MODELLING OF AEROBIC REACTORS FOR LANDFILL METHANE OXIDATION.

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EXTENDED ABSTRACT

Landfill gas is produced by anaerobic degradation of organic waste. Landfills are one of the principal anthropogenic sources of atmospheric methane, a strong greenhouse gas. At the present, abatement techniques of landfill biogas consist in the energy recovery for the production of electrical energy, when the percentage of methane is in the order of 40 - 50% v/v. In this case, the complete combustion and the subsequent functioning of the engine for the production of energy is ensured. For percentages of the order of 30% v/v, the extracted biogas is conveyed to a system of gas flare which ensures the complete thermal oxidation before entering into the atmosphere.
In all cases of low production of landfill gas or low methane concentration (small landfills or landfills in the terminal phase of stabilization), the combustion of biogas is difficult. In such conditions the biogas produced is often directly emitted into the atmosphere. Technical specifications for the operation of gas flares indicate a minimum flow of 50 Nm^3/h and a methane concentration of 30% v/v. A flow of this size is equivalent to an annual emission of approximately 3200 tons of CO_2eq.
It is however known that methane can be metabolized by specific CH_4-reducing microorganisms. The aim of this work is the evaluation of the efficiency of an aerobic bioreactor for the oxidation of methane, through the application of a mathematical model representative of the biological oxidation process, by implementing a calculation algorithm.
The developed mathematical model describes the evolution of the phenomenon of methane oxidation. It is able to evaluate the efficiency of the system under varying operating conditions with the aim of optimizing the performance of the "biofilter". Literature data have been used in order to build the model and to drawing up the equations that describe the process. Through the implementation of the model in the MATLAB software, good results on the performance of this system were obtained. The factors that mostly affect the efficiency of the process of methane oxidation and that actually regulate the entire process have been highlighted in this work. The results obtained from the mathematical model showed that the biofilter system is simple to implement and manage and allows the achievement of high efficiency of methane oxidation.

Keywords: Landfill gas, methane oxidation, methanotrophs microorganisms, biofilters, methane emission.

1. INTRODUCTION

Landfills must be equipped with systems capable of reducing the impacts during both phases of management and post-management. A series of control and abatement systems must be provided to minimize the environmental impact that may derive from landfills. The processes of decomposition of organic substances occur by means of anaerobic bacteria, which are present in landfills, and lead to the production of leachate and landfill gas (*LFG*). Their diffusion in the environment would cause pollution of soil,

water (surface and groundwater) and atmosphere. Landfill gas, which is mainly composed by methane and carbon dioxide, is the final product of the anaerobic degradation of organic waste. The production of biogas continues until the organic material has not been completely degraded and can also continue for decades.
CH_4 and CO_2 are classified as greenhouse gases (GHGs). The global atmospheric concentration of CH_4 has increased from a pre-industrial value of about 715 to 1732 parts per billion (ppb) in the early 1990s, and was 1774 ppb in 2005 (*IPCC, 2007*). The atmospheric concentration of CH_4 in 2005 exceeded the natural range of the last 650.000 years (320 to 790 ppb) as determined from ice cores (IPCC 2007). Current atmospheric methane levels are due to continuing anthropogenic emissions. The current contribution of methane to climate change is 18% of the total radiative balance of all long-lived greenhouse gases, LLGHG (*Forster et al., 2007*).
Many countries, in recent years, have recognized the contribution of landfill gas emission to the global climate change due to the greenhouse effect. Consequently most of the industrialized countries provide by law the extraction and treatment of landfill gas, especially in recently constructed installations. At the same time, scientific research has focused its attention on the development of new technologies that are able to balance the cost/benefit ratio and, at the same time, to adapt themselves to different scenarios.
The conventional method most known and most used for the treatment of landfill gas is the method of flaring. Alternatively, for large storage sites, the flaring operation is replaced with a recovery and reuse, often at the same site, of the methane present in biogas. This technique leads to a benefit from an environmental and economic point of view and energy saving. Conventional treatments, such as flaring, for small or old landfills are not applicable from a technical and economic point of view. Traditional systems, in fact, cannot be applied to large landfills in the first phase of cultivation and tail, when the concentrations of methane are too low. In recent decades, considerable research and testing laboratory have been conducted with the aim to identify a solution to the problem of inapplicability of traditional systems. A good solution can be represented by the biological filtration. The biofilter is a biological reactor classified as "immobilized biomass". Structurally it consists of a metal casing (biocontainer) containing a filling material, on which the methanotrophic biomass can develop. The biocontainer is connected to the landfill gas extraction network. It is necessary to promote the contact between landfill gas and microorganisms in order to ensure the functioning of the system. In fact, only in particular conditions, the methanotrophic microorganisms have growth rates such as to allow the achievement of high overall efficiencies of the system.
Structurally, there are two different types of biofilters, said up-flow and down-flow, depending on the input position of the landfill gas flow. The biogas supply to the biofilter can be "active" or "passive." In active systems, biogas is extracted from the landfill and sent to the biofilter through a conventional extraction system. Active systems generally operate at constant flow and ensure constant temperature. Passive systems, on the contrary, are based on the pressure difference between the atmosphere and the landfill body. It follows that, the flow is significantly variable as well as the temperature and the humidity. Typically, these systems operate at ambient temperature (Scheutz et al. 2009).
The costs for investment and operation of biofiltration decrease with the increase of the biofilter size. The average costs of investment of a biofilter of 10, 20, and 40 m^3 are 1800, 1500 and 1100 USD per m^3, respectively. The annual operational costs, including both fixed and variable costs, are 260, 220, 170 USD per m^3, respectively (Melse et al. 2005).
The aim of this work is the evaluation of the efficiency of an aerobic bioreactor for the oxidation of methane, through the application of a mathematical model representative of the biological oxidation process. The working group of the authors has also produced a full-scale prototype of the biofilter for the evaluation of the influence of macro-parameters on process efficiency. In this paper we report the results of numerical modeling.

2. MATERIALS AND METHODS

2.1 The process of CH_4 oxidation in the biofilter

The filling material of the biofilter must provide optimum conditions for methanotrophic microorganisms. Furthermore, a large specific surface area for mass exchange is required, i.e. the material had to be fine-grained. In addition, the clogging of the material, e.g. due to the production of exopolymeric substances (EPS), should be significantly reduced. In order to match these requirements, a filter material generally consists of a mixture of equal volumes of waste compost, peat, and spruce wood fibers (Streese at al., 2003).

Methanotrophic bacteria (or methanotrophs) are a subset of a physiological group of bacteria known as methylotrophs. They are unique in their ability to utilize CH_4 as a source of carbon and energy. The complete pathway for the microbial oxidation of CH_4 to CO_2 by methanotrophs consists in intermediate steps for oxidation of CH_4 to methanol, followed by oxidation of methanol to formaldehyde (CHOH) and the subsequent oxidation of formaldehyde to formate (CHOOH) and the finally oxidation of formaldehyde to CO_2. In recent years several studies have been done on the subject and mainly two types of methanotrophs have been distinguished: type I and type II (Scheutz et al. 2009). The methanotrophs type I use a particular enzyme defined pMMO. Most of methanotrophs type I are not able to fix nitrogen (N_2). The methanotrophs type II, instead, are able to fix nitrogen by using a soluble enzyme defined sMMO. Only type I methanotrophs grow at low temperatures (3 – 10°C), but both types grow at 20°C (Börjesson et al. 2004). It must be said, however, that it is not possible a 100% conversion of the methane in microbial biomass (Scheutz et al. 2009). The aerobic microbial oxidation of methane occurs in the biosphere, wherever CH_4 and O_2 are present at the same time. Aerobic CH_4 oxidation proceeds according to the following overall reaction:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + heat$$

$$\Delta°G = -780\ kJ\ mol^{-1}\ CH_4$$

In many studies (Scheutz et al. 2009, De Visscher et al. 2001 etc.), authors propose to adopt the Michaelis-Menten kinetics of the first-order with two limiting factors:

$$r = \frac{r_{max} \cdot C_{CH_4}}{K_m + C_{CH_4}} \cdot \frac{C_{o_2}}{K_m + C_{o_2}} \quad \textbf{(1)}$$

Where:

- *r = CH_4 oxidation rate [mol/(m^3*h)];*
- *r_{max} = maximum CH_4 oxidation rate [mol/(m^3*h)];*
- *K_m = Michaelis–Menten (or half-saturation) constant [mol/m^3];*
- *C_{CH4} = CH_4 concentration [mol/m^3];*
- *C_{O2} = O_2 concentration [mol/m^3].*

2.2 Environmental factors influencing the process

The biological oxidation of methane is a process that occurs normally in the cover layers of landfills. In these cases CH4 oxidation is controlled by a number of environmental factors: soil texture, temperature, soil moisture content, CH_4 and O_2 supply, nutrients, etc. Environmental conditions are very important for the effective CH_4 oxidation rate. Temperature has a deep effect on all biological processes, including CH_4 oxidation activity. Moisture is an essential factor for micro-organisms to sustain their activity as it is the transport medium for nutrient supply and also for removal of residual metabolic compounds (Park et al. 2002). Too much moisture may slow down gaseous transport processes in the soil because molecular diffusion in water is about 100 times slower than in the air (Bender et al. 1995). Another important factor that affects the process of methane oxidation within a biofilter is the presence of exopolymeric substances (EPS). EPS are high molecular weight compounds that consist mainly of polysaccharides and

are produced by many bacteria, including methanotrophs. Accumulation of EPS reduces, intrinsically, the porosity of the system by preventing, or at least reducing, the gaseous substrate diffusivity or even creating preferential channels for the gaseous flow. The regular biomass washing is used to overcome the problem (Scheutz et al., 2009).
As in most of the chemical reactions, the pH plays an important role for the success of the process: the optimal pH value for the growth of methanotrophic is between 5,5 and 8,5.
Due to the changes of the atmospheric pressure, passive landfill ventilation causes periodically the reverse of the gas flux. This phenomenon can cause the air flow from the biofilter into the landfill during periods of high atmospheric pressure (Gebert et al.,2001). This means that the methanotrophic population of the biofilter is regularly deprived of methane, sometimes for longer periods, with consequent lowering of the methan oxidation rate (Gebert et al., 2003).

2.3 The developed mathematical model

The simplifying assumption for the realization of the mathematical model provides that the biofilter is a Plug Flow Reactor (PFR) (Figure 1). The flow conditions are as follows:

- complete mixing in the transverse direction;
- absence of mixing in the longitudinal direction (i.e. along the z direction);
- absence of gradients of temperature in the system.
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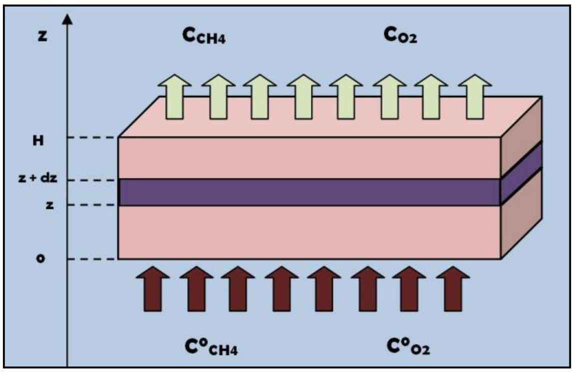

Figure 1 - Schematization of the reactor described by the mathematical model

According to the principle of the mass conservation:

IN – OUT ± GENERATION = ACCUMULATION ***(2)***

the input term indicates the methane mass flow rate which enters inside the control volume:

$$IN = W_{TOT.} \cdot y_{CH_4}\Big|_z$$

where $W_{TOT.}$ is the mass flow rate [$mol*h^{-1}$] and y_{CH4} is the methane mole fraction. $W_{TOT.}$ can be calculated with the following equation:

$$\frac{Q_0}{T_0}\frac{P_{TOT}}{R} = W_{TOT} = \left[\frac{mol}{h}\right]$$

where:

- Q_0 = *flow rate entering expressed in [Nm^3/h];*
- P_{TOT} = *atmospheric pressure = 1 [atm];*
- T_0 = *temperature in Normal Conditions = 273,15° [K]*
- *R = gas constant = $8.2*10^{-5}$ [(m^3*atm)/(mol * K)]*

The out term will be:

$$OUT = W_{TOT.} \cdot y_{CH_4}\Big|_{z+dz}$$

For the generation term it must be considered the diffusion process that occurs within the system (*Figure 2*).

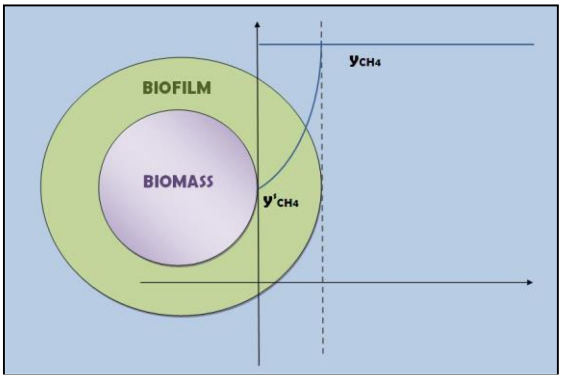

Figure 2 – Schematization of the transport phenomena through the biofilm

The methane flow, *N*, which effectively reaches the biomass can be indicated with the following expression: $N = k_g \cdot a \cdot \Delta C = k_g \cdot a \cdot \left(C - C^s\right)$ ***(3)***

- *k_g : methane transport coefficient [m/h];*
- *a : specific surface area [m^2/m^3];*
- *ΔC: concentration difference [mol/m^3].*

The accumulation term $ACC = \frac{dn_{CH4}}{dt} = 0$, assuming that the system is in steady state conditions.

Replacing the above terms in the equation **(2)**, we obtain:

$$W_{TOT.} \cdot y_{CH_4}\Big|_z - W_{TOT.} \cdot y_{CH_4}\Big|_{z+dz} - k_g \cdot a \cdot C_{TOT}\left(y_{CH4} - y^s_{CH4}\right) \cdot dV = 0$$

Now if we define:

- *Q = flow rate entering in the biofilter [m^3/h];*
- *S = effective biofilter surface [m^2];*
- *r = CH_4 oxidation rate [mol/(m^3*h)];*
- *$C_{TOT.}$ = total concentration = ($P_{TOT.}$)/(R*T) [mol/m^3];*
- *r_{MAX} = CH_4 maximum oxidation rate [mol/(m^3*h)];*
- *K_{CH4} = Michaelis–Menten or half-saturation constant [ad.]*

and recalling that the apex "*s*" indicates what actually comes to the biomass, we can obtain the end system of equations relative to the variation of the methane concentration along the biofilter height:

$$\begin{cases} \dfrac{dy_{CH_4}}{dz} = -\dfrac{k_g a}{Q}\left(y_{CH4} - y^s_{CH4}\right) \cdot S \\ y^s_{CH4} = y_{CH4} - \left(\dfrac{r_{CH4}}{k_g^{CH4} a \cdot C_{TOT}}\right) \\ r_{CH_4} = \dfrac{r_{MAX} \cdot y^s_{CH4}}{K_{CH_4} + y^s_{CH4}} \end{cases}$$

Finally, we defined the degree of methane conversion (x_{CH4}) such as:

$$x_{CH_4}[\%] = \left(\frac{y_{CH_4,0} - y_{CH_4}}{y_{CH_4,0}}\right) \cdot 100$$

2.4 Model's parameters

The first parameter is the transport coefficient k_g. The term (k_g*a) that appears in the equation ***(3)*** is defined transport volumetric coefficient, [h^{-1}]. As suggested by Seongyup et al. (2008), we considered that the numerical value of this coefficient is a function of the volumetric flow rate of gas, according to the following mathematical relationship:

$$k_g \cdot a = 69.42 \cdot (Q/S)^{0.46}$$

The relationship between r_{MAX} and T was determined according with the study of Cella Mazzariol et al. (2009):

$$r_{MAX} = 0 \qquad per\ T < -5°C$$

$$r_{MAX} = -3.91\text{E-}05 \cdot T^3 + 2.17\text{E-}03 \cdot T^2 + 8.05\text{E-}02 \cdot T + 3.48\text{E-}01 \quad per\ -5 < T < 82°C$$

$$r_{MAX} = 0 \quad per\ T > 82°C$$

The parameter K_{CH4}, i.e. the Michaelis–Menten (or half-saturation) constant, is also function of the temperature. The trend of K_{CH4} as a function of temperature was determined according with the data present in the work of De Visscher et al. (2001):

$$K_{CH4} = 0.000729 \qquad per\ T < 5°C$$

$$K_{CH4} = --1.62861\text{E-}07 \cdot T^3 + 9.26\text{E-}06 \cdot T^2 - 3.54\text{E-}06 \cdot T + 6.40\text{E-}04 \quad per\ 5 < T < 35°C$$

$$K_{CH4} = 0.005171 \quad per\ T > 35°C$$

After assigning the numeric values to the remaining parameters, such as vacuum degree (ε=0.5) and effective biofilter surface (S=16.25 m^2), we started the numerical simulation with the MATLAB software (The MathWorks).

For the technological units implemented the calculation parameters assume the following values:

- *filter effective height: H = 2.65 m;*
- *landfill gas flow rate: Q = 50 Nm^3/h;*
- *inside temperature: T = 50 °C;*
- *methane mole fraction in landfill gas flow: y_0 = 0.25;*
- *total concentration of methane present in the inflow: $C_{TOT.}$ = 43.84 mol/m^3.*

3. RESULTS AND DISCUSSION

The results of the simulations allow us to represent graphically the efficiency of the biofilter as a function of the height (Figure 3). The system loses quickly efficiency approaching the conditions of limiting substrate (CH_4), as we expected from the model of Michaelis-Menten. It is evident that the complete removal of methane by a biological system is not obtainable, as opposed to a thermal system. In real applications, the physiological loss of efficiency is compensated by the wider operating range as compared to thermal systems which are less flexible. The methane mole fraction decreases by a rate equal to 36.8%, for the system considered in this work (H=2.65 m).

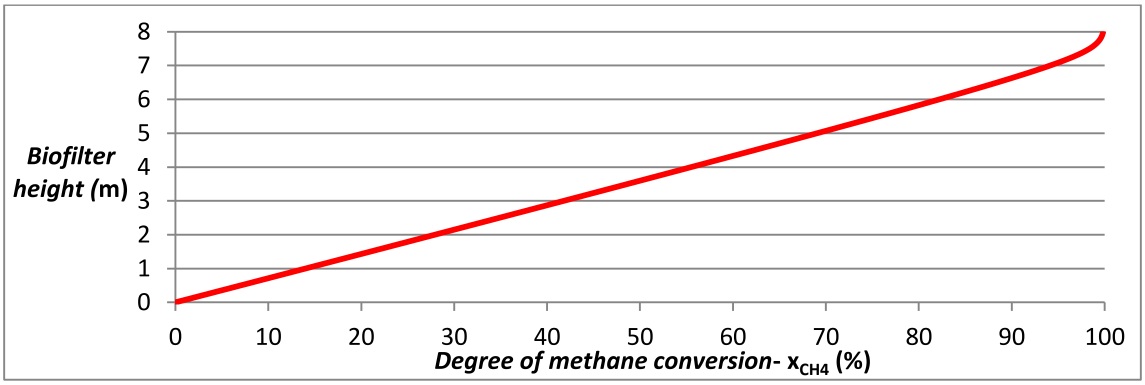

Figure 3 – Variation of the degree of methane conversion x_{CH4} as a function of the biofilter height

The obtained results can help evaluating the system response to the variation of important parameters that regulate the process of methane oxidation. Different operating conditions are represented in the following table:

Table 1 – Different operating conditions of the system

CASE	H (m)	T(°C)	Q(Nm^3/h)	y_0	$C_{TOT.}$(mol/m^3)
1	2.65	50	*Variable parameter*	0.1	43.84
2	2.65	50	50	*Variable parameter*	43.84
3	2.65	*Variable parameter*	50	0.1	43.84

The following figures show the graphic representation of the results for each operating conditions (Figures 4 and 5).

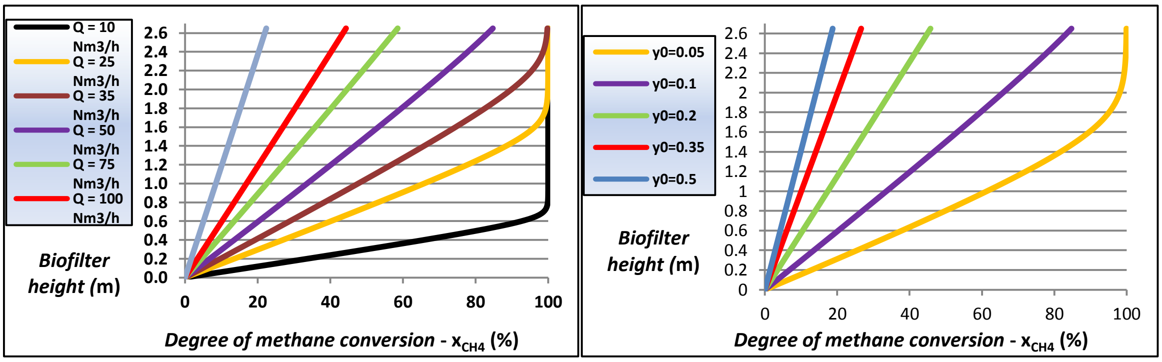

Figure 4 – A) Case 1: Variation of the degree of methane conversion x_{CH4} as a function of the biofilter height by varying the flow. B) Case 2: Variation of the degree of methane conversion x_{CH4} as a function of the biofilter height by varying the methane mole fraction.

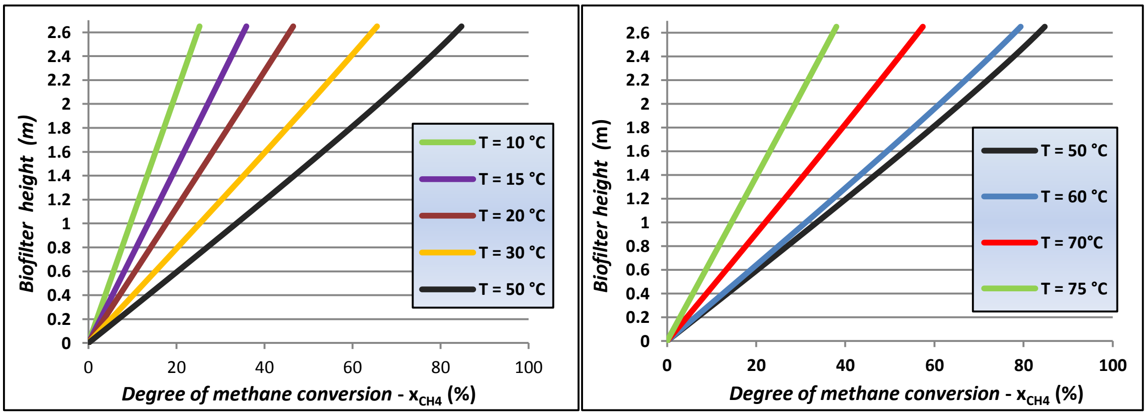

Figure 5 – Case 3: Variation of the degree of methane conversion x_{CH4} as a function of the biofilter height by varying the temperature: A) from -3°C to 50°C, B) from 50°C to 79°C.

The results demonstrate that the increase of the flow rate value involves a worsening of the oxidative process in terms of methane conversion. Also the increase of the methane concentration in the gaseous flow involves a worsening of the conversion yield. Finally, the biological processes have a strong dependence by the temperature changes, that affect the kinetic parameters of the biological reactions. Temperature is a parameter that greatly influences the process of methane oxidation. In detail we have that, for low temperatures, the degree of methane conversion is an increasing function of T: there is an improvement of the performance of the process. Instead, over 50°C (value corresponding to the maximum of the conversion) the increase of the temperature begins to have the opposite effect, i.e. it results in a decrease of the conversion in the system. When the biofilter is integrated into the landfill cover system and not externally heated, its temperature regime in general follows the changes of the ambient temperature, according to the thermal conductivity of the chosen filter materials (Gebert et al., 2006). Through this analysis, therefore, we can conclude that the temperature range in the biofilter should stand between 40°C and 60°C, in order to optimize the treatment system of the methane. The temperature control is easy but expensive. The reduction is always possible by operating on the ratio air/landfill gas, while the increase of the temperature can be made through a heat exchanger, but it is economically very expensive unless it has a flow residual heat (e.g. other systems using biogas). For these reasons, a strong insulation of the units is essential in order to avoid the temperature drop in winter periods. In these cases, a layer insulation equivalent of more than 5 cm, with a thermal conductivity equal to 0.034 [W/(m*K)], is required.

4. CONCLUSIONS

The proposed biological system is not antagonistic to the energy production systems from landfill gas, but falls into the category in which the reduced production of landfill gas (small landfills and/or landfills that have been closed for many years) does not allow the installation of energy recovery systems. The biological system has proved to be an economic system (ease of implementation and management) with good performances.
Moreover, the results of the simulations show that the landfill gas treatment through biological systems, in the above-mentioned conditions, have yields of methane abatement higher than 70%. The working group of the authors is working on a full-scale biofiltration system in the landfill of the municipality of Venosa (Potenza - Italy). The technical discussion about the first experimental results obtained will be postponed in the next papers.

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