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Effects of different aeration rate and oxygen concentrations on nitrogen removal of old waste in lab-scale simulated bioreactors landfill

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Para quem sempre apoia, colabora e motiva a concretização dos objetivos de vida dos seus filhos, a minha MÃE.

To the one who always supports, collaborates and motivates the achievement of the life goals of her children, my MOTHER.

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Resumo

A aplicação de arejamento *in situ* em aterros biorreatores é um método potencial para reduzir as emissões presentes e potenciais, provenientes dos resíduos, através da aceleração da redução de concentração de azoto amoniacal e matéria orgânica biodegradável no aterro sanitário.

Neste estudo, foram realizados testes à escala laboratorial de forma a investigar alternativas que apresentem melhores desempenhos na estabilização de resíduos e emissões de poluentes, com especial foco nos compostos de azoto, em relação às condições de re-deposição atuais dos resíduos sólidos urbanos provenientes do antigo aterro sanitário de Legnago. Em acréscimo, foi também estudada a viabilidade do uso da concentração de oxigénio no gás de saída como parâmetro de dimensionamento e operação da tecnologia de arejamento *in situ.*

Diferentes fluxos de ar foram estabelecidos e ajustados ao longo do tempo com o objetivo de criar diferentes concentrações de oxigénio no gás de saída em cinco aterros aeróbios simulados. Um biorreator de controlo foi operado em condições anaeróbias de forma a simular as condições atuais de re-deposição dos resíduos.

O biorreator anaeróbio apresentou os níveis de emissão de poluentes nos lixiviados mais elevados, com maiores concentrações de CQO, COT e azoto amoniacal. Melhores alternativas, em termos de remoção de azoto, foram obtidas com a simulação de aterros sanitários aeróbios.

Os resultados demonstraram que a concentração de oxigénio no gás de saída é um parâmetro de dimensionamento e operação mais apropriado do que o próprio fluxo de ar de forma a ajustar a intensidade de arejamento necessária para alcançar o melhor desempenho possível de aterros aeróbios. O melhor desempenho de eficiência de arejamento, em termos de remoção de azoto amoniacal no lixiviado em relação à quantidade de oxigénio fornecida, foi alcançado pelo reator alimentado com o segundo menor fluxo de ar e com um valor médio de 1.3% de oxigénio no gás de saída.

Termos chave: Arejamento *in situ*, Oxigénio no gás de saída, Remoção de Azoto, Lixiviado, Resíduos Sólidos Urbanos.

Abstract

The application of in situ aeration in bioreactor landfill is a potential method to reduce the actual emissions and the emission potential from the waste material. This is achieved by accelerating the reduction of ammonia nitrogen concentration and biodegradable organic mass matter in the landfill body.

In this study, lab-scale tests were carried out to investigate alternatives that can achieve better performances of waste stabilization and pollutants emissions, with particular focus on nitrogen compounds, regarding the current re-disposal conditions of municipal solid waste from the old Landfill of Legnago. In addition, the viability of using the oxygen concentration in the outlet gas as a dimensioning and operational parameter of in situ aeration technology was also studied.

Different air flow rates were established and adjusted over time, with the aim of creating different oxygen concentrations in the outlet gas on five simulated landfill bioreactors. One control bioreactor was operated under anaerobic conditions in order to simulate the current conditions of the waste disposal.

The anaerobic bioreactor landfill showed the highest level of leachate emissions, with the highest concentrations of COD, TOC and ammonium nitrogen. Better alternatives, in terms of nitrogen removal, were obtained by simulated aerobic bioreactors landfill.

The results showed that oxygen concentration in the outlet gas is a more proper dimensioning and operational parameter than aeration flow rate itself in order to adjust the intensity of aeration required to reach the best performance of aerobic bioreactor landfills. The best performance of aeration efficiency, in terms of ammonium nitrogen removal in the leachate regarding the amount of oxygen supplied, was obtained by the bioreactor provided with the second lowest air flow rate and with an average value of 1.3% of oxygen in the outlet gas.

Key words: In situ aeration, Oxygen in the outlet gas, Nitrogen removal, Leachate, Municipal Solid Waste.

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Glossary

MSW	Municipal Solid Waste
TOC	Total Organic Carbon
COD	Chemical Oxygen Demand
BOD	Biochemical Oxygen Demand
RI_4	Respiration Index for four days
TKN	Total Kjeldahl Nitrogen
TS	Total Solids
VS	Volatile Solids
DM	Dry Matter
$N\text{-}NH_4^+$	Ammonium nitrogen
$N\text{-}NO_3^-$	Nitrate nitrogen
$N\text{-}NO_2^-$	Nitrite nitrogen
NH_3	Ammonia
N_2	Nitrogen gas
N_2O	Nitrous Oxide
SO_4^{2-}	Sulphate
Cl^-	Chloride
O_2	Oxygen
CO_2	Carbon dioxide
CH_4	Methane

1 Introduction

For its most economical and simple means, landfill is the dominant method for the waste disposal and management on a global scale (Lou *et al.*, 2015; Sun *et al.*, 2017). In Europe, there are an estimated 150 000-500 000 active and closed landfills (Mönkäre *et al.*, 2017). However, due to continuous landfill gas and leachate long-term emissions from the deposited refuse, municipal solid waste (MSW) landfill are source of air, soil, and water pollution and it still poses a risk to human and the environment that lasts decades to centuries after landfill closure (Brandstätter *et al.*, 2015a; Sun *et al.*, 2017).

Nitrogen emissions from MSW landfills take place predominantly via leachate, where they pose a long-term major concern in conventional landfills in the form of ammonium (Nikolaou *et al*., 2010; Brandstätter *et al.*, 2015b). Under anaerobic conditions in traditional landfills, this pollutant has been indicated by the scientific community as the key parameter that will determine when landfill post closure monitoring may end (Raga and Cossu, 2013).

For this purpose, the question arises of how to exert a positive influence on the emissions behavior of MSW deposits in such a way that a controlled and accelerated pollutant reduction will be achieved.

In this respect, the application of in situ aeration in bioreactor landfill is a potential method to reduce both the actual emissions and the emission potential of the waste material by means of accelerating the reduction of the concentration of ammonia nitrogen and biodegradable organic mass matter in the landfill body. This application can be considered for the innovative management during the aftercare phase of traditional landfills, as a remediation tool for old landfill or as a pretreatment before landfill mining (Prantl *et al*., 2006; Ritzkowski *et al.*, 2006; Raga and Cossu, 2013).

A proper control of oxygen distribution, waste temperature and moisture content is required in order to increase the effectiveness of landfill in situ aeration (Raga and Cossu, 2013). Therefore, according to the results of lab scale and full scale tests, a proper management of air flow and water inlet in the landfill body should be considered. Although several lab and field scale studies focused on the nitrogen removal, considering the above mentioned parameters are available (Prantl *et al*., 2006; Ritzkowski *et al.*, 2006; Erses *et al*., 2008; Ko *et al.*, 2016; among others), there is no general consensus in the literature on the optimum aeration rate for aerobic landfills. This research has the peculiar characteristic of studying different oxygen concentrations in the outlet gas as an operational and design stabilization parameter on old waste in order to better standardize the management.

1.1 Objectives and scope of the research

In 2001 the University of Padua made some investigations about the quality of waste, leachate and biogas in the old MSW landfill of Legnago (Province of Verona, Italy). The landfill was made on the old Tartaro river bed and its first part was built without artificial impermeable bottom liner and leachate collection. Thus, considering the geological situation of the area and the characteristics of the landfill barrier system, the risk of groundwater pollution is very high.

According to the studies performed, Municipality of Legnago decided to remediate the old landfill by means of the in situ aeration technology, followed by waste excavation and re-disposal in the new operating anaerobic sector of the landfill, allowing the best removal of leachate accumulated at the bottom, reducing further contamination risk.

The objective of this study is to assess if there are better performances alternatives to the current re-disposal method in anaerobic sectors in terms of waste stabilization and pollutants emissions, with particular focus on nitrogen removal. Additionally, studying the feasibility of using oxygen concentration in the outlet gas as a dimensioning and operational parameter of in situ aeration technology was also investigated. Therefore, different aeration flow rates were established and adjusted over time with the aim of creating different oxygen concentrations in the outlet gas on five lab-scale simulated landfill bioreactors. One control bioreactor was operated under anaerobic conditions in order to compare and simulate the current conditions of the waste in the new sector of the landfill of Legnago.

The results are expected to be useful particular in the decision making process regarding the fate of the waste that is currently being excavated and re-disposed at Legnago, and in a broader perspective it should provide helpful information about the effectiveness and management of aeration technology method, with particular focus on its application on old waste from landfill mining.

1.2 Dissertation organization

This document is divided in eight chapters:

Chapter 1: Introduction: The first chapter describes the landfill and waste management general problems and its relevance. This section also establishes the scope, objectives and expected contribution of this dissertation.

Chapter 2: Municipal Solid Waste Landfill: In this chapter, the main priorities, environmental risks and general requirements of operating a landfill are described as well as the general evolution trend of landfill leachate and gas composition observed over the time course of municipal solid waste degradation process in conventional landfill.

Chapter 3: Bioreactor Landfill: This chapter describes the main features, technologies and processes available to operate a landfill as a bioreactor landfill. A comparison between different types of bioreactors landfill is established, where a description of each one advantages and disadvantages is performed.

Chapter 4: Nitrogen transformation and removal processes in bioreactor landfills: In this chapter, a review of the nitrogen transformation and removal pathways that can possibly occur in a bioreactor landfill according to different conditions is performed.

Chapter 5: Aerobic Bioreactor Landfill - research updates: This section describes related experiments done and its main results and conclusions as well as relevant studies in order to improve and understand the effects of different aeration rate and off-gas oxygen concentration in waste decomposition and leachate production and treatment.

Chapter 6: Materials and Methods: In this chapter, the analytical methods and equipment used during the experiment are described as well as experimental operations performed throughout the whole period of the research.

Chapter 7: Results and Discussion: This section shows the results obtained from the analytical methods performed over the time course of the experiment. Values of solid, leachate and off-gas determinations are described and several parameters are discussed and compared in order to achieve the objectives of this study.

Chapter 8: Conclusions and further developments: In this chapter, main conclusions of the research are described based on results and evolution trends discussed on chapter 7. The evaluation of the research objectives is performed and future studies are suggested.

2 Municipal Solid Waste Landfill

Today, a major environmental, economical and social problem worldwide exists in Municipal Solid Waste (MSW) management, mainly because the waste volume is growing faster than the world's population (Renou *et al*., 2002). According to EPA (2009), landfill is defined as "a waste disposal site used for the controlled deposit of solid waste onto or into land". Although waste management is following new trends as recycling and compost processes, the sanitary method of landfilling for the ultimate disposal of solid waste material continues to be widely accepted and used due to its economic advantages (Sun *et al*., 2017).

A fundamental concern often associated with conventional MSW landfills is that they remain biologically active for many decades (Brandstätter *et al.*, 2015a). Once a landfill has reached its design capacity, a final cover must be installed. The site owner is then required to monitor and maintain a closed landfill for what is referred to as the postclosure monitoring period. Postclosure monitoring includes leachate collection and treatment, groundwater monitoring, inspection of the final cover and maintenance as required, and monitoring to ensure that methane is not migrating off-site. The monitoring will be discontinued after landfill stabilization (Barlaz *et al*., 2002). According to Walsh and O'Leary (2002), "complete stabilization is when the waste material no longer breaks down into byproducts that are released into the environment".

2.1 Leachate pollutants composition

The risk of groundwater pollution is probably the most severe environmental impact from landfills because historically most landfills were built without engineered liners and leachate collection systems. More recently, regulations in many countries have required the installation of liners and leachate collection systems as well as a plan for leachate treatment (Kjeldsen *et al*., 2002).

Leachates are defined as the aqueous effluent produced as a consequence of rainwater percolation through wastes, biochemical processes in waste's cells and the inherent water content of wastes themselves (Renou *et al*., 2008). Stricter environmental requirements are continuously imposed regarding ground and surface waters; the treatment of landfill leachate becomes a major environmental concern. According to Christensen *et al.* (1994), landfill leachate contains pollutants that can be categorized into four groups:

1. Dissolved organic matter, quantified as Chemical Oxygen Demand (COD) or Total Organic Carbon (TOC), volatile fatty acids and more refractory compounds such as fulvic-like and humic-like compounds;
2. Inorganic macro components: calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}), potassium (K^{+}), ammonium (NH_4^{+}), iron (Fe^{2+}), manganese (Mn^{2+}), chloride (Cl^{-}), sulphate (SO_4^{2-}), and hydrogen carbonate (HCO_3^{-});

3. Heavy metals: cadmium (Cd^{2+}), chromium (Cr^{3+}), copper (Cu^{2+}), lead (Pb^{2+}), nickel (Ni^{2+}), and zinc (Zn^{2+});
4. Xenobiotics organic compunds (XOCs), falling from household and industrial chemicals; the concentration of each of them is less than 1 mg/L; they are represented by different aromatic hydrocarbons, phenols, Cl-aliphatic hydrocarbons, pesticides, medicines.

The removal of organic material based on COD, biochemical oxygen demand (BOD) and ammonium from leachate is the usual prerequisite before discharging the leachates into natural waters (Renou *et al*., 2008). The concentrations of these components may typically be up to a factor 1000 to 5000 higher than concentrations found in groundwater (Kjeldsen *et al*., 2002). However, the quality of landfill leachate is affected by many factors: age, precipitation, seasonal weather variation, waste type and composition (depending on the standard of living of the surrounding population). In particular, the composition of landfill leachates varies greatly depending on the age of the landfill (Baig *et al*., 1999). In this respect, young acidogenic landfill leachate is commonly characterized by high BOD (4000–13000 mg/L) and COD (30000–60000 mg/L) concentrations, and moderately high strength of ammonium nitrogen (500–2000 mg/L) (Yao, 2017).

High nitrogen concentrations in leachate lead to eutrophication and decrease of DO (dissolved oxygen) level in receiving watercourse (Parker, 1975). Inevitably, cost effective and environmentally sustainable treatment solutions should be considered as a priority for nitrogen removal from leachate for the protection of sensitive water bodies from eutrophication.

2.2 Degradation process

Biodegradation of MSW in a landfill occurs in chronological phase until it changes to the simplest fraction of leachate characteristics and landfill gases. Throughout this period an increasing understanding of the complex series of chemical and biological reactions that initiates with the burial of refuse in a landfill has been developed (Kjeldsen *et al*., 2002). According to Farquhar and Rovers (1973), biodegradations of MSW which produce liquid and gases occur in a landfill through five or more sub-phases. Figure 2.1 shows the gas and leachate composition as refuses decomposes in anaerobic degradation processes. The rate and characteristics of leachate produced and biogas generated from a landfill vary from one phase to another, and reflect the microbial mediated processes taking place inside the landfill. The phases experienced by degrading wastes are described below (Farquhar and Rovers, 1973; Kjeldsen *et al.,* 2002; Tamru, 2015):

Phase I: Aerobic phase: This phase is associated with initial placement of solid waste and accumulation of moisture within landfills; oxygen present in the void spaces of the freshly buried refuse is rapidly consumed, resulting in the production of CO_2 and maybe an increase in waste temperature; the initial adjustment phase takes place only for a short period after MSW landfilled because oxygen is not replenished once the waste is covered; during the aerobic phase, the waste is not typically at field capacity and an acclimation period is observed until sufficient moisture develops and supports an active microbial community.

Phase II: Transition phase: In the transition phase, the field capacity is sometimes exceeded, and a transformation from an aerobic to anaerobic environment occurs, as evidenced by the depletion of oxygen trapped in the refuse; by the end of this phase, measurable concentrations of chemical oxygen demand (COD) and volatile fatty acids (VFA) can be detected in the leachate.

Phase III: Anaerobic acid phase: The continuous hydrolysis (solubilization) of solid waste, followed by the microbial conversion of biodegradable organic content results in the production of intermediate VFA at high concentrations throughout this phase; a decrease in pH values is often observed and viable biomass growth associated with the acid formers (acidogenic bacteria), and rapid consumption of substrate and nutrients are the predominant features of this phase.

Phase IV: Methane fermentation phase: During phase IV, intermediate acids are consumed by methanogenic bacteria and converted into CH_4 and CO_2; the pH value is elevated, being controlled by the bicarbonate buffering system, and consequently supports the growth of methanogenic bacteria; heavy metals are removed by complexation and precipitation.

Phase V: Maturation phase: During the final state of landfill stabilization, nutrients and available substrate become limiting, and the biological activity shifts to relative dormancy; gas production drops dramatically and leachate strength stays steady at much lower concentrations; reappearance of oxygen and oxidized species may be observed slowly; however, the slow degradation of resistant organic fractions may continue with the production of humiclike substances.

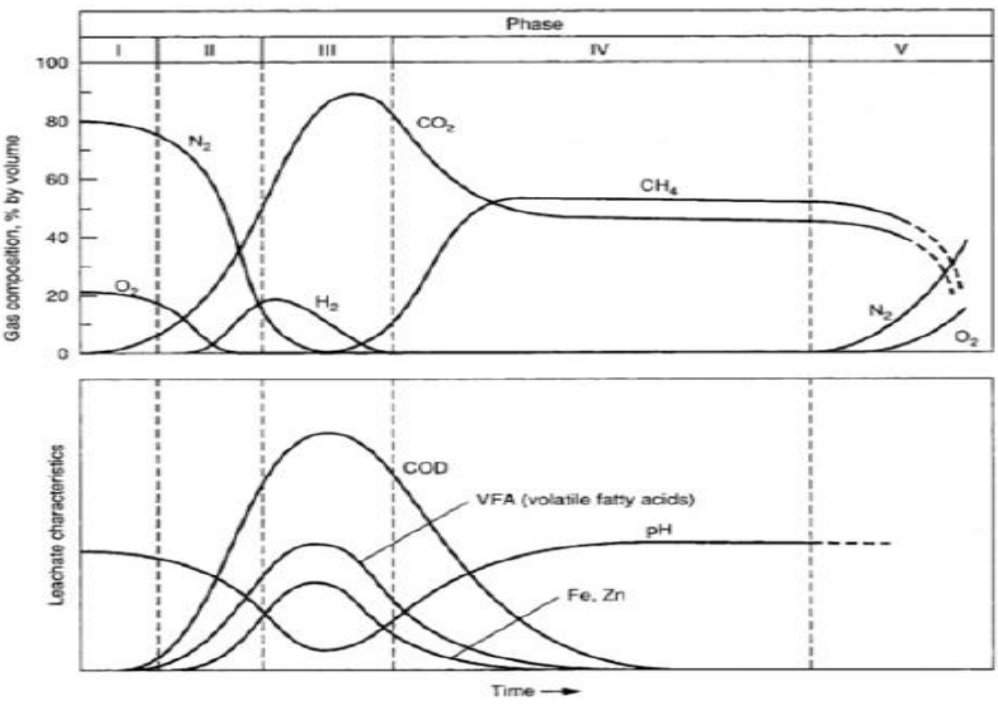

Figure 2.1 - General trends in landfill gas and leachate development (Tamru, 2015).

3 Bioreactor landfill

An essential goal in waste management worldwide is to create sustainable landfill with respect of the potential of terminating expensive perpetual landfill aftercare. Thus, recently, the focus of solid waste management has change from landfill thought as storage and containment systems to a landfill as a complex biological system capable of managing solid waste in a more proactive manner (Berge *et al*., 2005; Ritzkowski and Stegmann, 2012).

A bioreactor landfill is defined as a sanitary engineered landfill, which enhanced microbiological activity is promoted with the purpose to decompose and stabilize the incoming organic fraction of the municipal solid waste within a period of 5 to 10 years of implementation (Thampan and Chandel, 2015).

Leachate recirculation is considered to be an essential part of this technology due to the optimum moisture content maintenance necessary in the landfill body in order to improve leachate quality, enhancement of gas production rate and reduction of the time required for waste stabilization. At times, insufficient leachate is available and it is necessary to supplement with other liquids such as groundwater, storm water, wastewater, or surface water (Erses et al., 2008; Thampan and Chandel, 2015). Bioreactor systems' efficiency can also be increased with other factors such as pH adjustment, nutrient addition, waste pre-disposal and post-disposal conditioning and temperature control (Thampan and Chandel, 2015).

Because there is no degradation pathway for ammonia nitrogen in anaerobic environments, this pollutant tends to accumulate in both conventional landfill and bioreactor landfill systems. Due to moisture addition and/or leachate recirculation, ammonification rate is increased resulting in accumulation of higher levels of ammonia nitrogen in bioreactor landfills, even after the organic fraction of the waste is degraded. Thus, although the organic strength (i.e., chemical oxygen demand [COD] and biochemical oxygen demand [BOD]) of the leachate is significantly reduced in bioreactor landfills, ammonia nitrogen remains an issue (Barlaz *et al.*, 2002; Berge *et al*., 2005).

In general, the same degradation processes take place in bioreactor landfills as in conventional landfills, just at a faster rate and to a greater extent because of the optimization of in situ conditions (Berge *et al*., 2005). There are different operating schemes and technologies available to manage a bioreactor. Berge *et al.* (2005) refers that four types of bioreactor landfills have been explored: anaerobic, aerobic, facultative, and hybrid systems.

3.1 Anaerobic Bioreactor Landfills

According to Berge *et al*. (2005), anaerobic bioreactor landfills are those in which moisture addition is practiced and sources of liquid addition may include groundwater, storm water, infiltrating rainfall, or leachate.

A sketch of an anaerobic bioreactor landfill is illustrated in Figure 3.1. Leachate produced by the MSW is collected, stored and reinjected back into the landfill, redistributing nutrients and bacteria through the MSW mass and consequently promoting in situ anaerobic biological degradation. Additionally, moisture content adjustment results in enhanced methane production, which has been repeatedly demonstrated in several laboratory and field-scale studies. The total volume of gas produced also increases, as organics in the leachate are recycled and then biodegraded within the landfill. The majority of gas production may be confined to a few years, earlier in the life of the landfill, than traditionally occurs in conventional landfills. As the parameters are fitted for wet landfills, the time for 99% of the methane to be produced may decrease by almost 14-fold. Thus, anaerobic bioreactor allows more efficient landfill gas (LFG) capture and therefore the collection and use of CH_4 for energy may be more economical (Reinhart and Townsend, 1997; Berge *et al.*, 2005; Erses *et al.*, 2008).

Figure 3.1 - Design and operation features in anaerobic bioreactor landfill (Waste Management, 2004).

Although anaerobic bioreactor landfills are more effective at degrading the solid waste than conventional landfill, when compared to other types of bioreactor landfills, anaerobic system tend to have lower temperatures, slower degradation rates and may increase the potential risks to human health and the environment (Merz and Stone, 1970; Erses *et al.*, 2008).

The accumulation of ammonia nitrogen is a disadvantage of operating the landfill as an anaerobic bioreactor. The ammonia nitrogen present in the leachate requires ex situ treatment because this pollutant is continually returned to the landfill, where there is no degradation pathway for it in anaerobic environments (Raga and Cossu, 2013).

In anaerobic bioreactor the air is not added, therefore when compared to other bioreactor landfill types, the advantage of the anaerobic system is related to the operational costs which are less than what would be incurred aerobically (Berge *et al.*, 2005; Thampan and Chandel, 2015).

3.2 Aerobic Bioreactor Landfills

A new perspective on landfilling solid waste is the aerobic landfill technology as shown in Figure 3.2. In an aerobic bioreactor leachate is also recirculated into the landfill in a controlled manner. Air is injected into the waste mass, using vertical or horizontal wells, to promote aerobic activity and accelerate waste stabilization (EPA, 2017).

Adding air to landfills has been evaluated over the last few years to enhance degradation processes in landfills, as aerobic processes tend to degrade organic compounds typically found in municipal solid waste in shorter time periods than anaerobic degradation processes (Berge *et al*., 2005; Erses *et al.*, 2008).

The addition of air stops methane production, which is desirable in areas where the collection of this is not feasible. However, volatile acid and methane production may still occur in anaerobic pockets within the landfill. Methane is a potent greenhouse gas; thus, if it cannot be efficiently controlled and collected in anaerobic landfills, its production can be a local environmental concern (Berge *et al.*, 2005).

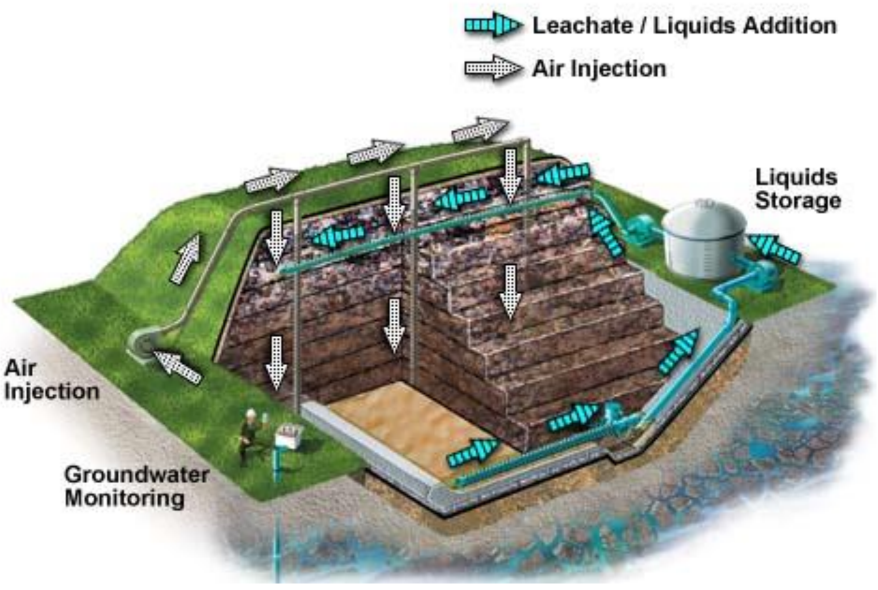

Figure 3.2 - Design and operation features in aerobic landfill bioreactor (Waste Management, 2004).

Under aerobic conditions, the ambient redox potential reverts from strongly negative to positive, which will affect metal speciation and movement and degradation of organic compounds. For example, aerobic conditions will limit fermentation reactions, which produce large amounts of acids and significantly reduce the pH, affecting solubility and sorption properties of organic and metal contaminants. Therefore, aerobic conditions reduce ex-situ leachate treatment required (Rittmann and McCarty, 2001).

Aerobic processes benefit many of the nitrogen transformation/removal process, including nitrification and ammonia air stripping or volatilization. Air stripping and volatilization may be favored in aerobic bioreactor landfills because of higher pH levels and temperatures that are inherent in an aerobic environment. The additional gas flow associated with air injection may also induce greater masses of ammonia nitrogen removal (Berge *et al.,* 2005).

The aerobic process generates a considerable amount of heat, leading to elevated in situ temperatures as high as 66ºC (Merz and Stone, 1970). The elevated temperatures increase evaporation, which results in a significant loss of leachate. As a consequence, there is less leachate to manage. Additionally, the combination of the high temperatures and presence of air may create a fire potential. However, by minimizing methane production and ensuring proper moisture contents, fire potential is decreased (Berge *et al.,* 2005).

Other advantage related with aerobic bioreactors is the reduction of odors often associated with anaerobic systems, such as from hydrogen sulfide and volatile acids. Aerobic processes do have some odor associated with them; however, it is an earthy smell (Berge *et al.,* 2005; Erses *et al.*, 2008).

From a technical point of view there are various aeration technologies and operation concepts, which have been reviewed by Ritzkowski and Stegmann (2012). According to this review, concepts range from high and low pressure aeration to semi aerobic applications, involving either continuous or intermittent air supply. Low pressure aeration can be further divided into active aeration with off-gas extraction, passive aeration (air venting) and energy self-sufficient long-term aeration.

Although landfill aeration is not a widely applied concept so far, according to Ritzkowski and Stegmann (2012), it has already been successfully applied to several landfills in Europe, North America and Asia.

3.3 Anaerobic-Aerobic (Hybrid) Bioreactor Landfills

Among the different types of landfill bioreactors, hybrid bioreactor landfill technology as illustrated in Figure 3.3 is of great promise. Hybrid bioreactor landfill is designed to accelerate waste degradation by combining attributes of the aerobic and anaerobic bioreactors. In this system the uppermost lift or layer of waste is aerated, while the lift immediately below it receives liquids. Landfill gas is extracted from each lift below the lift receiving liquids. Horizontal wells that are installed in each lift during landfill construction are used convey the air, liquids, and landfill gas (Waste Management, 2004; Berge *et al*., 2005; Xu *et al*., 2014).

The objective of the sequential aerobic-anaerobic treatment is to cause the rapid biodegradation of food and other easily degradable waste in the aerobic stage in order to reduce the production of organic acids in the anaerobic stage resulting in the earlier onset of methanogenesis. There are some components in both the waste and the leachate that are recalcitrant in anaerobic conditions but degradable in aerobic environments, such as lignin and aromatic compounds. Utilizing one of these hybrid techniques may allow for the leachate and/or waste to be treated more completely. Also, operating a bioreactor landfill as a hybrid system may serve to combine several nitrogen transformation and removal processes, such as nitrification and denitrification, potentially resulting in complete in situ removal of nitrogen from landfills (Berge *et al*., 2005; Xu *et al*., 2014).

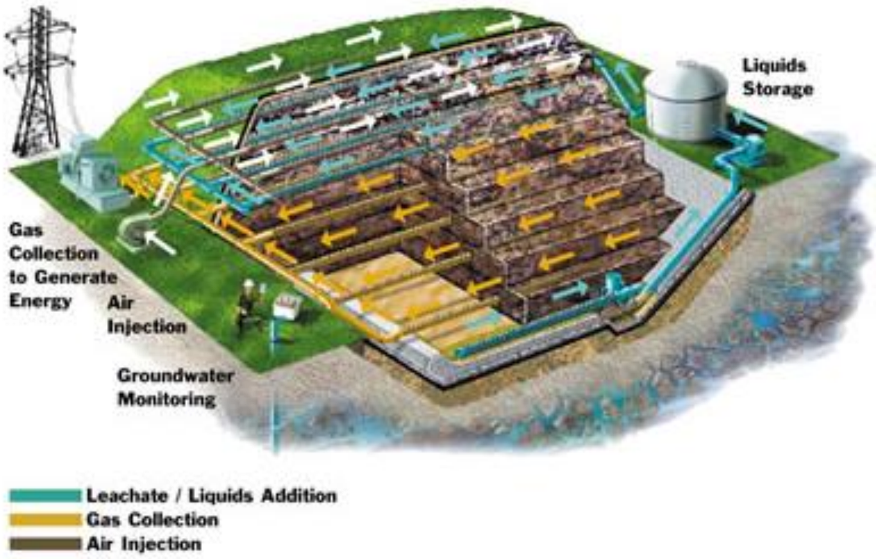

Figure 3.3 - Design and operation features in hybrid bioreactor landfill (Waste Management, 2004).

A system operated solely under aerobic conditions may increase the degradation kinetics of organic substances but inhibits completely methane generation and renders energy recovery impossible. Hybrid bioreactors operate under various combinations of aerobic and anaerobic conditions to achieve benefits from both. Researchers see combining the processes as a way to maximize the potential of a bioreactor landfill (Berge *et al*., 2005; Long *et al*., 2009; Xu *et al*., 2014).

3.4 Facultative Bioreactor Landfills

A sketch of a facultative system is illustrated in Figure 3.4. It combines conventional anaerobic degradation with a mechanism for controlling the high ammonia concentrations that may develop when liquids are added to the landfill. In this system leachate containing elevated levels of ammonia is treated using the biological process of nitrification. The nitrification process converts the ammonia in the leachate to nitrate. The treated leachate is then added to the landfill. Here certain microorganisms including the facultative bacteria can use the nitrate in the absence of oxygen for respiration. This process, called denitrification, can result in the production of nitrogen gas (N_2), which effectively removes nitrogen from the system (Berge *et al.*, 2005).

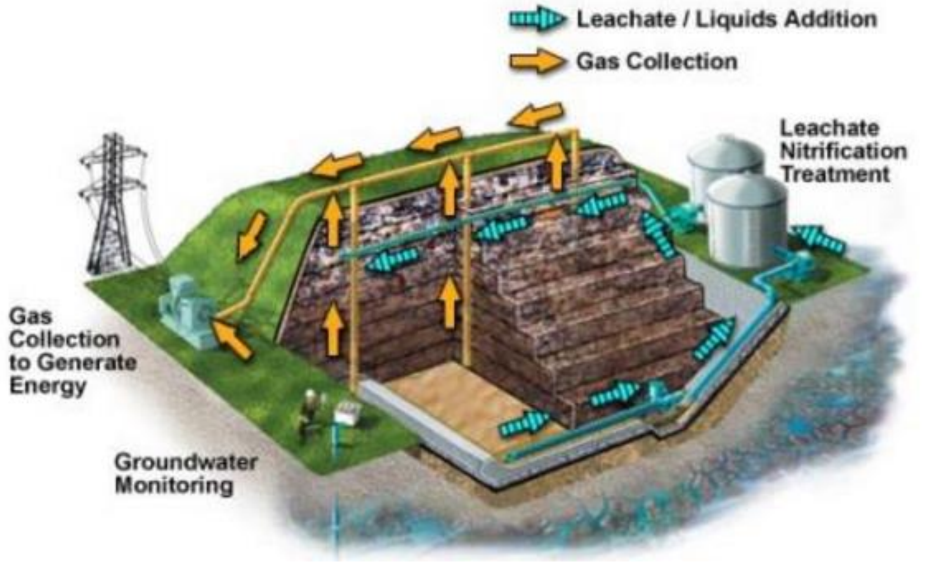

Figure 3.4 - Design and operation features in facultative bioreactor landfill (Waste Management, 2004).

A disadvantage of this technique is that external treatment of leachate for ammonia nitrogen removal must occur, which adds an extra step to the bioreactor landfill process and can be both difficult and costly because of high levels of ammonia-nitrogen in the leachate. Additionally, while denitrification of the leachate is occurring, methane production may be halted until the nitrate is consumed. It has been shown that methane production quickly resumes after nitrate is depleted (Berge *et al.*, 2005).

4 Nitrogen transformation and removal processes in bioreactor landfills

There are several ammonia nitrogen removal methods which often include complex sequences of physical, chemical, and/or biological processes, including chemical precipitation, nanofiltration, air stripping, and biological nitrification/denitrification via various reactor configurations. Thus, understanding the possible different nitrogen transformations is important when considering potential leachate management alternatives (Burton and Watson-Craik, 2002; Berge *et al.*, 2005). Figure 4.1 illustrates the potential nitrogen transformation and/or removal pathways that may occur in bioreactor landfills according to the nitrogen cycle.

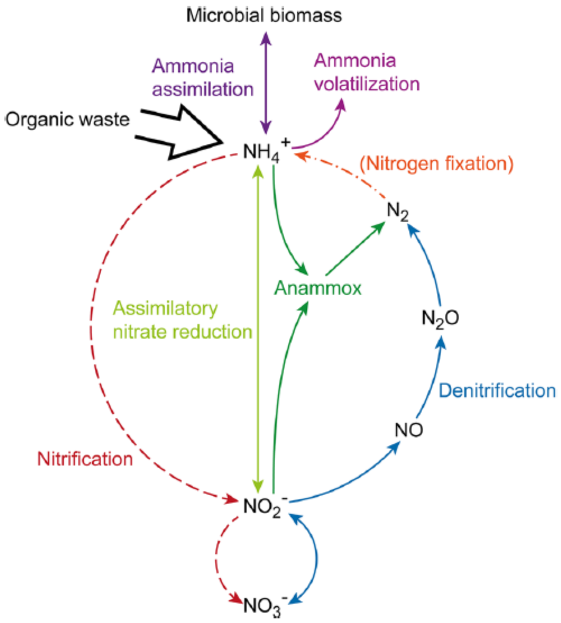

Figure 4.1 - Schematic illustration of the nitrogen cycle (Brandstätter *et al.,* 2015b).

4.1 Ammonification

Ammonia is released from the waste mainly by decomposition of proteins. Heterotrophic bacteria are responsible for the conversion of organic nitrogen to ammonia nitrogen in a process termed ammonification. This is a two-step process consisting of the enzymatic hydrolysis of proteins by aerobic and anaerobic microorganisms releasing amino acids and the subsequent fermentation of the acids to carbon dioxide, ammonia nitrogen, and volatile fatty acids (Kjeldsen *et al*., 2002; Berge *et al.,* 2005; Brandstätter *et al.*, 2015b).

After ammonification process, ammonia nitrogen is dissolved in the leachate and this component is ready to be transformed and/or removed via flushing, sorption, volatilization or biological processes within an aerobic environment (Berge *et al.,* 2005).

4.2 Ammonium Flushing, Sorption and Volatilization

The volume of water passed through the landfill, the nitrogen content of the waste, and the ammonia nitrogen concentration in the bulk liquid control the mass of ammonia nitrogen that can be leached from the waste. Addition of large amounts of water is required in order to reduce ammonia nitrogen concentrations by washouts and dilution to acceptable levels within a landfill (Berge *et al.,* 2005).

Flushing results in the removal of ammonia nitrogen from landfills by large volumes of water. However, with this method leachate must be treated externally and when operating the landfill as bioreactor, leachate recirculation is performed, and therefore ammonia nitrogen is continually reintroduced to the landfill while additional ammonia is solubilized into the leachate (Berge *et al.,* 2005).

Ammonium is known to sorb onto various inorganic and organic compounds. Thus, due to the high ammonium concentrations present, sorption of ammonia nitrogen to waste may be significant because sorption of ammonium to the waste will allow for temporary storage of ammonium prior to it being used in other processes, such as nitrification and volatilization, and may also result in the slow dissolution of ammonium over time (Heavey, 2003).

Sorption processes depends on pH, temperature, ammonium concentration, and ionic strength of the bulk liquid. Also, ammonia is only sorb to waste particles when it is in form of ammonium (NH_4^+). This way, a common procedure used to extract sorbed ammonium from particles involves the addition of a sodium or potassium sulphate solution (Berge *et al.,* 2005).

When free ammonia is present in the waste body volatilization may occur. The majority of the ammonia nitrogen present in solution is in the form of free ammonia gas at pH levels above 10.5 to 11.5. Due to the temperature dependence of the acid dissociation constant, as temperature increases, more of the ammonia is converted to free ammonia gas (Berge *et al.,* 2005). According to Tiquia and Tam (2000), at temperatures above 40ºC and at pH levels of 7 and above, the majority of nitrogen removed from compost is via volatilization.

Ammonia nitrogen volatilization is also influenced by the air flow introduced in the landfill. Because of its introduction, leachate begins to be agitated, creating a removal pathway for dissolved free ammonia to volatilize and leave the landfill (Berge *et al.,* 2005).

4.3 Nitrification

The two-step process in which ammonia nitrogen/ammonium is microbially oxidized to nitrite and nitrate is called nitrification (Berge *et al*., 2005). *Nitrosomonas* and *Nitrobacter* are the bacteria responsible for the biological nitrification process. Both of these groups are classed as autotrophic organisms. In the first step of nitrification, *Nitrosomonas* can oxidize ammonia to nitrite, but it cannot complete the oxidation to nitrate. The stoichiometric reaction for oxidation of ammonium to nitrite by *Nitrosomonas* is (Parker, 1975):

$$NH_4^+ + 1.5\,O_2 \rightarrow 2H^+ + H_2O + NO_2^- \qquad (1)$$

The second step reaction for oxidation of nitrite to nitrate by *Nitrobacter* is (Parker, 1975):

$$NO_2^- + 0.5\,O_2 \rightarrow NO_3^- \qquad (2)$$

These autotrophic organisms are distinguished from heterotrophic bacteria because inorganic carbon (carbon dioxide) is used for synthesis rather than organic carbon. Some heterotrophic microorganisms are able to nitrify; however their specific nitrifying rates are considered three to four orders of magnitude lower than that of autotrophs (Berge *et al*., 2005). Nitrification process results in the consumption of alkalinity as nitrous acid is formed (Berge *et al.,* 2005). According to Parker (1975), 7.14 mg of alkalinity as $CaCO_3$ is destroyed per mg of ammonia nitrogen oxidized.

The first step is often the limiting step but since complete nitrification is a sequential reaction, treatment processes must be designed to provide an environment suitable to the growth of both groups of nitrifying bacteria (Parker, 1975).

Because oxygen is a required element for nitrification, in landfills in which air is purposely added, nitrification can be a significant nitrogen removal pathway. On the other hand, it is an almost nonexistent process in conventional landfills and anaerobic bioreactor landfills (Berge *et al*., 2005). Temperature, heterotrophic bacteria competition, and potentially pH inhibition are also limiting factors of nitrification. According to Merz and Stone (1970), when air is added to landfills, in situ temperatures generally increase, often as high as 55 to 66ºC and may result in oxygen limitation (dissolved oxygen concentration declines with temperature increase) and thus reduce nitrification rates. Additionally, in areas within the landfill containing large amounts of organic carbon, oxygen may become limiting to nitrifiers due to competition with heterotrophic bacteria. At last, because nitrification destroys alkalinity, there may not be sufficient alkalinity present to buffer pH changes that would result from nitrification of high ammonia nitrogen leachates (Parker, 1975).

Berge *et al*. (2005) refers that is suspected that in situ nitrification may be optimized when operated in landfills cells containing older waste, because as the age of the waste increases the biological activity is reduced resulting in the decrease of the temperature of the system. Additionally, less competition with heterotrophs for oxygen will occur because older waste contains fewer biodegradable organics.

4.4 Denitrification

The conversion of nitrate nitrogen to a gaseous nitrogen species is the biological process termed as denitrification. Nitrogen gas is the primarily gaseous product but also may be nitrous oxide or nitric oxide formed (Parker, 1975).

A broad range of bacteria can accomplish denitrification, including *Psuedomonas, Micrococcus, Archromobacter and Bacillus.* The groups of denitrifiers are more robust than nitrifiers; However they require a sufficient organic carbon source for high nitrate removal rates (Parker, 1975, Berge *et al*., 2005).

Generally, the process has been termed as anaerobic denitrification. However, denitrification may also occur in portions of aerobic bioreactor landfill that air does not reach (Berge *et al*., 2005). Thus, the term anoxic denitrification is preferred, since it describes the environmental conditions of the absence of oxygen, without implying the nature of the biochemical pathways (Parker, 1975).

When air is added to landfills, biological processes such as nitrification traditionally found and expected only in landfill cover soils may now occur within the waste mass. Additionally, recirculating nitrified leachate allows for denitrification processes to occur in anoxic areas found in both anaerobic and aerobic bioreactor landfills (Berge *et al.,* 2005).

4.4.1 Heterotrophic Denitrification

As shown in the following reactions, denitrification is an anoxic process that reduces nitrate to nitrite, nitric oxide, nitrous oxide, and finally nitrogen gas (Berge *et al*., 2005):

$$NO_3^- + 2e^- + 2H^+ \rightarrow NO_2^- + H_2O \qquad (3)$$

$$NO_2^- + e^- + 2H^+ \rightarrow NO + H_2O \qquad (4)$$

$$2NO + 2e^- + 2H^+ \rightarrow N_2O + H_2O \qquad (5)$$

$$N_2O + 2e^- + 2H^+ \rightarrow N_2 + H_2O \qquad (6)$$

A potential advantage of this type of denitrification is related with the simultaneous carbon and nitrate removal without oxygen required. Denitrification also recovers the alkalinity consumed during nitrification. According to Parker (1975), bicarbonate is produced and carbonic acid concentration is reduced whenever nitrate or nitrite is denitrified to nitrogen gas. The stoichiometric quantity of alkalinity produced is 3.57 mg alkalinity as $CaCO_3$ produced per mg of nitrate or nitrite reduced to nitrogen gas.

4.4.2 Autotrophic Denitrification

Autotrophic denitrification may occur in environments with low organic carbon source and the presence of inorganic sulfur material, used as electron donor according to the reaction (Berge *et al.,* 2005; Berge *et al*., 2006):

$$2NO_3^- + 1.25\ HS^- + 0.75\ H^+ \rightarrow N_2 + 1.25\ SO_4^{2-} + H_2O \qquad (7)$$

During the autotrophic denitrification the nitrate decrease is usually coupled with an increase in sulphate concentration. Autotrophic denitrification may especially occur in older landfills or older portions of landfills where the carbon to nitrogen ratio may be low. In these situations, the nitrate removal via autotrophic denitrification is favored over heterotrophic denitrification (Koenig, 1996).

Autotrophic denitrification is advantageous, as it converts nitrate to nitrogen gas (N_2) in the absence of an organic carbon source and can utilize inorganic sulfur compounds (Berge *et al*., 2005).

4.5 Anammox

A process termed anammox (ANaerobic AMMonium OXidation) is the biological oxidation of ammonia nitrogen under anaerobic conditions. Bacteria capable of anammox use ammonium as the electron donor and nitrite as the electron acceptor according to the reaction (Berge *et al*., 2005):

$$NH_4^+ + 1.26\ NO_2^- + 0.085\ CO_2 + 0.02\ H^+ \rightarrow N_2 + 0.017\ H^+ + 0.24\ NO_3^- + 1.95\ H_2O \qquad (8)$$

According to Berge *et al*. (2005), there has been little research concerning anammox in solid waste environments; however, studies conducted in wastewater have shown that anammox readily occurs. Planctomycetales group are the microorganisms most often responsible for anammox process. Co-cultures of oxic and anoxic ammonia-oxidizing bacteria convert ammonia directly to nitrogen gas under oxygen limitation. Generally, this process is favorable in environments in which retention time is long, operation is stable, nitrite is present, and electron donors that would cause nitrite reduction via denitrification are not present. However, the growth rates of the anammox bacteria are extremely slow; thus, ammonia-nitrogen removal is slow as well (Jetten et al., 2001).

5 Aerobic Bioreactor Landfill – research updates

In order to improve and understand the effects of different aeration rate and off-gas oxygen concentration in the waste decomposition and leachate production and treatment, several lab-scale and field-scale studies have been done. The following section describes related experiments and its main results and conclusions.

5.1 Influence of aeration: lab-scale experiments

Prantl *et al.,* (2006) conducted a study where lab-scale investigations with column tests have been carried out. Gas proof columns (diameter: 20 cm; height: 65 cm) made of acrylic glass were filled with 10 - 15 kg waste material (dry mass) from an old landfill and operated under controlled temperature conditions (35ºC) in a climate chamber. The influences of water and different aeration intensities on biological degradation processes were investigated. Column S1 was operated as anaerobic bioreactor and two bioreactors S3 and S6 were operated with an aeration rate of 0.5 and 1 L/h, respectively. At day 270 of the experiment column S6 was established under anaerobic conditions. The runtime of the research was 513 days. Leachate recirculation was done (0.30 L/week).

The study's results of COD concentrations in the leachate are shown in Figure 5.1. The aerated waste is characterized by a rapid reduction of the COD to 350 mg O_2/L within 2 months of aeration, whereas the strongest decrease occurs in the first week. In this first phase, the influence of the aeration rate is obvious (S3 vs. S6). The anaerobic operated column shows a decrease in the COD, due to leaching processes and anaerobic degradation, although much slower. However, after 500 days, both the COD in the leachate of the anaerobic as well as of the aerated columns show similar concentrations. These results indicate a strong initial aeration effect, but after reaching a low level, the further COD reduction is rather caused by chemical-physical leaching processes.

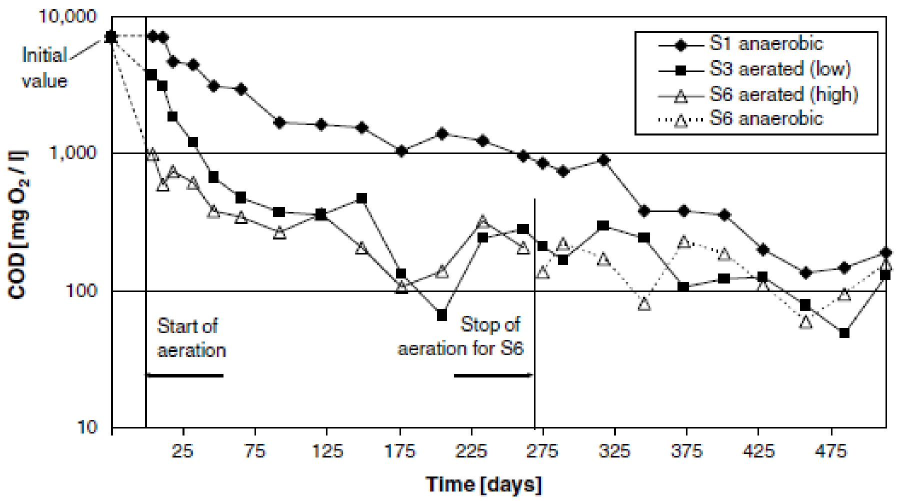

Figure 5.1 - COD concentrations in the leachate (Prantl *et al.*, 2006).

The results of ammonium nitrogen and nitrates nitrogen concentrations in the leachate are shown in Figure 5.2. Under anaerobic conditions, NH_4^+-N concentrations remain high over a long period of time. In contrast, ammonia nitrogen clearly declines within 2 months of aeration and remains at a very low level (<1.0 mg/L). The influence of the aeration rate is obvious in this phase (S3 vs. S6). Moreover, the stop of aeration after 270 days in column S6 causes a slight increase in ammonium concentrations, indicating that there is still a pool of degradable nitrogen in the waste. However, compared to the initial value and to the anaerobic control, these concentrations are low (<40 mg/L).

Nitrate (NO_3^-) as a product of nitrification was measured in the leachate of the aerated waste up to 10 mg/L in the starting phase and up to 100 mg/L later on, indicating two possible processes: The existence of anaerobic zones within the waste in the first months, leading to denitrification and the formation of elementary nitrogen, related to ammonia stripping via the gas phase. The subsequent increase of NO_3^--N indicates a decline of denitrification processes, as well as a possible increase of nitrification.

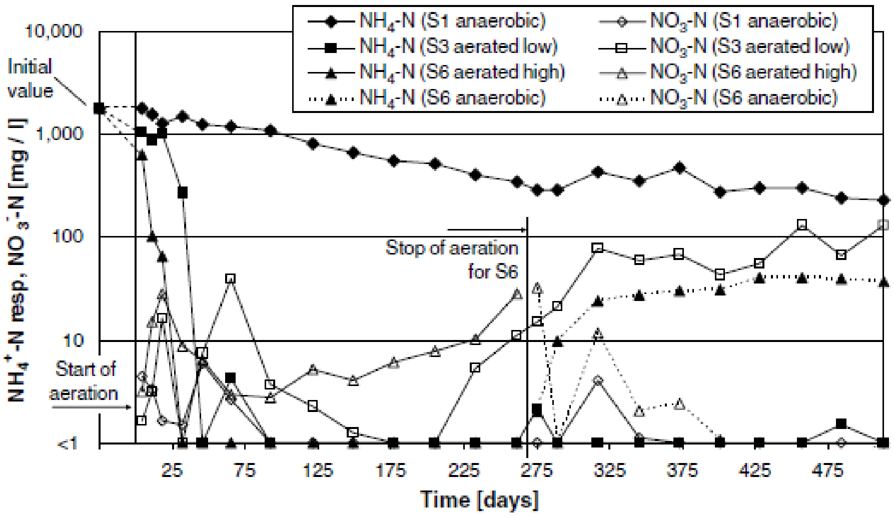

Figure 5.2 – NH_4^+-N and NO_3^--N concentrations in the leachate (Prantl *et al*., 2006).

The initial total nitrogen content of the solid samples were low and the changes were less significant compared to the ones regarding the TOC. Nevertheless, compared to the anaerobic column a slight decrease due to aeration could be pointed out.

In a similar study, Erses *et al*. (2008) conducted an experiment for almost 700 days where two landfill bioreactors were operated under aerobic and anaerobic conditions in a thermo-insulated room at a constant temperature of 32ºC. Reactors were filled with 19.5 kg of shredded synthetic solid waste prepared according to the average municipal solid waste compositions determined in Istanbul and operated under wet-tomb management strategy by using leachate recirculation (1 L/week). Moreover, 500 mL/week distilled water, corresponding to an equivalent of 20 cm/year rainfall, was added to the reactors. Each reactor had a diameter of 0.35 m and a length of 1 m (about 96 L).

Leachate COD concentrations results of the experiment for aerobic and anaerobic reactors are presented in Figure 5.3. The results of the study confirmed those of previous studies and indicated that approximately 90% of COD removal was complete by days 72 and 462 for aerobic and anaerobic reactors, respectively.

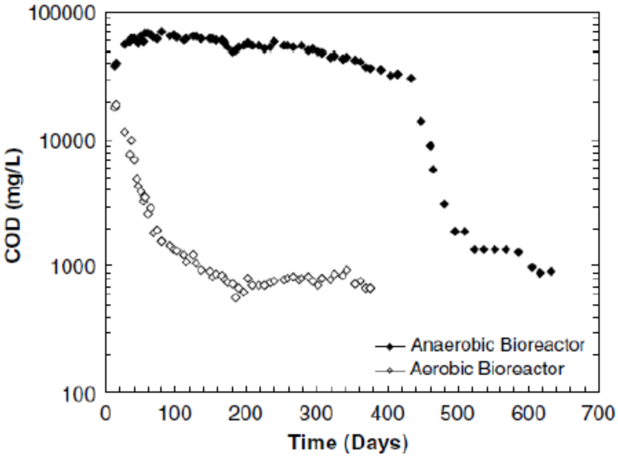

Figure 5.3 - Leachate COD concentrations (Erses *et al.,* 2008).

The TKN and ammonia nitrogen concentrations findings of Erses *et al.* (2008) for aerobic and anaerobic reactors are given in Figure 5.4. TKN and ammonia-nitrogen concentrations in the leachate of the aerobic reactor indicated the same decreasing trend. Initial TKN and ammonia nitrogen concentrations were measured as 620 and 399 mg/L, respectively. TKN concentration decreased to 140 mg/L on day 108 and 42 mg/L on day 178 and stayed constant throughout the study. NH_3-N concentrations, on the other hand, decreased to 132 mg/L on day 116 and 14 mg/L on day 175 and continued to decline slightly until reaching to 5 mg/L at the end. The recirculation practice in the anaerobic reactor reintroduces ammonia to the system, keeping its value almost constant throughout experiment.

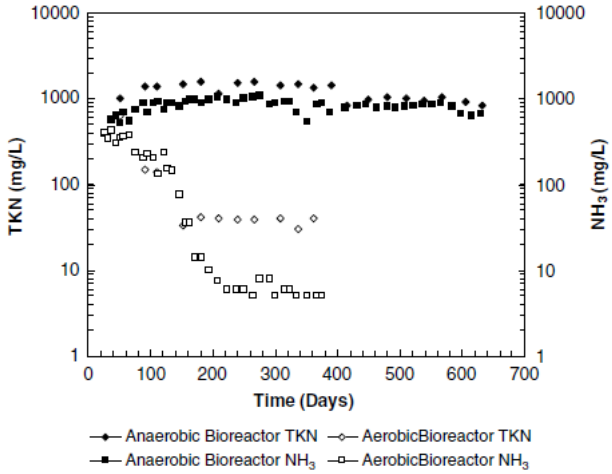

Figure 5.4 - Leachate TKN and ammonia nitrogen concentrations (Erses *et al*., 2008).

Similar results related to the influence of aeration on the degradation and stabilization of the waste material on lab-scale experiments are reported also by Cossu *et al*. (2003), Bilgili *et al*. (2006), Shao *et al*. (2008), Nikolaou *et al.* (2010), Slezak *et al*. (2010), He *et al*. (2011), Kim *et al*. (2011), Raga and Cossu (2013), and Nag *et al.* (2016), which experienced even much greater organic removal efficiency, faster stabilization and no ammonia accumulation in aerated reactors compared to the anaerobic ones.

5.2 Oxygen concentrations in the outlet gas

Several pilot and full-scale aerobic landfill studies were performed with a wide range of aeration rates and different results were obtained. According to the study of Prantl *et al*. (2006) above mentioned, the leachate quality of the simulated landfill with higher aeration (0.001 L/min.kgDM) was slightly better than those with lower aeration rate (0.0006 L/min.kgDM). Slezak *et al.* (2010) showed there were no significant differences among leachate qualities of bioreactors aerated with the flow rate range (continuous aeration) of 0.003 - 0.017 L/min.kg waste. The air flow rates at field scale reported in the literature also show different orders of magnitude. Hrad *et al*. (2013) used for a Landfill in Austria an in situ aeration system with a flow rate ranging from 0.00004 to 0.00006 L/min.kgDM, while Raga and Cossu (2014) used rates of 0.0002 L/min.kgDM.

There is no general consensus in the literature on the optimum aeration rate for aerobic landfills because the effect of MSW aeration depends on not only the quantity of aeration but also other factors, including MSW composition and conditions (organic content, moisture level, MSW age, temperature, etc.), the conditions of air (temperature and humidity), air distribution and off-gas collection systems (air injection technologies and off-gas collection systems), and moisture distribution system (Ko *et al.,* 2016).

Due to the wide range of aeration rates suggested for the solid waste in the literature, a few studies aim to define other bioreactor landfill operational parameters in order to better standardize the management. According to Bilgili *et al*. (2006), an airflow that provides an outlet CO_2 concentration of about 15% is sufficient for aerobic decomposition of solid waste. Cossu *et al*. (2016) studying biogas enhancement selected aeration rate and time adjusting it with the aim of monitoring specific chemical parameters capable of guaranteeing optimal conditions for methanogenic bacteria growth, setting an airflow which allowed $O_2\% > 1\text{-}2\%$ in the outlet gas, while Ritzkowski *et al*. (2006) adjusted the air flow in time according to the trend of the oxygen uptake rate during the duration of the test. Other experiments studied oxygen concentration evolution trend in the outlet gas for landfill aeration.

Ko *et al*. (2016) had conducted a research to investigate the effects of daily aeration frequency on leachate quality and waste settlement of a typical Chinese MSW. In this context, four laboratory-scale reactors were constructed and operated for about 10 months to simulate different bioreactors operations, including one anaerobic bioreactor and three hybrid bioreactors with different aeration frequencies (one, two, and four times per day). The bioreactors were constructed using 20-cm-diameter polyacrylic plastic pipe with a total height of 100 cm. Each bioreactor was initially packed with a total of 13.2 kg synthesized MSW. The three hybrid bioreactors A1, A2 and A3 were operated with an aeration frequency of 2, 4 and 8 h/day, respectively, with aeration flow rate of 30 L/h and having variation of oxygen concentrations in the outlet gas of approximately 2-17%, 4-17%, and 8-17%, respectively, at day 45 as shown in Figure 5.5. Leachate recirculation was done (500 mL/day).

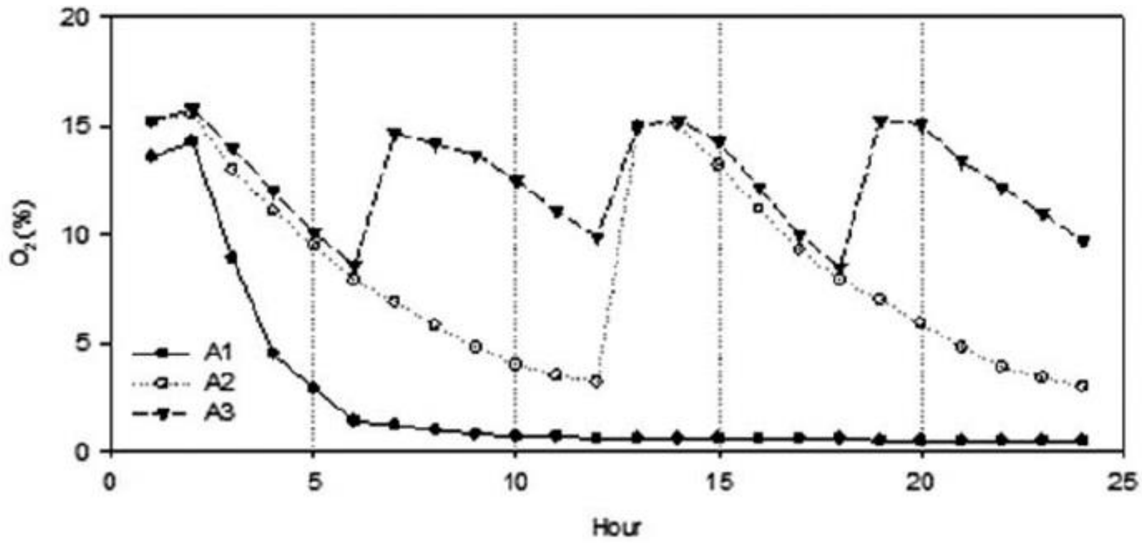

Figure 5.5 - Change of O_2 composition of A1, A2, and A3 during operation at day 45 (Ko *et al*., 2016).

The results of the experiment showed that 99% BOD_5 removal was achieved in A1, A2 and A3 at 284, 216 and 160 days, respectively. The BOD_5/COD ratios of A1, A2, and A3 at the completion of the experiment reached 0.15, 0.12, and 0.09, respectively. In the anaerobic reactor, COD and BOD_5 did not change much compared with the initial concentrations and BOD_5/COD ratio fluctuated around 0.7 during the experiment;

In the experiment, NH_3-N in leachate started to decrease around days 250, 100, and 50 in aerated bioreactors A1, A2, and A3, respectively. Time required for 95% NH_3-N removal in A2 and A3 were 190 and 142 days, respectively. Until the end of the experiment, NH_3-N removal in A1 had not achieved 95% yet. The NO_3^--N concentration in the anaerobic bioreactor was maintained at around 12mg/L during the experiment. The NO_3^--N concentration of A1, A2, and A3 increased to around 25, 30 and 40 mg/L, respectively. The concentrations of NO_2^--N in leachate of all bioreactors were minimal over the period of time.

The conclusions of this experiment reported that concentrations of NH_3-N with frequent aeration (higher oxygen concentrations in the outlet gas) were reduced quicker than that with a less frequent aeration.

Considering the cost of aeration MSW landfill, it was suggested to use low daily aeration frequency (less oxygen concentration in the outlet gas) if the landfill operator would target to remove organic carbon concentration and total nitrogen in the leachate. Performance-specific aeration approach was proposed: high aeration frequency for targeting fast nitrogen removal and low frequency for carbon removal.

Although several studies were performed with different aeration flow rates which lead to different oxygen concentration in the outlet gas, there is no study found in the literature that established different air flow rates with the aim of creating and evaluate different known oxygen content in the off-gas as an operational parameter in order to remove nitrogen compounds. This research has the peculiar characteristic of studying different oxygen concentrations in the outlet gas as an operational and design stabilization parameter on old waste in order to better standardize the management.

6 Material and Methods

6.1 Waste Samples

Waste samples were collected by excavating at 10 m depth in the old MSW landfill of Legnago, Province of Verona, Italy (Figure 6.1) and brought to LISA (*Laboratorio di Ingegneria Sanitaria Ambientale)*. The landfill of Legnago was made on the old Tartaro river bed and its first part was closed in 1990. It was built without artificial impermeable bottom liner where this barrier was composed by fine soil deposits of the old river bed. There wasn't leachate collection system. Bearing in mind the geological situation of the area and the characteristics of the landfill barrier system, the risk of groundwater pollution is very high (Cestaro *et al.,* 2006).

Figure 6.1 - Waste samples extraction, Legnago Landfill.

Mesh size sieves with 100, 50 and 20 mm were used in order to perform grain size distribution analysis on the excavated samples. Waste composition analyses were carried out considering the following categories: plastic, paper, wood, textile, metals, inerts (glass and stone), aggregates and fines (i.e. under sieve fraction, 0 - 20 mm).

Six reactors filled with approximately 30 years old waste samples collected from the landfill body were set up for the experiment. Before placing the material into the respective landfill simulation reactor, the so assembled waste samples were pooled and thoroughly mixed with shovels in order to ensure the best homogeneity inside the reactors. The placement of the waste samples in all reactors was performed with precision weighs following and recreating the initial waste composition.

In order to leave in each column the same air space at the top, and considering the high bulk density of the 30 years old waste (around 1000 kg/m^3 after low compaction), 30 kg to 35 kg of waste were prepared for each reactor. Because of the limited size of the columns, bulky material that could have created problems with its size as big stones and intact bottles were removed.

6.2 Equipment

Six column reactors used for the experiment were made of Plexiglas, having an internal height of 106 cm and a diameter of 24 cm. Columns C1, C2, C3, C4 and C5 were set as an aerobic reactors and column C0 as anaerobic reactor. A general scheme of aerobic and anaerobic reactors is shown in Figure 6.2. Three valves are located in the upper part of the columns in order to provide air introduction (in case of aerobic reactor), off-gas sampling, and water introduction and leachate recirculation. One valve is located in the lower part of the columns for leachate extraction.

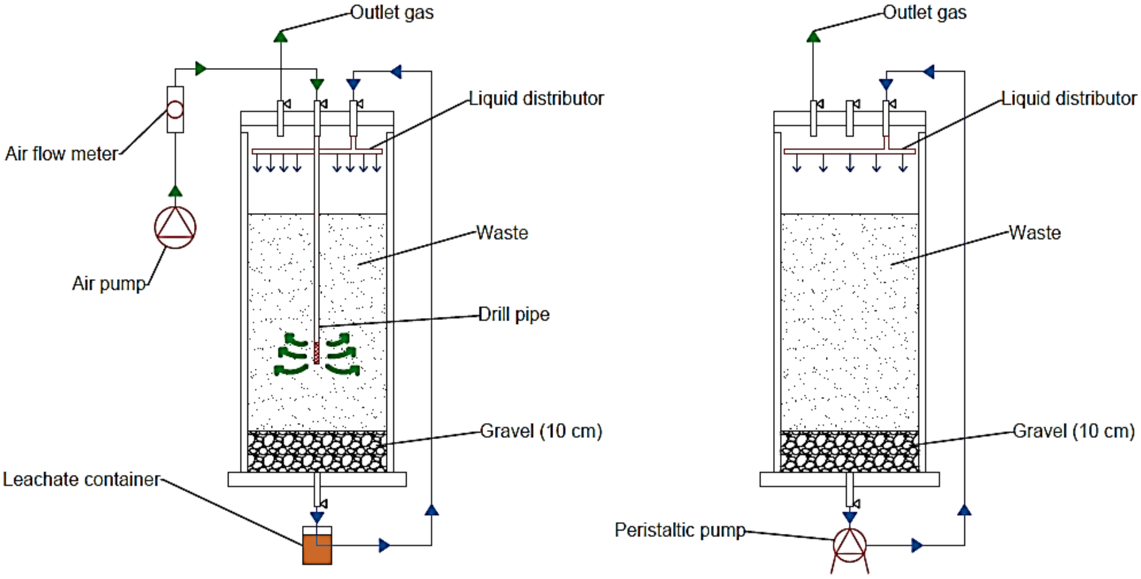

Figure 6.2 - Draught of aerobic reactors (left) and anaerobic reactor (right).

A leachate circular plastic pipe distributor uniformly perforated was installed in each column in order to let the drops spread all over the waste top layer ensuring the best moisture homogeneity inside the waste body avoiding preferential paths formation, while a 2 L leachate collection tank was installed at the bottom. A 10 cm thick gravel layer was used at the bottom as a drainage layer in order to avoid fines or other particles to block the valve. Recirculation in anaerobic column was done by means of peristaltic pump Heidolph PUMPDRIVE 5001.

The aeration was performed with three air pumps Prodac Air Professional 360 regulated by five Sho-Rate GT1335 flowmeter (Brooks Instruments). The aeration system was equipped with a vertical PVC tube with the purpose of air supply to the waste body. It was located at the center of the columns, 20 cm above the gravel and it had an open end and 10 cm length side perforations starting from the bottom. This system should guarantee the most uniform distribution of air throughout the column. Outlet gas composition analyses of carbon dioxide, methane and oxygen composition were performed by means of portable Telegan LFG 20 gas monitoring. Under anaerobic conditions air was not supplied into the column and the biogas produced was collected into a Tedlar 10 L sampling bag connected to the upper outlet gas valve.

6.3 Experimental operation

Before filling the columns, and after a preliminary cleaning, the body of the column has been checked and sealed with attention in order to avoid any leachate leak or air infiltration; old valves and components were replaced with new ones and all the junctions were sealed applying spreading silicone. Silicone has also been applied on very thin cracks found along the body of some of the columns.

After filling the six reactors with the waste samples, tap water was added and recirculated until waste field capacity was reached. In order to guarantee enough leachate for sampling and recirculation, an addition amount of tap water was added. Final landfill bioreactors columns set up is shown in Figure 6.3. Room temperature was fixed at 30ºC.

Figure 6.3 - Landfill bioreactors columns during the experiment.

Anaerobic environments were set in all the reactors until the day 44 with the aim of establishing the same starting conditions of aeration, with no oxygen in the outlet gas. At the start of aeration all reactors were aerated, except column C0 (maintained under anaerobic conditions). At the beginning of the aeration period, columns were operated under identical aeration condition (1 L/h) for two weeks in order to assess the oxygen consumption and its concentration in the outlet gas of the bioreactors in aerobic conditions and consequently choose different airflow rates with the purpose of creating different oxygen concentrations in the outlet gas on each column.

At day 64 of the experiment different air flow rates were set up: reactor C0 was used as control and therefore maintained under anaerobic conditions; reactors C1, C2, C3, C4 and C5 were operated with an air flow rate of 0.3, 0.5, 0.8, 1.0, and 1.2 L/h, respectively, corresponding to 0.22, 0.34, 0.54, 0.71, and 0.89 L/d.kg of waste, respectively. Air was supplied continuously during this experimental period. The whole running time period of the experiment lasted 120 days.

During the anaerobic period all the reactors remained sealed in anaerobic conditions, leaving the accumulated leachate on the bottom with no recirculation in order to ensure oxygen depletion. During the aeration phase of the experiment, 2.5 L/day of leachate recirculation per reactor was performed. This rate allows the recirculation of all processed water in the columns once a day. In reactors C1, C2, C3, C4, and C5 leachate recirculation of 0.5 L was executed manually five times a day: at 10h30, 11h30, 12h30, 15h00, and 16h00. In column C0 peristaltic pump with a rate of 10 rpm (i.e. 1.25 L/h) was switched on for 1h two times a day: at 10h30 and 15h00. Leachate recirculation in all columns was performed every day, except weekends and holydays.

Leachate samples (250 mL) were collected weekly for analyses (pH, alkalinity, TOC, COD, BOD, N-NH_4^+, N-NO_3^-, N-NO_2^-, SO_4^{2-}, Cl^-) and the same amount of tap water was replaced in the reactors. Outlet gas monitoring of CO_2, CH_4, and O_2 volume percentage was performed once every morning in all aerobic reactors before the first leachate recirculation in order to have steadier values and performed approximately once a week in anaerobic bioreactor before leachate recirculation as well. Off-gas monitoring was performed every day, except weekends and holidays.

6.4 Analytical methods

In order to compare the effect of aeration and the oxygen concentrations in the outlet gas on both waste stabilization and on nitrogen evolution in aerated bioreactors respectively to the anaerobic one, leachate monitoring were carried out throughout the entire experiment; and solid fraction analyses were performed at the beginning and at the end of the experiment. Italian standard methods were used for analytical methods on leachate and solid samples.

6.4.1 Leachate

Leachate samples were collected weekly for laboratory analyses. Most of the parameters (pH, alkalinity, sulphates, chlorides, total organic carbon, ammonium nitrogen, nitrates nitrogen, and nitrites nitrogen) were determinate weekly; while BOD, COD, and TKN analyses were performed monthly. The methods used for the analysis on leachate samples are shown in Table 6.1.

Table 6.1 - List of methods for the analysis on leachate samples.

Parameter	Method description
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
TKN	IRSA-CNR 29/2003, VOL 2, N.5030
N-NH_4^+	IRSA-CNR 29/2003, VOL 2, N.4030
N-NO_3^-	IRSA-CNR 29/2003, VOL 2, N.4040, A1
N-NO_2^-	IRSA-CNR 29/2003, VOL 2, N.4050
TOC	IRSA-CNR 29/2003, VOL 2, N.5040
Cl^-	IRSA-CNR 29/2003, VOL 2, N.4090, B
SO_4^{2-}	IRSA-CNR 29/2003, VOL 2, N.4140, B

6.4.2 Solid fraction

Laboratorial determinations on the waste samples were performed at the beginning and at the end of the experiment. The samples categories were shredded manually to smaller sizer in order to perform Total Solids (TS) and Volatile Solids (VS) determinations. The methods used for analysis on solid samples are shown in Table 6.2.

Table 6.2 - List of methods for analysis on solid samples.

Parameter	Method description
TS and VS	IRSA-CNR Q 64/84, VOL 2, N.2
TKN	IRSA-CNR Q 64/85, VOL 3, N.8, mod.

Tests of TS and VS were performed in triplicate on each category, except for metals and inerts (assumed as 100%TS and 0%VS) and results obtained as mean values. Respiration Index (RI_4) was determined by means of Sapromat respirometer. Analyses of TKN and RI_4 were determined on the fine fraction of the solid samples.

7 Results and Discussion

7.1 Waste characterization

After waste material samples excavation, waste composition analysis was performed. Physical and chemical determinations corresponding to the initial solid fraction analyses were done on waste for initial characterization. The following section shows the results of waste composition and initial solid fraction analysis.

7.1.1 Waste composition

The results of waste composition analysis are shown in Table 7.1. Around 400 kg of waste samples were collected from the Legnago landfill body. Grain size distribution analyses were performed on the excavated waste using 100, 50 and 20 mm mesh size sieves considering plastics, paper, textile, metals, aggregates, inerts (glass and stone), wood and fines (0 – 20 mm fraction).

Table 7.1 - Results of composition analysis of waste samples.

Category	**Screen (mm)**			**Total**	
	100	**50**	**20**		
	(kg)	(kg)	(kg)	(kg)	(%)
Plastics	28,71	9,25	7,42	45,38	**14,1**
Paper	3,71	3,19	3,47	10,37	**3,2**
Textile	4,10	1,90	1,10	7,10	**2,2**
Metals	0,97	1,16	0,87	3,00	**0,9**
Aggregates	11,68	1,38	3,36	16,42	**5,1**
Inerts	19,71	8,55	17,31	45,57	**14,2**
Wood	1,22	1,31	1,51	4,04	**1,3**
Fines	-	-	189,36	189,36	**58,9**

Studies on landfills have shown that landfills contain fine fraction that make up 40 - 70% (w/w) of landfills' content (Mönkäre *et al.,* 2017). The results from fractions separation confirmed that in this case the major constituent was the fine fraction (up to 59%). Comparable results are reported in the literature. Raga and Cossu (2013) had conducted a study in which waste composition analysis was performed on an approximately 15 years old waste from an Italian landfill and it was found that fine fraction represented up to 56% of the waste samples.

After waste composition analysis six waste samples were prepared to be loaded in the columns. Weight and composition of each waste sample prepared for the columns are reported in Table 7.2.

Table 7.2 - Weights and composition of the waste loaded in each column.

Category	Column					
	C0	**C1**	**C2**	**C3**	**C4**	**C5**
	(kg)	(kg)	(kg)	(kg)	(kg)	(kg)
Plastics	3,38	3,94	4,02	4,24	4,07	3,72
Paper	1,02	1,49	1,39	1,48	1,97	1,49
Textile	0,61	0,94	1,06	0,75	0,75	0,85
Metals	0,37	0,26	0,37	0,37	0,56	0,31
Aggregates	0,86	0,73	1,78	1,49	0,95	1,48
Inerts	4,19	4,76	5,37	4,78	4,17	2,80
Wood	0,40	0,46	0,54	0,38	0,59	0,31
Fines	19,99	20,42	20,83	22,11	20,95	21,22
Total	**30,82**	**33,00**	**35,36**	**35,60**	**34,01**	**32,18**

The placement of the waste samples in all reactors was performed with precision weighs following and recreating the initial waste composition bearing in mind the percentages results shown in Table 7.1.

7.1.2 Initial solid fraction analyses

Physical and chemical analyses were performed on the waste for an initial characterization. Table 7.3 shows the results of analysis of density, total solids (TS), volatile solids (VS), moisture content, total Kjeldahl nitrogen (TKN) and respiration index for four days (RI_4). The values of TS, VS, Moisture, TKN and RI_4 reported in the following table are based on analyses on one initial solid sample.

Table 7.3 - Results from initial physical and chemical solid fraction analyses.

Parameter	Column					
	C0	**C1**	**C2**	**C3**	**C4**	**C5**
TS (%)	79,0	78,4	78,5	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
Density (kg/m^3)	1,1	1,1	1,2	1,1	1,1	1,2
RI_4 (mgO_2/gTS)	1,1	1,1	1,1	1,1	1,1	1,1
TKN (gN/kgTS)	2,2	2,2	2,2	2,2	2,2	2,2

Due to waste material age and since previous in situ aerobic biological degradation processes decreasing the organic content had already occurred, it should be expected that the initial reactivity potential of the waste material at the investigated landfill site would be quite low at the beginning of the experiment.

The material was characterized by a low respiration index (RI_4 = 1,1 mgO_2/gTS) that confirms the advanced level of previous bio-stabilization which took place under the 30 years of anaerobic conditions in the landfill. Other landfill aeration projects reported results in a similar dimension. For waste samples taken from the landfill of Modena in northern Italy the average value of RI_4 was 1.6 mgO2/gTS (Raga *et al*., 2015); Hrad *et al*. (2013) reported a median RI_4 value of 1.7 mgO2/gTS for waste samples derived from an old landfill near Vienna, Austria; and Brandstätter *et al.* (2015a) found an average RI_4 value of 1.7 mgO2/gTS for 40 year old waste from a former MSW landfill in Austria. No previous in situ aeration was performed in the above mentioned studies, thus the results of RI_4 are slightly higher than the values obtained in this study.

Although volatile solids determination is not a measure of available organic matter, this parameter analysis is a way to assess the potential degradability of waste excavated from a landfill (Hull *et al*., 2005). The volatile solids content of the excavated waste into each column ranged from 17.2% to 20.5%, suggesting a considerable amount of potential degradability. Considering the age of the waste and the previous aerobic treatment, TKN concentrations are still relatively high, suggesting low efficiency of previous aeration applied and/or slow degradation of landfill bottom layers.

According to different studies, the wastes moisture content in Europe ranged between 20% and 30% (Jani *et al*., 2016). The moisture content of the excavated waste in the columns is in accordance to the values in the literature, ranging 21.0% to 23.0% into each bioreactor.

7.2 Gas composition

7.2.1 Off-gas characterization

Composition of columns' outlet gas in terms of volume percentage of CO_2, CH_4 and O_2 are reported in Figure 7.1, Figure 7.2, and Figure 7.3, respectively. Gas composition analyses were performed frequently for all columns since the beginning of the experiment and on a daily basis on the aerated columns from the first days of the aeration throughout the whole experiment.

The results of carbon dioxide production trend in all columns is clear. At the beginning of the experiment, different concentrations were reached. At day 20 of the experiment, during the anaerobic period, CO_2 concentrations in reactors C0, C1, C2, C3, C4, and C5 were 9.5%, 15.0%, 13.7%, 13.0%, 10.9%, and 8.8%, respectively, and at day 42 it reached 12.1%, 20.0%, 15.7%, 15.3, 12.1%, and 11.7%, respectively. These values corresponded to different biological activity present in the columns, showing faster and higher biological activity in reactors C1, C2, and C3.

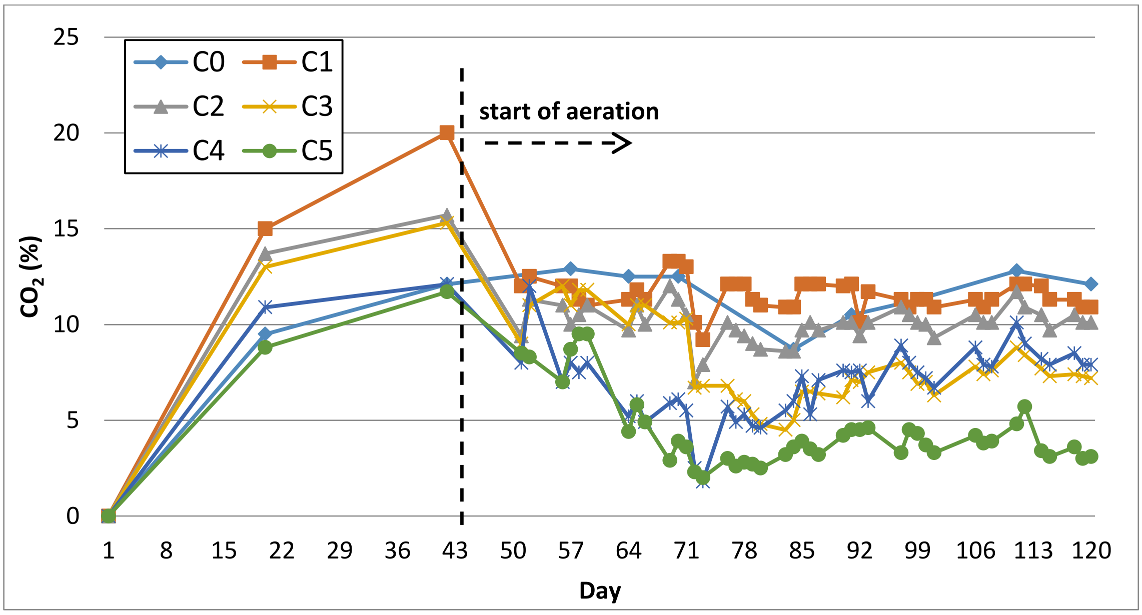

Figure 7.1 - Outlet gas composition for CO_2 in the bioreactors.

During aerobic degradation of MSW, biodegradable materials are converted mostly to carbon dioxide and water (Berge *et al.,* 2005). At the beginning of aeration carbon dioxide concentrations dropped as the columns were being flushed by air. When the air flow rates were adjusted in the columns to the definitive set (i.e. 0.3, 0.5, 0.8, 1.0, and 1.2 L/h, in C1, C2, C3, C4, and C5, respectively) CO_2 concentration in the outlet gas in the columns were less with higher amount of air injected. It should be noted that although column C4 was set with higher air flow rate comparing to C3, from day 83 of the research carbon dioxide production in column C4 increased to similar or slightly higher values than C3 throughout the experiment, suggesting a higher microbiological activity present in column C4 respect to C3 and/or the existence of air preferential pathways. Anaerobic bioreactor kept values between 8 – 13% until the end of the experiment.

The different biological activity present in the bioreactors was more evident when methane fermentation phase started (Figure 7.2). At day 42 of the experiment, methane production was detected in bioreactors C1, C2, and C3; however, with clearly different production between the three, being the value of its concentration in bioreactor C1, C2, and C3 of 39.1%, 22.3%, and 4.7%, respectively, showing advanced methane fermentation phase in C2 and particularly in C1.

As aeration period started, CH_4 concentrations dropped due to the presence of oxygen in the columns inhibiting its production (Kjeldsen *et al.*, 2002). During this period, methane concentrations in column C1 (air flow rate of 0.3 L/h) reached values of 1.9%, suggesting the presence of anaerobic spots within the bioreactor. The same compound was detected at day 50 in the anaerobic bioreactor and its concentration increased throughout the entire experiment reaching the maximum value of 20.7%. No methane production occurred in bioreactors C2, C3, C4, and C5 during the aeration phase.

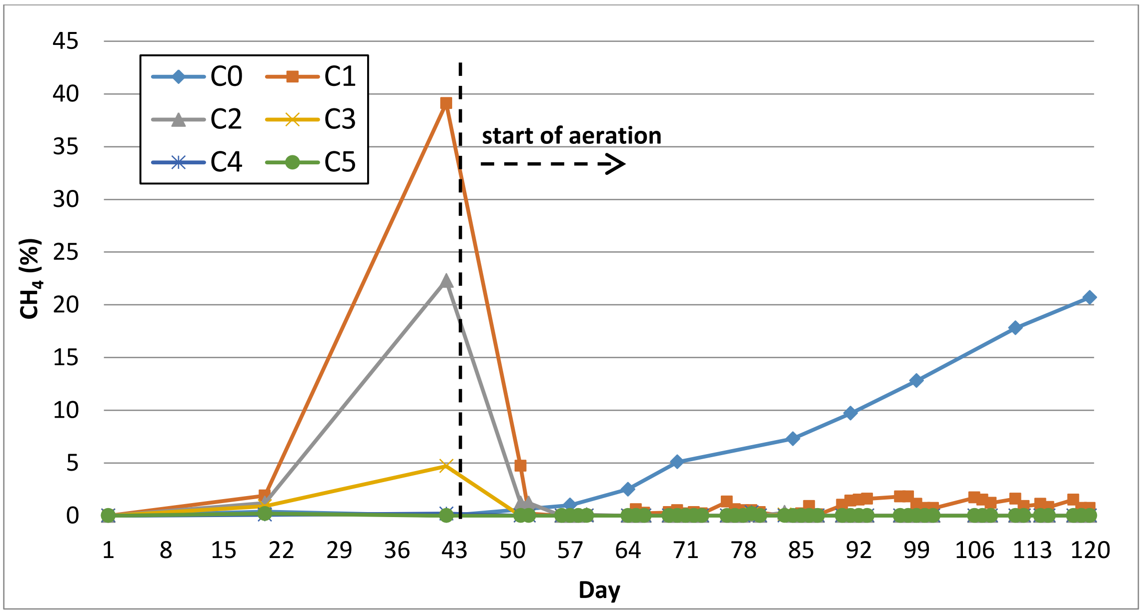

Figure 7.2 - Outlet gas composition for CH_4 in the bioreactors.

The results of oxygen concentration in the outlet gas (Figure 7.3) show a rapid decrease of its concentration during the anaerobic period. At day 20 of the experiment O_2 content in the off-gas in columns C0, C1, C2, C3, C4, and C5 was 0.4%, 0.4, 0.0%, 0.1%, 1.3%, and 0.0%, respectively, and at day 42 its concentration reached 0.0% in all columns.

After an initial aerobic phase characterized by high oscillations in terms of O_2 concentrations in the outlet gas of the aerobic columns, relatively stable values started to occur when definite air flow rates were set up in the bioreactors. The amount of oxygen present in the off-gas of the aerated reactors was directly dependent to the respective inlet air flow, being its concentrations higher with higher aeration flow rate; average values of O_2 content in the off-gas of the aerobic bioreactors C1, C2, C3, C4, and C5 were 0.4%, 1.3%, 7.4%, 9.0%, and 14.6%, respectively, during the period of definite air flow rates, while presence of oxygen was never detected in the anaerobic bioreactor.

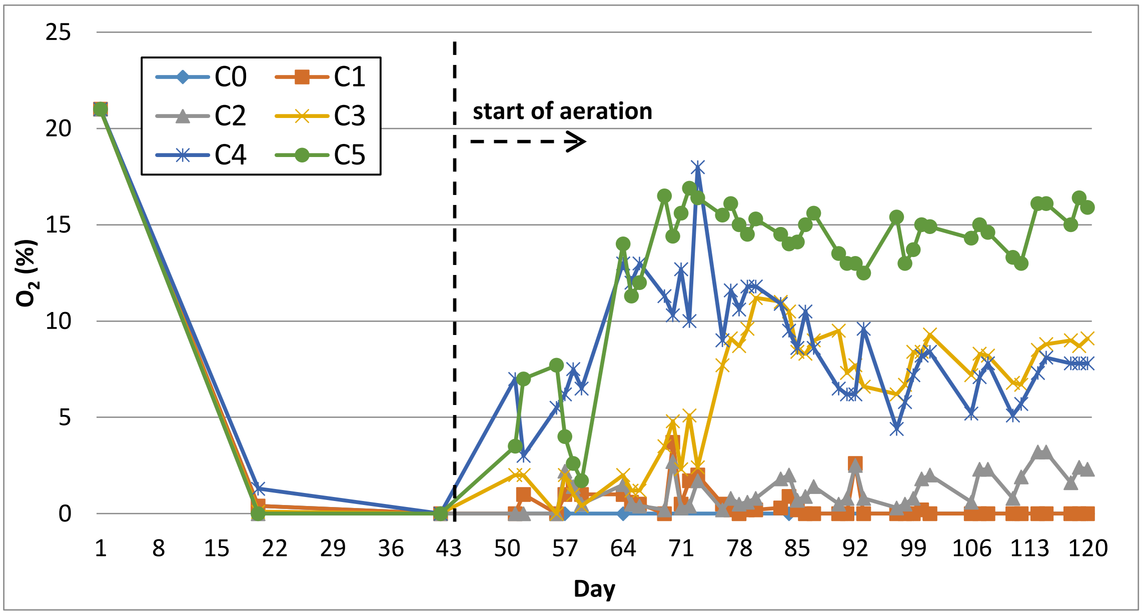

Figure 7.3 - Outlet gas composition for O_2 in the bioreactors.

Although column C3 and C4 air flow rate were set with 0.8 and 1.0 L/h, respectively, it was noticed that from day 90 of the experiment oxygen content in the outlet gas of column C3 reached values slightly higher than C4 throughout the research. These results reveal higher oxygen requirements in column C4 comparing to C3 and/or the existence of air preferential pathways within the waste material as suggested with the carbon dioxide production observed in both columns. Additionally, from day 101 of the experiment O_2 content in the off-gas of C1 was not detected until the end of the research indicating an insufficient air supply to complete the aerobic microbiological activity.

7.2.2 Oxygen utilization rate

Oxygen has been used in different amounts according to the aeration flow rate (oxygen input), biological activity in the columns and air distribution within the bioreactors body. The amount of oxygen supplied into each bioreactor and its quantity of utilization during the aeration period are reported in Figure 7.4. The results were calculated based on the oxygen available (oxygen input) and the mean values of oxygen concentration in the outlet gas during the first period of aeration (i.e. when airflow rate of 1L/h was set in all columns) and during the period when final air flow rate set up were operated in the reactors.

The results report that oxygen uptake is not proportional to the air flow rates established. During the aeration phase, the values show that columns C1, C2, C3, C4, and C5 used 5.5, 6.5, 6.8, 6.7, and 5.5 LO_2/kg of waste, respectively, corresponding to 97.2%, 94.8%, 73.6%, 59.9%, and 40.0%, respectively, of the total amount of oxygen available in each column during the same period.

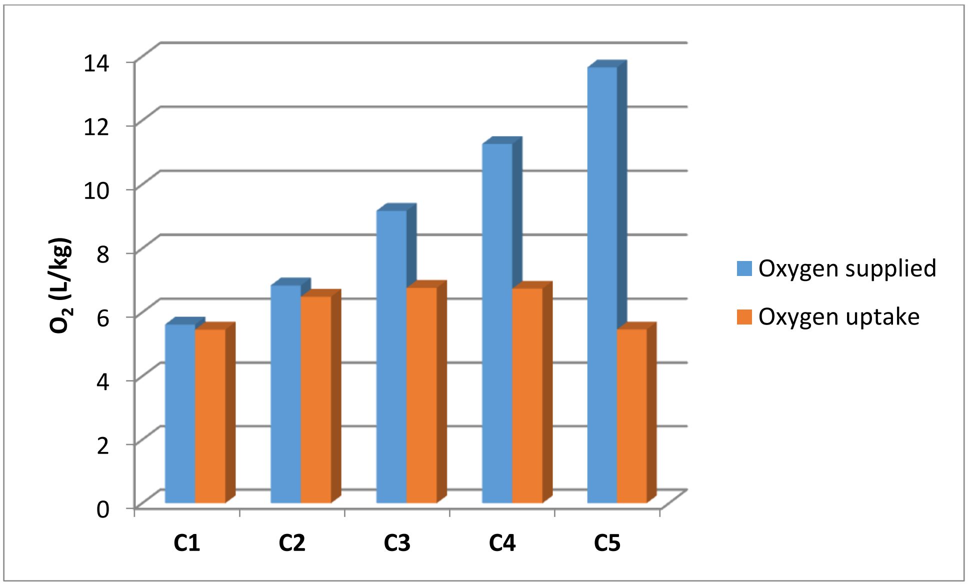

Figure 7.4 - O_2 supplied and uptake into the bioreactors during the aeration period.

It should be noted that 26%, 40%, and 60% of the oxygen injected into the columns C3, C4, and C5, respectively, was not used and escaped in the off-gas. These results show that the amount of oxygen supplied into the columns were greater than the bioreactors needs most likely due to lower microbiological activity requirements of oxygen respect to its availability and/or because the existence of air preferential pathways. The values obtained show that even with higher air flow rate into column C5 the oxygen uptake was significantly lower respect to the aerated columns C2, C3, and C4, suggesting that higher aeration intensity doesn’t ensure higher oxygen uptake.

According to the results of methane production (Figure 7.2) and oxygen uptake compared to its availability (Figure 7.4), it is also possible to note that the oxygen supplied into the bioreactor C1 (the least aerated one) was not enough to complete the aerobic microbiological activity, indicating an existence of anaerobic spots within the waste body of the aerated bioreactor.

7.3 Leachate dissolved organic matter

Results of the parameters concerning organic substance analysed in leachate are reported in Figure 7.5, Figure 7.6, and Figure 7.7 for TOC, COD, and BOD_5, respectively.

At the beginning of the experiment all columns' TOC concentration in the leachate ranged similar values, except for column C1. At day 6 of the research bioreactors C0, C2, C3, C4 , C5 showed values of 444, 500, 585, 541, and 521 mg/L, respectively, while C1 had almost the double of the others (935 mg/L) due to heterogeneous nature of solid waste as commonly observed (Berge *et al.*, 2005). However, concentrations of TOC measured in the leachate of all columns are in a range of relatively low values as expected due to the age of the waste and previous degradation processes.

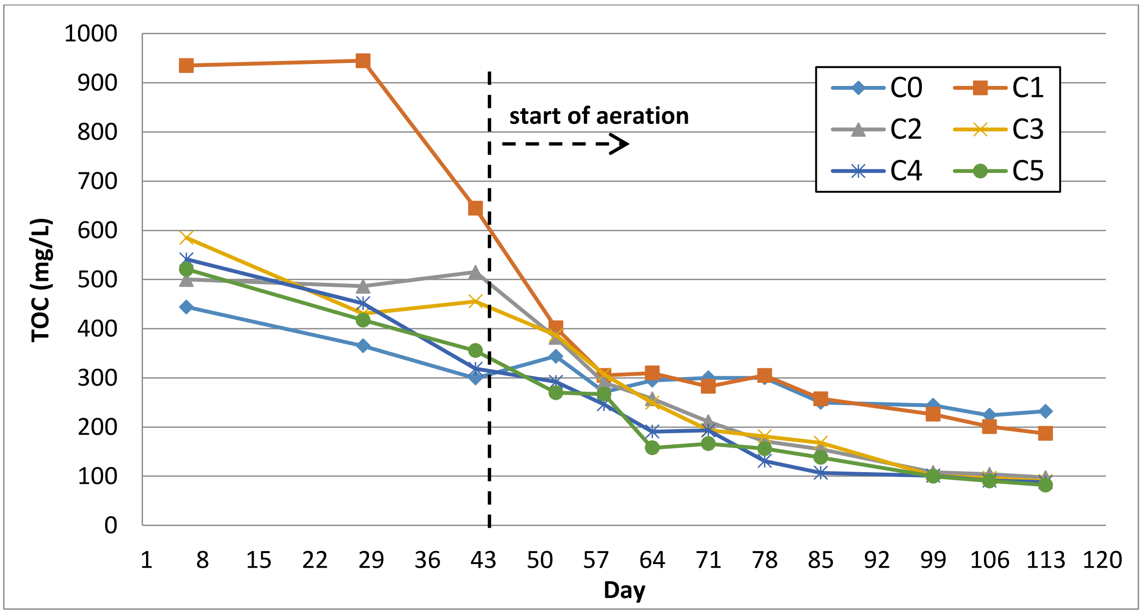

Figure 7.5 – TOC concentration evolution in the leachate.

At the beginning of aeration a decrease of TOC content in the leachate occurred in all aerated bioreactors with higher removal efficiency obtained in column C1. Since aerobic microorganisms are able to decompose organic compounds, which are resistant to anaerobic fermentation processes (Prantl *et al.*, 2006) this decrease was expected in the aerobic columns. At day 52 of the test TOC content in the aerated bioreactors C2, C3, C4, and C5 were 382, 387, 292, and 270 mg/L, respectively, and its concentration decreased to around 100 mg/L in the same columns after 47 days of aeration and remained stable towards the end of the research. The least aerated bioreactor (C1) had a concentration value of 402 mg/L at day 52 and it decreased to 183 mg/L at the end of experiment. The anaerobic bioreactor reported a slightly TOC decrease during the experiment, showing the highest final concentration (232 mg/L) in respect to the others reactors.

The results of COD concentration evolution show the same trend behaviour compared to the values obtained in total organic carbon analyses. The beginning of the experiment is characterized by similar low values in all columns, except C1 with a concentration of 1662 mg/L at the day 28 of the test (almost the double of the others reactors). During the aeration period higher decrease occurred in the column C1; however, final measured values of COD concentration were higher in the anaerobic bioreactor (472 mg/L) and in the least aerated one (392 mg/L). The last results of COD content in the leachate analysed in bioreactors C2, C3, C4, and C5 were 324, 302, 280, and 274 mg/L, respectively, presenting lower COD concentrations with higher air flow rates. Similar trend behaviours of COD in the leachate are reported in several experiments performed comparing anaerobic and aerobic bioreactors (Borglin *et al*., 2004; Prantl *et al*., 2006; Erses *et al.,* 2008; Raga and Cossu, 2013).

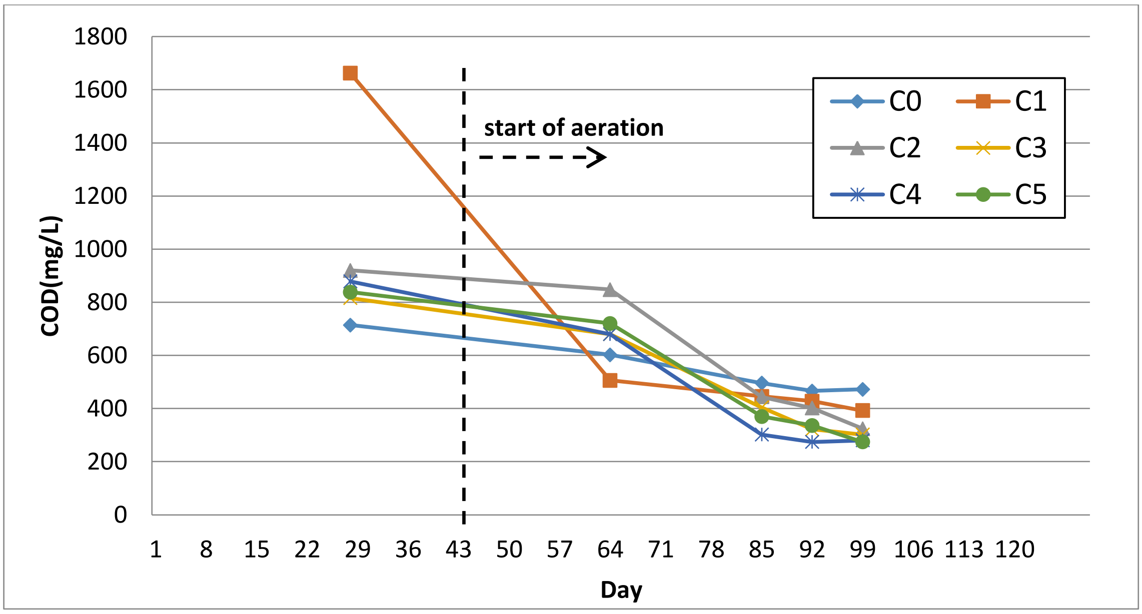

Figure 7.6 – COD concentration evolution in the leachate.

The values of BOD_5 concentration obtained at the beginning of the experiment were extremely low in all columns due to the age of the waste material and previous in situ aeration performed in the Legnago landfill. The results obtained correspond to the methane production behaviour trend observed. CH_4 composition obtained at day 42 of the test in columns C1, C2, and C3 were 39.1%, 22.3%, and 4.7%, respectively, while the BOD_5 concentration obtained at day 28 were 373.0, 133.0, and 98.7 mg/L, respectively. At the beginning of aeration a strong decrease occurred in all aerated bioreactors, principally in C1.

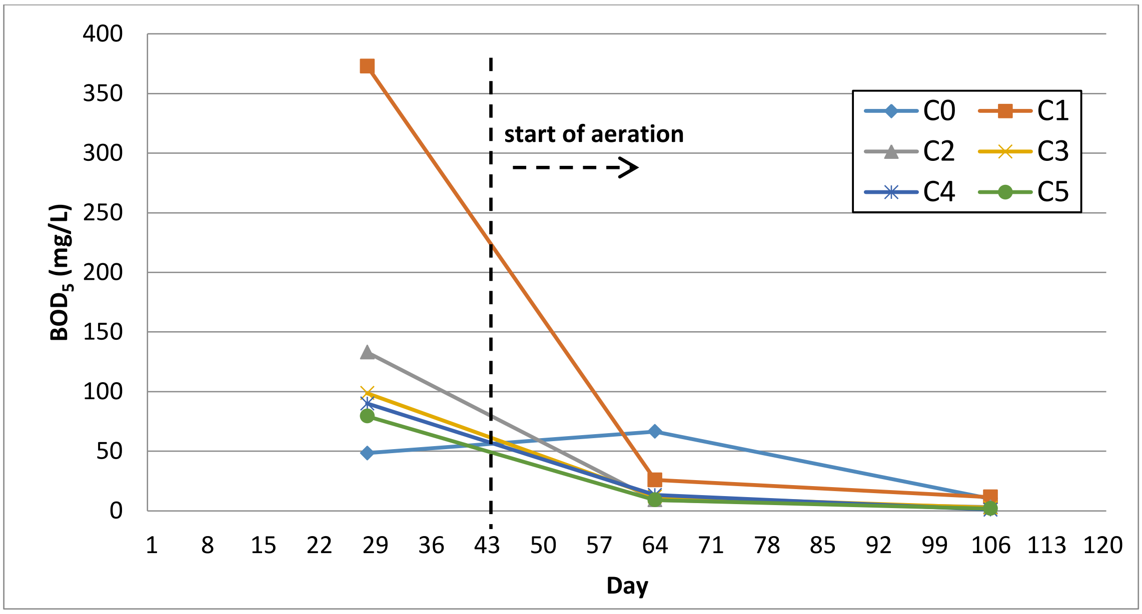

Figure 7.7 - BOD_5 concentration evolution in the leachate.

Although a slower and less efficiency of BOD_5 removal were expected in column C0, it should be noted that at day 64 of the experiment a value of 66.5 mg/L was obtained in the anaerobic bioreactor and its concentration decreased to 10.1 mg/L at day 106 of the test. At day 64 in which aeration flow rates were adjusted to the final set up, BOD_5 concentrations in the leachate of C1, C2, C3, C4, and C5 were 25.9, 9.1, 11.9, 13.3, and 9.12, respectively, and a similar values were observed at day 106 in which concentrations were 11.5, 3.13, 2.6, 0.89, and 1.82, respectively. These results reveal that very low values of BOD_5 were present in the leachate of the aerated columns during the aeration period.

7.4 Leachate pH and Alkalinity

The results of variation of pH and alkalinity present in the leachate during the experiment are reported in Figure 7.8 and Figure 7.9, respectively. The first samples analysis performed on both parameters were done on the 28th day of the running test and carried on throughout the end of the experiment.

At day 28 of the experiment pH values of all bioreactors were around 7.5. From this day to the day 42 of the research, pH in leachate of all columns dropped to values slightly above 7 indicating a small accumulation of organic acids in anaerobic phase. At the start of the aeration and leachate recirculation an overall increase has been reported showing the same trend and similar values in all bioreactor's leachate. The increase of the value in the anaerobic column could be explained by the start of methane production. As the methane gas production rate increases, hydrogen, carbon dioxide and volatile fatty acid concentrations decrease (Murphy *et al*., 1995). The conversion of fatty acids causes the pH within the waste cells to increase (Warith, 1999).

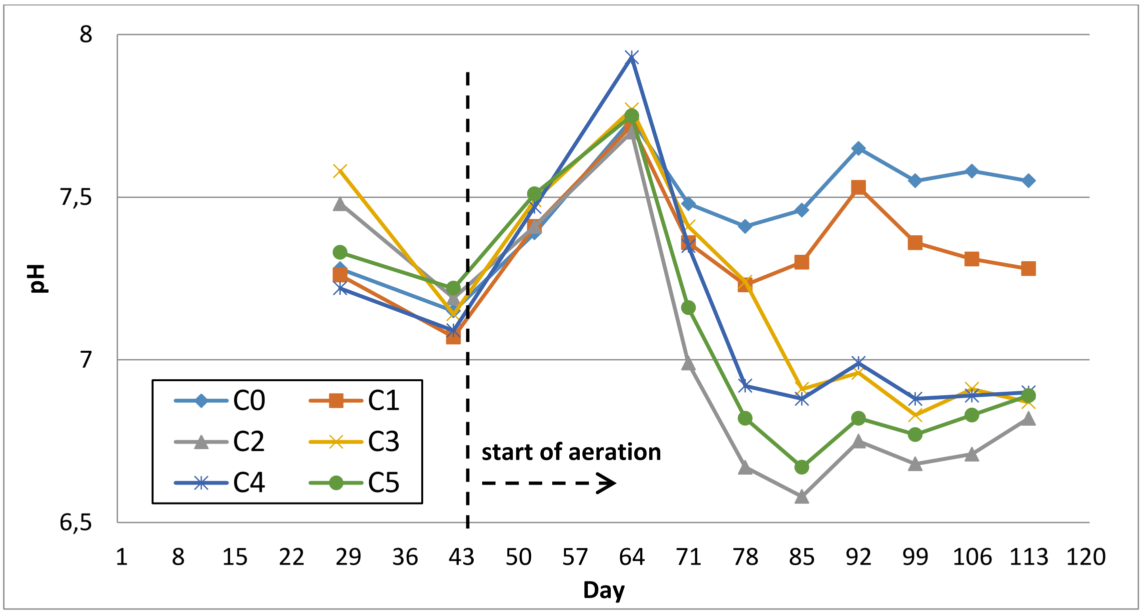

Figure 7.8 – pH evolution in the leachate.

Although mostly aeration leads to an increase of pH in the leachate (Xu *et al*., 2015), the results of the present study show a drop of pH in the most aerated bioreactors reaching values inferior to 7.0 after day 64, while the anaerobic one and the least aerated column having a pH drop to values around 7.5 after the same day. The results obtained could be explained by the strong nitrification processes and consequently higher and faster alkalinity consumption (Figure 7.9) in the most aerated bioreactors. Under aerobic conditions, ammonium nitrogen can be converted into NO_3^--N and release H^+, as shown in the equation (9) (Ko *et al*., 2016):

$$NH_4^+ + O_2 + H_2O \rightarrow NO_3^- + 5H^+ + 4e^- \qquad (9)$$

On the other hand, the NH_4^+ in leachate can be air stripped during the aeration process, resulting in pH decreasing as shown in equation (10) (Ko *et al*., 2016):

$$NH_4^+ \leftrightarrow NH_3 + H^+ \qquad (10)$$

Therefore, due to the high aeration flow rate, the pH in the leachate of columns C2, C3, C4, and C5 were lower than C0 (anaerobic) and C1 (the least aerated) after the establishment of final air flow rates set up in the columns.

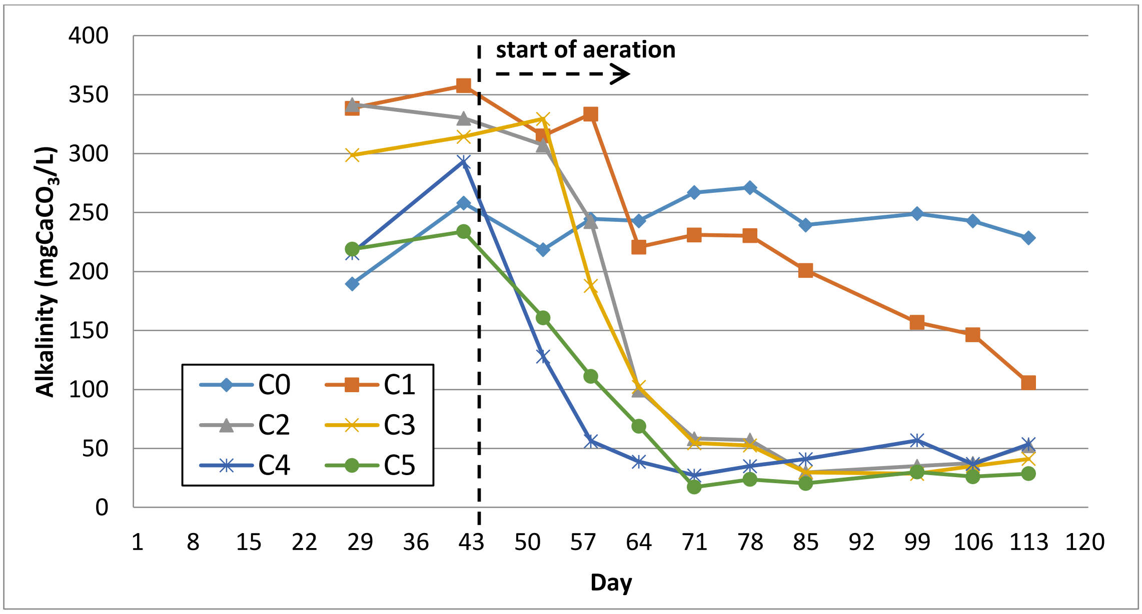

Figure 7.9 – Alkalinity concentration evolution in the leachate.

Alkalinity is mainly consumed due to the nitrification process, where 7.14 mg of alkalinity as $CaCO_3$ is destroyed per mg of ammonia nitrogen oxidized (Parker, 1975). The results obtained show a decrease of alkalinity in the leachate of all aerated columns after the start of aeration; however, faster and higher drop due to nitrification process is reported in the highly aerated bioreactors (C2, C3, C4, and C5). In this columns, alkalinity reached values inferior to 50 $mgCaCO_3/L$, while C1 reached a minimum value of 101 $mgCaCO_3/L$. The results of ammonium nitrogen oxidized that confirm the nitrification process are reported in the following chapter. Alkalinity in the anaerobic bioreactor remained around 250 $mgCaCO_3/L$ during the aeration period.

Research conducted by Raga and Cossu (2013) show similar results in terms of pH and alkalinity trend present in the leachate of aerated and anaerobic bioreactors. Berge *et al*., (2006) had also observed a drop in pH in aerobic systems, suggesting nitrification had occurred, since alkalinity is destroyed during nitrification.

7.5 Nitrogen removal

7.5.1 Ammonium nitrogen and TKN in the leachate

In order to understand the effects of different aeration rates and oxygen concentrations on nitrogen removal in the leachate, results of TKN and ammonia nitrogen concentrations in the bioreactors' leachate throughout the experiment are reported in Figure 7.10 and Figure 7.11, respectively. The form of NH_3-N present in solution is dependent on the solution pH. During the study, the pH was below 8.0; therefore, the dominant form of ammonia nitrogen is ammonium nitrogen (N-NH_4^+) (Berge *et al.*, 2006).

Before the start of aeration TKN concentrations values in the leachate were similar in all bioreactors, ranging from 834 mg/L to 1040 mg/L. As soon as the aeration started an evident decrease was observed in all aerated columns. A marked drop due to the amount of oxygen injection into the columns was even clearer when final air flow rates were set up in the bioreactors; the lowest TKN concentration results were obtained with higher air flow rate. In this respect, at day 92 of the experiment columns C2, C3, C4, and C5 showed values of 86, 82, 56, and 32 mg/L, respectively, while the least aerated one showed similar results in respect to the anaerobic one at the same day (759 mg/L and 801 mg/L in C1 and C0, respectively).

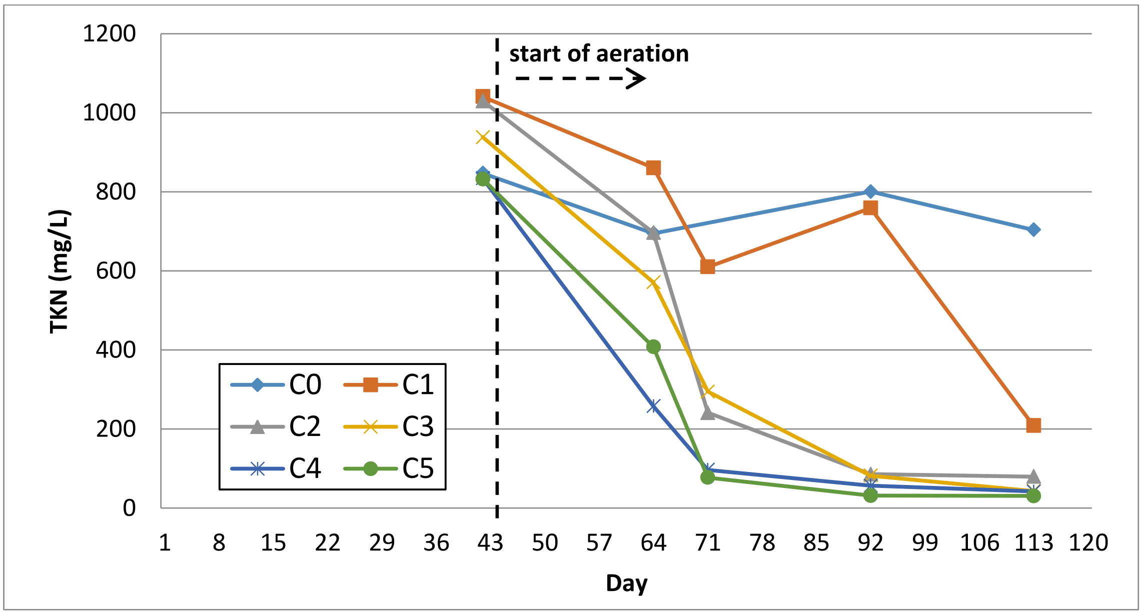

Figure 7.10 - TKN concentration evolution in the leachate.

In contrast to TOC concentration removal trend previously observed, the highest decrease of TKN concentration in column C1 occurred at the final part of the aeration period in which a drop from 759 mg/L at day 92 to a value of 208 mg/L at day 113 was observed, suggesting that at the beginning of aeration phase microbiological activity used the oxygen available mainly to TOC removal and at the end for nitrogen reduction. The values obtained in the anaerobic bioreactor remained relatively constant over the time course of the experiment.

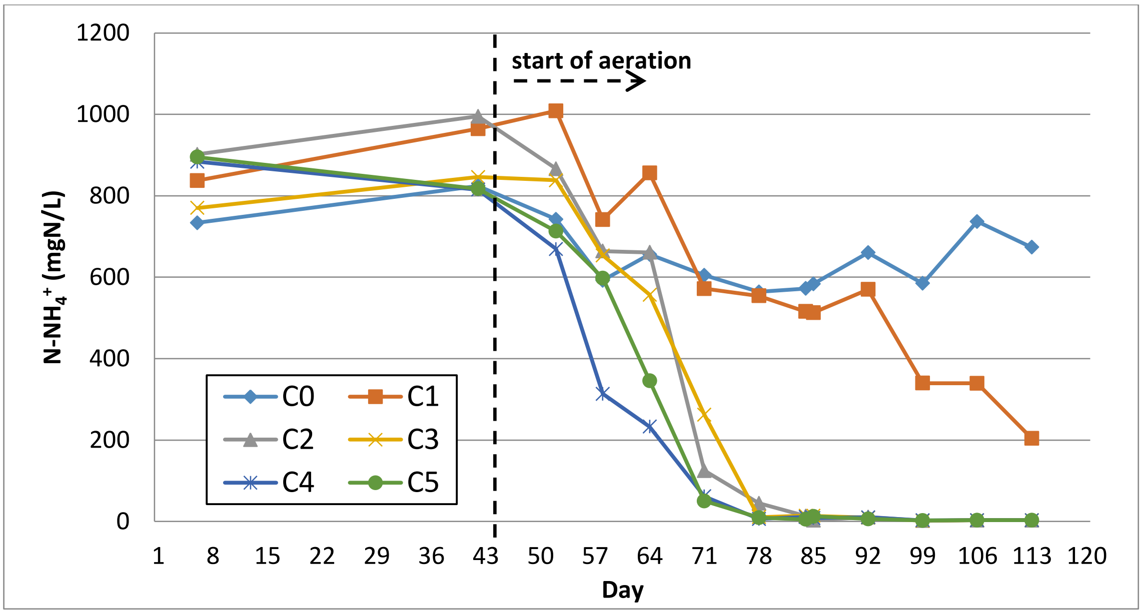

Figure 7.11 - Ammonium nitrogen concentration evolution in the leachate.

Before the start of aeration, ammonium nitrogen concentrations ranged from 815 mg/L to 995 mg/L and accounted from 70% to 96% of TKN. The same trend of TKN concentration behavior in leachate was observed as soon as the aeration started. After 55 days of aeration 99% of ammonium nitrogen removal was reached in columns C2, C3, C4, and C5. The aerobic bioreactor C1 behaved differently reporting an accumulation of ammonia nitrogen at the beginning of aeration followed by a efficiency removal of 75% at the end of the experiment, showing a less sharp decrease starting when other columns reached already an almost complete NH_4^+ depletion. As expected, ammonium nitrogen concentration in the leachate of anaerobic reactor remained relatively stable over the time course of the experiment because there is no degradation pathway for it in anaerobic environments (Berge *et al.*, 2005; Raga and Cossu, 2013).

7.5.2 Nitrogen transformation and removal processes

Analysis of nitrites and nitrates concentrations were performed in order to assess the nitrification and denitrification process that are generally expected to be the major cause for ammonium nitrogen removal in the leachate (Friedrich and Trois, 2016). Additionally, results for nitrites and nitrates concentration in leachate allow for a better comprehension of nitrogen flows and reactions inside the reactors in respect to oxygen content. Both parameters are reported in Figure 7.12 and Figure 7.13, respectively.

Nitrification is a two-step process in which ammonium nitrogen is firstly oxidized to nitrites and then nitrites to nitrates via microbiological activity within the waste body (Berge *et al*., 2005). The results are in accordance with nitrification process, showing that when oxygen started to be available, in the first time only nitrites have been produce through ammonium nitrogen oxidation. If oxygen is not available in sufficient amount to complete the oxidation into nitrates, nitrification process can be stopped at its first step (Parker, 1975).

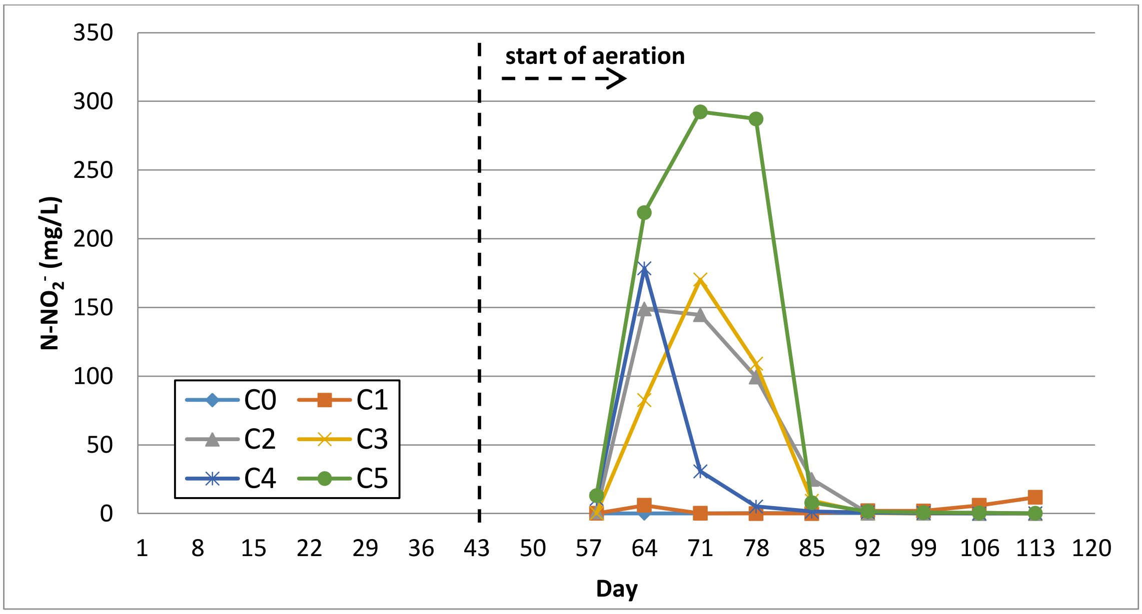

Figure 7.12 – Nitrites concentration evolution in the leachate.

Nitrites were found in the aerated bioreactors although its concentration value in column C1 was lower than 10 mg/L at day 64 and it was not detected again until day 105 of the research, indicating a late start of nitrification process in the least aerated column. The most aerated reactor reported the highest concentration of nitrites, having a peak of its value at day 71 of the experiment with 292.4 mg/L, while C2, C3, and C4 showed similar peak concentration values of approximately 160 mg/L.

According to the results of nitrates concentrations only the four columns with the highest air flow rate reported a significant concentration of nitrates in leachate indicating a complete nitrification process allowing ammonia oxidation into nitrates, having peak of its concentrations value of 12.9 mg/L in column C2 at day 71, 40.5 mg/L in bioreactor C3 at day 85, 221,3 mg/L in C4 at day 78, and 359.6 mg/L in C5 at day 92 of the experiment. Since alkalinity is destroyed when ammonia nitrogen is oxidized (Berge *et al*., 2005), the nitrification process in the four most aerated columns is in accordance with the evolution trend of alkalinity concentration in the leachate previously observed.

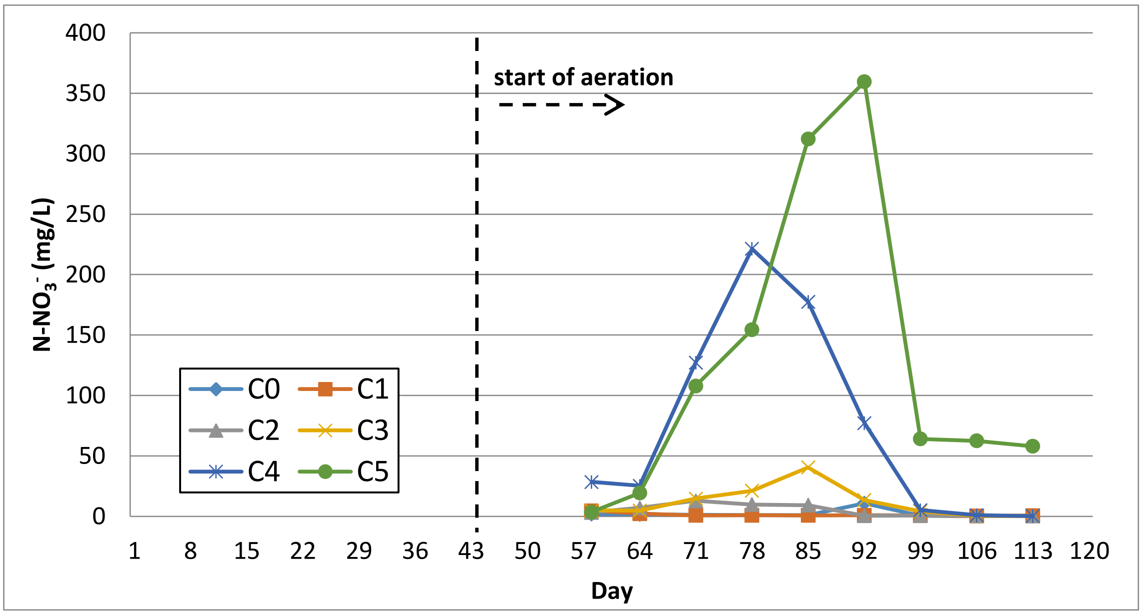

Figure 7.13 – Nitrates concentration evolution in the leachate.

Denitrification occurs through a biological process where denitrifying bacteria uses nitrate as electron acceptor if there is a lack or absence of oxygen (Kristanto *et al*., 2017). No matter the efficiency of aeration system, anaerobic or anoxic pockets might exist. In these microenvironments, sequential nitrification (in aerobic zone) and then denitrification (in anoxic/anaerobic zone) could occur (Tong *et al*., 2015). Results of the present study show a decrease of nitrates and nitrites concentration indicating that denitrification was actually occurring too, most likely due to the presence of anoxic spots within the waste mass of the columns, leading the transformation of nitrates into nitrogen gas (N_2) which is consequently dispersed in the outlet gas. Also, there exists the possibility that denitrification may happen in an aerobic condition which produces N_2O gas rather than N_2 gas (Takaya *et al*., 2003).

It should be noted that nitrates concentration in leachate of bioreactor C5 remained as high as 65 mg/L from the day 99 of the test until the final sample determination, suggesting that denitrification process stopped from that day probably due to the high aeration rate applied in which may have caused the absence of anaerobic conditions which are required for an optimum denitrification process. Additionally, the reach of stable nitrates concentrations in reactor C5 as well as the decrease to zero observed in reactors C2, C3, and C4 is due to the ammonium nitrogen complete removal preventing any new production of nitrites nitrogen and nitrates nitrogen.

Since heterotrophic denitrification requires high carbon source (Berge *et al*., 2006) the results of low carbon content in the present study indicate that autotrophic denitrification might have dominate the nitrate removal observed.

Although complete nitrification and denitrification process were not observed in column C1, ammonium nitrogen in the leachate was removed. Additionally, the values of nitrites and nitrates in the most aerated columns were not as high as predictable respect to the amount of ammonium nitrogen removed if these removal pathways were the only responsible for ammonium depletion. These results suggest that other processes were also affecting ammonium nitrogen removal.

The formation of free ammonia from ammonium ions may have occurred due to the increase of pH at the beginning of the aeration period (Canziani *et al*., 2006). It is highly possible that aeration agitated the leachate of the aerobic bioreactors, creating a removal pathway for dissolved free ammonia to volatilize. Similar findings are reported in Nikolaou *et al*. (2010). Additionally, it is possibly ammonium sorption in waste mass occurred through the leachate recirculation, creating a transformation pathway for ammonium nitrogen.

In reactor C1 there was no evidence that complete nitrification took place, since there was absence of oxygen and no significant changes were observed in nitrates concentrations during the experiment. At some point, an anaerobic mechanism appears to have started in C1. Possibly, production of nitrogen gas through anammox process may have happen in column C1.

7.5.3 Ammonium nitrogen removal and oxygen concentrations

In general, in situ aerobic stabilization processes have a significant potential for reducing landfill emissions but when operating at field-scale, costs can vary considerably, depending highly on site specific conditions (Ritzowski *et al.*, 2006). This way, it is very important to understand the pollutant removal efficiencies related to the amount of air injected (energy supply) into the landfill.

Because ammonium nitrogen is both persistent and toxic, it will likely influence when the landfill is biologically stable and when postclosure monitoring may end (Berge *et al.*, 2006). Ammonium nitrogen removal efficiencies in the leachate for each bioreactor respect to the oxygen supplied are reported in Table 7.4. The values reported correspond to day 99 of the experiment (i.e. 55^{th} day of aeration), when column C2, C3, C4, and C5 reached more than 99% of ammonium nitrogen removal in the leachate. The amount of oxygen supplied and uptake into each column before the air flow rates final adjustment were considered in order to obtain the results reported in the table. The oxygen content in the outlet was obtained as an average value.

Table 7.4 – Ammonium nitrogen removal aeration effiency at the 55^{th} day of aeration.

Column	**Air flow rate** (L/h)	**O_2 outlet gas** (%)	**O_2 uptake** (LO_2/kg)	**$N\text{-}NH_4^+$ removal efficiency** (%)	**Aeration efficiency** (mg $N\text{-}NH_4^+$ removed/ L O_2 supplied/kg)
C1	0,3	0,4	4,5	59,4	106,8
C2	0,5	1,3	5,1	99,8	168,4
C3	0,8	7,4	5,5	99,8	113,1
C4	1,0	9,0	4,9	99,6	108,1
C5	1,2	14,6	4,9	99,7	91,9

As expected, according to the results reported on the table above it is clear that the worst performance in terms of aeration efficiency was achieved by column C5 due to the higher excess amount of air injected related to its requirements (14.6% of O_2 in the outlet gas). Also, when comparing column C5 to the other aerated reactors, bioreactor C5 showed lower values of oxygen uptake over the time course of aeration period respect to the amount of air injected, suggesting lower oxygen needs due to lower microbiological activity and/or the existence of preferential pathways of the air injected which results in higher amount of waste not reached by the oxygen.

The results clearly show the best performance of reactor C2 in terms of ammonium nitrogen removal respect to the amount of air injected, being its value of 168.4 mg $N\text{-}NH_4^+$ removed/LO_2 supplied/kg of waste. With an average of 1.3% of oxygen content in the outlet gas during the aeration phase, this bioreactor was supplied with the second lowest air flow rate (0.5 L/h) which means lower costs in terms of energy supply required to maintain optimal conditions at field-scale.

Similar aeration efficiencies were obtained in reactors C1, C3, and C4, being its values of 106.8, 113.1, and 108.1 mg N-NH_4^+ removed/LO_2 supplied/kg, respectively. The results of column C1 show that an average of oxygen concentration in the outlet gas of 0.4% might be lower than the oxygen requirements for a faster ammonium nitrogen removal in the leachate compared to higher O_2 concentrations. This reactor showed the lowest values of oxygen uptake (4.5 LO_2/kg) indicating less use of oxygen compared to the other aerated columns due to the lowest O_2 availability. Only 59% of the ammonium nitrogen in the leachate of reactor C1 was removed at the 55th day of aeration period, while the others bioreactors reached more than 99% at the same day most likely because the lower amount of oxygen supplied into C1 delayed the nitrification process requirements. However, looking at the trend of ammonium nitrogen in leachate of C1 higher removal efficiency is observed, even though in a much longer time span.

7.5.4 Final solid analysis

Analyses on the waste mass of each bioreactor were carried out at the end of the experiment in order to compare the initial and final conditions. The results of Total Kjeldahl Nitrogen (TKN) and Respiration Index (RI_4) at the beginning and at the end of experiment are reported in Table 7.5.

Table 7.5 - Initial and final analysis of RI_4 and TKN on solid samples.

Parameter	**Column**					
	C0	**C1**	**C2**	**C3**	**C4**	**C5**
Start RI_4 (mgO_2/gDM)	1,1	1,1	1,1	1,1	1,1	1,1
End RI_4 (mgO_2/gDM)	0,7	0,8	0,5	0,4	0,3	0,5
Initial TKN (gN/kgTS)	2,2	2,2	2,2	2,2	2,2	2,2
End TKN (gN/kgTS)	1,4	1,8	1,8	1,6	1,1	0,9

According to the results of the analysis on solids samples at the end of the experiment it is clear that a decrease of respiration index in four days was observed in all reactors. However, lower values were obtained in the most aerated bioreactors C2, C3, C4, and C5, being its results of 0.5, 0.4, 0.3, and 0.5 mgO_2/kgTS, respectively. It should be noted that the value obtained in the most aerated column (C5) is the same as C2 and higher than C3 and C4. These results could be explained due to the existence of air preferential pathways within the waste mass which lead to portions of waste material not reachable by the oxygen.

The values obtained in the anaerobic bioreactor C0 and the least aerated one (C1) were 0.7 and 0.8 mgO_2/kgTS, respectively. It was expected to observe lower values of RI_4 in reactor C1 than C0. Similar results observed could be explained due to the same trend behavior evolution of many parameters analyzed on both reactors over the time course of the experiment, indicating the presence of anaerobic spots within the waste mass of reactor C1. However, very low values of RI_4 were obtained in all columns at the end of the research.

Many of the nitrogen transformation/removal process are favored by aerobic processes, including nitrification and ammonia air stripping or volatilization (Berge *et al*., 2005). In this respect, higher decrease in TKN on the solid sample at the end of the experiment was observed on the columns with the two highest air flow rate (i.e., C4 and C5). However, higher decrease of TKN concentration on the solid sample was observed in anaerobic bioreactor in respect to column C1, C2 and C3 most likely due to higher TKN content removed from leachate sampling in the anaerobic one over the time course of the research and, also, the waste is heterogeneous and portions of the landfill may contain different amounts of nutrients (Berge *et al.*, 2005) even if all the efforts have been done to ensure the best homogeneity of waste samples and identical analysis conditions. Therefore, more samples of different parts of the columns' waste body should have been collected and analyzed at the start and at the end of the experiment.

Nitrogen mass balance should be performed in order to have a better comprehension on nitrogen removal pathways and emissions. In this experiment, nitrogen gaseous compounds such as N_2, N_2O, and NH_3 were not monitored in the outlet gas over the time course of the running test. Therefore, a complete nitrogen mass balance was not performed.

7.6 Chlorides and sulphates in the leachate

Chloride is a non-degradable conservative parameter and the change of its concentration is commonly used to assess the variation of leachate dilution (Bilgili *et al*., 2006). Also, chloride may also be of major importance to aquatic toxicity (Clément and Merlin, 1995). According to Kjeldsen *et al.* (2002), decreasing trend in concentration of pollutant chloride with time could be due to wash out by the leaching.

The evolution of chlorides concentrations in the leachate are reported in Figure 7.14. According to the results observed there is no considerable change in Cl^- concentrations of leachate generated from all bioreactors. Similar decreasing trend was obtained due to the same amount of water added after sampling and same recirculation applied to the reactors.

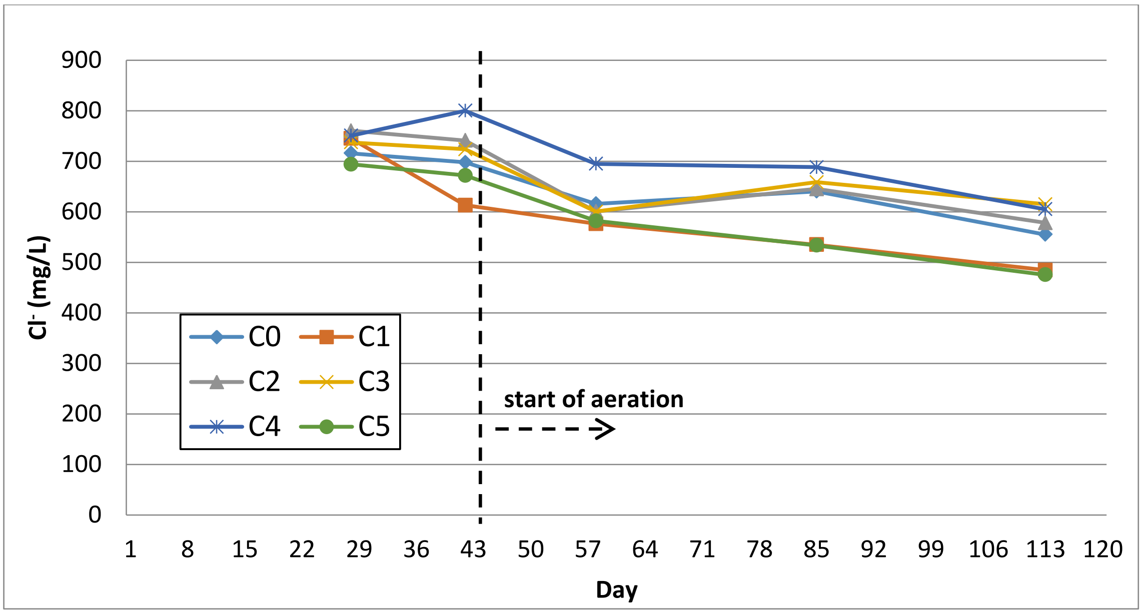

Figure 7.14 - Chlorides concentration evolution in the leachate.

Figure 7.15 shows the variations of sulphates concentrations throughout the experiment. With the oxygen provided into the aerobic reactors and the degradation of organic matter, higher sulphates concentrations were obtained in those characterized by higher oxygen concentrations, increasing to maximum values of 4286, 4398, 4698, and 5074 mg/L in reactors C2, C3, C4, and C5, respectively, after 30 days of aeration; while column C1 reached to its maximum value of 1006 mg/L after 22 days of aeration. The dramatic production of sulphate during aeration was expected and probably partly due to autotrophic denitrification processes (Berge *et al*., 2007).

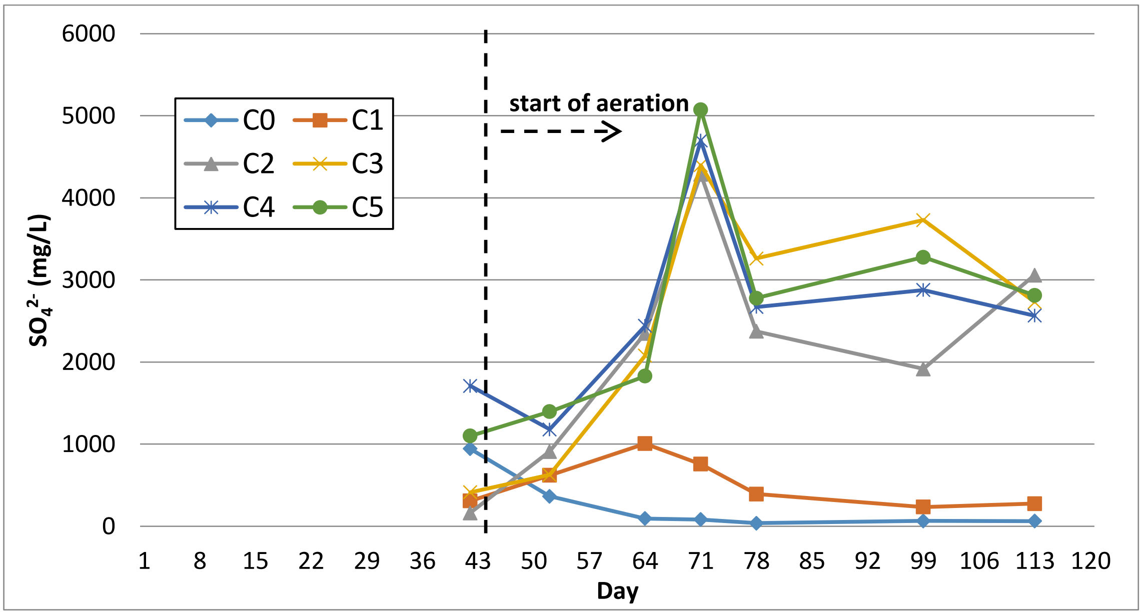

Figure 7.15 - Sulphates concentration evolution in the leachate.

Under anaerobic conditions, sulphate reducing bacteria can use organic compounds as an electron donor and sulphate as an electron acceptor, reducing sulphate to sulphide (Nikolaou *et al*., 2010). Thus, SO_4^{2-} concentration remained low in reactor C0 and a decline trend over the time course of the experiment was observed. Since column C1 showed similar behaviors in other parameters investigated during the test in respect to the control bioreactor, suggesting the existence of anaerobic spots within the waste mass, from the day 64 of the experiment until the end sulphate concentration in the leachate decrease trend in C1 was probably due to the microbial reduction of sulphate to sulphide under anaerobic conditions. By the end of the research the value of C1 was at the initial concentration level.

From day 78 of the research in the aerobic columns C2, C3, C4, and C5 sulphates concentration started to decrease gradually. The aeration of those reactors during the last 35 days did not have a significant impact the on the SO_4^{2-} concentration.

8 Conclusions and further developments

Before applying in situ aeration on a field-scale, column tests, such as those performed in this investigation, are useful to determine dimensioning criteria, such as the intensity of aeration required to reach an adequate stability. A comparison of landfill bioreactors operated under different aeration rates and one anaerobic, monitoring leachate and off-gas over the time course of the experiment led to different effects and evolution trends in terms of leachate reduction of emissions, remaining emission potential and aeration efficiency in respect to oxygen availability.

According to the results of this experiment, the anaerobic bioreactor landfill with municipal solid waste from Legnago Landfill, simulating the current re-disposal conditions, shows the highest level of leachate emissions, with the highest concentrations of COD, TOC and ammonium nitrogen. Better alternatives, in terms of nitrogen removal, were obtained with simulated aerobic bioreactor landfill.

Nitrification and denitrification process proved to be a crucial cause for ammonium nitrogen removal in the leachate on the most aerated bioreactors. However, nitrates accumulation was observed in the one operated with the highest air flow rate. It is possible that ammonium removal also occurred because aeration agitated the leachate, creating a removal pathway for dissolved free ammonia to volatilize. Ammonium transformation possibly happened due to ammonium sorption in waste mass through the leachate recirculation. In the least aerated column there was no evidence that complete nitrification took place and production of nitrogen gas through anammox process may have happen.

This study proved that oxygen concentration in the outlet gas is a more proper dimensioning and operational parameter than aeration flow rate itself in order to adjust the intensity of aeration required to reach the best performance of aerobic bioreactor landfills. It has been noticed that higher air flow rate doesn’t ensure higher oxygen consumption, probably due to the existence of air preferential pathways within the waste mass and/or because the heterogeneous nature of solid waste results in different oxygen requirements at distinct portions of the landfill. Therefore, the same air flow rate per kilograms of waste at separate portions of the same landfill may result in different performances. Adjusting the aeration intensity over time, according to the oxygen content in the off-gas, could allow the best performance of aeration efficiency in respect to pollutants removal.

It has been proved that the best performance of aeration efficiency, in terms of ammonium nitrogen removal regarding the amount of oxygen available, was obtained by the bioreactor supplied with the second lowest air flow rate and with an average value of 1.3% of oxygen in the outlet gas during the period of the definitive aeration rate set up. This bioreactor reached more than 99% of ammonium nitrogen removal in the leachate at the same day as the highest air flow rate columns. Additionally, it has been proved that lower aeration, which led to an average value of 0.4% of oxygen content in the outlet gas, might limit the nitrification processes. Therefore, the time span needed to reach the same ammonium removal efficiency as the others aerated bioreactors increases. However, in this case, leachate production tends to behave more similarly to anaerobic leachate conditions, resulting in no sulphate accumulation which means less ex situ treatment costs.

Further similar studies should be performed monitoring oxygen concentration within the waste mass in order to achieve a better comprehension of oxygen distribution which could allow for a better understanding of nitrification and denitrification processes. Additionally, in order to assess the feasibility of oxygen concentration in the outlet gas as a bioreactor landfill management parameter of aeration intensity, similar studies should be done on young waste. Also, gas monitoring of nitrogen compounds, such as N_2, N_2O and NH_3, allowing a nitrogen mass balance, should be performed in order to have a deeper comprehension of the nitrogen removal pathways.

9 References

Baig, S., Coulomb, I., Courant, P., and Liechti, P. (1999). Treatment of landfill leachates: Lapeyrouse and Satrod case studies. *Ozone Science Engineering*, 21, 1–22.

Barlaz, M.A., Rooker, A.P., Kjeldsen, P., Gabr, M.A., and Borden, R.C. (2002). A critical evaluation of factors required to terminate the postclosure monitoring period at solid waste landfills. *Environmental Science and Technology*, 36, 3457-3464.

Berge, N. D., Reinhart, D. R., and Townsend, T. (2005). The fate of nitrogen in bioreactor landfills. *Critical Reviews in Environmental Science and Technology*, 35, 365–399.

Berge, N.D., Reinhart, D., Dietz, J., and Townsend, T. (2006). In situ ammonia removal in bioreactor landfill leachate. *Waste Management*, 26, 334-343.

Berge, N.D., Reinhart, D.R., Dietz, J.D., and Townsend, T., (2007). The impact of temperature and gas-phase oxygen on kinetics of in situ ammonia removal in bioreactor landfill leachate. *Water Research*, 41, 1907–1914.

Bilgili, M.S., Demir, A., and Ozkaya, B. (2006). Influence of leachate recirculation on aerobic and anaerobic decomposition of solid wastes. *Journal of Hazardous Materials*, 143, 177-183.

Brandstätter, C., Laner, D., and Fellner, J. (2015a). Carbon pools and flows during lab-scale degradation of old landfilled waste under different oxygen and water regimes. *Waste Management*, 40, 100–111.

Brandstätter, C., Laner, D., and Fellner, J. (2015b). Nitrogen pools and flows during lab-scale degradation of old landfilled waste under different oxygen and water regimes. *Biodegradation*, 26, 399-414.

Burton, S., and Watson-Craik, I. (2002). Ammonia Fluxes in Landfills. *R&D Technical Report P1-306/TR*. Environment Agency, Rio House, Waterside Drive, Aztec West, Almondsbury, BRISTOL.

Canziani, R., Emondi, V., Garavaglia, M., Malpei, F., Pasinetti, E., and Buttiglieri, G. (2006). Effect of oxygen concentration on biological nitrification and microbial kinetics in a cross-flow membrane bioreactor (MBR) and movingbed biofilm reactor (MBBR) treating old landfill leachate. *Journal Membrane Science*, 286, 202–212.

Cestaro, S., Rossetti, D., and Cossu, R. (2006). Full-scale application of aerobic in situ stabilization of an old landfill in north of Italy. *Forth Intercontinental Landfill Research Symposium*, Gällivare, Sweden, 14-16 June.

Christensen, T.H., Kjeldsen, P., Albrechtsen, H.-J., Heron, G., Nielsen, P.H., Bjerg, P.L., and Holm, P.E. (1994). Attenuation of landfill leachate pollutants in aquifers. *Critical Reviews in Environmental Science and Technology*, 24, 119.

Clément, B. and Merlin, G. (1995). The contribution of ammonia and alkalinity to landfill leachate toxicity to duckweed. *The Science of the Total Environment*, 170, 71-79.

Cossu, R., Morello, L., Raga, R., and Cerminara, G. (2016). Biogas production enhancement using semi-aerobic pre-aeration in a hybrid bioreactor landfill. *Waste Management*, 55, 83-92.

Cossu, R., Raga, R., and Rossetti, D., (2003). The PAF model: an integrated approach for landfill sustainability. *Waste Management*, 23. 37-44.

EPA - Environmental Protection Agency. (2017). *Bioreactor Landfills*. From URL: https://www.epa.gov/landfills/bioreactor-landfills (Acceded: 08-07-2017).

EPA – Environmental Protection Authority. (2009). *Waste guidelines – Waste definitions*. From URL: https://www.google.pt/url?sa=t&rct=j&q=&esrc=s&source=web&cd=5&cad=rja&uact=8&ved=0ahUKEwiEltDZwa7WAhVIrxoKHRgCCnsQFghLMAQ&url=http%3A%2F%2Fwww.epa.sa.gov.au%2Ffiles%2F4771336_guide_waste_definitions.pdf&usg=AFQjCNF5hKMiKNqe6JjwuXYJsjkQmI8GMQ (Acceded: 18-09-2017).

Erses, A.S., Onay, T.T., and Yenigun, O. (2008). Comparison of aerobic and anaerobic degradation of municipal solid waste in bioreactor landfills. *Bioresource Technology*, 99, 5418–5426.

Farquhar, G.J., and Rovers, F.A. (1973). Gas production during refuse decomposition. *Water, Air, and Soil Pollution*, 2, 483-495.

Friedrich, E., and Trois, C. (2016). Current and future greenhouse gas (GHG) emissions from the management of municipal solid waste in the Thekwini Municipality e South Africa. *Journal Cleaner Production*, 112, 4071-4083.

He, P., Yang, N. Gu, H., Zhang, H., and Shao, L. (2011). N_2O and NH_3 emissions from a bioreactor landfill operated under limited aerobic degradation conditions. *Journal of Environmental Sciences*, 23. 1011-1019.

Heavey, M. (2003). Low-cost treatment of landfill leachate using peat. *Waste Management*, 23, 447-454.

Hrad, M., Gamperling, O., and Huber-Humer, M. (2013). Comparison between lab- and fullscale applications of in situ aeration of an old landfill and assessment of long-term emission development after completion. *Waste Management*, 33. 2061-2073.

Hull, R. M., Krogmann, U.M., and Strom, P.F. (2005*).* Composition and Characteristics of Excavated Materials from a New Jersey Landfill. *Journal of Environmental Engineering*, 131, 478-490.

IRSA-CNR - Istituto di Ricerca sulle Acque Consiglio Nazionale delle Ricerche. (2003). *Metodi analitici per le acque.* APAT, Roma, Italy.

Jani, Y., Kaczala, F., Marchand, C., Hogland, M., Kriipsalu, M., Hogland, W., and Kihl, A. (2016). Characterisation of excavated fine fraction and waste composition from a Swedish landfill*. Waste Management & Research*, 34, 1292–1299.

Jetten, M.S.M., Wagner, M., Fuerst, J., van Loosdrecht, M., Kuenen, G., and Strous, M. (2001). Microbiology and application of the anaerobic ammonium oxidation ('anammox') process. *Current Opinion Biotechnology*, 12, 283-288.

Kjeldsen, P., Barlaz, M.A., Rooker, A.P., Baun, A., Ledin, A., and Christensen, T.H. (2002). Present and Long-Term Composition of MSW Landfill Leachate: A Review*. Critical Reviews in Environmental Science and Technology*, 32, 297–336.

Ko, J.H., Ma, Z., Jin, X., and Xu, Q. (2016). Effects of aeration frequency on leachate quality and waste in simulated hybrid bioreactor landfills*. Journal of the Air & Waste Management Association*, 66, 1245-1256.

Koenig, A., and Lui, H. (1996). Autotrophic denitrification of landfill leachate using elemental sulphur. *Water Science Technology,* 34, 469-476.

Kristanto, G.A., Rialdi, H., and Gusniani, I. (2017). Nitrogen removal from landfill leachate via ex-situ nitrification and in-situ denitrification in laboratory scale bioreactor. *Procedia Engineering*, 171, 425-433.

Long, Y., Long, Y.-T., Liu, H.-C., Shen, D.-S. (2009). Degradation of refuse in hybrid bioreactor landfill. *Biomed. Environ. Sci*. 22, 303-310.

Lou, Z.Y., Wang, L.C., Zhu, N.W., et al., (2015). Martial recycling from renewable landfill and associated risks: A review*. Chemosphere*, 131, 91–103.

Merz, R.C., and Stone, R. (1970). Special studies of a sanitary landfill. *National technical information service*, Washington, DC, Report NTIS PB 196 148.

Mönkäre, T.J., Palmroth, M.R.T., and Rintala, J.A. (2017). Screening biological methods for laboratory scale stabilization of fine fraction from landfill mining. *Waste Management*, 60, 739–747.

Murphy, R.J., Jones, D.E., and Stessel, R.I. (1995). Relationship of microbial mass and activity in biodegradation of solid waste. *Waste Management and Research*, 13, 485-497.

Nag, M., Shimaoka, T., and Komiya, T. (2016). Impact of intermittent aerations on leachate quality and greenhouse gas reduction in the aerobic–anaerobic landfill method*. Waste Management*, 55, 71-82.

Nikolaou, A., Giannis, A., and Gidarakos, E., (2010)*.* Comparative studies of aerobic and anaerobic treatment of MSW organic fraction in landfill bioreactors*. Environmental Technology*, 31, 1381-1389.

Parker, D.S. (1975). *Process Design Manual for Nitrogen Control*. Brown & Caldwell, Walnut Greek, California.

Prantl, R., Tesar, M., Huber-Humer, M., and Lechner, P. (2006). Changes in carbon and nitrogen pool during in-situ aeration of old landfills under varying conditions. *Waste Management*, 26, 373-380.

Raga, R., and Cossu, R. (2013). Bioreactor tests preliminary to landfill in situ aeration: A case study. *Waste Management*, 33, 871-880.

Raga, R., and Cossu, R. (2014). Landfill aeration in the framework of a reclamation project in Northern Italy. *Waste Management*, 34, 683–691.

Raga, R., Cossu, R., Heerenklage, J., Pivato, A., and Ritzkowski, M. (2015). Landfill aeration for emission control before and during landfill mining. *Waste Management*, 46, 420-429.

Reinhart, D.R., and Townsend, T.G. (1997). *Landfill Bioreactor Design and Operation.* Lewis Publishers: New York.

Renou, S., Givaudan, J.G., Poulain, S., Dirassouyan, F., and Moulin, P. (2008). Landfill leachate treatment: Review and opportunity. *Journal of Hazardous Materials*, 150, 468–493.

Rittman, B.E., and McCarty, P.L. (2001). *Environmental Biotechnology: Principles and Application.* McGraw Hill, New York.

Ritzkowski, M. Stegmann, R. (2012). Landfill aeration worldwide: Concepts, indications and findings. *Waste Management*, 32, 1411-1319.

Ritzkowski, M., Heyer, K.-U., and Stegmann, R. (2006). Fundamental processes and implications during in situ aeration of old landfills. *Waste Management*, 26, 356–372.

Shao, L-M., He, P.-J., and Li G.-J. (2008). In situ nitrogen removal from leachate by bioreactor landfill with limited aeration*. Waste Management*, 28. 1000-1007.

Slezak, R., Krzystek, L., and Ledakowicz, S. (2010). Simulation of aerobic landfill in laboratory scale lysimeters – effect of aeration rate. *Chemical Papers*, 64. 223-229.

Sun, X., Zhang, H., and Cheng, Z. (2017). Use of bioreactor landfill for nitrogen removal to enhance methane production through ex situ simultaneous nitrification-denitrification and in situ denitrification. *Waste Management*, 66, 97-102.

Takay, N.M.A.B., Catalan-Sakairi, Y., Sakaguchi, I., Kato, Z. and Zhou, Z. (2003). Aerobic denitrifying bacteria that produce low levels of nitrous oxide. *Applied Enviromental Microbiology*, 69, 3152-3157.

Tamru, A. T. (2015). Effects of Landfilled MSW Stabilization Stages on Composition of Landfill Leachate: A Review. *National Conference on Recent Advancement in Civil & Environmental Engineering RACEE-2015*, 28-29 November.

Thampan, A., and Chandel, M.K. (2015). Bioreactor Landfill Technology. *International Journal of Science and Research*, 4, 6.

Tiquia, S.M., and Tam, N.F.Y. (2000). Fate of nitrogen during composting of chicken litter. *Environmental Pollution*, 100, 535-541.

Tong, H., Yin, K., Giannis, A., Ge, L., and Wang, J.-Y. (2015). Influence of temperature on carbon and nitrogen dynamics during in situ aeration of aged waste in simulated landfill bioreactors. *Bioresource Technology*, 192, 149-156.

Tong, H., Yin, K., Giannis, A., Ge, L., and Wang, J-Y. (2015). Influence of temperature on carbon and nitrogen dynamics during in situ aeration of aged waste in simulated landfill bioreactors. *Bioresource Technology*,192, 149–156.

Warith, M. A. (1999). Advantage of leachate recirculation on municipal solid waste biodegradation: experimental and field results. *Transactions on Ecology and the Environment*, 26, 1743-3541.

Waste Management. (2004). *The bioreactor landfill – Next generation landfill technology*. From URL: http://www.wm.com/thinkgreen/pdfs/bioreactorbrochure.pdf (acceded: 11-07-2017).

Xu, Q., Jin, Z., Ma, Z., Tao, H., and Ko, J.H. (2014). Methane production in simulated hybrid bioreactor landfill. *Bioresourource Technology*, 168, 92–96.

Xu, Q., Y. Tian, S.Wang, and J.H. Ko. (2015). A comparative study of leachate quality and biogas generation in simulated anaerobic and hybrid bioreactors. *Waste Management*, 41, 94-100.

Yao, P. (2013). Perspectives on technology for landfill leachate treatment. *Arabian Journal of Chemistry*, 10, 2567–2574.