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Influence of oxygen concentrations and different aeration flow rates in carbon content of old waste: Lab-scale bioreactor landfills

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Aos meus pais, Dina e Paulo, pelo vosso apoio e energia positiva que me proporcionaram durante este período, sem o vosso amor esta etapa não estaria concluída.

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Resumo

A operação de um biorreator com arejamento *in situ* foi destacado como um método apropriado para o aceleramento da degradação da matéria orgânica e subsequentemente, para alcançar uma rápida estabilização e compactação dos RSU.

Resíduos com 30 anos, provenientes do aterro de Legnago, foram investigados à escala laboratorial de modo a desenvolver novas alternativas para a recolocação dos RSU.

Este estudo teve como objetivo, a otimização da estabilidade dos resíduos e, por conseguinte, a minimização das emissões, evidenciando a remoção de carbono. O balanço de carbono foi determinado de modo a analisar os percursos de remoção deste componente. Conjuntamente, a concentração de oxigénio no gás de saída foi analisada, com o propósito de avaliar este parâmetro como uma ferramenta benéfica para o dimensionamento e operação de um aterro, de acordo com a intensidade de arejamento.

Cinco diferentes fluxos de ar foram ajustados nos biorreatores, de maneira a proporcionar concentrações de oxigénio no gás de saída estáveis. Apenas um, foi configurado com condições anaeróbias, de modo a simular as condições reais do aterro em estudo.

As concentrações dos componentes de carbono e de azoto, no lixiviado, verificaram-se superiores no biorreator anaeróbio do que nos aeróbios, evidenciando um melhor desenvolvimento nos resíduos com a injeção de ar.

Durante a experiência, a coluna arejada fornecida com 5.6 L O_2/(kg de resíduos) e com um output médio de 0.4% de oxigénio no gás de saída, apresentou o melhor desempenho relativamente à eficiência de arejamento em termos de remoção de carbono, analogamente ao oxigénio fornecido.

De acordo com o balanço de carbono, foi registado uma maior remoção de carbono pelo gás do que pelo lixiviado. Mais de 90% do carbono removido foi convertido em dióxido de carbono, devido à degradação aeróbia.

No final do estudo, verificou-se que a definição da concentração de oxigénio no gás de saída é uma ferramenta apropriada e benéfica para o processo de conceção e de operação de um biorreator aeróbio.

Palavras-Chave:

RSU, Biorreator, Arejamento *in situ*, Concentração de oxigénio no gás de saída, Remoção de carbono, Balanço de carbono

Abstract

Operating a bioreactor with *in situ* aeration has been consider as a proper method to accelerate the degradation of organic matter and consequently, to have a rapid stabilization and settlement of MSW.

Lab-scale tests were carried on a 30-year-old waste, from Legnago landfill, to study the improvement of new alternatives for the current re-disposal of the waste.

This research aimed to accomplish a better stabilization of the waste and, subsequently, a reduction of the emissions, focusing on carbon content removal. Carbon mass balance was performed to assess the carbon removal pathways. Additionally, oxygen concentrations in the outlet gas were evaluated to understand if can be considered as a beneficial tool for the landfill dimensioning and operation, in order to adjust the aeration rate.

In six bioreactors, different aeration rates were adjusted over time to provide stable oxygen concentrations in the outlet gas on five bioreactors, and one column was set-up under anaerobic conditions to simulate the real conditions of the waste in the landfill.

Concentrations of carbon compounds and ammonia nitrogen were higher in the leachate of the anaerobic bioreactor than the aerated ones, which acknowledges a better development with air injection on the waste.

During the experiment, the lowest aerated column with an inlet of 5.6 L O_2/kg of waste and a mean value of 0.4% O_2 in the outlet gas reported the best performance of aeration efficiency in terms of carbon removal, regarding the oxygen supplied.

Concerning the carbon balance, it was recognized that most of carbon content was removed via gas than via leachate. More than 90% of carbon removed was converted into carbon dioxide due to aerobic degradation processes.

At the end of the study, defining oxygen concentrations in the outlet gas turned out to be an appropriate and a beneficial tool to design and operate an aerobic bioreactor.

Key words

MSW, Bioreactor, *In situ* aeration, Oxygen concentration in the outlet gas, Carbon removal, Carbon balance

Index

List of figures

List of tables

Glossary of abbreviations

BOD	Biochemical oxygen demand
CH_4	Methane
Cl^-	Chloride ion
COD	Chemical oxygen demand
CO_2	Carbon dioxide
DM	Dry matter
FWS	Former waste disposal site
GHG	Greenhouse gas
MSW	Municipal solid waste
NH^+_4	Ammonium ion
NO^-_2	Nitrite ion
NO^-_3	Nitrate
O_2	Oxygen
RI	Respiration index
SO^{2-}_4	Sulphate ion
TKN	Total kjeldahl nitrogen
TOC	Total organic carbon
TS	Total solids
VFA	Volatile fatty acids
VS	Volatile solids

1 Introduction

During the years the waste management has suffered an evolution from a former waste disposal site to landfilling, recycling and compost processes.

The landfilling has been the main play role for disposing municipal solid waste (MSW) in Europe since it provides an easy economic and constructive view for the MSW disposal (Berge[b] *et al.,* 2009; Mönkare *et al.,* 2015), nevertheless the risks of the environmental content is still a potential problem due to the long-term emissions relative to the landfill gas and leachate (Hrad *et al.,* 2013).

A traditional landfill is considered at the bottom of the waste management hierarchy, therefore the conception of a sustainable landfilling started to be the aim of the waste management as like the potential of promoting the waste minimization, recycling and biological treatment (Nikolaou *et al.,* 2010; Ritzkowski *et al.,* 2012).

The application of *in situ* aeration in bioreactor landfill is one of the strategy that deals with this problematic, since it has more environment benefits, e.g., more efficient in terms of the leachate and gas treatment, acceleration of biodegradation of the organic matter what provides the stabilization of the waste with low carbon and nitrogen content and reduce the long-term emissions (Berge[b] *et al.,* 2009; Raga[a] and Cossu, 2014). To accomplish these outcomes, the system is control by leachate recirculation, addition of water and some nutrients (Mertoglu *et al.,* 2006).

In the past few years lab - and full - scale applications have been carried out for the evaluation of the effects of aeration on organic matter removal in old waste. In the North of Italy, a high quantity of the carbon was discharge via gas from the landfill body (Raga[a] and Cossu, 2014) and according with Hrad *et al.,* 2013 a lab-scale was performed on an old waste from Austria to evaluate the long-term emission development after completion. These studies had a satisfactory result relative to aeration as an efficient and cost-benefit treatment of the waste, however there still are some questions to acknowledge regarding to this approach.

In general, this technique provides the improvement of the leachate quality respect to organic pollutants as chemical and biochemical oxygen demand (COD and BOD), decrease the methane (CH_4) gas emission potential which is consider as a greenhouse gas (GHG) and reduce the total organic carbon (TOC) in the solid fraction (Hrad *et al.,* 2013**;** Nag *et al.,* 2015).

1.1 Objectives and scope of the dissertation

The University of Padua started to investigated the quality of the waste, biogas and leachate from the old landfill of Legnago, in 2001.

Considering that the landfill didn't had the artificial impermeable bottom liner and leachate collection system, and also the geological situation of the area in the Providence of Verona, it was indicated a significant high risk of the groundwater pollution. Therefore, the landfill in study started to be remediate with the technology of *in situ* aeration, and after a period was followed by waste excavation and re-disposal in a new sector of the landfill, with the aim of reducing further contamination risk.

This research had three main goals, during six months:

- Develop new alternatives for the re-disposal of the MSW in study in a new site for non-hazardous in Legnago, to achieve better performances in terms of the waste stabilization and settlement, and subsequently, in the reduction of the pollutants emissions, focusing on carbon removal.

- Determine the carbon mass balance to understand the carbon removal pathways in the waste, the gas and the leachate.

- Additionally, evaluate if the set-up of different and stable oxygen concentrations in the outlet gas can be an appropriate and a beneficial tool for dimensioning and operating a landfill.

To achieve the objectives of the study, one lab-scale simulated landfill bioreactor was set-up with anaerobic conditions to simulate the actual conditions of the MSW in the new sector of the old landfill, and five different aeration flow rates were established after an air injection trial and were adjust over time, to produce different oxygen concentrations in the outlet gas of the five bioreactor landfills.

1.2 Dissertation organization

The present document is divided in five chapters:

Chapter 1 - Introduction: describes the evolution of the waste management such as the improvement of sustainable alternatives for the MSW disposal and their relevant problems; also establishes **the objectives and the scope of the dissertation**.

Chapter 2 - Literature review: is divided in five sub-chapters which resume the actual performance of the **municipal solid waste management**, with focus on the hierarchy of the waste treatment. The **conventional sanitary landfill** is compare with a **bioreactor landfill** (sustainable landfill), that has four different operations types of this new landfill design. Additionally, establishes a review of the organic reactions into waste mass with focus on **carbon content**, and the pathways that this organic compound take inside of a landfill. The **state of art of the effects of aeration flow rate and oxygen concentrations** in the outlet gas is performed.

Chapter 3 – Materials and methods: describes the landfill site were the waste was excavated, and the materials and the equipment used during the lab-tests. Also, it establishes the analytical methods used during the waste, leachate and off-gas samples, and the set-up of the equipment. Additionally, describes the determination of the carbon that was discharge via gas, which was used in the determination of the carbon mass balance. Also, the carbon extracted from the leachate and the solid fraction was taken in account for the mass balance.

Chapter 4 – Results and discussion: is divide into four sub-chapters, which shows the results of the analysis in the solid fraction to **characterize the waste excavated**, **the off-gas samples** according to carbon dioxide and methane production and oxygen content, and the **leachate quality.** Moreover, the **efficiency of carbon removal** related with the carbon mass balance and the oxygen inlet are also discussed in order to understand if the dissertation objectives were accomplished.

Chapter 5 – Conclusions and future perspectives: a conclusion of this project is described in order of the discussion of the results made in chapter 5. Some recommendations for the improvement of the objectives are suggested.

2 Literature review

2.1 Municipal solid waste management

Over the years, the solid waste generation has been growing as a global issue due to the excessive population, and subsequently, an increase of consumption of the natural resources to support life and the disposal of waste.

In 2012, an estimation of global MSW generation levels were, approximately, 1.3 billion ton/years and were expected to increase 69.3%, to approximately 2.2 billion ton/year by 2025. Still, these global averages are conditioned by regions, countries and cities, due to the influence of the affluence in every region, (Kawai and Tasaki, 2015) as **Table 2.1** shows.

Table 2.1 – Actual waste production in different regions in the world (Hoornweg and Bhada-Tata, 2012).

Region	OECD	EAP	LAC	ECA	MENA	SAR	AFR
Waste generation (%)	**44**	**21**	**12**	**7**	**6**	**5**	**5**

OECD: Organization for Economic Cooperation and Development **EAP: East Asia and Pacific**

LAC: Latin America and the Caribbean **ECA: Eastern and Central Asia**

MENA: Middle East and North Africa **SAR: South Asia**

AFR: Africa

In every region, MSW production are influenced by many strands, such as economic development, public habits, local climate, the degree of industrialization and living standards, e.g., urban residents produce approximately, twice as much waste as the rural population, because higher the economic progress and the urbanization rate, greater the consumption of goods and services as does the waste generated (Hoornweg and Bhada-Tata, 2012).

Table 2.2 reports that the high income level in the countries produce a high quantity of waste per capita and the low income countries produce less urban waste per capita. However, the lower middle income produces more than the upper middle income level, due to the inclusion of only the urban residents, e.g., China have a disproportionately high urban waste generation rates per capita (lower middle income) relative to overall economic status since they have a major portion of poor rural populations (Hoornweg and Bhada-Tata, 2012).

Table 2.2 - Currently and projected waste generation according with the Income Capital Level (Hoornweg and Bhada-Tata, 2012).

Region	Current Available Data			Projections for 2025			
	TUP (millions)	Urban Waste Generation		Projected Population		Projected Urban Waste Generation	
		Per Capita (kg/capita/d)	Total (tons/d)	TP (millions)	UP (millions)	Per Capita (kg/capita/d)	Total (tons/d)
LI	**343**	**0.60**	**204 802**	**1 637**	**676**	**0.86**	**584 272**
LMI	**1 293**	**0.78**	**1 012 321**	**4 010**	**2 080**	**1.3**	**2 618 804**
UMI	**572**	**1.16**	**665 586**	**888**	**619**	**1.6**	**987 039**
HI	**774**	**2.13**	**1 649 547**	**1 112**	**912**	**2.1**	**1 879 590**
Total	**2 982**	**1.19**	**3 532 256**	**7 647**	**4 287**	**1.4**	**6 069 705**

LI: Lower income **LMI: Lower middle income** **UMI: Upper middle income** **HI: High income**

TUP: Total urban population **TP: Total population** **UP: Urban population**

According with the EU's Landfill Directive, 1999, MSW is defined as the waste from households and other type of waste, that it's nature or composition is similar to waste from household. The composition of this type of waste it's categorize by organic and inorganic as its report in the COM 2000/532/EC – European List of Waste, which generally is classify by organic, paper, plastic, glass and others.

Waste composition is influenced by several factors: economic development, culture norms, energy sources, climate, and geographic location, e.g., as a country grows in urbanization rate and the quality of life improves, production of inorganic waste as plastics, paper and aluminium have an upsurge, while the organic fraction decrease. Therefore, the highest income in the production of organic matter are the lower and the middle level whereas the middle and higher income are the main-role in the consumption of the inorganic, such as plastic, paper, metal fractions and glass (Hoornweg and Bhada-Tata, 2012).

The concern of the increase of MSW generation and quality requires an improvement of the solid waste management options, based on the hierarchy of solutions: waste prevention, re-use, recycling/composting, energy recovery and landfilling.

Preventing the waste production is the best way to manage the MSW and reduce the waste production, since what isn't produced doesn't have to be disposed of. Though this step in the hierarchy, it is the most challenging option, because with the population grow and the affluences in the regions it turns more difficult to follow this concept. There are some tools to encourage waste prevention as eco-design and awareness-raising campaigns to educate the public and encourage

consumers to demand greener products and guide the creation of a more resource-efficient market (EU, 2010).

Re-use is the second step in the pyramid hierarchy and it consists in the repeated use of products and components for the same purpose, e.g. re-use of second-hand car components in company car fleets in Netherland (EU, 2010).

To reduce the waste production, recycling is the third choice to manage, since not just decreases the amount of waste in the disposal sites, but also provides the industries with significant supplies recovered such as paper, glass, plastic and metals (EU, 2010).

Incinerating the waste is consider one of the options to alternative energies, which can produce electricity, steam and heating for buildings and, also can be used for certain industrial processes as fuel. However, this energy recovery need to have some delicate conditions, because an incomplete incineration of the waste can put in risk the health of the humans and the environment, through the release of hazardous chemicals (dioxins and acid gases) (EU, 2010).

In the bottom of the hierarchy there is the landfill, the oldest way of waste treatment. This form has been considered the least desirable option because of the airtight conditions of landfill sites (EU, 2010).

2.2 Conventional sanitary landfill

The conventional landfilling techniques promote in biological, physical and chemical processes the anaerobic degradation of the waste mass, obtaining leachate and landfill gas during the life period of the landfill. It has been the major worldwide waste disposal method, specifically in developing countries due to the offer of a simpler and faster way to the solid waste dumping at practical costs (Bilgili *et al.,* 2006**;** Cossu, 2009).

The structure of a sanitary landfill consists in cells and lifts with liners, drains, gas vents, leaks detection systems with intermediate and final covers. However, in the past, the old landfills didn't had pre-treatment as the base sealing systems and cover layers that protect the atmosphere, subterranean/superficial water, and the soils; resulting in organic and inorganic emissions which represents potential risks to the environment (Prantl *et al.,* 2006). According with the EU's Landfill Directive, 1999, the protection of these three strands must be achieved by the combination of a geological barrier and a bottom liner during the operational/active phase, and the combination of a geological barrier and a top liner during the passive phase/post closure. Even with the protective layers the degradation of solid waste can represent a risk, if emissions of landfill gas and landfill leachate aren't controlled (Erses *et al.,* 2008).

Leachate has been recognized as a serious pollutant from the bottom of the landfill, which is composition it's influence by the nature of the solid waste disposed, biochemical and chemical processes and the moisture content in the waste, having high concentrations of TOC and T-N. While

the biogas has been recognized with high levels of greenhouse gases (GHGs) and intensive odours problems (Nag *et al.,* 2015).

So currently, regulations and legislations required: a collection system of leachate for treatment before release to the environment, since it contains organic and inorganic compounds and suspended particles, which threats the soil and the ground water quality; and collective and monitor systems of the landfill long-term emissions (biogas) to limit the release of methane and other volatile organic compounds (Borglin *et al.,* 2004; Naveen *et al.,* 2016).

Therefore, the improvement of sustainable landfills concept has been the main focus in the waste management worldwide, due to the performance of a conventional landfill as a container of pollution and to develop the potential of terminating expensive perpetual landfill aftercare (Bilgili *et al.,* 2006). Besides there are evidences that landfilling has decreased by almost 40 million tonnes (**Figure 2.1**), comparing with the other techniques in the EU's hierarchy of waste management between 2001 and 2010 (EEA, 2013).

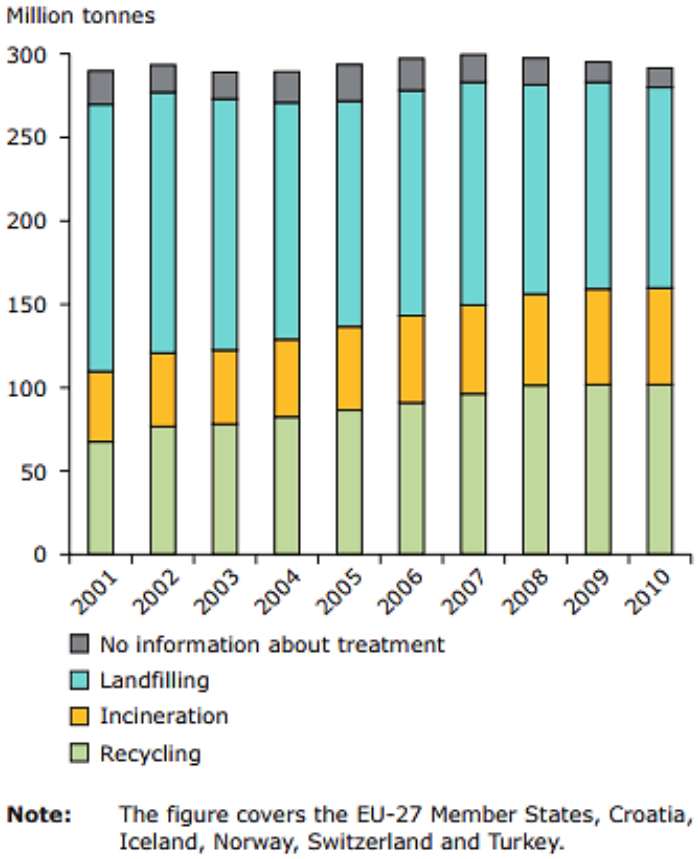


Figure 2.1 - Development of municipal waste management in 32 European countries, 2001-2010 (EEA, 2013)

2.3 Bioreactor landfill concept

Bioreactor landfill is one of the new and emerging techniques to operate a landfill in the waste management as a process-based approach, providing the optimization of the conditions for microbial decomposition and, subsequently, accelerating the stabilization and the settlement of the waste mass, thus allowing for additional municipal solid waste disposal or faster land re-use, when the biological operations are finish (Borglin *et al.,* 2004).

This engineered concept is design not just to be advantageous in the minimization of the environmental impacts and the public health, but also have the potential to be more economical than a conventional sanitary landfill.

Regarding the environmental component, the bioreactor landfill is beneficial for the reason of (Warith *et al.,* 2001):

- maximizing landfill gas (LFG) generation rates under controlled conditions, which improves the quality of the gas composition;
- minimizing leachate migration into the subsurface and the impact on the superficial water by containing this liquid product;
- improving the neighbouring environment by controlling the LFG emissions and the odour;
- improving the re-use of the cells by removing the inert end-product, through periodical engineered mining and the end-product could be used as compost.

Concerning an economical strand, this kind of technique is able to (Berge[b] *et al.,* 2009):

- overall of landfilling costs by saving outlays from not require new landfills sites every 15-20 years, since can be built in modules to increase the waste capacity in the cells, subsequently, including extension of the active life of the landfill;
- reduction of leachate treatment, operations and disposal costs, since it's beneficial to improve the biological and chemical transformation of organic and inorganic components within the efficiency of the landfill airspace utilization;
- reduction in post-closure care, maintenance and risk due to the decrease landfill-monitoring activities of LFG and leachate;
- decrease in contaminant concentrations during the operating period;
- increase the efficiency gas collection resulting in larger revenues from energy production.

Bioreactors are defined by use of series tools to assurance the optimization of the biological and chemical processes in the waste mass including: shredding the MSW, air injection, addition of nutrients and sludge, controlling temperature and moisture content, and leachate recirculation. However, liquid addition (leachate, tap water or distilled water) is one of the most significant aspects to

guarantee the efficiency of the operation, because it provides the distribution of nutrients and enzymes, the pH buffering, the recycling and distribution of methanogens, the dilution of inhibitory compounds, evaporation opportunities and liquid storage (Bilgili *et al.,* 2006**;** Hrad *et al.,* 2013; Warith *et al.,* 2001).

Four types of bioreactors landfill are generally considered as far as the metabolic pathway is concerned: anaerobic, aerobic, hybrid and facultative bioreactors (Berge *et al.,* 2005; Morello *et al.,* 2017).

2.3.1 Anaerobic bioreactor

Anaerobic bioreactor landfills are the most commonly used, characterized by the absence of oxygen in the system and by the moisture content adjustment to 35 - 45 percent, with addition of leachate, groundwater, infiltrating rainfall and storm water (Berge *et al.,* 2005; Waste Management, 2004).

Anaerobic conditions are easily reached in the waste mass when the MSW is dumped in the bioreactor, because without air addition and the waste compaction, oxygen can't enter inside of the bioreactor, therefore the operational costs are less and doesn't need any intervention.

Comparing with anaerobic conventional landfill: moisture addition increase LFG production rate, more exactly, methane generation, and the time required for waste degradation is less by the recirculation of the organic matter into the waste mass, resulting also in the improvement of leachate quality (Berge *et al.,* 2005; Erses *et al.,* 2008).

Regarding other types of bioreactor landfills, this system has some disadvantageous, such as: tendency to have lower temperatures resulting of a slower stabilization process of the waste; the majority of the gas will be produced just early after closing the landfill, more or less 20 years; putrification and deamination processes are present; formation of hydrogen sulfide; and the most significant is the accumulation of ammonia-nitrogen (Berge *et al.,* 2005; Borglin *et al.,* 2004).

The high levels of ammonia-nitrogen in the waste mass is due to the absence of pathways for ammonia removal, because with the continually returned of this component in the bioreactor and without oxygen there isn't any removing process. Therefore, with the ammonium accumulation the bioreactor system requires treatment prior to ultimate discharge of the leachate, increasing the operational costs (Berge *et al.,* 2005; Onay and Pohland, 1997).

Figure 2.2 reports a view of an anaerobic bioreactor with high ammonium concentration in the leachate. The LFG is produce by the degradation of the waste and is collected in the pipes within the waste, and then is used to generate energy. The leachate is removed via pipes from the bottom of the landfill to reach the biological treatment facility. Around the area of the landfill the groundwater is monitor (EPA, 2017).

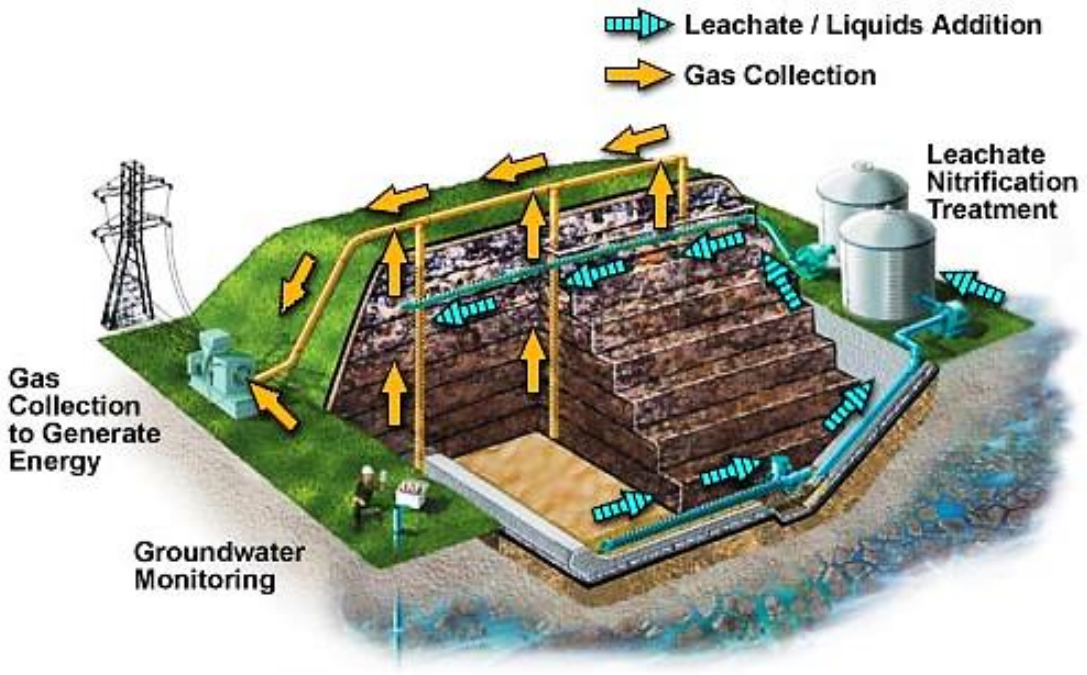


Figure 2.2 - Anaerobic bioreactor landfill design (Waste Management, 2004)

2.3.2 Aerobic bioreactor

Aerobic bioreactors have been considered as an indispensable tool for a sustainable landfill management. The design of it, is characterized by the presence of oxygen with air injection or natural entry inside of the waste mass, and with water addition and/or recirculation of leachate (Berge *et al.,* 2005).

This technique can operate as a tool during the aftercare phase of conventional landfills, like a remediation instrument for old landfills or as pretreatment before landfill mining, since is used for controlling the long-term impact of landfilling due to the presence of organic matter in the MSW (Raga and Cossu, 2012).

According with Berge *et al.,* 2005; Borglin *et al.,* 2004 and Erses *et al.,* 2008, aerobic bioreactor landfills have many advantageous comparing with the anaerobic technique: aerobic biodegradation rates are more rapid and can potentially decrease the time of stabilization and increase the settling of the MSW; decrease methane gas production and control costs; the volatile organic compounds and odor emissions are less; reduce off site leachate treatment, since the treatment inside of the bioreactor is more efficiency; the redox potential transform from negative to positive which will affect metal mobility to decreasing; and will limit the fermentation reactions, producing more acids and decrease the pH, influencing solubility and sorption properties of organic and metal contaminants.

Many researchers already had studied carbon and nitrogen balance and the enhancement of waste stabilization during in situ waste aeration at lab and full scale as Ritzkowski[a] and Stegmann, 2013; Erses *et al.,* 2008; Raga and Cossu, 2012 and Berge *et al.,* 2005, and others. When the bioreactor

starts to have aerobic conditions in the waste mass, nitrogen removal rate start to increase due to nitrification, ammonia air stripping or volatilization, and the additional gas flow associated with air injection may also induce this removal process (Berge *et al.,* 2005). The degradation of organic matter is accelerated by oxidative respiration when the air is injected or is inside of the waste mass, causing a decrease in the formation of methane and in the carbon component of the waste, which increase the amount of carbon being released in gas form as carbon dioxide, CO_2, and decrease the BOD concentration in the leachate (Brandstätter *et al.,* 2005).

As **Figure 2.3** shows, aeration start by the pumps injecting the air through vertical or horizontal well located in the top layer into the waste mass, improving the biodegradation. The leachate is removed from the bottom layer as like in the anaerobic bioreactor (**Figure 2.2**) and it's piped to a storage tank and then it's recirculated to the landfill to be collected in the end (Waste Management, 2004).

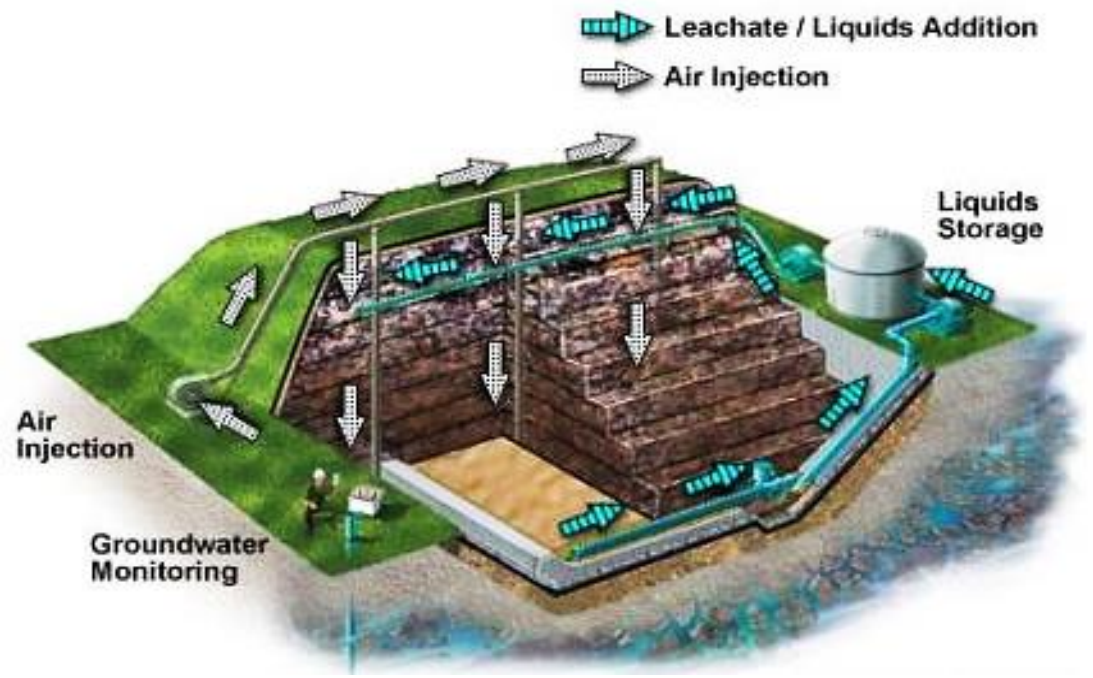


Figure 2.3 - Aerobic bioreactor landfill design (Waste Management, 2004)

The effectiveness of the aerobic bioreactor operation depends on proper control of oxygen distribution, waste temperature and moisture content (Raga and Cossu, 2012). Waste temperature is essential because aerobic process tend to increase the temperature, leading to evaporation of the leachate resulting in a significant loss of quantity (Berge *et al.,* 2005).

There are three concepts for aeration in the bioreactor, according with Ritzkowski and Stegmann, 2012, to control the effect in the stabilization of the waste: high pressure aeration; low pressure aeration with active aeration and off-gas extraction, active aeration without off-gas extraction, passive aeration, energy self-sufficient long-term aeration; and semi aerobic concept.

2.3.3 Hybrid bioreactor

Hybrid bioreactor landfill involves an on-off aeration cycles, in other words, an intermittent aeration with aerobic and anaerobic conditions. Under the combination of each condition there is a potentiality of enhancing biochemical processes which lead to methane production as well as nitrification and denitrification of ammonium nitrogen (Morello *et al.,* 2017 and Ko *et al.,* 2016).

The main objective of hybrid conditions is usually to remove nitrogen from leachate using biological nitri-denitrification processes, since there aren't so many studies available focus on the influence of waste degradation and gas generation (Xu *et al.,* 2015).

Two types of these cycles have been explored according with Berge *et al.,* 2005, short-term cycling of air injection into the bioreactor that is characterized by the repeat alternation of *in situ* aerobic and anaerobic conditions, through the life time of the landfill; and sequencing of aerobic and anaerobic conditions, which include an initial aerobic phase and in the end of the active life of the landfill an anaerobic phase.

As **Figure 2.4** shows, the aerobic-anaerobic management employs the aeration in the top layer of the landfill to improve the degradation of the waste, while the pipes to collect the gas are in the lower part of the bioreactor and it's collected to produce electricity. The leachate has the same method as the aerobic bioreactor in the case of recirculation: is collected in the lower portion to a tank storage and then, is deposited in the upper part of the bioreactor.

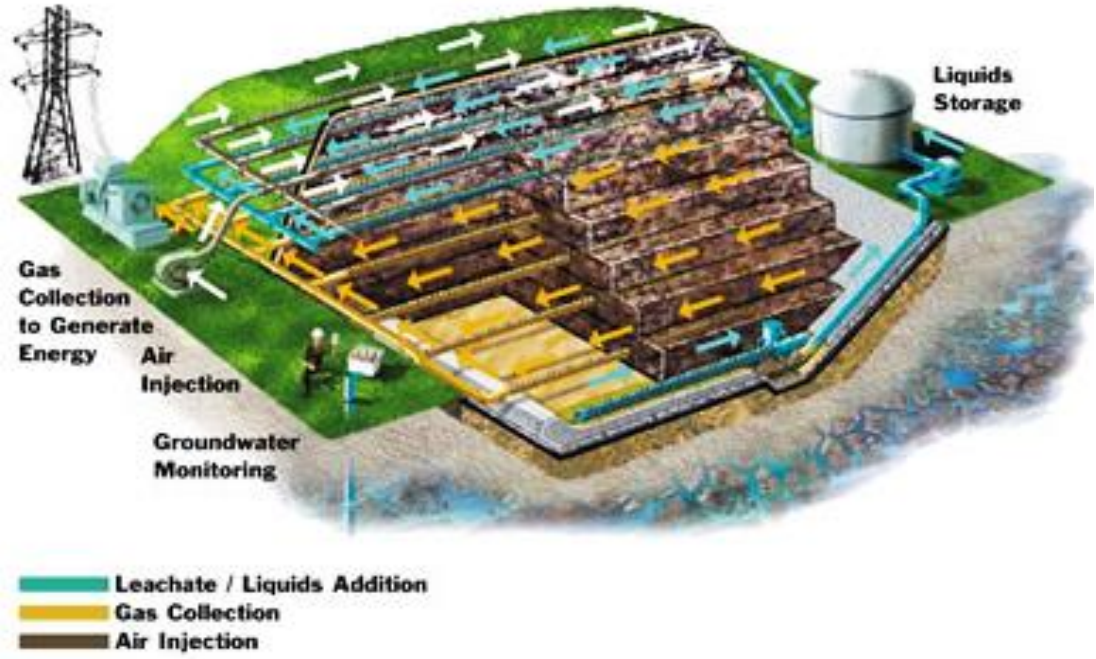


Figure 2.4 - Hybrid bioreactor landfill design (Waste Management, 2004)

2.3.4 Facultative bioreactor

The operation of a facultative bioreactor consists in combining conventional anaerobic degradation of the MSW with a mechanism for controlling high ammonia nitrogen levels that can occur when water addition is manage in the landfill (Waste Management, 2004).

The leachate of a facultative bioreactor (**Figure 2.5**) usually has high concentration of ammonia and it's removed from the bottom layer to an ex-situ treatment system to suffer biological nitrification and then, it returns to the bioreactor with less ammonia nitrogen and a high content of nitrate. So, inside of the waste mass denitrification occurs, because certain microorganisms as facultative bacteria use the nitrates in the place of oxygen for respiration (Berge *et al.,* 2005; Waste Management, 2004).

The leachate nitrification treatment is considered has an economic disadvantage, since the costs increase with *ex situ* treatment, besides of the operational management that needs; and also, until the nitrate is remove/consume the methane production is cease (Berge *et al.,* 2005).

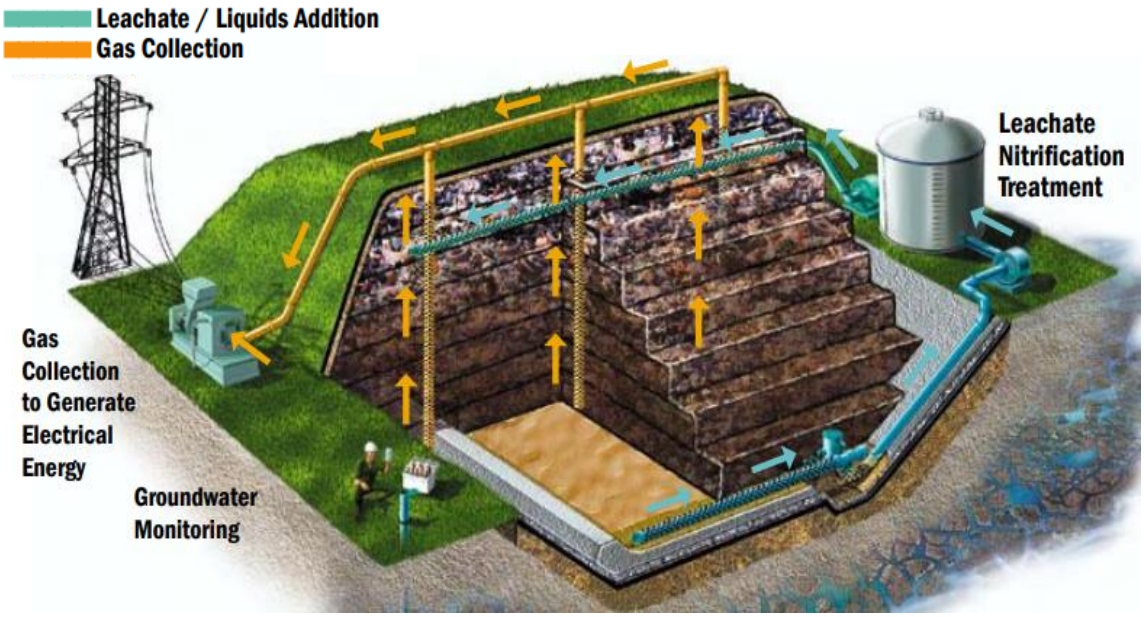


Figure 2.5 - Facultative bioreactor landfill design (Waste Management, 2004)

2.4 Carbon content

Landfilling has been characterized to be, supposedly, the last option in waste disposal as the lasts chapters had reported, since the pollutants can cause different effects in the environment and human health. However, with the protective layers in the composition of the landfill, these trace pollutants can be diluted in the waste mass, so the real problem are the family of the elemental species in great concentrations of the waste, leachate and gas, as organic compounds: carbon and nitrogen; and as inorganic compounds: sulphur, chlorides and heavy metals.

This chapter will explain and report the carbon flux in the waste mass, leachate and gas composition, in order to implement the carbon balance. Carbon mass balance is important to understand the mobilization and stabilization of the organic matter, their biological and chemical reactions which can influence the stability of other compounds and their oxidative states. And, also to observe the removal pathways in biogas, leachate and waste.

2.4.1 Organic reactions into waste mass

Landfilled waste is composed by organic material as paper, cardboard, food and, garden and park waste. These types of waste have in general: 50% of cellulose, 15% of lignin, 10% of hemicellulose and 5% of protein, starch, pectin and other soluble sugars (Erses *et al.,* 2008; Hull *et al.,* 2005), which represent the composition of the total organic carbon, TOC.

Lignin is a tough cell wall material and it's the last material to be degraded, since is extremely resistant to attack. Also, the cellulose is significantly resistant, and it's defined as a polymer. Hemicellulose is a polysaccharide that is very susceptible to attack by the microorganism, because it's composed by 50 - 150 sugar units (Biddlestone and Gray, 1975).

The major reactions (**Figure 2.6**) which occurs in the solid waste are responsible for the formation and quality of leachate and biogas: hydrolysis and biodegradation of the organic matter.

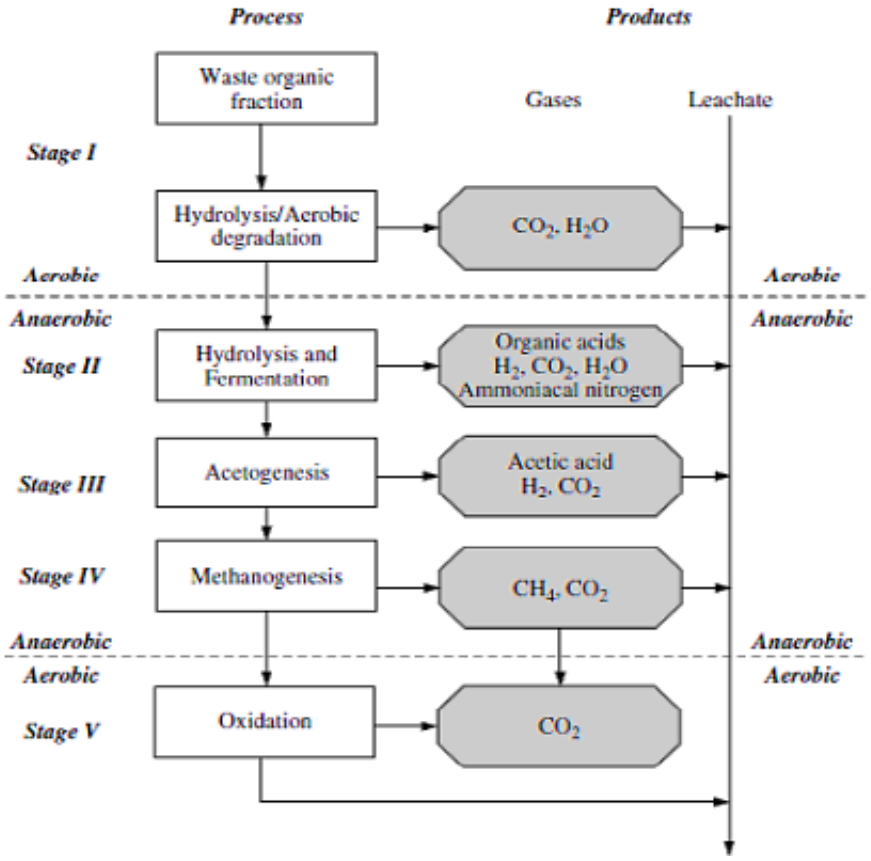


Figure 2.6 - Three principal reactions of degradation in landfills (Waste Management Paper 26B, 1995)

2.4.1.1 Hydrolysis process

After the MSW has been disposed in the landfill, hydrolysis can be the first process occurred. Hydrolysis of complex organics as cellulose and hemicellulose with or without the presence of oxygen, enhance biodegradation rate and convert the organic matter, in the waste mass, into simple monomers with stabilized humic material remaining in the MSW (Erses *et al.,* 2008**;** Östman, 2008).

As **figure 2.6** reports, when there is the absence of oxygen, hydrolysis and fermentation (first step in anaerobic degradation) produces organic acids, carbon dioxide, water, hydrogen and ammonia nitrogen. And with aerobic conditions, only carbon dioxide and water are produced in the gas.

2.4.1.2 Aerobic degradation

Microorganisms start using the oxygen for the aerobic respiration as an electron acceptor, and subsequently, to oxidize the organic matter into simple molecules, e.g. glucose is a product of the cellulose and hemicellulose degradation that is converted into carbon dioxide and water, as it shown in **Equation 2.1** (Brändstatter *et al.,* 2015; Townsend *et al.,* 2015).

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O \qquad \textbf{Equation 2.1}$$

Intense aerobic degradation generates high temperatures with heat, and can reach, approximately, 70ºC. However, if the waste mass is well compacted in the landfill, the oxygen pathways are less, resulting in low temperatures and anaerobic processes, so aerobic degradation is limited by the availability of oxygen (Östman, 2008; Ritzkowski[a] and Stegmann, 2013).

2.4.1.3 Anaerobic degradation

Anaerobic degradation is a complex process without oxygen for the conversion of organic carbon and it's characterized by four processes as **figure 2.6** shows: hydrolysis, fermentation, acetogenesis and methanogenesis (Metcalf and Eddy, 2003):

- Hydrolysis as in **sub-chapter 2.3.1.1** reports, is when the particulate material is converted to soluble compounds that can be hydrolyzed into simple molecules, so in this phase, chemical oxygen demand, COD, increase, since it is a soluble product of the hydrolysis;

- Fermentation, also referred as acidogenesis, consists in the degradation of aminoacids, sugars and some volatile fatty acids to produce acetate, hydrogen, carbon dioxide (**Equation 2.2**), ammonia nitrogen, propionate and butyrate. However, the organic substrates can serve as electron donors or acceptors, since the fermentation of propionate and butyrate can produce acetate, H_2 and CO_2; usually this process is operated with mesophilic temperature range with 30-35ºC;

$$3CH_2O + H_2O \rightarrow CH_3COOH + CO_2 + H_2$$ **Equation 2.2**

- Acetogenesis is defined as the stage where the products of fermentation are oxidized into acetic acid, hydrogen and carbon dioxide. A*cetogens* bacteria can use carbon dioxide to oxidize the hydrogen and, subsequently, produced acetic acid for the fourth stage;
- Methanogenesis is characterized by two group of microorganisms, *aceticlastic methanogene* and hydrogen-utilizing *methanogene*. The first family, fragment the acetate into methane and carbon dioxide (**Equation 2.3**) and the other group use the hydrogen as the electron donor and carbon dioxide as the electron acceptor to produce methane. Major of methane is produced by the acetate formation.

$$CH_3COOH \rightarrow CH_4 + CO_2$$ **Equation 2.3**

During the active life of the landfill, the microbial activity is intense in the beginning, leading to a great biogas production, however with the advancing of the landfill age, the microbial activity starts to decline, causing the decrease of methane production. With the dropping of the gas pressure, air start to enter inside of the landfill through diffusion and, subsequently, the waste mass start to slowly oxidize, which carries the risk of metal ions becoming more mobile and then leaching out to a greater extent than under anaerobic conditions (Östman, 2008).

2.4.2 Carbon pathways

When the waste is disposed into the landfill the carbon component can be converted into more stable compounds, contributing for the formation of a geological deposit or be discharge into the biogas, such as methane and carbon dioxide, and be leached in the form of leachate composed by soluble organic compounds: VFA, humic and fulvic acids (Prantl *et al.,* 2006).

2.4.2.1 Leachate

Landfill leachate consist in a complex matrix of organic matter, organic trace pollutants, inorganic salts and heavy metals, where each concentration are influence by physical, chemical and microbiological processes occurring inside the landfill (Moody and Townsend, 2016). BOD, COD, DOC and TOC are the components measured to characterize the organic content of the leachate.

Biochemical oxygen demand involves the measurement of the dissolved oxygen used by microorganisms in the biochemical oxidation of organic content. In other words, the aerobic degradation of the waste will reach the end, if the oxygen available is sufficient during three processes: oxidation of a portion of the waste into end products to obtain energy for cell maintenance

and for synthesis of new cell tissue; simultaneously some of the waste is converted into new cell tissue using part of the energy released; and finally, when the organic content is consumed the new cells begin to consume their own cell tissue to obtain energy for cell maintenance (endogenous respiration). So, BOD is used to determine the quantity of oxygen that will be required to biologically stabilize the organic matter during these reactions (Metcalf and Eddy, 2003).

Chemical oxygen demand is a component used to measure the oxygen equivalent of the organic material in waste that can be oxidized chemically. As **Figure 2.7** shows, the COD have two principal fractions: the particulate and the soluble. The readily biodegradable soluble COD is often fractionated further into complex COD that can be fermented to VFA (Metcalf and Eddy, 2003).

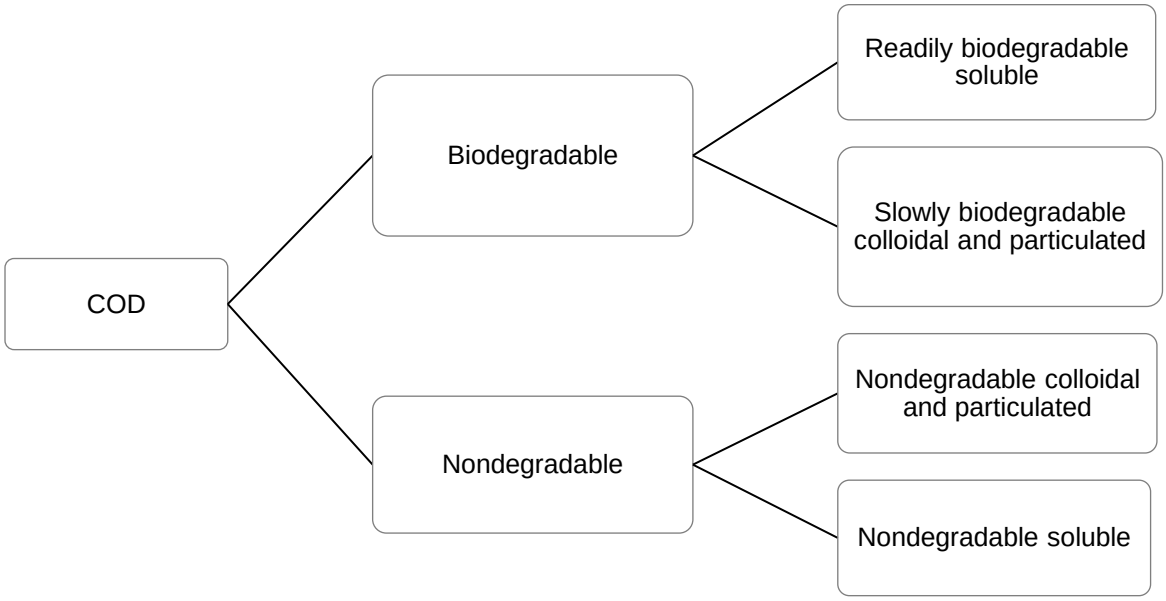


Figure 2.7 - Fractions of COD (Metcalf and Eddy, 2003)

Dissolved organic carbon is produced by the anaerobic degradation of the organic waste in the landfill and consist in a complex component of groundwater and leachate that includes high molecular weight humic and fulvic acids as like a small portion of VFA such as acetate (Mohammadzadeh *et al.,* 2005). DOC is a component that it's not just traceable with great concentration on old leachates, but also can influence the behaviour of other contaminants by its: participation in redox-processes, capacity for connect hydrophobic contaminants, and its ability to form complexes with heavy metals (Christensen *et al.,* 1997).

In general, the quality of landfill leachate changes with the age of the waste having four phases: transition, acid-formation, methane fermentation and final maturation. The limit concentrations of the parameters that characterized the organic carbon compounds of the leachate during the years are presented in **Table 2.3**. In the initial stage, leachate tend to be acidic due to the presence of VFA and over time, the biodegradation of the waste turns from a shorter initial period to a longer degradation period, transforming the concentration of leachate constituents. The fact that COD continues to have

high concentrations between 10-20 years is due to the presence of humic and fulvic acids that aren't easily degradable (Aziz *et al.,* 2010).

Table 2.3 - Concentration of leachate compounds during the life time of a landfill (Aziz *et al.,* 2010)

Leachate parameters	Transition phase (0-5 years)	Acid-formation phase (5-10 years)	Methane fermentation phase (10-20 years)	Final maturation phase (>20 years)
BOD_5	**100-11000**	**1000-57000**	**100-3500**	**4-120**
COD	**500-22000**	**1500-71000**	**150-10000**	**30-900**
TOC	**100-3000**	**500-28000**	**50-2200**	**70-260**
Ammonia	**0-190**	**30-3000**	**6-430**	**6-340**

Leachate can be treated inside of the landfill defined as *in-situ* or can be collected to a wastewater treatment plant (WWTP) and be treated (*ex-situ*).

In-situ treatment can consist in: aerobic conditions as lagoons or bioreactor landfills and in leachate recirculation. The *ex-situ* treatment in the WWTP consist in physico-chemical treatment as: chemical precipitation, chemical oxidation, active carbon adsorption, coagulation-flocculation and membrane processes (Aziz *et al.,* 2010**,** Williams, 2013; Wu *et al.,* 2013).

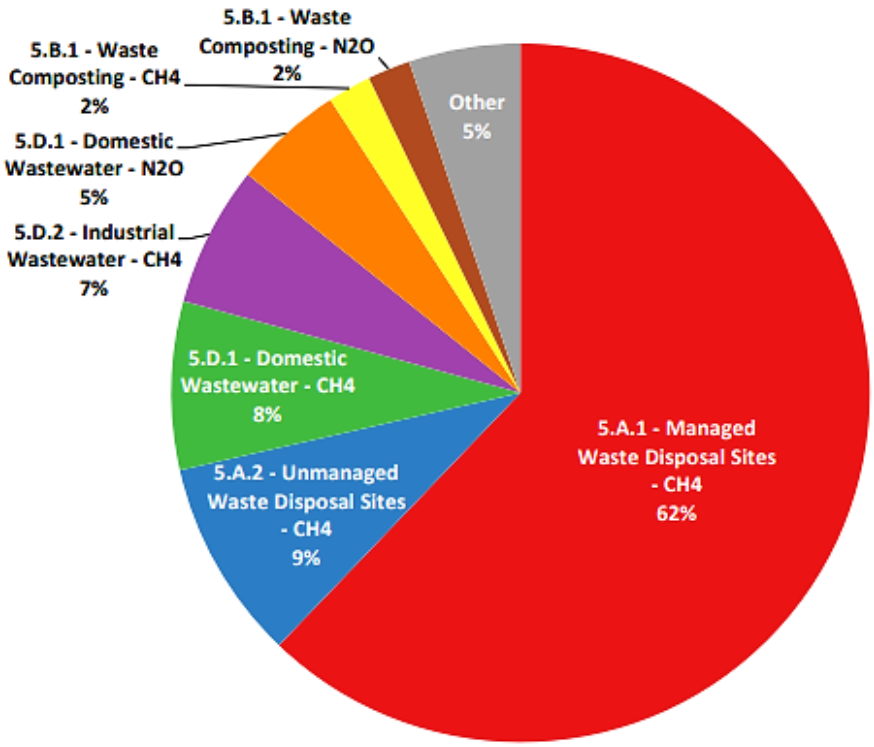
Usually after the leachate is treated and if a sewer line of the municipal is available, leachate is discharge into the sewer system or can be also discharge without treatment and be treated into the WWTP of the municipal (Williams, 2013).

2.4.2.2 Landfill gas

Usually 90% of the total organic carbon in the waste mass is degraded in a bioreactor landfill and it's converted into landfill gas, while only 10% remains in the dissolved organic carbon load of the leachate (Huber-Humer *et al.,* 2011).

The greenhouse gas emissions consist in methane and carbon dioxide, but CO_2 is considered as effect-neutral due to is biogenic origin and the negligible amount compared to other sector, such as industry and transport. While CH_4 has a 23-fold higher global warming potential because of is stronger molar absorption coefficient for infrared radiation and longer atmospheric residence time (Huber-Humer *et al.,* 2011**;** Prantl *et al.,* 2006).

LFG is the fourth largest emission in European Union contributing 3.2% to total GHG emissions in 2015 comparing with other methods for waste treatment, since it produced 62% of methane (**Figure 2.8**).



The category Other includes CH_4 emissions from uncategorized waste disposal sites (5.A.3), CO_2, CH_4 and N_2O emissions from waste incineration and open burning of waste (5.C), N_2O emissions from industrial wastewater treatment and emissions reported under 5.E. other, also CH_4 and N_2O from 5B2 Anaerobic digestion at biogas facilities and CH_4 and N_2O for 5D3 other wastewater treatment and discharge, all other categories in the waste sector are contributing to a EU key source

Figure 2.8 - Methane emissions from landfill sites (EEA[b], 2017).

The main gases from the organic load in the landfill are CH_4 and CO_2 with, respectively, 45-55% and 30-40%. However, there is a wide range of other gases that can potentially be produced. These gases can be characterized into saturated and unsaturated hydrocarbons, acidic hydrocarbons, organic alcohols, aromatic hydrocarbons, sulphur compounds as organic esters, organo-sulphur compounds and hydrogen sulphide, and inorganic compounds (Rasi, 2009).

Biogas composition is influence by the degradation stages of the waste disposed, climate conditions and landfill age (Hrad *et al.,* 2016**;** Prantl *et al.,* 2006):

- Under anaerobic conditions, more specifically, stable methanogenic phase, the concentration of methane is higher than carbon dioxide, with 50-60%, because of the acetate transformation into methane and, also the oxidation of hydrogen with carbon dioxide;
- In the beginning of the aeration, carbon dioxide declines approximately 15%, because the main oxygen is used in the respiration of the microorganisms. However, during further course of aeration, carbon dioxide increases in 90% due to the acceleration of the discharge of carbon (approximately five times more than anaerobic conditions);

- When the aeration stops in the landfill, after a long time, there are low gas generation without methane, indicating that the organic content was already degraded, and it's stabilized.

After the biogas been collected it can be flare or use for energy recover using the methane and other contaminants has a combust.

2.4.3 Carbon mass balance

Mass balance is considered a beneficial tool for achieving the sustainable landfill concept, by studying the emissions from a landfill in a long term and by determining the influence of different alternatives and conditions for waste and landfill management (Cossu *et al.,* 2015). So, using the mass balance for the carbon is useful to understand the removal efficiency of this component into the leachate and biogas.

The principle of mass balance considers the fate of the inputs and outputs of the system in various ways, where the inlet are the waste, the sludge and the rainfall, and the outlet are the biogas and the leachate.

The modelling approach to the mass balance tries to simplify the system with a CSTR – Continuous Stirred Tank Reactor (Cossu *et al.,* 2015):

$$accumulation = input - output \pm reaction \quad \textbf{Equation 2.4}$$

Where:

Accumulation	components that weren't degraded after the time *dt*;
Input	waste mass deposited;
Output	components that were mobilized and transferred into the leachate and the biogas;
Reaction	production and consumption of components inside the waste.

So, to determine the carbon mass balance (**Figure 2.9**):

$$\frac{dx}{dt} fix + \frac{dx}{dt} mob = \sum_i (X_{Si} Q_i) - (x_L Q_{Lr} + x_L Q_{Ld} + x_B Q_{Br} + x_B Q_{Bd} + rV) \quad \textbf{Equation 2.5}$$

Where the *accumulation* is:

$\frac{dx}{dt}fix$ accumulation of stable non- extractable compound;

$\frac{dx}{dt}mob$ accumulation of compounds mobilized and transferred.

The *input* of the landfill consists:

$\sum_i(X_{Si}Q_i)$ sum of X_{Si}, the carbon content in the solid phase (mg TOC/t waste) multiply by Qi, the waste mass (t/year).

The *output* consists into the carbon content after the physic-chemical processes in the leachate and the biogas:

x_LQ_{Lr} carbon content in the collected leachate: X_L consist in the carbon fraction in leachate (mg TOC/L) and Q_{Lr} consist in the amount of leachate collected (L/year);

x_LQ_{Ld} carbon content that migrated in an uncontrolled way through the barrier of the system: Q_{Ld} is the leachate that reach the protective layers (L/year) and X_L is the carbon portion in leachate (mg TOC/L);

x_BQ_{Br} carbon content in the collected biogas: X_B consist in the carbon fraction in biogas (mg TOC/m³) and Q_{Br} consist in the amount of biogas collected (m³/year);

x_BQ_{Bd} carbon content that migrated in an uncontrolled way: Q_{Bd} is the biogas that escaped (m³/year) and X_B is the carbon portion in biogas (mg TOC/m³).

The *reaction* is:

rV degradation of the waste mass in the bioreactor plus the kinetic constant.

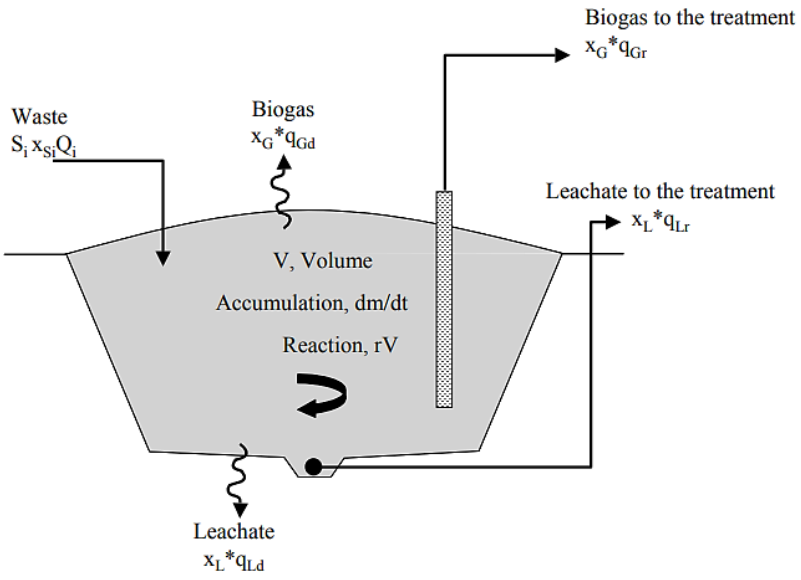


Figure 2.9 - Terms of the landfill mass balance (Cossu *et al.,* 2015)

To reduce all the uncontrolled emissions of carbon and have a sustainable management of a landfill some actions can be provided (Cossu *et al.,* 2015):

- Reduce the amount of waste mass deposited into the landfill or improve the quality;
- Increase the amount of leachate and biogas collected to minimize the uncontrolled flux;
- Maximize the accumulation of stable components and the stabilization processes;
- Improve the increase of the degradation rate of the organic compounds, e.g., aerobic conditions.

2.5 Effects of aeration flow rate and oxygen concentrations: state of art

The study of Slezak *et al.,* 2009**,** had the aim to investigate the influence of aeration rate on the degradation of organic matter present in the MSW, more specific the changes of carbon content in gas and leachate produced.

This lab-scale study was carried out by five glass cylinder lysimeters with an internal diameter of 15 cm and a height of 1.15 m. Each lysimeter had 15 L of old waste with 28% of organic, 19% of paper, 12% of plastics, 4% of textiles, 27% of compost and 10% of other inorganic. Once a day for 15 min with a volumetric flow rate equal to 1 mL/s, leachate was recirculated in all lysimeters. And off-gas were collected every day.

The lysimeters started with anaerobic conditions so the waste could use the oxygen present inside. After this period, each column had different values of air flow that were given at standard pressure and temperature conditions with 23ºC (**Table 2.4**).

Table 2.4 - Operational data for the experiment (Slezak *et al.,* 2009)

Columns	R0	R1	R2	R3	R4
Air flow rate (L/h)	**0**	**10**	**6**	**4**	**2**
Anaerobic period (d)	**221**	**8**	**8**	**8**	**8**
Aerobic period (d)	**0**	**213**	**213**	**213**	**213**

During the whole experiment, BOD_5 index reported similar values for all aeration rates (**Figure 2.10**). Through anaerobic conditions, the values were similar to 9000 mg/L and after 26 days of aeration, the reduction for R1, R2, R3 and R4 were, respectively: 99.5%, 98.2%, 99.2% and 98.7%. In the end, the lysimeters achieved concentrations from 3-9 mg/L. For the anaerobic lysimeter, the reduction wasn't

so significant as the aerobic lysimeters, since it started with 10000 mg/L and in the end of the experiment remained at 121 mg/L.

Similar trends were observed also by Erses *et al.,* 2008, that carried out a similar study with an aerobic bioreactor with an inlet of 2.2 L/min for 5 hours in a day and an anaerobic bioreactor. In the end of the experiment the concentration of BOD_5 was equal to 4 mg/L.

Comparing with the BOD_5, COD index reported a slight influence by the aeration (**Figure 2.10**).

Initial values for the reactors began with a range of 13800-19000 mg/L and then, after 15 days of aeration was reported a great decrease equal to: 91.3% in R1, 85.6% in R2, 88.2% in R3 and 92.2% in R4. In the end of the experiment, values of the COD index on the completion of aeration were for R1, R2, R3 and R4, respectively: 790 mg/L, 680 mg/L, 950 mg/L and 550 mg/L. The lowest aeration flow rate, R4, had the highest decrease of COD levels and the second lowest, R3, had the worst removal comparing with the air flow rate of 10 L/h, R1.

The anaerobic lysimeter had an increase of COD due to the presence of acid phase and then, started to decrease. So, under this condition the COD index assumed higher values than under aerobic conditions.

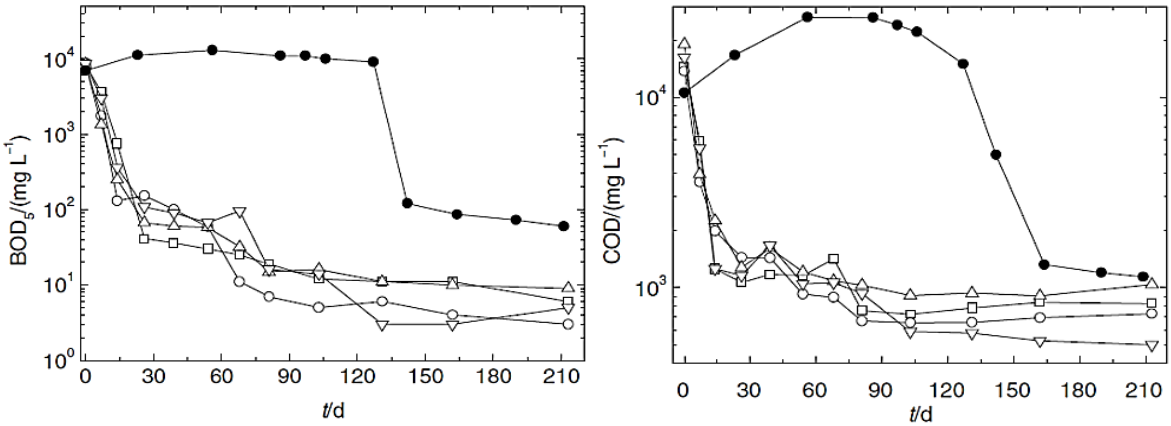


Figure 2.10 - BOD_5 and COD results in leachate (Slezak *et al.,* 2009)

Carbon quantity released by off-gas was determine considered only CO_2 as in the course of aeration (**Figure 2.11**). The amount of carbon dioxide produced was referred to 1 kg of dry mass of waste. The aeration rate affected the carbon dioxide production rate, which: R2 had the lowest C-discharge with a value of 66 g/kg DM and R1 reported the highest amount of carbon release, 140 g/kg DM.

The amount of air supplied to each lysimeter affected the carbon conversion rate into CO_2 and COD removal in the leachate.

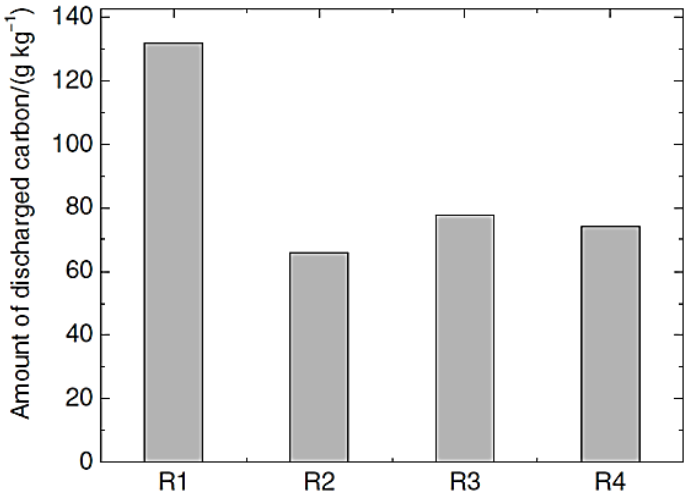


Figure 2.11 - Carbon release by off-gas in the aerated lysimeters (Slezak *et al.,* 2009)

Another study that started to investigate the changes of carbon compounds during *in-situ* aeration of an old landfill under various aeration regimes and also the effect in nitrogen compounds was Prantl *et al.,* 2006, with a lab-scale experiment.

The experiment was set-up with acrylic glass columns with a diameter of 20 cm and a height of 65 cm. The gas proof columns were loaded with 10-15 kg waste (dry mass) and operated under controlled temperature conditions, 35 ºC in a climate chamber. Leachate samples were weekly taken, and off-gas samples were measured continuously. Column S1 had anaerobic conditions for 513 days and S3 and S6 were aerated with, respectively: 0.5 L/h of air for 513 days and 1 L/h of air for 270 days. However, S6 after the aeration period for 243 days started to be anaerobic.

Figure 2.12 reports an obvious influence of the different air flow rate in S3 and S6 for COD development.

The three columns started with high COD concentrations, above 7000 mg O_2/L, before the aeration. After 2 months of aeration, columns S3 and S6 had a rapid decrease to 350 mg O_2/L. During this phase, the lowest aerated bioreactor had the worst improvement than S6. After two months the aeration started to become less influence.

S1 reported a decrease, because of the leaching processes and anaerobic degradation, however in the end of the experiment, both the bioreactors showed similar COD concentrations.

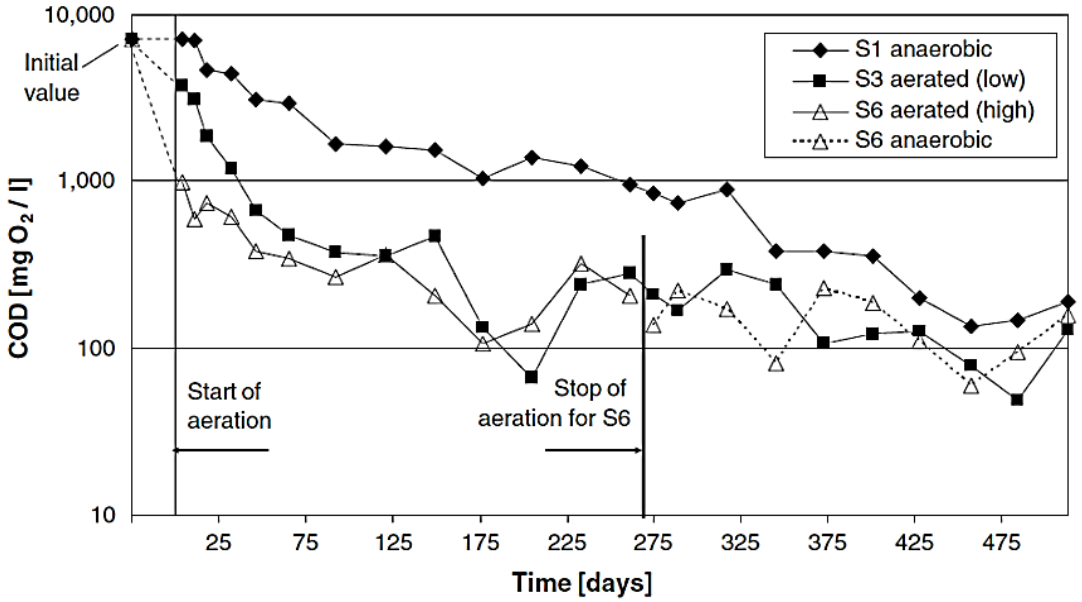


Figure 2.12 - Effects by aeration rates on COD concentration in leachate (Prantl *et al.,* 2006)

Not only leachate quality, but also off-gas samples (**Figure 2.13**) showed a slight effect in carbon-discharge by the different aeration effects: S6 (highest aeration rate) had approximately more C-discharge than S3, at day 270. And then at day 513, the carbon content increase for the lowest air flow rate than for the highest, since for S6 the aeration was stop. Particularly, it was reported that more than 90% of carbon was discharged as CO_2 than CH_4.

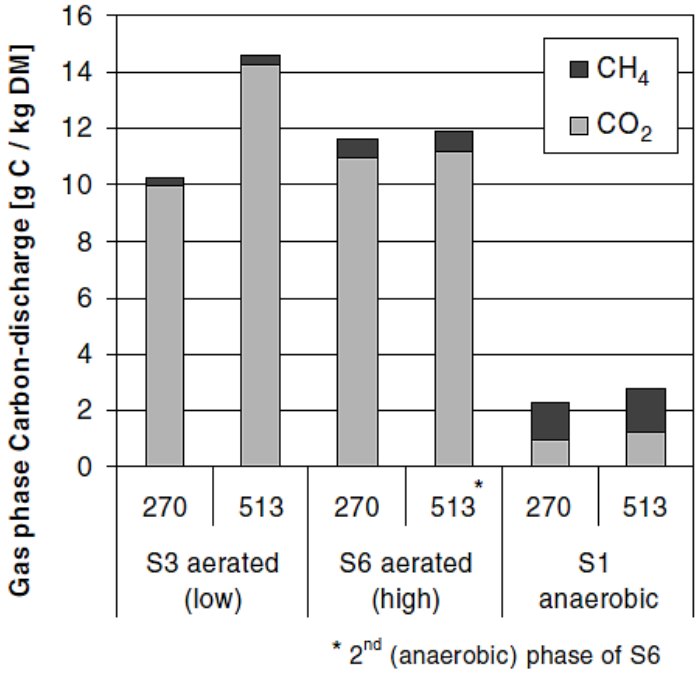


Figure 2.13 - C-discharge in the gas phase for the anaerobic and aerobic columns (Prantl *et al.,* 2006)

However, with so many ranges of aeration like the studies reported, and Bilgili *et al.,* 2006**,** with 0.084-0.086 L/min/kg waste and Borglin *et al.,* 2004**,** with 0.04 L/min/kg waste, it is difficult to define an optimum air flow rate to the stabilization of the waste, because there are many factors that influence the aerobic degradation: temperature, humidity, air distribution, MSW composition and conditions and others (Ko *et al.,* 2016).

An adequate determination of oxygen concentrations in the outlet gas was consider by some researchers an essential criterion to achieve bio-stabilization.

Slezak[a] *et al.,* 2015 had investigated another study with the aim of carrying an experimental simulation of the processes observed in the municipal landfills under both anaerobic and aerobic degradation.

The experiment was set-up with three PVC cylinder lysimeters: A1, A2 and AN with 15 L of waste. A1 and A2 were conducted under aerobic conditions with the same air flow rate: 4.41×10^{-3}L/min.kg for 196 days; while AN was anaerobic. Leachate recirculation was applied daily with a rate of 24.9 and 1.58 L/m^3.d for A1 and A2, respectively.

Comparing with other studies, the aeration rate was smaller in order to check if small amounts would be sufficient to achieve the waste stabilization, e.g., Bilgili *et al.,* 2006**,** Borglin *et al.,* 2004 and Erses *et al.,* 2008, applied aeration rates in a range of 0.012-0.22 L/min.kg and for leachate recirculation rate a range of 0.35-144 L/m^3.d, however the rate of leachate recirculation in A2 was similar to the study of Erses *et al.,* 2008.

Figure 2.14 reports, that during the aeration, oxygen concentration in the outlet gas had the tendency of an intensive reduction from the start of the experiment until day 20. The lysimeters started with a similar value of 4.28 g O_2/kg DM and then after 196 days reduced to: 0.62 g O_2/kg DM in A1 and 0.59 g O_2/kg DM in A2. These results lead to an average concentration of O_2 in the exhaust gas of 12.67% in A1 and 11.54% in A2. Also, Bilgili *et al.,* 2006, reported similar values of oxygen concentration in the off-gas samples with a range of 8 to 14 vol.%.

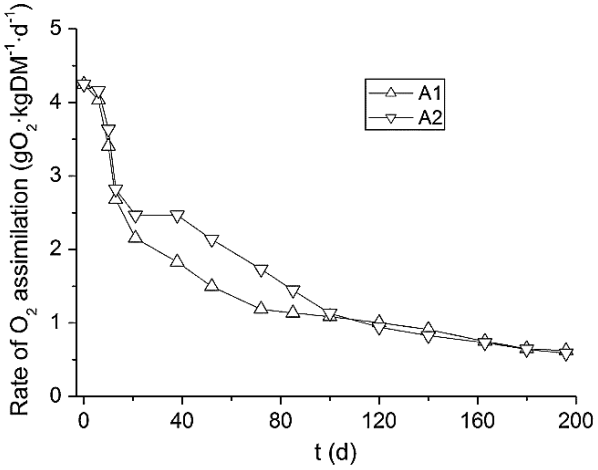


Figure 2.14 - Oxygen assimilation rate in the aerobic lysimeters (Prantl *et al.,* 2006)

The study revealed some impacts on the leachate composition and on the gas production: A1 reported 75% of COD removal earlier than A2 that in contrast had more oxygen assimilation; ammonium

nitrogen, in the end of the experiment, had a concentration of 4.8 mg N/L in A1 and 7.1 mg N/L in A2; column A2 reported more assimilation of oxygen concentrations and more production of carbon dioxide, respectively: 301.1 g O_2/kg DM and 101.2 g C/kg DM, than A1 with a concentration of, respectively: 265.2 g O_2/kg DM and 82.5 g C/kg DM.

Also, Ritzkowski and Stegmann, 2012, had investigated the influence of adjusting the aeration rate in time according to oxygen concentrations in off-gas samples and assimilation, during the experiment to bio-stabilize the biodegradable organic carbon (BOC): an average of 80% oxygen conversion quota was determined for the acceleration effect of the biodegradation processes associated with significantly shorter aeration periods. Ko *et al.,* 2016, measured values of oxygen concentration of approximately 17% in the exhaust gas with an aeration flow rate of 30L/h.

3 Materials and methods

3.1 Landfill description

The Legnago landfill was built in 1981 on the Tartaro river bed, located on the southern Legnago County (Providence of Verona, Italy), on the Bergantino border. The firsts sectors of this non-hazardous waste disposal landfill (Sector I and II) were built on an old river bed without some minimum requisites to the construction of a landfill (Le. Se., 2017).

In the bottom part, it wasn't designed an artificial impermeable bottom liner and the leachate collection system, which respectively had the function of, preventing infiltrations of superficial and/or subterranean waters and of precipitation for the base and slope of the landfill, and providing a minimum level for leachate accumulation inside of the site (Cestaro *et al.,* 2006).

Since the sector was constructed above an aquifer and didn't respected the legible criterions, the waste was excavated and went to further analyses to observe if it's appropriate to put in a new disposal site (**Figure 3.1**) characterized with the environmental protective systems, which provides a better management of the landfill and avoid the contamination in the subterranean water/aquifers, atmosphere and soil.

Figure 3.1 - Old sector without protective systems (on the left) and the new sector according with the legislation criterias (on the right) (Google Maps, 2017)

3.2 Waste samples

The MSW samples were excavated and collected from 10 m landfill body depth, corresponding to approximately, 30 years of age of the waste. So, the waste sample used for the experiment was therefore a mixed MSW from the 80's. Around 400 kg of waste were collected with the excavator and

put into 8 sealed plastic bins for further analysis in LISA, Laboratorio di Ingegneria Sanitaria Ambientale. **Figure 3.2** shows the collection operation of the waste in the Legnago landfill.

Figure 3.2 - Excavation layer for the MSW samples in study

Grain size distribution analysis was manually performed, using mesh size sieves to separate: 100, 50 and 20 mm. Waste composition analysis was carried out considering the eight categories: fines (under sieve, with < 20 mm), plastic, paper, metals, aggregates (mixture of unknown materials), inerts (glass and stones), textiles and wood.

After the grain size distribution analysis, the waste was mixed and weighted in order to guarantee the homogeneity of the waste samples, and to simulate the same waste composition inside of the landfill in each bioreactor.

3.3 Equipment

The six cylindrical column reactors were made by Plexiglass® with an intern diameter of 24 cm, an external diameter of 26 cm and a total height of 106 cm (**Figure 3.3**). The bottom part was equipped by the leachate output to collect the samples and the upper flange had two inputs, for the introduction of the air and the leachate recirculation or tap water addition, and one output for the gas-off samples.

The bioreactors were filled with gravel, as a drainage layer, and with a mix of each category of the solid fraction, in a range of: 30.8 – 35.6 kg, in order to maintain the homogeneity of the waste categories for all reactors.

Figure 3.3 - Six bioreactors used for the lab-scale tests

C1, C2, C3, C4 and C5 were operated with aerobic conditions with different aeration flow rates, through three Prodac Air Professional 360 air pumps, regulated by five Sho-Rate GT1335 flowmeter (Brooks Instruments). The air was loaded into the columns by a PVC pipe perforate 10 cm in the down part to have a uniform distribution from the bottom to the upper part, and it was fixed in the middle of the columns starting in 20 cm above the gravel (without contact with the leachate). Five different aeration flow rates were set-up for the columns to stablished different oxygen concentrations in the exhaust gas. C0 was operated with anaerobic conditions. **Figure 3.4**, illustrates the concept of the aerated columns (left side) and the anaerobic column (right side).

The recirculation of the leachate for the aerated bioreactors, was made manually with a funnel and a tank with 2 L of volume. For C0, the recirculation was channelled with a peristaltic pump Heidolph PUMPDRIVE 5001.

Gas composition was evaluated with Telegan LFG 20 and under anaerobic conditions the quantity of the gas produced was collected by Tedlar 10 L bags.

During the experiment, the room temperature was maintained at 30ºC for all the pilots and the input for measured the temperature in the columns was sealed.

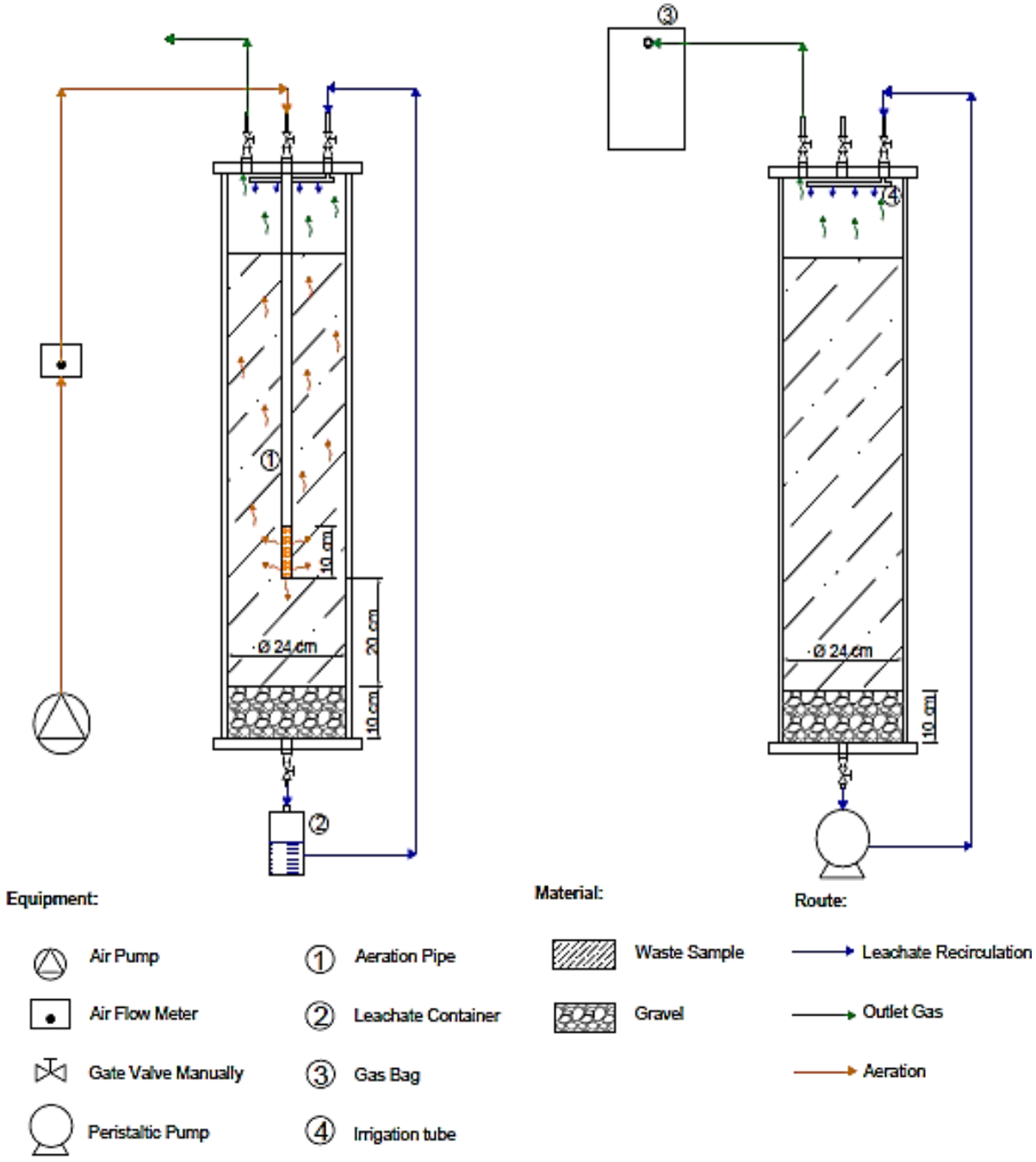


Figure 3.4 - Ilustration of the experiment equipment

3.4 Methodology

Firstly, all the columns were loaded with 10 cm of gravel in the bottom layer (in a range of 9-10 kg) and after, for C0, C1, C2, C3, C4 and C5 the waste height were, respectively: 0,62 cm; 0,68 cm; 0,68 cm; 0,72 cm; 0,70 cm and 0,62 cm.

After loading the pilots with a range of waste density of 1.07-1.15 kg/m^3, the field capacity of each was determined adding tap water and recirculated until this parameter was reach in an average of fifteen minutes for each column.

The management of the columns was divided in two phases, for 120 days: Phase I – Anaerobic conditions – Phase II – Anaerobic and aerobic conditions.

In Phase I, all the columns were set-up under anaerobic conditions, for 44 days, without recirculation of leachate, in order to begin the aeration of the bioreactors with the same conditions.

In Phase II, a trial test was made with 1 L/h of air injected, with the purpose of understand the different behaviours of oxygen consumption and to create different oxygen concentrations in the outlet gas for each bioreactor. After this test, at day 65, C1, C2, C3, C4 and C5 were established with a continuous aeration rates, respectively: 0.22 L/d.kg of waste, 0.34 L/ d.kg of waste, 0.54 L/ d. kg of waste, 0.71 L/ d. kg of waste, 0.89 L/ d. kg of waste. C0 was set-up as anaerobic to represent the real situation of Legnago landfill and to stand as a control pilot. This phase lasted 76 days.

Throughout this phase, 0.5 L of leachate was manually recirculated for all the aerobic columns at: 10:30 h, 11:30 h, 12:30 h, 15:00 h and 16:00 h. This time table was set-up to avoid the saturation of the waste. For the anaerobic column, a rate of 10 rpm equivalent to 1.25 L/h was set-up for two hours, at: 10:30 h and 15:00 h. The recirculation was executed every week achieving 2.5 L/day to maintain the humidity of the waste.

Off-gas samples were analysed for dioxide carbon (CO_2), methane (CH_4) and oxygen (O_2), every morning in the week of the experiment, at 10:00 h, before the recirculation period, except for weekends and holydays.

Leachate samples were taken three times in phase I, and for phase II were collected weekly with a volume of 250 mL to analyse: TOC, BOD_5, COD, TKN, ammonium-nitrogen, nitrite, nitrate, pH, alkalinity, chloride and sulphur. The same amount was replaced for all columns with tap water.

3.5 Analytical methods

Italian standard methods were applied for analysis determination on leachate and solid samples, and off-gas samples were collected.

3.5.1 Waste Samples

In order to characterize the waste samples some parameters were measured to assess the original composition from the landfill and in the end of the experiment to understand the behaviours of the organic content.

TS and VS analysis was based in the method IRSA-CNR Q 64/84 Vol. 2, n.2, and were made in triplicate on each category, except for metals and inerts. With the values of the TS, moisture content was determined (100% - TS%). The method for the TOC determination is described in UNI EN 13137 and samples of fines for each bioreactor were analysed. And the Respiration index was determined with an average of three samples of the undersieves by the Sapromat apparatus, for four days.

3.5.2 Off-gas samples

The composition from the gas (% volume) was analyse for three parameters: CO_2, CH_4 and O_2.

3.5.3 Leachate Samples

Table 3.1 shows the method description for every parameter used to characterize the leachate and the frequency of the analysis.

Table 3.1 - Methods for the anaylsis of the compounds in leachate

Parameter	Method description	Weekly analysis	Monthly analysis
pH	**IRSA-CNR 29/2003, VOL 1, N.2060**	✖	
Alkalinity	**IRSA-CNR 29/2003, VOL 1, N.2030**	✖	
COD	**IRSA-CNR 29/2003, VOL 2, N.5130**		✖
BOD_5	**IRSA-CNR 29/2003, VOL 2, N.5120**		✖
TOC	**IRSA-CNR 29/2003, VOL 2, N.5040**	✖	
TKN	**IRSA-CNR 29/2003, VOL 2, N.5030**		
$N\text{-}NH_4^+$	**IRSA-CNR 29/2003, VOL 2, N.4030**	✖	
$N\text{-}NO_3^-$	**IRSA-CNR 29/2003, VOL 2, N.4040, A1**	✖	
$N\text{-}NO_2^-$	**IRSA-CNR 29/2003, VOL 2, N.4050**	✖	
Cl^-	**IRSA-CNR 29/2003, VOL 2, N.4090, B**		✖
SO_4^{2-}	**IRSA-CNR 29/2003, VOL 2, N.4140, B**	✖	

3.6 Calculations

3.6.1 C-Discharge via gas

In order to calculate the anaerobic C-discharge based on carbon dioxide and methane production, the volume and gas composition was measured obtaining the volume of each component by

multiplication. For aerobic treatment with the set-up of air flow meter and the gas composition for 76 days, the volume of CO_2 or CH_4 was determined.

The general gas equation (**Equation 3.1**) was applied:

$$n = \frac{pV}{RT} \quad \textbf{Equation 3.1}$$

n	amount of CO_2 or CH_4 (mol);	R	universal gas constant 0,082 (L.atm/K.mol);
T	temperature (K);	p	atmospheric pressure 1 (atm);
V	volume measured of gas (L).		

For calculating the carbon mass in grams mass mole formula (**Equation 3.2**) was applied:

$$n = \frac{m}{M} \quad \textbf{Equation 3.2}$$

M molar mass of CO_2, CH_4 or C, respectively, 44 g/mol, 16 g/mol and 12 g/mol;

m weight of CO_2, CH_4 or C (g).

3.6.2 Mass balancing

The carbon remained in the solid sample was measured at the start and at the end of the experiment, denoted as, respectively, TOC_{is} and TOC_{fs}.

The C-discharge via gas was calculate as the sum of methane and carbon dioxide discharge in phase I and phase II ($C_{gas\ (anaer+aer)}$).

For the carbon that was discharge via leachate, the sum of the extracted sample in 250 mL and the leachate that remained inside of each reactor was applied (respectively, TOC_{ls} and TOC_{lr}). In C0, C1, C2, C3, C4 and C5 the volume of leachate inside was, respectively: 4.6 L, 5.6 L, 5.4 L, 5.3 L, 5.4 L and 5.0 L.

The total mass balance of organic carbon for each column (**Equation 3.3**) was determined as (g C/kg TS):

$$Error_{TOC} = TOC_{is} - TOC_{fs} - TOC_{ls} - TOC_{lr} - C_{gas\ (anaer+aer)} \quad \textbf{Equation 3.3}$$

The $Error_{TOC}$ consist in the carbon missing in the carbon mass balance.

4 Results and discussion

4.1 Waste characterization

The following two sub-chapters shows the results of the excavated material collected in the Legnago landfill and the composition of the solid fraction used for each bioreactor.

4.1.1 Composition of the excavated material

After the waste were excavated from the landfill, the composition of the handsorted samples were analysed. **Table 4.1**, reports the results of the grain size distribution in 8 categories: plastic, paper, textile, metals, aggregates, inerts, wood and fines.

Table 4.1 - Particle size distribution of the excavated waste from Legnago

Waste category	Particle size (mm)			Total	
	< 100	< 50	< 20	(kg)	(%)
Plastic (kg)	**28.7**	**9.3**	**7.4**	**45.4**	**14.1**
Paper (kg)	**3.7**	**3.2**	**3.5**	**10.4**	**3.2**
Textile (kg)	**4.1**	**1.9**	**1.1**	**7.1**	**2.2**
Metals (kg)	**1.0**	**1.2**	**0.9**	**3.0**	**0.9**
Aggregates (kg)	**11.7**	**1.4**	**3.4**	**16.4**	**5.1**
Inerts (kg)	**19.7**	**8.6**	**17.3**	**45.6**	**14.2**
Wood (kg)	**1.2**	**1.3**	**1.5**	**4.0**	**1.3**
Fines (kg)	**0.0**	**0.0**	**189.4**	**189.4**	**58.9**
Total (kg)	**70.1**	**26.7**	**224.4**	**321.2**	**100.0**

Fines were the major fraction in weight of the samples with 58.9% of total weight. Also, the studies of Hull *et al.,* 2005 and Kaartinen *et al.,* 2013, have found out similar amounts of fines. According to Monkäre *et al.,* 2015, the amount of fines (under sieves) increase when the age of the waste increase because of the decomposition of the waste. Additionally, inerts and plastic reported also a great quantity in the excavated material, comparing with the remain categories.

Table 4.2 indicate the results of the analytical methods for the moisture, total solids and volatile solids matter. The selected characteristics can give an indication of the environmental conditions, the degree of degradation in the landfill and the quality of the categories selected.

Table 4.2 – Physical parameters of the excavated waste from Legnago

Waste Category	Parameters (units)		
	Moisture (%)	TS (%)	VS (%)
Fines	**20.4**	**79.7**	**6.4**
Wood	**31.1**	**68.9**	**91.4**
Paper	**54.6**	**45.4**	**46.4**
Textile	**49.4**	**50.6**	**54.6**
Aggregates	**34.5**	**65.6**	**72.7**
Plastic	**33.2**	**66.8**	**32.8**
Total	**21.7**	**78.3**	**20.4**

Hull *et al.,* 2005, suggested that moisture content can determine the environmental conditions in the landfill and, also can consist as a decisional parameter for further biological or thermal treatment of the excavated material.

As expected paper and textile were the major fraction in moisture content, because these categories can absorb moisture (Hull *et al.,* 2005). Relating these values with the grain size analyses (**Table 4.1**), it was showed that the major fraction with humidity content weren't the most significantly in weight, so supposedly in these landfill sector where the waste was excavated, the moisture content was low.

Since the TS content is the opposite from moisture content, paper and textile were the lowest fraction and fines and wood had the highest value of total solids.

Volatile solids are used as a measure of the degree of biodegradation of the organic fraction (Hull *et al.,* 2005).

Wood and aggregates had the highest values for VS and the fines was the category with a low percentage. According with Hull *et al.,* 2005, over the lifetime of a landfill, due to degradation of organic matter, dry mass of waste deposited in a landfill is reduced. The undersieve fraction (fines) represents a significant amount of organic matter, so in this study it was confirmed that the waste excavated had already suffered degradation processes for 30 years resulting in low trends of VS in this fraction.

4.1.2 Solid fraction in the bioreactors

After the determination of the weight of each category in total by the grain size distribution method, it was possible to correlate the grain size distribution in each bioreactor, having the same trend of the solid sample weight, so 6 mixtures of the solid fraction were made and loaded into the bioreactors (**Figure 4.1**). The fines, plastic and inerts were the most dominant fraction in each column.

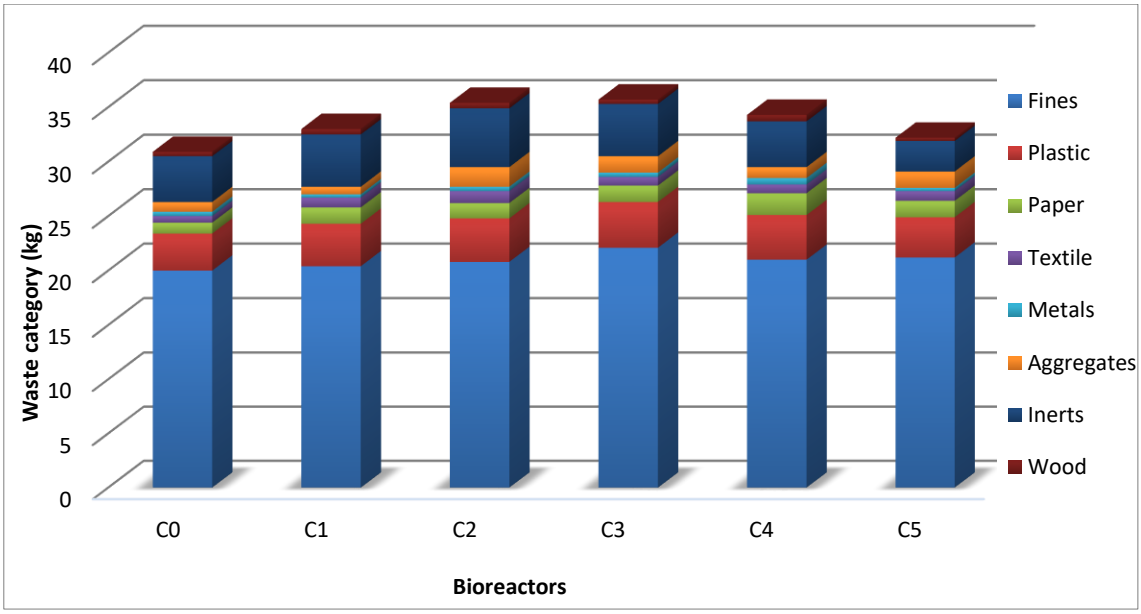


Figure 4.1 – Composition of the waste loaded in each bioreactor

After weighting the waste for each column, a correlation for the moisture, TS and VS content was made, in order to understand the behaviour in the start of the experiment. **Table 4.3**, reports the values of these parameters which characterize all columns after manual compaction.

Table 4.3 - Correlating values for TS, VS and Moisture content for the six columns

Parameters (units)	Bioreactors					
	C0	C1	C2	C3	C4	C5
Weight (kg)	**30.8**	**33.0**	**35.4**	**35.6**	**34.0**	**32.2**
TS (%)	**79.0**	**78.4**	**78.4**	**78.3**	**77.7**	**77.0**
TS (kg)	**24.4**	**25.9**	**27.7**	**27.9**	**26.4**	**24.8**
VS (%TS)	**17.2**	**18.4**	**20.4**	**19.1**	**19.7**	**20.5**
VS (kg)	**4.2**	**4.8**	**5.7**	**5.3**	**5.2**	**5.1**
Moisture (%)	**21.0**	**21.6**	**21.6**	**21.7**	**22.3**	**23.0**
Moisture (kg)	**6.5**	**7.1**	**7.6**	**7.7**	**7.6**	**7.4**

As referred the VS is a measure of the potential degradation of the organic content and the calculation of VS/TS denoted that the dry matter had a lower ratio, indicating also, a low organic content in the columns (Hull *et al.,* 2005).

C0 had the highest value of TS (79%) therefore the VS/TS was the lowest (17.2%), comparing to C5 that reported the highest value of VS/TS (20.5%). There were different proportion of organic content between the bioreactors, suggesting, in general, to the heterogeneity of the material.

For the start and the end of the experiment, RI_4 and TOC were determined to understand the evolution of the reactions in the excavated waste, considering the different aeration rates and oxygen concentrations in the outlet gas. **Table 4.4**, reports these values.

Table 4.4 – Initial and final chemical analysis for each bioreactor

Parameters (units)	Bioreactors					
	C0	C1	C2	C3	C4	C5
$RI_{4\ initial}$ (mg O_2/kg TS)	**1.1**	**1.1**	**1.1**	**1.1**	**1.1**	**1.1**
$RI_{4\ final}$ (mg O_2/kg TS)	**0.7**	**0.8**	**0.5**	**0.4**	**0.3**	**0.5**
$TOC_{initial}$ (g C/kg TS)	**15.0**	**14.4**	**13.7**	**14.5**	**14.5**	**15.6**
TOC_{final} (g C/kg TS)	**10.9**	**9.3**	**9.0**	**8.8**	**8.6**	**9.1**

The waste material had a respiration index of 1.1 mg O_2/kg TS on the 4th day, indicating a relative high stability of the waste. These values were considered low comparing with the study of Raga and Cossu, 2012 and Tran *et al.,* 2015, due to a progressive reduction of biodegradable content over the lifetime of the landfill, since the waste had 30 years old, the organic matter already suffered degradation processes with anaerobic conditions.

In the end of the experiment, the aerated columns suffered a significant reduction in the RI_4, ranging from 22 – 69%. C1, was the column with the lowest reduction, indicating that if the experiment hadn't stop, aerobic degradation could continue stabilizing even more, the waste (Raga and Cossu, 2012). The anaerobic column didn't have a great decrease, since anaerobic degradation take more time to reduce the organic material.

TOC in the beginning were still relatively high, considering the age of the waste and the pre-treatment with air injected, suggesting that for 30 years the efficiency of removing organic compounds were low, which RI_4 values can also corroborated. C0 and C5, started with higher values than the other reactors. After the waste had suffer anaerobic degradation, in phase I, and aerobic degradation during more time (phase II), on the 120th day it was observed a decrease in the TOC content: 36% in C1, 35% in

C2, 39% in C3, 40% in C4 and 42% in C5. Only the anaerobic reactor had a slight decrease of organic carbon with a value of 28% due to the slow degradation.

These TOC values measured on the waste material were consider for the evaluation of the carbon balance.

4.2 Off-gas development

The influence of waste aeration rate on the changes of carbon dioxide and methane concentration in off-gas samples were measured to define the processes of degradation and, additionally to determine the quantity of carbon released in the carbon mass balance.

Methane and carbon dioxide are the principal gases produced during the decomposition of organic fraction of waste under anaerobic conditions (Erses *et al.,* 2007). While, under aerobic conditions, methane isn't produced, and carbon dioxide is the major component in the gas (Brandstätter *et al.,* 2015).

Daily gas production of the aerobic and the anaerobic columns have been given in **figure 4.2** for the CO_2 and **figure 4.3** for the CH_4. **Figure 4.4**, illustrates oxygen concentrations in the outlet-gas samples for all the bioreactors.

4.2.1 Carbon dioxide production rate

During phase I, carbon dioxide started to be produced, achieving different concentrations with a range of 8.8-15%. Until day 44th, CO_2 had a great production achieving maximum values of: 12.1% in C0, 20.0% in C1, 15.7% in C2, 15.3% in C3, 12.1% in C4 and 11.7% in C5, suggesting that methanogenic bacteria started to fragment acetate, so gas production rate started to increase (Erses *et al.,* 2007). This process is more evident in C1, C2 and C3, since the CO_2 concentration was higher than in C0, C4 and C5.

The onset of aeration, in phase II, caused a considerable decrease of the carbon dioxide concentration in the off-gas, because with the start of oxygen injection in the waste mass, anaerobic degradation started to be inhibited, reducing carbon dioxide production. Also, Berge *et al.,* 2005 and Slezak *et al.,* 2009, had reported this tendency when aeration conditions were set-up in the bioreactors, because of the drop of biodegradable organic matter in the excavated waste.

In the study of Prantl *et al.,* 2006, carbon dioxide declined immediately to 15% under aerobic conditions, while in these tests, CO_2 suffered a significant reduction ranging from 27 – 43%.

The highest aerated bioreactors with an inlet of 1.0 L/h and 1.2 L/h, reported a lower carbon dioxide production in the off-gas samples, comparing with C1, C2 and C3. Slezak *et al.,* 2009, also reported this situation under different aeration rates: the reactors with an air flow rate of 10 L/h and 6 L/h had a concentration of, respectively, 0.8% and 0.6%, while the less aerated columns with an inlet of 4 L/h

and 2 L/h reported values of, respectively, 0.8% CO_2 and 1.6% CO_2. However, during the 83th – 120th day, C4 and C3 changed their behaviour: CO_2 production in C4 increased more than C3, probably due to a lower aerobic degradation activity or to the presence of anaerobic spots, providing the inhibition of oxidation of the organic matter.

C0 had a constant behaviour ranging from 8-13% of CO_2. But during the period of 69th - 83th day, a decrease – increase behaviour was observed, remaining constant until the end of the experiment.

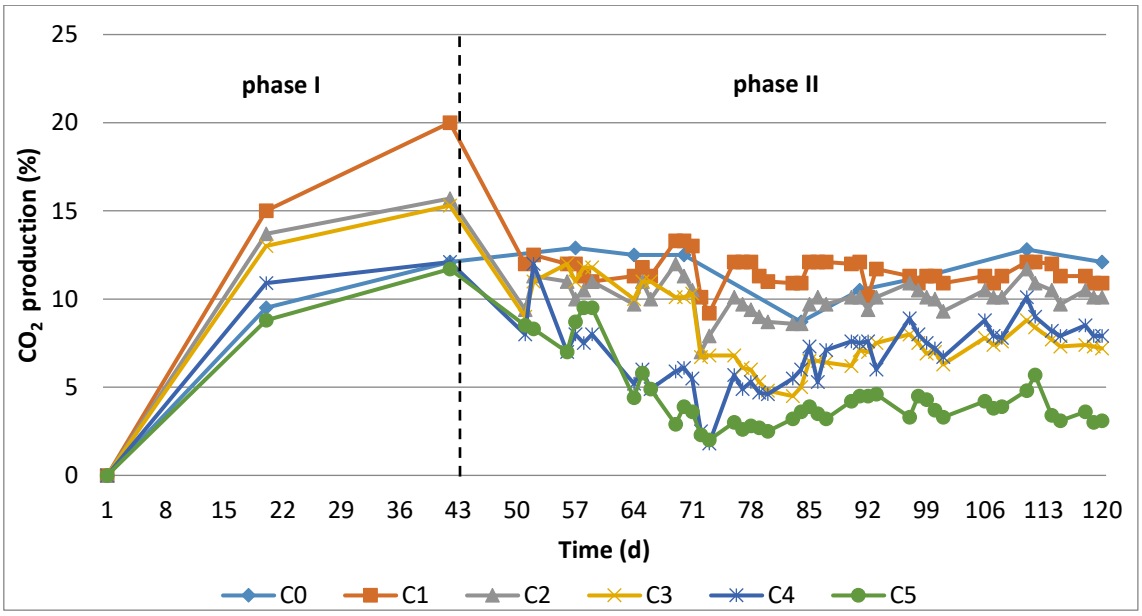


Figure 4.2 – Carbon dioxide production in off-gas during the experiment

4.2.2 Methane production rate

During the first three weeks, no active methane generation was observed, until day 20 ranging from 0.2 - 1.9% CH_4.

On the 42th day, methane production had a great increase in C1, C2 and C3, corroborating with the values of dioxide carbon, because of the high metabolic activity of microorganisms in anaerobic digestion (methanogenic phase). C1, C2 and C3 reported, respectively: 39.1%, 22.3% and 4.7% indicating an advanced methanogenesis, while C0, C4 and C5 had no methane production at all. This result indicated that more organic matter was converted to methane in the bioreactors C1, C2 and C3

When phase II started, CH_4 stopped almost completely in the bioreactors set-up under aerobic conditions, after one week. The lack of methane emissions in the off-gas was caused by the oxidation of organic matter under the presence of oxygen, reaching values, approximately, of 0% CH_4.

However, C1, the lowest aerated column (0.3 L/h) reached a range of values of 0.3 - 1.9% CH_4 until the end of the experiment, probably because of the presence of anaerobic spots in the waste mass (Borglin *et al.,* 2004**;** Xu *et al.,* 2015).

Since C0 was run under anaerobic conditions, anaerobic degradation occurred for 120 days, leading to the fragmentation of the acetate into carbon dioxide and methane, and to the combination of hydrogen and carbon dioxide to produce methane (Hrad *et al.,* 2016**;** Prantl *et al.,* 2006). On the 57th day, CH_4 concentration started to increase, reaching a concentration of 20.7% CH_4, at the end of the experiment.

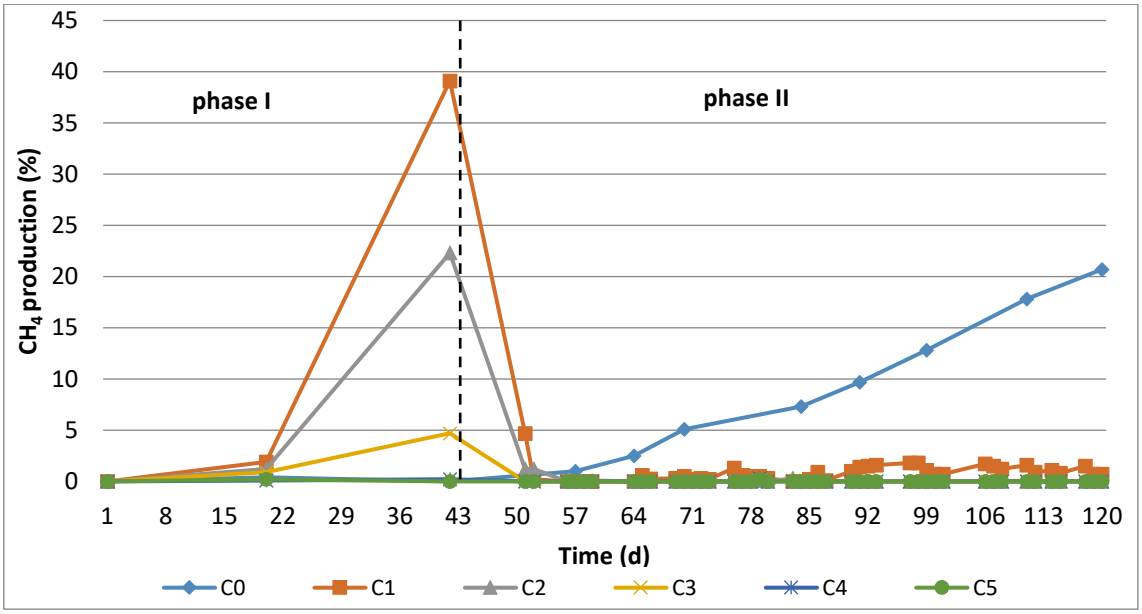


Figure 4.3 - Methane production in off-gas during the experiment

4.2.3 Oxygen concentration

The waste material in each column started with 21% of oxygen, because, before the samples were loaded in the bioreactors, all the fractions composing the waste matter were in contact with the atmospheric air.

In the starting phase of anaerobic conditions, oxygen concentrations had a significant decrease to: 0.4% in C0 and in C1, 0% in C2, 0.1% in C3, 1.3% in C4 and 0% in C5. All the reactors reached 0% of oxygen in the outlet gas, since the aerobic microorganism used all the available oxygen to cellular respiration.

During the aeration trial, significant oscillations of oxygen content was reported in the off-gas. Then, when air flow rates were set-up definitive to: 0.3 L/h in C1, 0.5 L/h in C2, 0.8 L/h in C3, 1.0 L/h in C4 and 1.2 L/h in C5, the O_2 content started to show stable concentrations correlating with the aeration rates.

Oxygen concentration in the off-gas, showed a direct relation with the respective flow rates, ranging from: 0.4%, 1.3%, 7.4%, 9.0% and 14.6%, in other words, by increasing the air flow rates, oxygen content also increases. Additionally, it was noticed an inverse relationship between O_2, CO_2 and CH_4.

When the oxygen started to increase carbon dioxide dropped and methane production stopped (Wu[a] *et al.,* 2016).

The evolution of bioreactor C3 and C4, reported an inverse tendency regarding the air flow rates, because comparing the lowest aerated column with the highest, the expected behaviour would be that C4 would had the highest content of oxygen in the off-gas, which didn't happen. Carbon dioxide production tendency also showed this trend, between C3 and C4. Berge *et al.,* 2005, suggested that this tendency can be because of the waste heterogeneities and differences in waste compaction which creates preferential flow pathways resulting in different rates of microbial degradation.

Almost two weeks before the experiment was finished, oxygen concentrations weren't detected in the off-gas of C1, suggesting that an inlet of 0.3 L/h of air wasn't enough to complete the oxidation of the organic matter.

Since C0 was defined with anaerobic conditions, the absence of oxygen was clear during all the experiment.

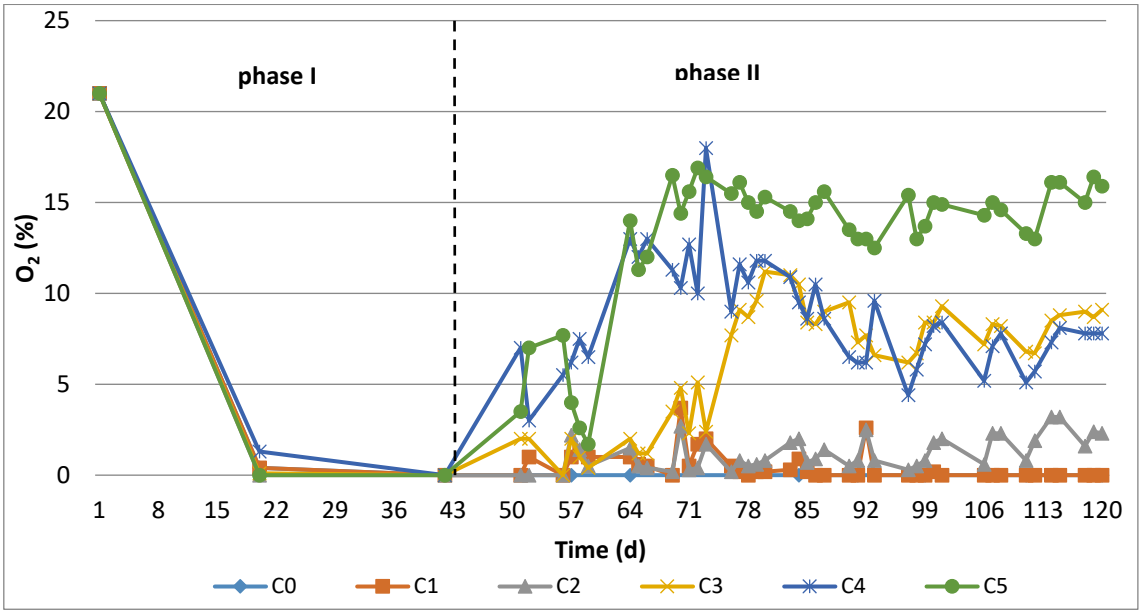


Figure 4.4 - Oxygen content in the outlet gas, during the experiment

4.2.4 Oxygen uptake in the reactors

Oxygen consumptions were determined to understand if the oxygen inlets were enough to the microbial activity requirements. The calculation consisted in the difference between the oxygen supplied for each air flow rate and the mean value of oxygen content in the outlet gas by the waste mass inside of each column. **Figure 4.5**, represents the results of this determination.

At the start of phase II, oxygen consumption had different concentrations in each aerated bioreactor, accordingly to the air flow rates chosen.

Two periods were considered to determine the oxygen uptake in the reactors:

- the aeration trial with 1 L/h of air supply for all the columns, for 20 days;
- the set-up of different air flow rates: 0.3 L/h in C1, 0.5 L/h in C2, 0.8 L/h in C3, 1.0 L/h in C4 and 1.2 L/h in C5, for the lasts 56 days.

The columns with higher quantities of air supply (higher inlets of air) reported highest oxygen contents available for the aerobic microorganisms, such as: 13.7 L O_2/kg waste in C5 > 11.3 L O_2/kg waste in C4 > 9.2 L O_2/kg waste in C3 > 6.8 L O_2/kg waste in C2 > 5.6 L O_2/kg waste in C1.

However, the consumption of oxygen had a different trend, probably because of the heterogeneity of the waste or oxygen preferential pathways. It is showed that the consumption of oxygen started to have an increase performance with the raise of the air flow, until the inlet of C3, and then the highest aerated column reported lower values of consumption: 5.5 L O_2/kg waste in C1, 6.5 L O_2/kg waste in C2, 6.8 L O_2/kg waste in C3, 6.7 L O_2/kg waste in C4 and 5.5 L O_2/kg waste in C5.

The oxygen consumption ratio of C1, C2, C3, C4 and C5 were, respectively: 97.2%, 94.8%, 73.8%, 59.9% and 40.0%. So, for the lowest air flow rate a major quantity of oxygen was consumed by the microorganisms letting less than 10% escaped by the biogas and the highest aerated bioreactor reported more than 50% escaped by gas.

Moreover, C1 reported that 0.3 L/h of air wasn't enough for aerobic degradation, because the consumption of oxygen was almost 100%, leading to an increase of methane. If oxygen isn't enough, anaerobic conditions can be created in some spots of the waste mass and, subsequently, anaerobic digestion will happen.

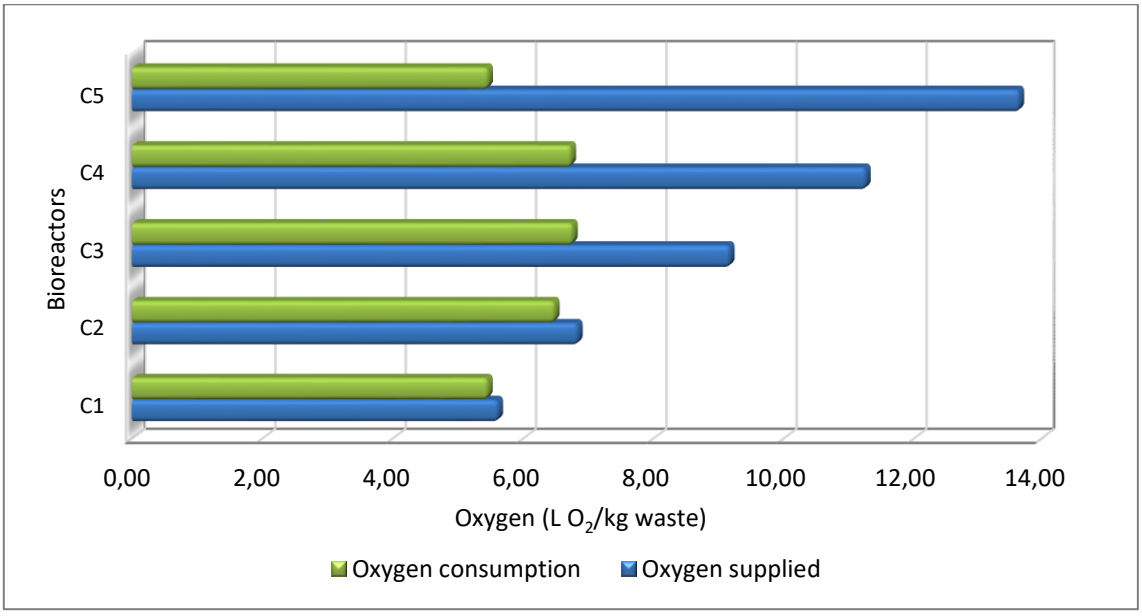


Figure 4.5 - Oxygen consumption during aerobic degradation in each reactor

4.3 Leachate quality

Sampling for leachate characterization started after five days from the beginning of phase I until, approximately, the end of phase II, on the 113th day.

The development of some relevant organic and inorganic compounds in the leachate are reported in the next sub-chapters.

4.3.1 Acidity/Alkalinity

According with Naveen *et al.,* 2016, the degradation of organic materials in the MSW is the critical reaction which can influence the leachate pH range, because it produces carbon dioxide and a small amount of ammonia, and additionally results in the formation of ammonium ions and carbonic acid. The carbonic acid dissociation produces hydrogen cations and bicarbonate anions, which have influence in the acidic or the alkaline pH range. Moreover, this parameter is also influence by the partial pressure of the carbon dioxide production that is in contact with the leachate.

Figure 4.6 gives the changes in leachate pH of the anaerobic bioreactor and the aerobic bioreactors.

In the beginning of the experiment, both bioreactors started off in alkaline conditions, ranging from similar pH values of 7 – 7.6.

For 30 years, this waste material suffered an anaerobic treatment, and accordingly with the results, it suggests that methanogenic activity was already onset. Also in the study of Erses *et al.,* 2008, the last phase of anaerobic digestion was reported with pH values between 7.0 – 7.5.

When aeration started, pH values began to increase until, approximately, 8.0 at day 64, when was the higher peak. Also, the anaerobic bioreactor had the same performance, which suggest that VFA had decrease, leading to the increase of pH. According with Warith, 2001, as the methane gas production rates increase during the methanogenic activity, carbon dioxide and VFA decreases, which the conversion of VFA causes the pH increase. Also, Berge *et al.,* 2005, suggested that with aeration, VFA production decrease because the anaerobic fermentation processes are limited.

After day 64, the aerated bioreactors reported the same significant decrease trend, because carbon dioxide was produce, and nitrification processes occurred.

At the end of the experiment, bioreactors C0 and C1 had similar pH values of, respectively, 7.6 and 7.3. The pH of the other bioreactors was less alkaline (neutral) than C0 and C1, with values of: 6.7 in C2, 6.9 in C3, 6.9 in C4 and 6.8 in C5. Supposedly, the aerated bioreactors should have pH values more alkaline than the anaerobic column. This decrease could be explained by the alkalinity consumption due to a strong nitrification processes detected in the well aerated bioreactors (Berge[a] *et al.,* 2005).

A similar behavior was reported in the research of Raga and Cossu, 2012, when the aerated bioreactors had lower pH values, comparing with the anaerobic columns for all the experiment.

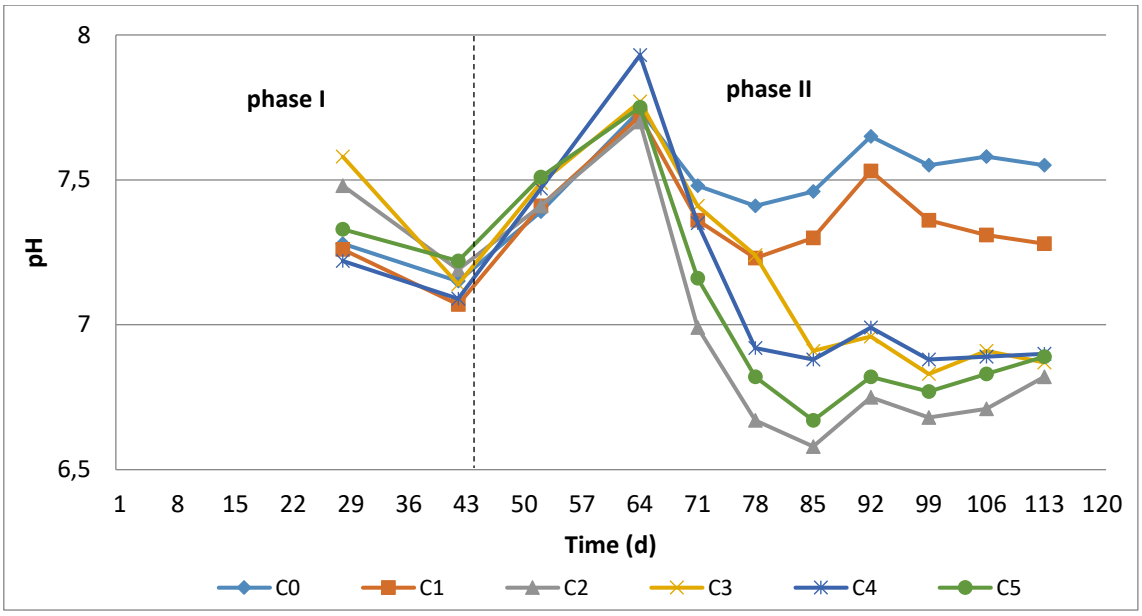


Figure 4.6 - pH evolution during phase I and phase II in the six bioreactors

Adequate alkalinity is necessary to maintain a stable pH in the landfill for optimal biological activity (Erses *et al.,* 2008). The results for this parameter are reported in **Figure 4.7**.

Initial alkalinity of the bioreactors was: 258.1 mg $CaCO_3$/L in C0, 357.6 mg $CaCO_3$/L in C1, 330.0 mg $CaCO_3$/L in C2, 314.3 mg $CaCO_3$/L in C3, 293.2 mg $CaCO_3$/L in C4 and 233.9 mg $CaCO_3$/L in C5.

After the onset of phase II, the aerated columns reported a significant drop. The decline of alkalinity had a correspondence with the range of air injected in each column, such as: the columns with the highest aeration flow rate (C4 and C5) had a faster drop in terms of calcium carbonate than C2 and C3 that reached at the lowest value after one week. Leachate alkalinity measured was: 57.1 mg $CaCO_3$/L in C2, 52.6 mg $CaCO_3$/L in C3, 27.1 mg $CaCO_3$/L in C4 and 17.3 mg $CaCO_3$/L in C5.

On the other hand, C0 and C1 had the lowest peak earlier, on the 64th day.

According with Raga and Cossu, 2012, the alkalinity is consumed when the ammonium is being removed under aerobic conditions, which also occurred in this study, during phase II. Undeniably the results showed that the bioreactor with the highest aeration rate had the highest alkalinity depletion.

The measured leachate alkalinity reported an inverse performance relating with the pH. For the beginning of phase I, the pH started with alkaline conditions since the alkalinity had higher values of calcium carbonate. When the tests were carried out under aerobic conditions, the alkalinity started to be consumed and therefore the pH dropped. Aerobic bioreactors suffered a higher decrease in alkalinity, stablishing a neutral side of pH, and for C0 and C1, the conditions of alkaline side remained, because alkalinity remained stable.

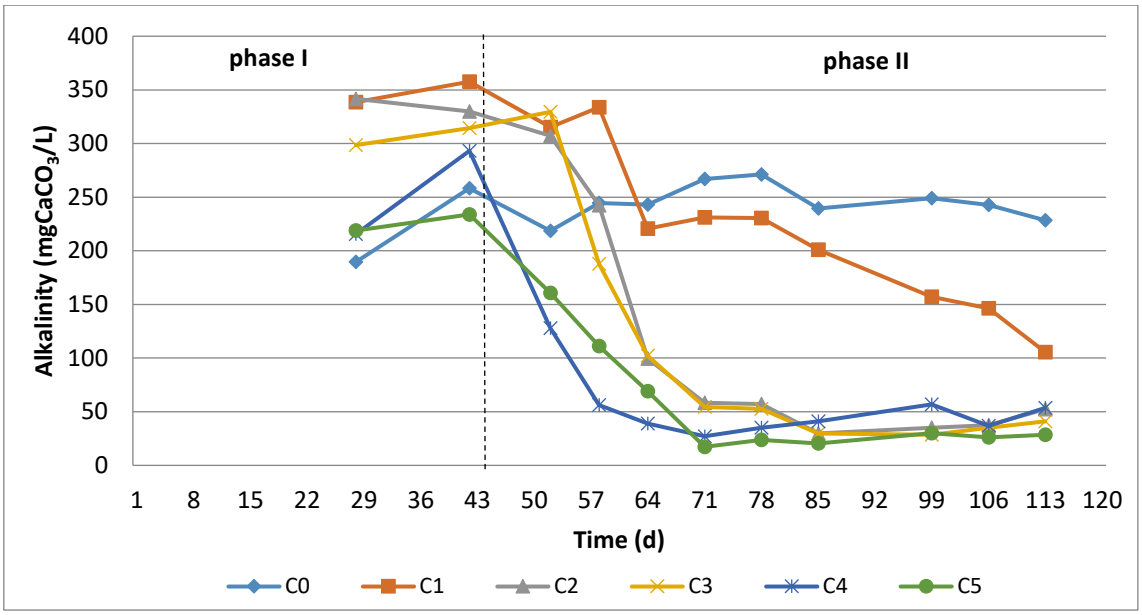


Figure 4.7 - Alkalinity evolution during phase I and II in the six columns

4.3.2 Nitrogen content

Nitrogen cycle is composed by four possible stages: ammonification, volatilization, nitrification and denitrification.

Ammonification occurs when the proteins and amino acids are degraded from the organic matter, producing ammonia-nitrogen by heterotrophic bacteria's (Bilgili *et al.,* 2006**)**. Nitrification, generally, occur under aerobic conditions when the ammonium have started to be consumed and nitrates and nitrites are produced, however when e.g., the carbon source or dissolved oxygen content is small, this process is repressed (Sun *et al.,* 2016). Denitrification can occur by two processes: autotrophic denitrification, that might lead to dominate nitrate removal if the rate of carbon-nitrogen is small, since heterotrophic denitrification requires a vast carbon source (Kristanto *et al.,* 2017).

The ammonium, TKN, nitrites and nitrates concentrations for phase I and phase II are given in, respectively, **figure 4.8**, **figure 4.9**, **figure 4.10** and **figure 4.11**.

At the start of the experiment, C0, C1, C2, C3, C4 and C5 started with a similar range of ammonium values, respectively, 734 mg N/L, 837 mg N/L, 902 mg N/L, 770 mg N/L, 884 mg N/L, 895 mg N/L.

According with Erses *et al.,* 2008, as a result of decomposition of organic matter containing nitrogen, initial ammonium concentrations increased under anaerobic conditions.

During phase II, ammonium nitrogen had a significant decay on the aerated bioreactors, for 5 weeks, with C1 as an exception, since only 45.1% of ammonium was remove. C2, C3, C4 and C5 had an efficiency of ammonium removal of, respectively, 94.8%, 98.7%, 99.1% and 98.6%.

In the end of the experiment, ammonium nitrogen concentration reached less than 4 mg N/L on C2, C3, C4 and C5. Bioreactor C1, was the only aerobic reactor where ammonium started to decrease slowly, even on the last day of the experiment had a value of 204.3 mg N/L.

The observed ammonium reduction after phase II, was already described in many *in situ* aeration studies as Erses *et al.,* 2008, Prantl *et al.,* 2006 and Raga and Cossu, 2012.

According with Tran *et al.,* 2015, under anaerobic conditions, the stabilization process is relatively slow and there is no pathway for the transformation of ammonium, which result in the slow decline of this organic compound. This trend was observed in this study, on C0, until the 78th day, where ammonium concentration started to be produced, reaching to 673.7 mg N/L.

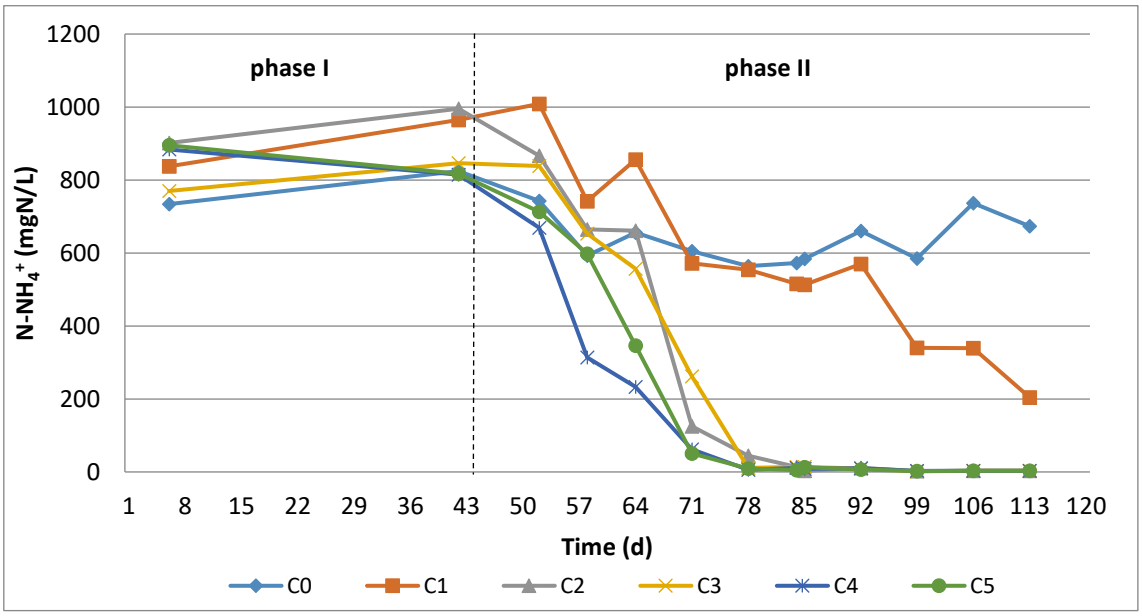


Figure 4.8 - Ammonium nitrogen evolution in phase I and II in the six reactors

According with Bilgili *et al.,* 2006, TKN have a similar evolution as the ammonium, because of the degradation of the proteins and amino acids. Comparing the **figure 4.8** with **figure 4.9** it was also shown, a parallel behaviour with these nitrogen components.

In the end of the first phase, the bioreactors started with similar values, ranging from: 832 – 1040 mg N/L.

TKN and ammonia-nitrogen concentrations in the leachate of the aerobic bioreactors indicated the same decreasing trend, until the end of the experiment. Additionally, the bioreactor run under anaerobic conditions had the same slow decrease trend.

At the end of the experiment, C0, C1, C2, C3, C4 and C5 reached, respectively, to: 602 mg N/L, 208 mg N/L, 80 mg N/L, 43 mg N/L, 42 mg N/L and 31 mg N/L.

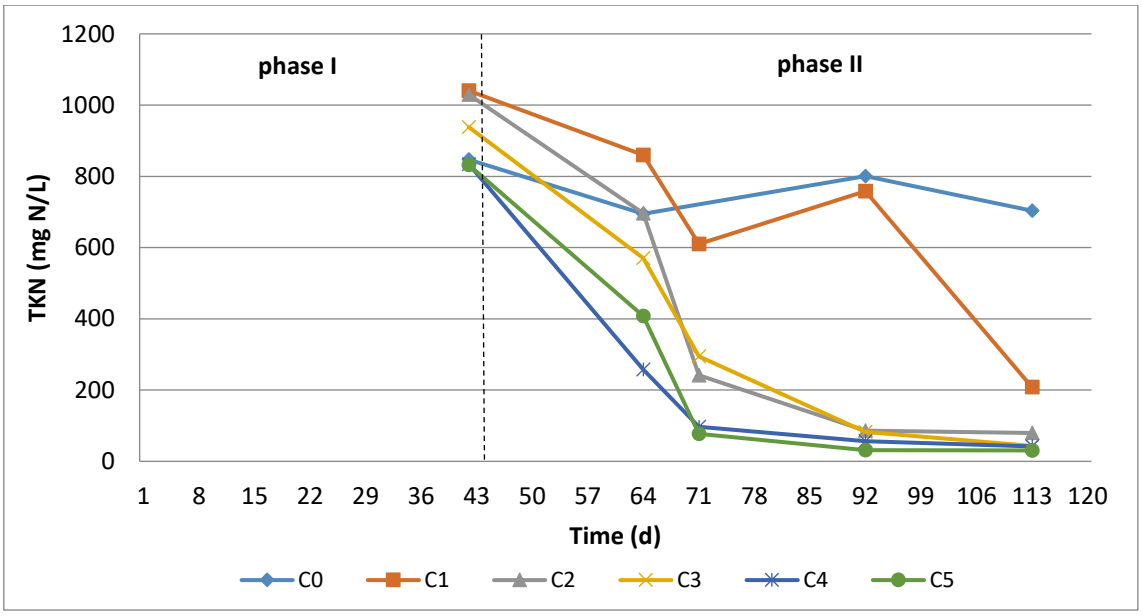


Figure 4.9 - TKN evolution in phase I and II in the six reactors

When phase II started, (**Figure 4.10 and Figure 4.11**) nitrates and nitrites started to be produced through ammonium oxidation, with C0 and C1 as an exception.

The highest aerated column had a better performance of nitrites and nitrates production with a value of, respectively, 292 mg $N\text{-}NO_2$/L and 360 mg $N\text{-}NO_3$/L, while the bioreactor with a lowest inlet of air, had a production of nitrites and nitrates under 1 mg $N\text{-}NO_2$/L.

The evolution of the columns with high air flow rate, indicates that a complete nitrification process was achieved, subsequently leading to ammonia oxidation into $N\text{-}NO_3$ (maximum concentrations), such as the study of Ko *et al.,* 2016.

During the experiment the nitrates and nitrites were produced and removed, showing that nitrification and subsequently denitrification had occurred.

Bioreactor C5 didn't complete nitrates removal during the experiment, reporting a stable value of 58 mg $N\text{-}NO_3$/L. This evolution suggests, that denitrification process wasn't enhance and, consequently, a possible increase of nitrification occurred.

The denitrification can occur when there was the absence of oxygen such as in anaerobic spots in the waste mass. This process is consisted by the transformation of nitrates into nitrogen gas (N_2), and additionally, nitrates and nitrites wouldn't be detected anymore due to the ammonium nitrogen depletion (Kristanto *et al.,* 2017).

For the anaerobic column, such as nitrates and nitrites concentrations had the lowest values, since the ammonium nitrogen wasn't oxidized.

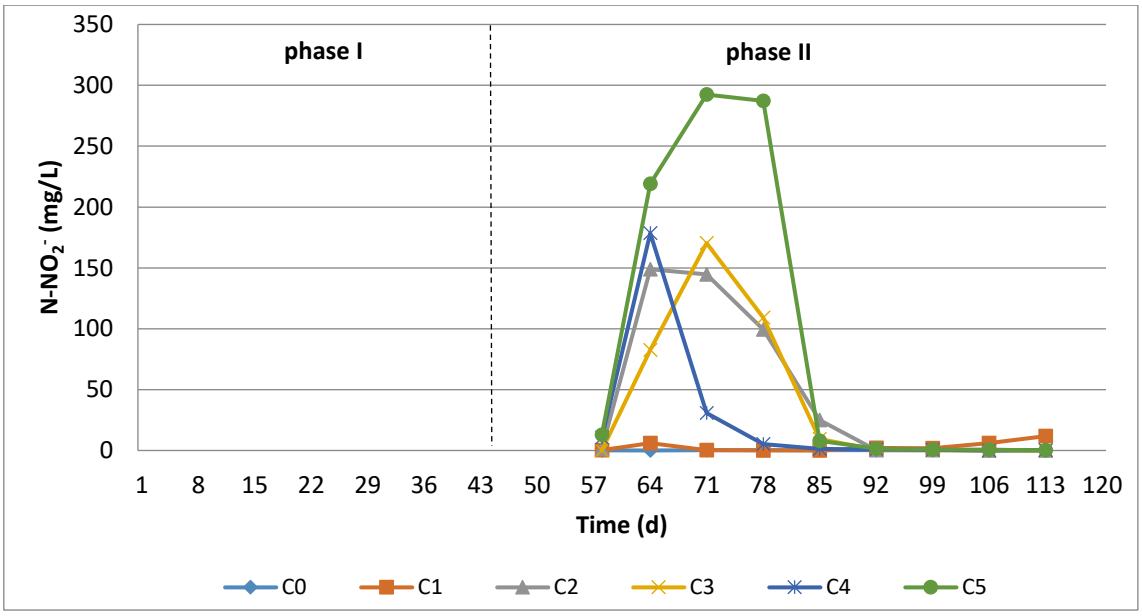


Figure 4.10 - Nitrites evolution in phase I and II in the six reactors

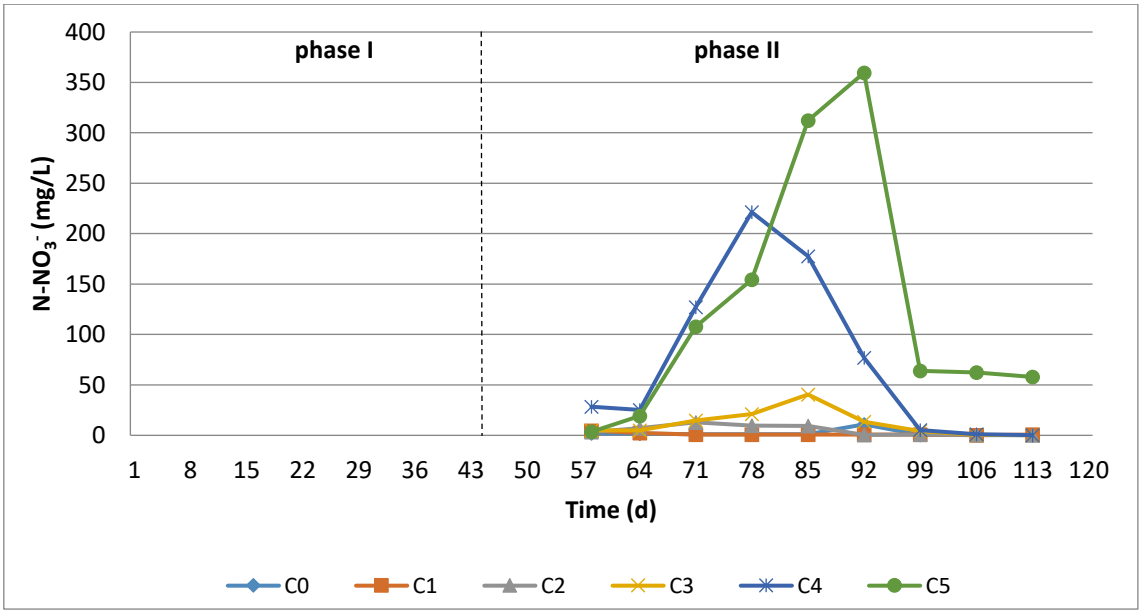


Figure 4.11 - Nitrates evolution in phase I and II in the six reactors

4.3.3 Inorganic ions

Sulphate ion was measured as a tracer of the autotrophic denitrification. The denitrification microorganisms use inorganic sulphur as a source, e.g., hydrogen sulphide, sulphur and sulphur dioxide to reduce nitrates into nitrogen gas and to produce sulphate (Berge *et al.,* 2005 and Raga and Cossu, 2012).

Figure 4.12 illustrates the sulphate concentrations for all the experiment.

In the end of phase I, C0, C1, C2, C3, C4 and C5 started with a concentration of, respectively: 943 mg SO_4^{2-}/L, 308 mg SO_4^{2-}/L, 161 mg SO_4^{2-}/L, 414 mg SO_4^{2-}/L, 1711 mg SO_4^{2-}/L and 1100 mg SO_4^{2-}/L.

Sulphate ion reported an increase trend when the bioreactors started to be provided by oxygen, reaching a peak on the 71th day with concentrations above 4500 mg SO_4^{2-}/L. This upsurge was because of the inhabitation of the anaerobic sulphate reduction bacteria, due to the aeration, which is expected to lead to less anoxic spots in the waste mass reducing the probability of sulphate reduction processes (Raga and Cossu, 2012). After 4 weeks of aeration, a significant decrease was observed before the end of the experiment.

During the study, C0 reported a slow decreasing process reaching to stable values, such as in the experiment of Raga and Cossu, 2012, which suggested that, probably, sulphur reduction had occurred in anoxic spots at the waste mass.

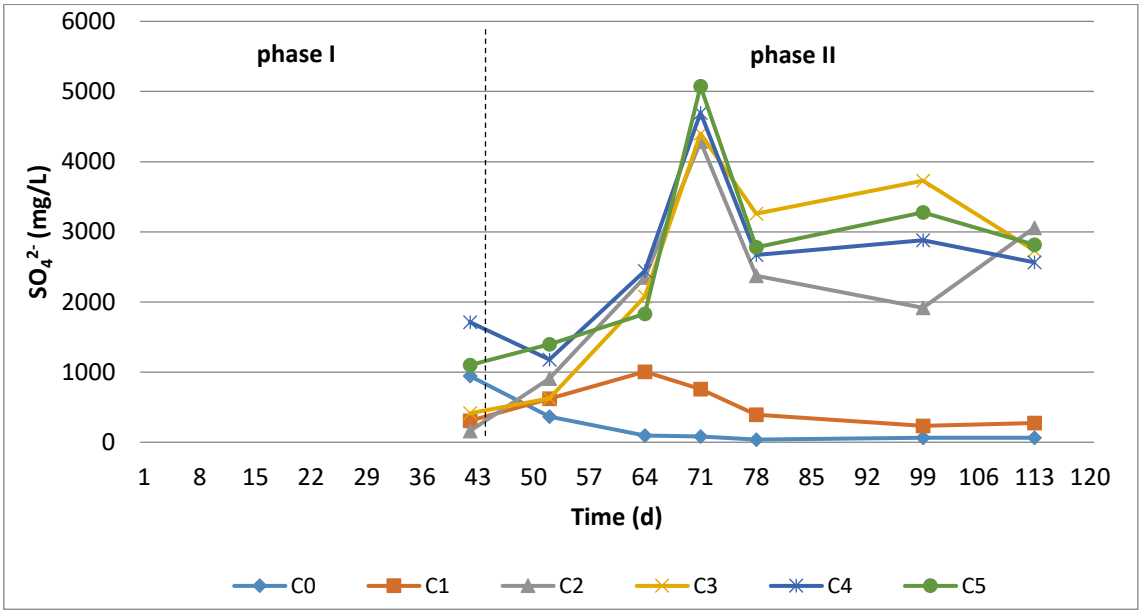


Figure 4.12 - Sulphates evolution in phase I and II in the six reactors

Chloride was measured to evaluate the variation of leachate dilution and washout effects, as like in the studies of Bilgili *et al.,* 2006, Erses *et al.,* 2008 and Nikolaou *et al.,* 2010.

Figure 4.13 shows that during the experiment, all the columns had an identical decreasing trend, even for the aerobic and the anaerobic bioreactors. Probably, this tendency was because of the same leachate recirculation rate which led to chloride removal (Erses *et al.,* 2008).

Moreover, the different aeration rates didn't affect the chloride content, as like in the study of Raga and Cossu, 2012.

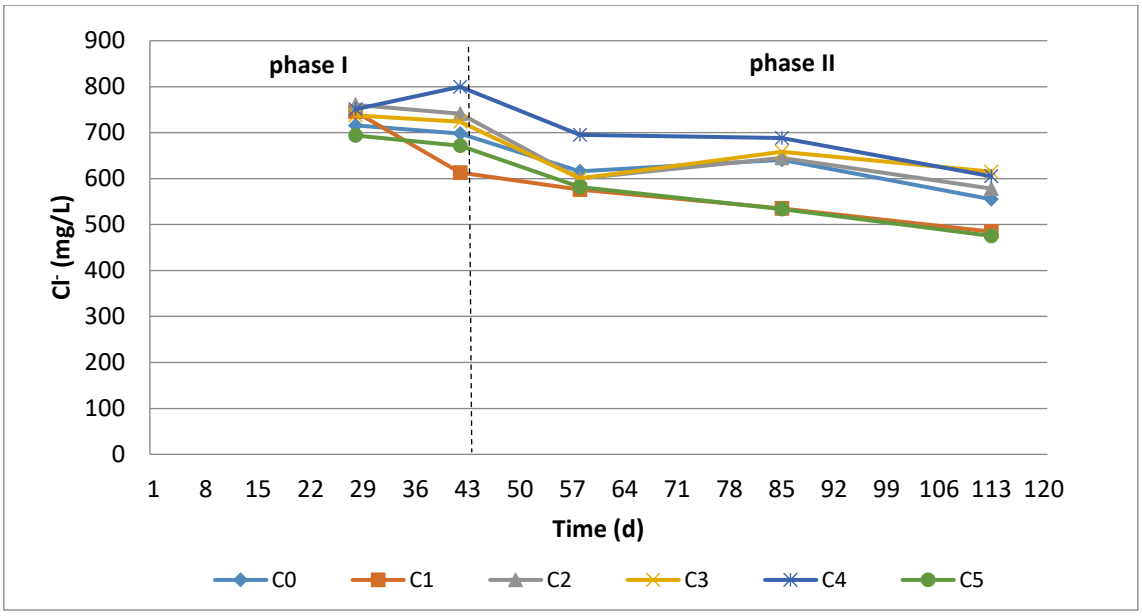


Figure 4.13 - Chloride evolution in phase I and II in the six reactors

4.3.4 Carbon content

Usually, a fresh material of MSW have high concentrations of organic content: TOC, COD and BOD_5, however, as respectively, **figure 4.14**, **figure 4.15** and **figure 4.16** report, this experiment was investigated using an old MSW sample which lead to low concentrations of the referred parameters.

4.3.4.1 TOC evolution

All the columns began with similar concentrations of TOC, while C1 reported the highest carbon content: 444 mg C/L in C0, 935 mg C/L in C1, 500 mg C/L in C2, 585 mg C/L in C3, 541 mg C/L in C4 and 521 mg C/L in C5.

During phase I, the TOC concentration in the bioreactors C0, C1, C4 and C5, declined in accordance with the progression of anaerobic degradation. This drop was also confirmed with the increase of carbon dioxide and methane (Erses *et al.,* 2008). Only C2 and C3 showed an increase tendency, before phase II to, respectively: 515 mg C/L and 456 mg C/L. Probably due to the heterogeneity of the solid waste mass, as Prantl *et al.,* 2006, reported in his study.

When phase II started, all the aerated bioreactors suffered a significant decrease of TOC concentration, except C0, since was subjected to anaerobic conditions.

After 7 days of aeration, the lowest aerated bioreactor, C1, had the best performance of TOC removal, given it started with higher concentration and reached to similar values as to the other bioreactors. So, at the 52^{th} day, C1, C2, C3, C4 and C5 share the same trend of values, which were, respectively: 402 mg C/L, 382 mg C/L, 387 mg C/L, 292 mg C/L and 270 mg C/L. After 10 weeks of aeration, these

columns continued to have a smooth decreasing trend, reaching at the end of the study with: 187 mg C/L in C1, 98 mg C/L in C2, 90 mg C/L in C3, 88 mg C/L in C4 and 82 mg C/L. Bioreactor C1, has already was reported, showed the presence of anaerobic in the waste mass, leading to higher concentrations of TOC in the end of the experiment, comparing with the other aerated bioreactors.

Regarding the bioreactor, C0, for phase II it was reported stables values of TOC, reaching 232 mg C/L at the 113th day. The anaerobic bioreactor had the highest organic content in leachate comparing with the aerated columns, because even for an old waste material that had small quantities of TOC content, aeration had accelerated the degradation of the organic matter for the aerated bioreactors.

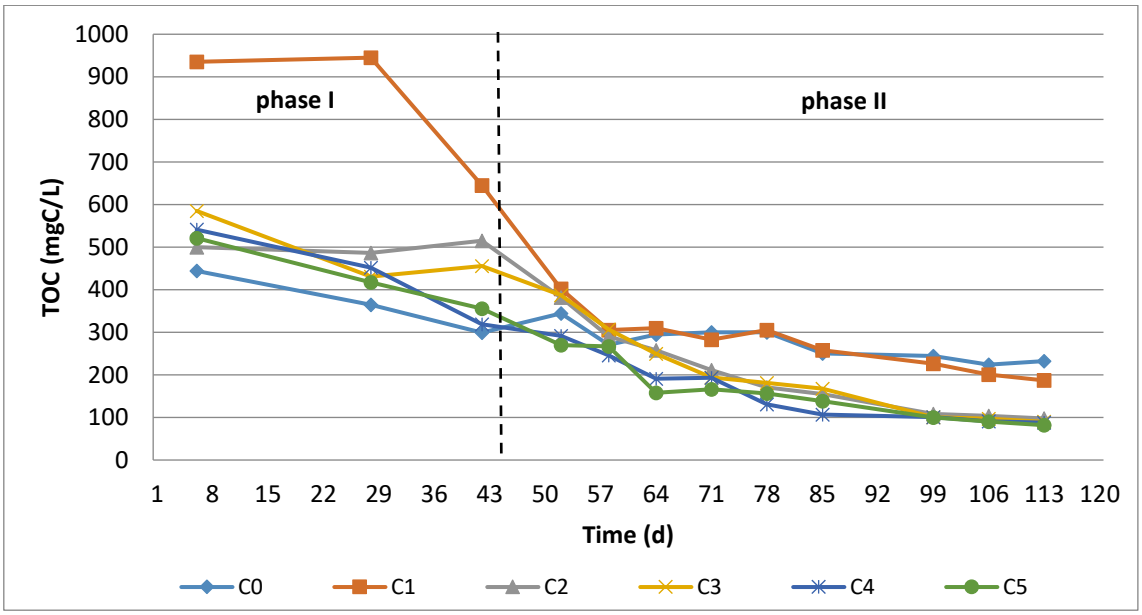


Figure 4.14 - TOC evolution during phase I and II in the six reactors

4.3.4.2 COD evolution

COD concentrations showed a similar trend to TOC content, as demonstrated in the study of Erses *et al.,* 2008.

In the beginning of phase I, C1 started with higher concentration of COD, when compared with the rest of the bioreactors, that were: 714 mg O_2/L in C0, 1662 mg O_2/L in C1, 920 mg O_2/L in C2, 816 mg O_2/L in C3, 879 mg O_2/L in C4 and 838 mg O_2/L in C5. During anaerobic conditions, COD content started to decrease, triggered by the methanogenic phase, which is confirmed by the production of gas and the pH values (Erses *et al.,* 2008**;** Slezak *et al.,* 2009).

When aeration started, COD continued to drop until the end of the experiment, exhibiting the same behavior of the TOC content, reaching values of: 392 mg O_2/L in C1, 324 mg O_2/L in C2, 302 mg O_2/L in C3, 280 mg O_2/L in C4 and 274 mg O_2/L in C5. Accordingly, with Prantl *et al.,* 2006, when COD concentration have suffered a significant decrease it is probably, due to anaerobic digestion in some

anaerobic spots inside of the solid fraction or/and to leaching processes. This situation occurred in bioreactor C1, considering it started with much higher COD content than the other bioreactors and consequently, reached to similar values as the other ones, at the end of the experiment.

The anaerobic bioreactor, showed higher COD concentration than the aerated bioreactors, due to the slow performance of anaerobic degradation.

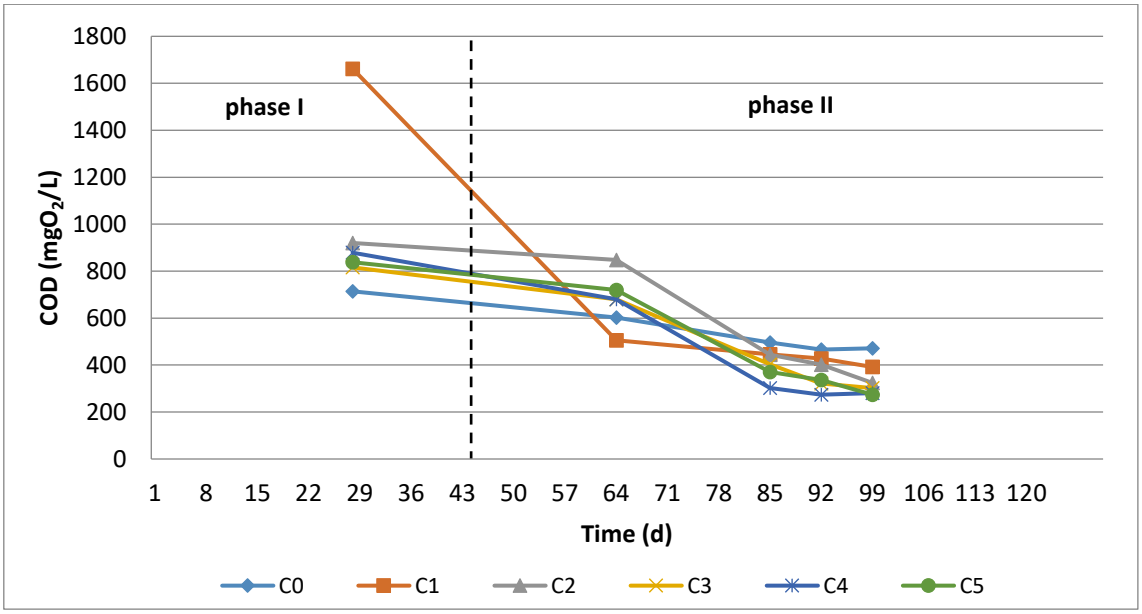


Figure 4.15 - COD evolution during phase I and II in the six reactors

4.3.4.3 BOD_5 evolution

BOD_5, followed the same trend as COD and TOC concentrations: all the aerated columns decreased its BOD_5 content, during the experiment, but the anaerobic operated column first had suffered a slightly increase and then started to decrease on the 64th day.

C0, C2, C3, C4 and C5 started with similar concentrations of BOD_5, such as, respectively: 48 mg O_2/L, 133 mg O_2/L, 99 mg O_2/L, 90 mg O_2/L and 79 mg O_2/L, while C1, as expected, began with the highest concentration: 373 mg O_2/L.

In the anaerobic phase, occurred a fast reduction of the BOD_5 which was caused by intensive gas production (Slezak *et al.,* 2009). Given the age of the waste mass sample excavated from an old landfill, these low values of BOD_5 were expected, since a pre-treatment with aeration was made.

After phase II started, BOD_5 content in aerated bioreactors started to drop to concentrations below or equal to 3 mg O_2/L, only C1 remained with higher content, more specifically, with 12 mg O_2/L. The anaerobic bioreactor had an equal concentration to the lowest aerated bioreactor, C1.

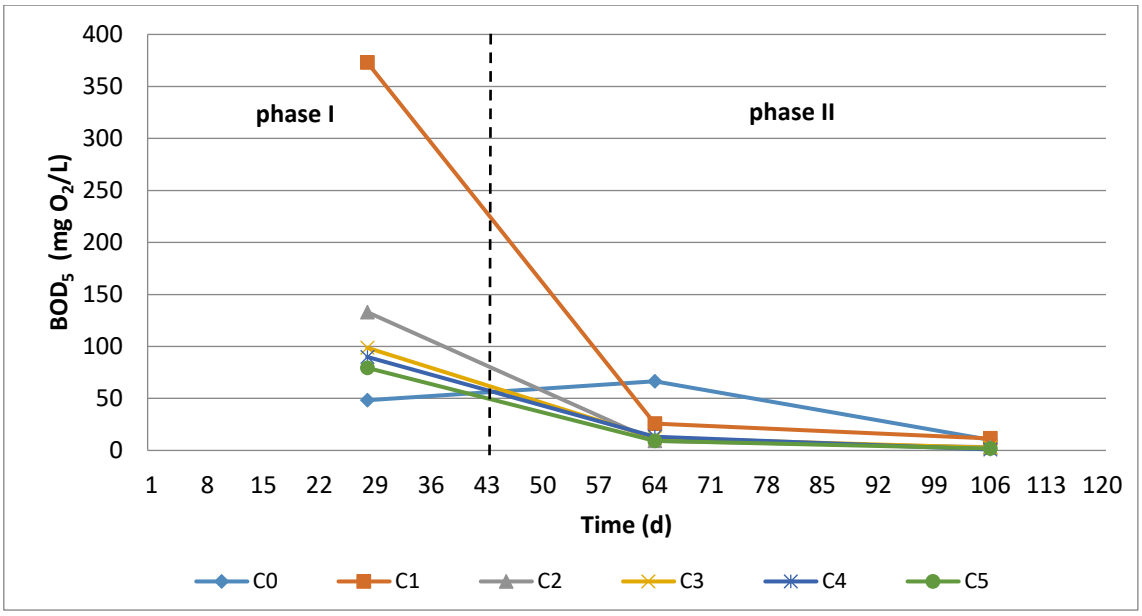


Figure 4.16 - BOD_5 evolution during phase I and II in the six reactors

4.3.4.4 BOD_5/COD index

BOD_5/COD ratio was determined in many studies such as Aziz *et al.,* 2010, Erses *et al.,* 2008 and Morello *et al.,* 2017, to assess the amount of biodegradable compounds still present in leachate, and thus to understand the degree of landfill stabilization.

Table 4.5 – BOD_5/COD index during phase I and II

Time (day)	Bioreactors					
	C0	C1	C2	C3	C4	C5
28	**0.07**	**0.22**	**0.15**	**0.12**	**0.10**	**0.10**
64	**0.11**	**0.05**	**0.01**	**0.02**	**0.02**	**0.01**

Table 4.5 reports BOD_5/COD index values. The 28th day, represent the BOD_5/COD index for phase I, when the leachate where subjected to anaerobic conditions. The 64th day, consist the value of the index when the bioreactors where run under aerobic conditions, more specifically, were set-up with different aeration rates: 0.3 L/h, 0.5 L/h, 0.8 L/h, 1 L/h and 1.2 L/h.

On the 28th day, the organic index started with values below 0.2, suggesting that leachate began with low biodegradable organic carbon, and possibly, relatively high in hard-to-biodegrade organic

compounds such as humic substances. So, the leachate was approximately on a stable level, given the treatment suffered and the age of the landfill.

In phase II, there was a drop in all the aerated bioreactors, reaching ratios below or equal to 0.05, because with air injection, the degradation of the remain organic content turned the leachate more stabilized than already was. Also, TOC content showed a higher reduction in organic compounds of leachate, with air supply.

On the other hand, relatively high organic index was obtained from the anaerobic bioreactor (C0), comparing to the bioreactors injected by air, possibly due to the leachate recirculation, which led to the accumulation of the organic content inside of the waste mass of the bioreactor.

The values estimated by **Azis *et al.,* 2010** and Erses *et al.,* 2008, were, respectively, BOD_5/COD ratio below to 0.10 and between 0.02 – 0.13, for old landfills. Comparing the results with the ones from these studies is clear that leachate has a high level of stabilization due to low concentrations of organic compounds.

4.4 Efficiency of carbon removal

The depletion of carbon content was determined by the influence of oxygen supplied in each aerated bioreactor in order to conclude which air flow rate and oxygen concentration in the outlet gas is more efficient, in terms of total organic carbon removal and, as well which amount of oxygen in the outlet gas is more viable in efficacy-economic benefits trends for a full-scale landfill.

Additionally, carbon mass balance was determined to understand the pathways that carbon presented.

4.4.1 Carbon mass balance

In order to understand the major pathways where carbon escaped to, carbon balance was computed (**Table 4.6**).

Additionally, with **figure 4.17** and **table 4.7** it was possible to assess and understand the performance of both aerobic and anaerobic bioreactors in the carbon removal via leachate and via gas, specifically in the carbon conversion to carbon dioxide and methane.

In the discussion of this determination, it was taken into account the inhomogeneity of the waste in each bioreactor, due the different quantity of the solid fraction and its composition which was slightly different for each set-up of the bioreactors

Table 4.6 - Carbon mass balance

Parameters (g C/kg TS)	Bioreactors					
	C0	C1	C2	C3	C4	C5
TOC_{is} (measured)	**14.97**	**14.40**	**13.71**	**14.46**	**14.45**	**15.62**
TOC_{fs} (measured)	**10.85**	**9.31**	**8.98**	**8.84**	**8.65**	**9.14**
TOC_{lr}	**0.044**	**0.040**	**0.019**	**0.017**	**0.018**	**0.017**
TOC_{ls} (measured)	**0.037**	**0.048**	**0.030**	**0.029**	**0.026**	**0.027**
C $gas_{(ae)}$	**0.46**	**0.99**	**1.06**	**1.20**	**1.29**	**0.99**
C $gas_{(anae)}$	**0.008**	**0.186**	**0.091**	**0.027**	**0.011**	**0.006**
C $gas_{t\ (ae+anae)}$	**0.47**	**1.17**	**1.16**	**1.23**	**1.30**	**1.00**
TOC_t	**11.41**	**10.57**	**10.18**	**10.12**	**9.99**	**10.18**
$Error_{TOC}$	**3.57**	**3.83**	**3.53**	**4.35**	**4.46**	**5.43**

TOC_{is} **initial TOC measurement in the solid fraction**
TOC_{fs} **final TOC measurement in the solid fraction**
TOC_{lr} **TOC in the leachate inside of the bioreactor**
TOC_{ls} **TOC of the leachate extracted (sample)**
C $gas_{(ae)}$ **C-discharge in aerobic conditions**
C $gas_{(anae)}$ **C-discharge in anaerobic conditions**
C $gas_{t\ (ae+anae)}$ **total C-discharge via gas**
TOC_t **total TOC via gas, leachate and solid**
$Error_{TOC}$ **TOC losses**

The anaerobic and aerobic bioreactors showed a clear difference of the degradable carbon quantity. More specifically, column C0 reported the highest value of carbon that didn't suffered degradation: 72.5% of carbon remained in the solid fraction at the end of the experiment, due to the slow activity of the anaerobic microorganisms.

It was noticed that with the increase of the oxygen inlet in the aerobic bioreactors, the carbon remained in the solid started to decrease: 64.6% in C1, 65.5% in C2, 61.1% in C3, 59.8% in C4 and 58.5% in C5. Only the bioreactor C2 didn't respect this trend.

Literature values for similar experiments, had determined that most of the carbon was removed by gas: Prantl *et al.,* 2006, reported that a range of 12 – 19 g C/kg TS were discharged via gas, for a duration of 342 - 513 days, in a waste with an age between 8 and 17 years; and Raga and Cossu, 2012, had indicated a value around 12.7 g C/kg TS for a waste material with 15 years old. Also in this study was determined that the majority of the carbon removed was discharge via gas than extracted via leachate. However, the values of Prantl *et al.,* 2006 and Raga and Cossu, 2012, were higher than the quantity obtained in this experiment, because the waste material in subject were much younger than the waste excavated from Legnago.

In the two phases of the experiment, the carbon was mainly removed from the system as carbon dioxide, as **Table 4.7** reports it:

Table 4.7 - Carbon conversion into CO_2 and CH_4 during anaerobic and aerobic conditions

Period	Phase I		Phase II	
Bioreactors	C into CO_2 (%)	C into CH_4 (%)	C into CO_2 (%)	C into CH_4 (%)
C0	**99.0**	**1.0**	**46.5**	**53.5**
C1	**34.4**	**65.6**	**93.7**	**6.3**
C2	**43.4**	**56.6**	**98.9**	**1.1**
C3	**77.6**	**22.4**	**99.9**	**0.1**
C4	**98.5**	**1.5**	**99.9**	**0.1**
C5	**99.6**	**0.4**	**99.9**	**0.1**

In phase I, most of the carbon discharged via gas was converted to CO_2 than CH_4. Usually, under anaerobic conditions the reverse is expected: methane production should be higher than the carbon dioxide, because methanogenic phase was already run-off in the waste material. However, it should be considered that: phase I only lasted 44 days, which probably is a short time for anaerobic degradation, and also methane was detected in the last days of this phase or wasn't detected at all, in most of the bioreactors. Bioreactor C0, C4 and C5 had the highest conversion of carbon into carbon dioxide, with a ratio of, respectively: 99.0%, 98.5% and 99.6%. The rest of the bioreactors had a conversion less than 90%.

When the columns started to be aerated, the ones with higher air flow rates resulted into 99.9% of carbon that was transformed into CO_2.

Methane had a great development during phase I, on C1 and C2, with values of, respectively, 65.6% and 56.6%.

During phase II, the reactor that remained with anaerobic conditions, had the highest percentage of carbon transformation into CH_4. However, considering the evolution of the aerated bioreactors, C1 was the only that had more than 6% of methane production, as was observed in the outlet gas. This situation can be explained due to the anaerobic spots, which led to the methane formation.

Considering the data of the carbon conversion into CO_2 and CH_4 and **figure 4.17**, it was clear that the anaerobic bioreactor had the lowest quantity of carbon discharged via gas, because anaerobic reactions can take more time to convert the carbon into carbon dioxide and methane, comparing to the aerobic activity of the microorganisms to degrade the organic matter, more specifically the carbon.

Regarding the aerobic bioreactors, it should be noted that with the increase of the air flow rate carbon removed via gas should increase, which didn't occur in the experiment.

Bioreactor C1 reported a slight higher quantity of carbon discharged via gas than bioreactor C2, which probably was because during phase II, column C1 reported methane formation due to the anaerobic spots, leading to a raise of the amount of carbon degraded and removed via gas.

The highest aerated bioreactor with an oxygen inlet of 13.7 L O_2/kg of waste, reported the lowest carbon content removed via gas, because during phase I methane production was, approximately, 0% comparing to the other bioreactors. Also during phase II, the evolution of bioreactor C5 indicated a lower degradation process of the carbon content leading to a lower carbon dioxide production in the biogas, because only 5.5 L of oxygen was consumed per kilogram of waste, which comparing with the rest of the bioreactors was a small amount of oxygen uptake relating to the air supplied.

Only a minor amount was discharge via leachate (sum of TOC_{lr} and TOC_{ls}): 0.080 g C/kg TS in C0, 0.089 g C/kg TS in C1, 0.049 g C/kg TS in C2, 0.046 g C/kg TS in C3, 0.044 g C/kg TS in C4 and 0.044 g C/kg TS in C5. The contribution given by the leachate is very low due to the low amount of the liquid weekly pulled out.

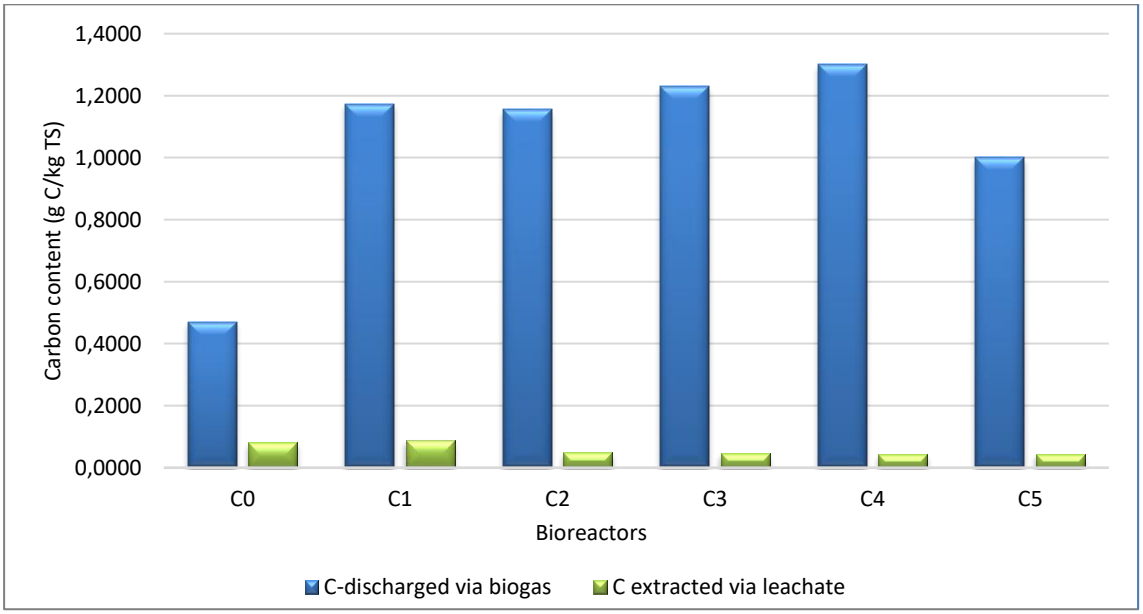


Figure 4.17 - Carbon removal pathways via gas and via leachate

It should be considered that a significant amount of carbon suffered a deviation between solid, gaseous and leachate losses, ranging from 24 – 35%. These errors could be derived by some measurement errors on the analysis and by the method used for the final solid fraction collection in the six bioreactors, more specifically, it should had been taken from the superficial, the middle and the bottom part of the bioreactor and then should have been mixed, which in the reality was only taken from the superficial part of the bioreactor.

4.4.2 Carbon removal vs oxygen inlet

Air injection has been considered an effective operation of bioreactor landfills which contributes towards an accelerated, controlled and sustainable conversion of conventional anaerobic landfills into a biological stabilized state and for carbon trade mechanisms (Berge[b] *et al.,* 2009 and Ritzkowski and Stegmann, 2012). However, in terms of costs and efficiency of carbon removal this methodology becomes an interesting tool to understand the right amount of air injected.

4.4.2.1 Via leachate

Aeration efficiency in carbon removal was determined with the difference between the initial TOC concentration and the final TOC concentration by the oxygen supplied for each air flow rate, considering the aeration trial and the set-up of each aeration rate.

This parameter was calculated for two periods, for phase II:

- Period L - during the day 44 until the day 113, to observed which aeration flow rate is better to a long-term efficiency;
- Period F – starting at the beginning of aeration, on the 44th day, until the 71th day when occurred the faster decrease of carbon in all the aerated bioreactors, via leachate.

Phase L

Table 4.8 reports the aeration efficiency values for each oxygen inlet for period L, in which:

- C1 had the best performance by achieving an aeration efficiency of carbon removal, with a result of 81.5 mg C removed/L O_2 supplied.kg of waste, and since the air inlet was the lowest, economic benefits can be achieved in order to reach optimal conditions for aerobic degradation in a landfill, with a mean value of 0.4% of O_2 content in the outlet gas;
- C5 had the worst development with a value of 20.0 mg C removed/L O_2 supplied.kg of waste during this period, suggesting that with an inlet of 13.7 L O_2/kg of waste, the microorganisms would not need so much oxygen to degrade the organic matter leading to a consumption of only 5.5 L O_2/kg. So, a higher amount of O_2 injected had escaped to the outlet gas with a mean value of 14.6 O_2%;
- C2 was the bioreactor with the second higher efficiency respecting the oxygen inlet, being its value of 61.0 mg C removed/L O_2 supplied.kg of waste. However, more oxygen escaped via gas with a mean value of 1.3% O_2. Without considering the aeration rate, this column had the best performance in removing organic carbon, with an efficiency of 81.1% TOC;
- C3 and C4 had similar oxygen consumption ranging from 6.7 – 6.8 L O_2/kg of waste, removing amounts of approximately, 74% in C3 and 66% in C4 of TOC in the leachate, but in order of

aeration efficiency, C4 showed a lower improvement with a value of 20.5 mg C removed/L O_2 supplied.kg of waste and C3 had 40.0 mg C removed/L O_2 supplied.kg of waste. A high quantity of injected air led to a higher amount of oxygen in the outlet gas with 7.4 O_2% in C3 and 9.0 O_2% in C4.

Table 4.8 – Carbon removal aeration efficiency via leachate for phase L

Parameters (units)	Bioreactors				
	C1	C2	C3	C4	C5
Air flow rate (L/h)	**0.3**	**0.5**	**0.8**	**1.0**	**1.2**
O_2 inlet (L O_2/kg)	**5.6**	**6.8**	**9.2**	**11.3**	**13.7**
O_2 outlet (L O_2/kg)	**0.2**	**0.4**	**2.4**	**4.5**	**8.2**
O_2 outlet (%)	**0.4**	**1.3**	**7.4**	**9.0**	**14.6**
O_2 uptake (L O_2/kg)	**5.5**	**6.5**	**6.8**	**6.7**	**5.5**
TOC removal efficiency (%)	**71.0**	**81.1**	**80.3**	**72.4**	**77.0**
Aeration efficiency (mg C removed/L O_2 supplied.kg)	**81.5**	**61.0**	**40.0**	**20.5**	**20.0**

Phase F

In t**able 4.9** the aeration efficiency in terms of carbon removed was determined during period F:

- Even in a shorter period, the best performance of aeration efficiency was obtained by C1, being its value of 107.4 mg C removed/L O_2 supplied.kg of waste. This result show that, with a small amount of air supply it is possible to remove high quantity of TOC via leachate which, at field-scale, means less operational costs;

- In this case, C4 had the worst development of carbon removal according with 11.3 O_2 supplied, since it had 31.4 mg C removed/L O_2 supplied.kg of waste. While the highest aerated column, C5, with an inlet of 4.5 L O_2/kg of waste, removed more organic carbon with a difference of 11.2 mg C removed/L O_2 supplied.kg of waste;

- C2 and C3 were respectively, the 2th and the 3th bioreactor with a higher aeration efficiency, comparing to C4 and C5 (higher aerated columns), however without considering the inlet of oxygen, C2 was the best bioreactor with a value of 59% TOC removed than C1 that had 56.2% TOC removed.

Table 4.9 - Carbon removal aeration efficiency via leachate for phase F

Parameters (unit)	Bioreactors				
	C1	C2	C3	C4	C5
Air flow rate (L/h)	**0.3**	**0.5**	**0.8**	**1.0**	**1.2**
O_2 inlet (L O_2/kg)	**3.4**	**3.4**	**3.6**	**4.0**	**4.5**
O_2 outlet (L O_2/kg)	**0.1**	**0.1**	**0.3**	**1.6**	**1.7**
O_2 outlet (%)	**0.4**	**1.3**	**7.4**	**9.0**	**14.6**
O_2 uptake (L O_2/kg)	**3.2**	**3.2**	**3.3**	**2.4**	**2.7**
TOC removal efficiency (%)	**56.2**	**59.0**	**57.4**	**39.4**	**53.1**
Aeration efficiency (mg C removed/L O_2 supplied.kg)	**107.4**	**90.8**	**72.2**	**31.4**	**42.6**

4.4.2.2 Via gas

Aeration efficiency in terms of carbon converted into CO_2 and CH_4 was evaluated on a long-term period (period L) during the 44 - 120th day, as **Table 4.10** reports. The calculation consisted in the sum of carbon conversion into CO_2 and CH_4 for this period divided by the oxygen inlet of each aeration rate.

Table 4.10 – Carbon removal aeration efficiency via gas for phase L

Parameters (unit)	Bioreactors				
	C1	C2	C3	C4	C5
Air flow rate (L/h)	**0.3**	**0.5**	**0.8**	**1.0**	**1.2**
O_2 inlet (L O_2/kg)	**5.6**	**6.8**	**9.2**	**11.3**	**13.7**
O_2 outlet (L O_2/kg)	**0.2**	**0.4**	**2.4**	**4.5**	**8.2**
O_2 outlet (%)	**0.4**	**1.3**	**7.4**	**9.0**	**14.6**
O_2 uptake (L O_2/kg)	**5.5**	**6.5**	**6.8**	**6.7**	**5.5**
C conversion in CO_2 and CH_4 (g C)	**25.5**	**29.5**	**33.5**	**34.1**	**24.6**
Aeration efficiency (mg C converted/L O_2 supplied.kg)	**4541.9**	**4311.4**	**3656.3**	**3026.7**	**1804.7**

Comparing with carbon removal in leachate (Period L) similar results were observed.

C1 had the best performance of carbon being removed via gas respecting to the oxygen supply with a result of 4541.9 mg C converted/L O_2 supplied.kg of waste.

In terms of conversion, with the raise of the oxygen supplied for the bioreactors the aeration efficiency turned out to be lower. However, bioreactor C2, C3 and C4 had higher amounts of carbon that was used to produced carbon dioxide and methane in the outlet gas, with values of, respectively: 29.5 g C, 33.5 g C and 34.1 g C, but in terms of aeration efficiency bioreactor C2 reported a higher value than the bioreactor C4.

Bioreactor C5, had also the worst development in carbon removal by biogas in respect of the oxygen inlet, since it had a result of 1804.7 mg C converted/L O_2.kg of waste.

With higher amounts of air supply, less efficient is the carbon removal considering the O_2 in the gas, leading to more amounts of oxygen escaped via gas, subsequently less the oxygen is used to the degradation processes in the waste.

5 Conclusions and future prespectives

Lab scale tests in bioreactors landfill were carried out on an old waste, that is being re-dispose in a new landfill with anaerobic conditions, in order to evaluate the effects produced by different aeration flow rates and different oxygen concentrations in the outlet gas, monitoring leachate and biogas throughout the duration of the experiment, with specific regard to carbon turnover.

Based on the simulations conducted in this study, it has been proved that considering oxygen concentration in the outlet gas is an appropriate tool to reach optimal conditions of designing and operating a landfill at field-scale, and subsequently to achieve financial benefits such as minimizing the costs of air supply and leachate ex-situ treatment.

Aeration affected significantly waste, leachate and biogas quality in the bioreactors. Aerated columns had better performances in terms of carbon removal than the anaerobic column in which had a slow degradation of organic matter, over the time course of the experiment. Therefore, beneficial effects of in situ aeration can be expected for Legnago landfill, such as a considerably improvement of leachate quality, resulting in a significant decrease of COD, BOD_5, BOD_5/COD index and ammonium nitrogen.

The results obtained reported that high aeration flow rates with higher amounts of oxygen content in the outlet gas doesn't ensure the best performance in carbon removal, because even with more oxygen availability it turned out that the consumption of oxygen was lower or equal than the lowest aerated columns, probably due to preferential air pathways in the columns and/or the heterogeneity of waste in each reactor, which led to different microbial activity and velocity.

The best performance of carbon removal efficiency via leachate and via gas with respect of oxygen inlet in each column was obtained by the C1, the bioreactor with an inlet of 5.6 L O_2/kg of waste and an oxygen outlet with a mean value of 0.4%, during the experiment. This reactor had a carbon removal of 81.5 mg C/L O_2 supplied.kg of waste in leachate and 4541.9 mg C/L O_2 supplied.kg of waste via biogas.

Regarding the carbon mass balance, majority of carbon was discharge via gas than via leachate, considering all the pilots. The bioreactor with the second highest aeration rate, C4, had the best performance in the conversion of carbon removed into carbon dioxide and methane, with a result of 1.30 g C removed/kg TS, during all the experiment. In general, a greater amount of carbon was converted into carbon dioxide in the outlet gas than methane, reaching values above 90% of conversion in the aerated columns.

For further investigations, a field-scale verification should be done in order of the results collected in this experiment, to evaluate the absolutely benefits in a landfill with an oxygen concentration in the outlet gas of 0.4%. Also in lab-scale tests, using only the fine fraction, to assess a better reactivity of the waste and to ensure the homogeneity of the material, would be a good approach in parallel of monitoring the oxygen content during the experiments into the waste mass, in order to understand the evolution and effects of preferential flow of oxygen and of carbon.

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