concentration.
C_{ij}^0	Initial concentration of waste category i landfilled in year j .
D	Diffusivity, $\text{year}^{-1} \text{m}^2$.
d	Euclidean dimension.
d_s	Fracton dimension.
d_w	Fractal dimension of the path of the random walk.
ϕ	Fill porosity.
k_a	Methane generation parameter, year^{-1} .
k_i	Kinetics constant of waste category i , year^{-1} .

L_0	Potential methane yield of MSW, m^3/tonne under standard conditions.
M	Mass of the liquid clusters, kg.
M_{ij}	Mass of waste category i landfilled in year j , kg.
P	Average refuse acceptance rate, tonne/year .
Q_{CH_4}	Methane generation rate, m^3/year under standard conditions.
R	Root mean square displacement, m.
r	Characteristic length scale of liquid clusters, m.
R_S	Characteristic longitude of leachate islands, m.
$S(t)$	Averaged number of distinct sites visited by a molecule after time t in a fractal space.
S_W	Leachate porous space saturation.
t	Time, year.
t_j	Time from the year of burying j , year.
V	Volume trap-free regions, solid-phase volume, m^3 .
V_T	Fill volume.

producer is important from the point of view of hazard control and the estimate of the eventual methane contribution on the climatic global change in next years. Also, a reliable method of estimating methane production from landfill over time is obviously needed if valorisation landfill gas projects are to be seen as sound investment [6].

The calculus of methane production from landfills is usually performed with models assuming total conversion, and homogeneous spatial chemical reactivity, like USEPA model [7] and Hoeks model [8], both models will be succinctly introduced in Section 2. Nevertheless, there are experimental evidences of heterogeneous spatial chemical reactivity in landfills (at this respect, please consult Ref. [9] and references therein). In fact, among the different variables that affect fermentation in landfills, free water content appears to be the single most important thermodynamic variable. Free water content is the water held by capillarity in the refuse and intermediate cover layers, as well as water in transit through the landfill by downward percolation or under upward evapotranspirative flow gradients. Free water content is assumed to promote mass transfer of inoculum and evening out any local shortage of nutrient or excess of toxins or inhibitors, at the same time it provides the aqueous environment essential to microorganisms. Certainly, free water content is important, high levels appear to be beneficial for methane production, while biodegradation almost ceases at moderate levels. Hence, irrigation or leachate recycle is highly stimulatory for methane production, moderately compaction (minor than $800 \text{ kg}/\text{m}^3$) promotes also free water content by increasing the capillary forces of the system, but high compaction (higher than $800 \text{ kg}/\text{m}^3$) is not recommended for methane production because it reduces the free water content by destroying the landfill porous space. However, most modern landfills are intentionally well compacted and covered in order to minimize leachate formation, so their

free water content is usually very poor (inferior to 20% on mass). In this scenario, water essentially flows via landfill pores, and the resulting water spatial distribution is not homogeneous, i.e. it is possible to distinguish quite moistened regions and dry regions, in both horizontal and vertical direction [10]. As it is well known, this kind of spatial structure is not efficient for mass transport all the way through liquid-phase, and then it hinders the circulation of nutrients and bacteria in the site. However, water is not the only mass transfer medium, solid-phase diffusion is slower but may be important in practice [11]. In brief, poor free water content in landfill (not stirred system) outcomes a reaction system characterized by a spatially heterogeneous chemical reactivity, there mass diffusion in solid-phase of organic substrate must be the reaction rate limiting mechanism.

It is pertinent to remark that at present time there are no available field data, which allow a quantitative validation of any equation to calculate methane production due to: (i) no one has determined convincingly the final fermentation efficiency in landfill, the hypothesis of 100% of conversion is not acceptable because in well-compacted landfills is common to find MSW in their original form years after they were buried [12,13], and (ii) no one has made a satisfactory determination of the efficiency of gas capture systems. Generally it is assumed, without enough justification, that only a half of gas produced is captured [6,14]. Therefore, assorted studies have been performed on smaller and more controllable systems as anaerobic digesters without agitation and with high solid content, i.e. the study of fermentation under similar conditions to landfill predominant conditions [15–18]. Recently, the digestion under this set of conditions has been standardized as solid state digestion (SSD) [9]. Although the accumulated experience signals a wide variability [11,16], a typical trend of methane production from SSD has been established: first methane

production rises slowly to a classical peak, and then an asymptotic decline follows, there very high reaction orders have been observed and final conversion is usually poor [15,16]. By analogy, methane production in landfill must rise (years) to a peak, and then a stage of deceleration (decades) follows, with a poor final conversion. This last stage of gas production is the most important one for methane recuperation [1,6,19], and following [8] the work presented here is particularly oriented to model it. It is pertinent to remark that there are approaches considering the balance between the rates of polymer hydrolysis and methanogenesis [11,20], what is particularly adequate to model the early stages of methane production in SSD.

The purpose of this work is to introduce a fractal-like equation for methane landfill production from MSW composition and site history. This fractal-like chemical kinetics equation considers the heterogeneous nature of fermentation (i.e. inefficient transport of hydrolyzed nutrient towards the methanogenesis reaction zone, the solid–liquid interface) under the conditions imposed by the modern operation of landfills.

This manuscript presents the material as follows. First the antecedents are briefly presented through two equations widely used in the industrial work to predict the behaviour of the methane production in landfill. Second, a fractal-like variant of the Hoeks equation is introduced. Third, the computed methane production results using the different equations are compared each other by means of a numerical application on a hypothetical problem. Their differences and similarities are discussed.

2. Published equations

As before mentioned, it is important to be able to predict with reasonable certainty the rate of methane production available at a given landfill site. In the past, both empirical and semi-fundamental forecasting equations have been developed with this end; however, they cannot yet be relied on to predict accurately landfill gas production [21]. Empirical models are particularly site-dependent. Conversely, the more fundamental models describe the decomposition process with a set of sequential microbial reactions, beginning with aerobic decay and then proceeding through the stages of anaerobic degradation, from hydrolysis through to methanogenesis. Although this latter approach may be sounder, these models suffer from a lack of credible data relating to microbial activity. They also tend to become complex, which often results in high computing demands.

Since there is, as yet, no rigorous approach to modelling landfill gas production, simple empirical models are the most common. The approach most often employed is to assume a first order decay of organic material. This is a reasonable first approximation since the volume of methane produced versus time curve apparently approximates to this form (dying exponential). A typical example of this kind of

approach is the USEPA model equation; it has the form [7]

$$Q_{\text{CH}_4} = L_0 P \{ \exp(-k_a c) - \exp(-k_a b) \} \quad (2)$$

Where Q_{CH_4} is the methane generation rate in m^3/year , and L_0 is the potential methane yield of MSW in m^3/tonne of MSW, both under standard conditions. k_a is a methane generation parameter in year^{-1} , b is the time from the initial MSW placement, and c is the time elapsed since landfill closure ($c = 0$ for an active landfill), both in years. The average value of refuse acceptance rate during the active life of a landfill, P in tonne of MSW by year, is in this model assumed constant. The major limitation of this approach is that the methodology is strictly site specific, gas measurements must be taken at each site to find appropriate rate constants.

Now it is presented an example of a semi-fundamental approach, the Hoeks model [8]. Here, the MSW is partitioned in four kinetic categories: (1) readily degradable (food waste) with a half-life time ≈ 1 year, (2) moderately degradable (yard waste) with a half-life time ≈ 5 years, (3) slowly degradable (paper, textiles and wood) with a half-life time ≈ 15 years, and (4) inert materials (plastics, glass, metals, ash, rock and dirt). These half-life values were estimated under good reaction conditions (i.e. a well mix system with enough water, pH control, etc.).

There is field evidence that the concentration of glucose polymers in landfill decreases in quasi-exponential way as a function of time [22,23]. Therefore, fermentation rate of waste in category i is mathematically described as a first order chemical process. From the given half-life times, kinetics constants take the values 0.69 ± 0.23 , 0.14 ± 0.23 , and $0.05 \pm 0.23 \text{ year}^{-1}$ for the waste categories 1, 2, and 3, respectively [21].

Let M_{ij} the mass of waste category i landfilled in year j . It is assumed that waste landfilled during the year j begins its methane production in the year $j + 1$; that agrees with the accumulated experience [2]. Let C_{ij}^0 the initial concentration of waste category i landfilled in year j , and t_j the time in years elapsed from year j . If linearity is assumed, then Q_{CH_4} is the sum over all the wastes categories and over all years of landfill activity

$$Q_{\text{CH}_4} = L_0 \sum_j \sum_i M_{ij} k_i C_{ij}^0 e^{-k_i t_j} \quad (3)$$

Therefore, Eqs. (2) and (3), based on hypothesis of homogeneous reactivity and total efficiency, are not really suitable to model the methane yield from landfill. The equation introduced in Section 3 seems to be more adequate to describe the main features cited above.

3. Fractal-like kinetics equation

Here, it is assumed the conventional understanding of landfill processes, methane production occurs in liquid-phase or at solid–liquid interface, i.e. at the porous space saturated

by water. Given the heterogeneous and poor free water distribution in modern landfills, mass transfer by diffusion in liquid-phase is not efficient, so methane production kinetics must be controlled by organic substrates diffusion in solid-phase towards solid–liquid interface. Notice that in landfill the nature of solid-phase is clearly heterogeneous, and so mass diffusion presents anomalous characteristics, for instance hydrolyzed organic species cannot access the volume occupied by glass, metals, rocks and plastic; these materials are always held in MSW (Table 1). Indeed, organic matter should be first hydrolyzed and second transported in solid-phase towards solid–liquid interface [24]. At the beginning, hydrolyzed substrates located in the neighbourhood of solid–liquid interface are quickly transported to liquid-phase, but this material is fast exhausted and biodegradable organic matter should be transported from farther. Evidently, this transport process becomes early inefficient due to slow diffusion in solid-phase, which contains permeable and impermeable areas. Consequently, when bacteria consume the biodegradable organic matter in liquid-phase, organic substrates are not really reinstated, and a significant decreasing of organic matter content in liquid-phase occurs [15,16]. The resulting fermentation kinetics has a pronounced decline of reaction rate due to reactant separation (i.e. the substrates have to diffuse, in solid-phase, a long way to the site of reaction), it produces very anomalous results in which rate constants depend on time [25]. A workable mathematical approach for this behaviour is a fractal-like kinetics model (Appendix A). A fractal variant of the Hoeks model is next introduced.

Field capacity is that water content that a porous material (for instance, refuse or soil cover) absorbs and stores within its pores by capillarity. If a quantity of water is added to a material already at its field capacity, an equal quantity will drain out of it to restore moisture equilibrium. In terms of a water balance and the definition of field capacity, one might imagine the water stored in a landfill gradually accumulating until the overall field capacity had been reached. Thereafter any further water added at the top of the landfill would result in the production of an equal quantity of leachate at the base. Let us consider that just

Table 1
Typical water content and composition (mass percentages as discarded), as well as biodegradability of MSW from Mexico City

Waste	Mass (%)	Water content	Biodegradability
Food	39	70	Readily
Paper	22	6	Slowly
Plastics	6	2	Inert
Textiles	2	10	Slowly
Wood	1	20	Slowly
Yard	6	60	Moderately
Glass	8	2	Inert
Metals	4	3	Inert
Ash, rock and dirt	12	8	Inert

Adapted from Ref. [32].

the porous space saturated by leachate is accessible to methane generative bacteria. Therefore, their habitat volume is given by $V_T \phi S_W$, where V_T , ϕ , and S_W are the fill volume, the fill porosity and the leachate porous space saturation, respectively. So, in function of the site operation (impermeable covering, irrigation, compaction, etc.) bacterial habitat could be constituted by: (i) finite leachate clusters, when the field capacity of the fill is not surpassed-poor free water content, or (ii) ‘percolating’ leachate clusters (percolating means here that the cluster spans all the space of interest), when the field capacity of the filling is surpassed. For various finite clusters, lattice animals, and mono-disperse islands (square and linear), computer simulations have indeed given unbelievably large reaction orders (from 3 to 75). Thus any diffusion-controlled reaction that occurs on clusters or islands is expected to be anomalous and fractal-like [26]. In this scenario, the trapping problem is fundamental to the understanding of the kinetics of reaction. Assume a random walker in a medium, which contains a finite concentration of randomly distributed static trapping sites (finite leachate clusters caught by capillarity into the fill porous space). The random walker represents the biodegradable organic specie, i.e. a biodegradable organic substratum diffusing into the solid-phase. The question of interest is what is the trapping rate or, equivalently, the survival probability, or how the concentration of random walkers decays with time. It is assumed that trapping occurs immediately upon the encounter of a random walker with solid–liquid interface (trapping centres), so that the process is limited by the diffusion of the biodegradable species in solid-phase. In this case, Weiss and Havlin [27] proposed elsewhere that the probability of survival of random walkers is proportional to

$$P(V, t) \propto \exp\left[-A \frac{t}{V^{2/d_s}}\right] \quad (4)$$

Where A is a constant value, V is the volume trap-free regions, $V = V_T(1 - \phi)$, and d_s is the solid-phase fracton dimension, its value is given by $d_s = 2d_f/d_w$, d_f and d_w are the fractal dimension and the fractal dimension of the path of the random walk, respectively, both referred to solid-phase. We encourage the reader to look at Appendix A.

Moreover, the free-trap volume depends of the characteristic longitude of leachate islands, R_s , as $V \propto (R_s)^{d_f}$. Introducing the two last relationships in Eq. (4), the following is obtained

$$P(V, t) \propto \exp\left[-A \frac{t}{R_s^{d_w}}\right] \quad (5)$$

So the concentration of the biodegradable organic substrates as a function of time could be expressed as

$$C(t) = BC^0 t^{-d_s/2} \exp\left[-A \frac{t}{R_s^{d_w}}\right] \quad (6)$$

Where B is a constant (one of its tasks is to conserve the dimensional homogeneity of Eq. (6)), C^0 is the initial organic reactant concentration, and the factor $t^{-d_s/2}$ is the diffusional contribution (reaction controlled by diffusion through the solid-phase). Finally, the introduction in the Hoeks model of $C_{ij}(t_j)$, via Eq. (6), for all waste categories and over all years of landfill activity gives the following equation, it is analogous to Eq. (3)

$$Q_{CH_4} = BL_0 \sum_j \sum_i M_{ij} C_{ij}^0 k_i(t_j)^{-d_s/2} \exp\left[-A_i \frac{t_j}{R_s^{d_s}}\right] \quad (7)$$

To keep the dimensional homogeneity of Eq. (7), the values of A and B must be chosen as $A_i = x k_i R_s^{d_s/2}$ and $B = y \times \text{year}^{(1-d_s/2)}$; $x, y \in \{\text{real numbers} > 0\}$. The values of these constants are found via the condition: if $d_s \rightarrow 0$ (mixture), then Eq. (7) tends to Eq. (3). So $x = y = 1$, and Eq. (7) becomes

$$Q_{CH_4} = L_0 \sum_j \sum_i M_{ij} C_{ij}^0 k_i(t_j)^{-d_s/2} \exp[-k_i t_j] \quad (8)$$

In Section 4, the differences among the methane production values of the diverse formulations, Eqs. (2), (3) and (8) are analyzed and discussed.

4. Numerical application and discussion

In order to compare the methane production versus time curves prediction of the different equations, a virtual study is developed on a hypothetical site landfilled during 9 years with MSW from Mexico City. The average MSW composition is given in Table 1, and the mass landfilled over a 9 year period was 7500 ktonne. So $P = 833.33$ ktonne/year. From Table 1, it is easily derived that there are 368 kg of degradable organic matter by tonne of MSW, where 114 kg of readily degradable, 12 kg of moderately degradable and 242 kg of slowly degradable organic matter. Thus, from Eq. (1) the fermentation of 1 tonne of MSW produces 125.856 m^3 of methane at standard conditions. On the other hand, the values of k_a go from 0.02 year^{-1} for a temperate climate to 0.04 year^{-1} for tropical climate [7]. Fig. 1 shows the sensitivity of USEPA equation, Eq. (2), to this parameter. Notice that the landfill completion corresponds to maximum of methane production and a bigger value of k_a means a faster rate of methane production. However, in the three studied cases, this equation predicts a very long period of production after landfill completion. Particularly, a significant methane generation 90 years after landfill end is unrealistic for a tropical climate, where gas landfill production is generally finished before 50 years from site completion [7].

For Hoeks model, both classical and fractal-like equations, simulation begins with a fed-batch behaviour (landfilling stage), and goes on with batch behaviour with a specific methane production in each lift (MSW landfilled

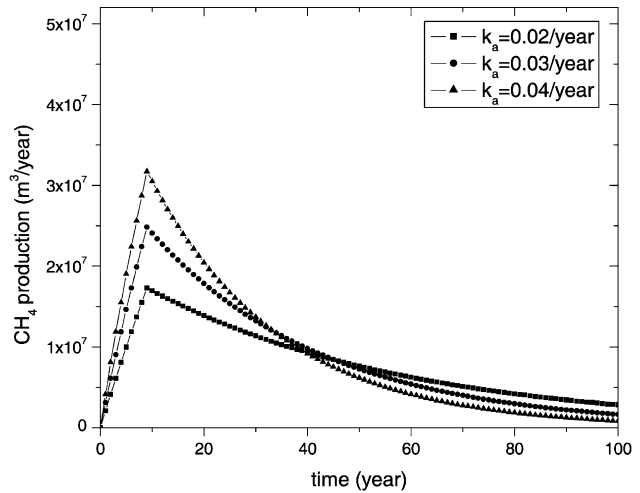


Fig. 1. Prediction of methane production by USEPA equation, Eq. (2), sensitivity to k_a parameter. k_a is a function of temperature.

during one year). In the case of Hoeks equation, Eq. (3), Fig. 2 shows that during the landfilling stage and also during the first 10 years after landfill completion, methane production is essentially due to fermentation of readily and slowly degradable organic fractions; and after that, methane production is entirely due to fermentation of slowly degradable fraction. In this case, the contribution of moderately degradable fraction is always unimportant because the poor (12 kg/tonne) concentration of this waste category in Mexican MSW. Here, the maximum of production corresponds to 1 year later the site closing. Notice that 60 years after landfill completion methane production is unimportant.

Fig. 3 compares the sensitivity of the fractal-like equation, Eq. (8), to d_s parameter. There have been a number of works trying to demonstrate which is the value for d_s . The conjecture of author in Ref. [28] says that d_s equals an almost constant value very close to $4/3$ for any dimension and for the case of a big ‘percolating’ fractal

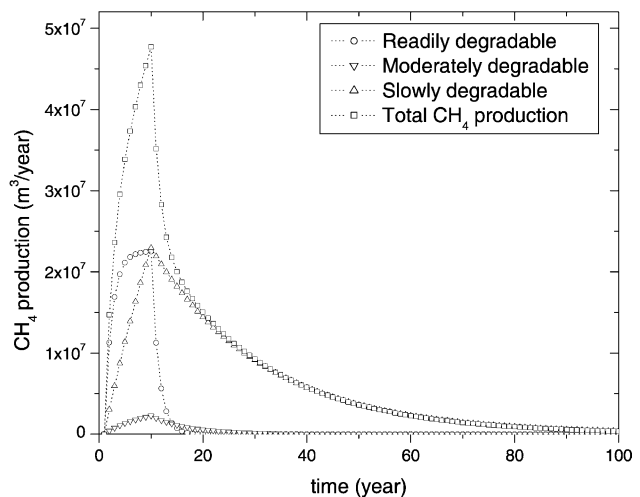


Fig. 2. Prediction of methane production by Hoeks equation, Eq. (3), total methane production and the contribution of each waste category.

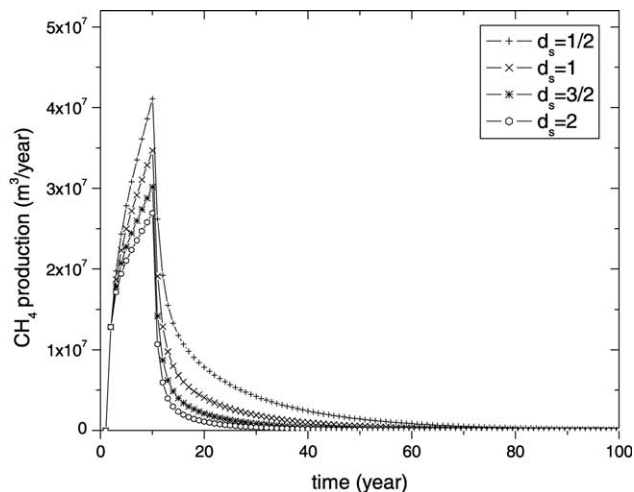


Fig. 3. Prediction of methane production by fractal-like kinetics equation, Eq. (8), sensitivity to d_s parameter. With vigorous stirring $d_s = 0$, and for diffusion-limited reactions in fractal spaces one always has $d_s > 0$. However, a reaction medium does not have to be a geometrical fractal in order to exhibit fractal kinetics [25].

cluster. Notice that the values $d_s = 4/3$ is in between the curves presented in Fig. 3. A detailed analysis for distributions of fractal clusters with the same fractal dimension but a broad distribution of sizes (as it is in our present case) indicates that this conjecture is no longer valid [29]. Thus, because we cannot yet estimate d_s experimentally, in Fig. 3 we present results for different possible values of it. In particular, the value $d_s = 1$ corresponds to the result that gives the analysis performed in Ref. [30]. In that work, the author relates the conjectured value $4/3$ for d_s with the one it should have for the case of a broad distribution of clusters with different sizes, i.e.: $d_s(\text{broad distribution}) = 4/3(1 - \beta/(\beta + \gamma))$, where β and γ are very well known critical exponents from percolation theory [28,31]. For three dimensions, they attain the values $\beta = 0.41$ and $\gamma = 1.80$, thus $d_s(\text{broad distribution}) \cong 1.08$, for this reason, we choose $d_s = 1$ in Fig. 3. Note there that: (i) as Hoeks equation, 1 year later the site closing corresponds to the maximum of methane production, (ii) a higher value of d_s (less efficient mix) corresponds to a lower efficient fermentation, i.e. a minor area under the production curve, and (ii) the four studied cases, $d_s = 1/2, 1, 3/2,$ and 2 , predict a worthless production scarcely 50 years after the site closing, this in good agreement with accumulated industrial experience.

Fig. 4 compares the methane production versus time curve predictions of the different equations. Note there that: (i) the curve shape in all three models follows the typical trend of methane production from landfill, i.e. first methane production rises (years) to a peak, and then a stage of deceleration (decades) follows, (ii) only the fractal-like equation produces high reaction orders and a fermentation efficiency smaller than 100%, (iii) during landfilling stage, the three equations signal a significant methane production, more than 1/4 of the potential methane yield, during this

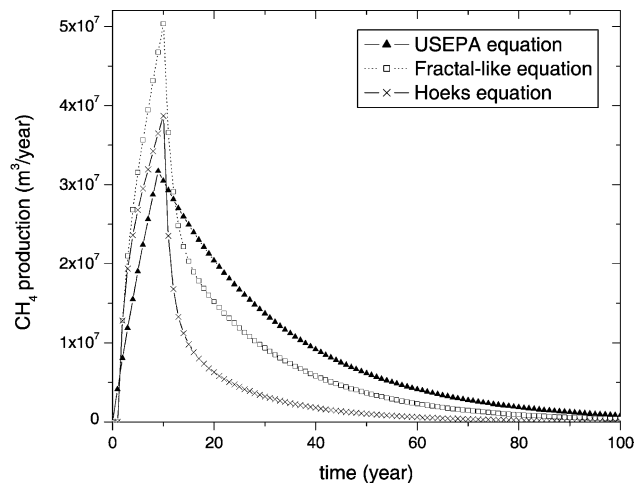


Fig. 4. Comparing methane production prediction from Hoeks equation, Eq. (2), USEPA equation, Eq. (3) with $k_a = 0.04 \text{ year}^{-1}$, and fractal-like equation, Eq. (8) with $d_s = 1$.

step Eq. (3), Hoeks equation, predicts the highest production value, meanwhile USEPA and fractal models present similar areas under the curves of methane production, and (iv) after site completion, USEPA equation predicts the highest methane production, but its production lapse is too large; duration predicted by the other models are more plausible in the context of a tropical climate, but the lack of reliable field data do not make possible validate the results of the simulations. Nevertheless fractal-like equation is not based on homogeneous conditions of reaction hypothesis and 100% of conversion hypothesis, both of doubtful justification in the context of modern landfills. That in principle confers it a bigger reliability.

Two alternatives of model verification will be tried: (i) an experimental work will be carried out on anaerobic reactors below SSD conditions, reactors will be filled with the same organic matter and with inert materials (e.g. rocks), the goal is to study the effect of size and spatial distribution of inert materials (changing solid-phase transport properties) on fermentation behaviour, the drop of the biogas production must furnish the value for d_s , and (ii) an automaton simulation study on SSD considering both, inhibitory and symbiotic relations between acidogenic and methanogenic bacteria, and a substratum of heterogeneous biodegradability kinetic.

5. Conclusions

Modern landfill designs and operation tend to limit fermentation by restricting infiltration in order to minimize leachate generation, thus heterogeneous reactivity conditions are developed into the landfill. It is not uncommon to observe well-conserved waste years after the landfill closure. However, traditional methane production equations, e.g. Hoeks equation and USEPA equation, suppose both: (i) spatially homogeneous

chemical reactivity, and (ii) 100% of conversion. The virtual analysis performed here, suggests that the estimations of methane emissions with traditional models are too high. Improving the estimate of methane emissions from landfills requires the development of methane production equations based on more realistic hypotheses. The equation introduced here considers explicitly way the heterogeneous reactivity characterizing fermentation in landfill. Particularly, this equation signals that the poor and erratic methane production usually observed in modern landfills, is likely due to the inefficient transport by diffusion of hydrolyzed nutrient in a heterogeneous solid-phase characterized by a wide range of diffusivities, and the fact that methanogenesis reaction happens at a solid–liquid interface with complex geometry.

The introduced equation assumes synchronized processes of waste conversion into gas in the total volume of landfill. A wide variety of methane production behaviour (e.g. the breadth of the peak) can be obtained considering non-synchronized fermentation processes. This version of the model could explain a more puzzling observation, landfills producing methane at the same time as acidic leachate, this is readily explicable if methanogenesis occurs only in a portion of water get by capillarity in the landfill porous space, while acid production occurs in the rest of the landfill liquid-phase.

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Appendix A

For those reader who are not familiar with fractal terminology, let us remember some few important aspects concerning diffusion on a fractal structure [30,31]. When, for instance, a diffusing substrate molecule is performing a random walk through a medium without any disorder, its root mean square displacement, R , grows proportional to the time squared. This is called a diffusion law and usually is denoted as: $R \propto t^n$; $n = 1/2$ or equivalently $R^2 = Dt$, where D is the diffusivity. This law is commonly referred to as ‘normal diffusion’. For a disordered medium, where the diffusing molecule does not have access to every place through out it (like in a fractal geometry) the exponent n is no longer $1/2$, but takes on lower values. This is called ‘anomalous diffusion’. In landfill, hydrolyzed organic species cannot access the volume occupied by glass, metals,

rocks and plastic. These materials are always held in MSW (Table 1). When one is dealing with a medium that presents heterogeneities, like, for instance, a collection of ‘liquid islands’ made up of wet regions of the waste deposit space, one can say that ‘disorder’ in the problem consists in the presence of a great number ‘liquid clusters’ (wet regions) of different sizes, towards the diffusing molecule should displace. All these clusters present the same fractal geometry characterized by a fractal dimension, d_f , i.e. their mass, M , will grow as: $M \propto r^{d_f}$, where r is their characteristic length scale and d_f is lower than the Euclidean dimension ($d = 3$ here). More clearly, when a fractal entity grows, it will not ‘fill’ the space in the same way that an Euclidean object will do. This marks the difference between homogeneous and heterogeneous space properties and this important difference must be taken into account in any model of a chemical process occurring in this kind of media [26]. In this scenario, the diffusion phenomenon will be characterized by an anomalous diffusion law that can be written as: $t \propto R^{d_w}$; $d_w = 1/n$. Where d_w can be visualized as the fractal dimension of the random walk that the diffusing molecule is doing in the fractal structure. Following De Gennes [28], the averaged number of distinct sites, $S(t)$, visited by the molecule after time t in a fractal space will be proportional to: $S(t) \propto t^{d_s}$, where d_s is the *fracton* or *spectral* dimension of the problem. $S(t)$ will be inversely proportional to the probability for the diffusing molecule to reach a certain distance R after time t [28]. The terms fracton and spectral were introduced by Alexander and Orbach [29] in 1982 and are widely used in fractal heterogeneous chemistry models [26]. As said above, d_s is related to d_w and d_f by: $d_s = 2d_f/d_w$. In order to have a ‘feeling’ of its meaning, one can say that d_s takes into account the way that a diffusing molecule ‘sees’ the heterogeneities present in the medium during its random walking transit.

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