João Filipe Valverde Cardoso

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Fate of nitrogen in bioreactor landfills: Lab-scale *in situ* aeration in well decomposed MSW

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Orientador: Prof. Doutora Ana Isabel Espinha da Silveira, Professor Auxiliar, Faculdade de Ciências e Tecnologias – Universidade Nova de Lisboa
Co-orientador: Prof. Doutor Roberto Raga, Assistant Professor, DICEA – Università degli Studi di Padova

Júri:

Presidente: Prof. Doutora Maria da Graça Madeira Martinho
Arguente: Prof. Doutor António Pedro de Macedo Coimbra Mano
Vogal: Prof. Doutora Ana Isabel Espinha da Silveira
Vogal: Prof. Doutor Roberto Raga

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À minha madrinha

(To my godmother)

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Resumo

Atualmente na Europa a gestão de resíduos sólidos urbanos prossegue novas tendências como a reciclagem e a compostagem. Contudo, os aterros sanitários continuam a ter um papel importante nessa gestão, de facto, de acordo com o SOER 2012, no ano 2010 37% dos resíduos sólidos urbanos tiveram como destino final a deposição em aterro sanitário na Europa a 27. A perspetiva futura demonstra que a deposição de resíduos em aterro manter-se-á uma opção válida nos próximos anos.

Os aterros sanitários têm um elevado período de pós-encerramento sendo que pelo menos 30 anos de monitorização são legalmente exigidos. Um dos principais parâmetros para atingir a estabilização de um aterro sanitário é: o lixiviado não deverá conter elevadas concentrações de matéria orgânica, azoto amoniacal e metais pesados.

Sendo assim, a operação de um aterro sanitário como um bioreactor aeróbio tornou-se uma técnica aceitável para diminuir o período de pós-encerramento, reduzindo também os custos do tratamento de lixiviado.

No presente estudo seis reactores cheios com resíduos sólidos urbanos muito degradados foram arejados e várias injecções quer de azoto amoniacal quer de nitrato (1000mg N/l) foram realizadas com o intuito de compreender as transformações do azoto sob estas condições. Nomeadamente os processos de nitrificação e desnitrificação, e a possível volatilização de amónia foi igualmente monitorizada.

Os resultados demonstraram que o azoto amoniacal foi removido com sucesso dentro de um intervalo de 99,0 a 99,7%. O nitrato, aquando da presença de carbono facilmente degradável, foi removido num intervalo de 89,9 a 99%, no entanto sob condições de resíduos sólidos urbanos decompostos apenas 40,8 a 56,6% de remoção de nitrato foi atingido.

Quer a desnitrificação autotrófica quer a heterotrófica foram avaliadas com o objetivo de compreender se a primeira ocorre e que eficiência ambas revelam na remoção de nitrato.

Palavras-chave: Aterro sanitário aeróbio, remoção de azoto, desnitrificação autotrófica e heterotrófica, recirculação de lixiviado.

Abstract

In Europe nowadays waste management is following new trends as recycling and compost processes. However, landfilling continues to have an important role in waste management, in fact, according to SOER 2012, by the year of 2010 37% of MSW was landfilled on EU-27 countries. The future perspective shows that landfilling will continue to be a valid option in the years to come.

Landfills have an elevated post-closure time, since at least 30 years of monitoring are legally required. One of the main parameters to achieve landfill stabilization is: the leachate should not contain high concentrations of organics, ammonia, or heavy metals.

With this regard operating a landfill as an aerated bioreactor as became an acceptable technique to diminish the aftercare period in the landfill, reducing also the costs of the leachate treatment.

In this study six reactors filled with well decomposed MSW are aerated and several ammonium nitrogen and nitrate nitrogen injections (1000 mg N/l) were performed in order to understand the fate of nitrogen under these conditions. Specifically, nitrification and denitrification processes, and a possible volatilization of free ammonia was also monitored.

The results shows that ammonium nitrogen was successfully removed in a range of 99,0 to 99,7%. Nitrate, when in the presence of readily available carbon, was removed in a range of 89,9 to 99%, however under well decomposed MSW conditions only 40,8 to 56,6% of nitrate nitrogen removal was achieved.

Both autotrophic and heterotrophic denitrification were also assessed in order to understand whether the first occur and which is the obtained efficiency of nitrate removal in both cases.

Key words: Aerobic landfill, nitrogen removal, Autotrophic and heterotrophic denitrification, leachate recirculation.

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Glossary of abbreviations

MSW	Municipal Solid Waste
LFG	Landfill Gas
BOD_5	Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
TOC	Total Organic Carbon
NH_4^+	Ammonium Ion
NO_3^-	Nitrate Ion
SO_4^{2-}	Sulphate Ion
N_2	Nitrogen Gas
CH_3COONa	Sodium Acetate
CH_3COONH_4	Ammonium Acetate
NH_4Cl	Ammonium Chloride
KNO_3	Potassium Nitrate
$CaCO_3$	Calcium Carbonate

1 Introduction

In Europe nowadays waste management is following new trends as recycling and compost processes. However, landfilling continues to have an important role, in fact, according to SOER 2012, by the year of 2010 37% of waste was landfilled on EU-27 countries. The future perspective shows that landfilling will continue to be a valid option in the years to come.

Thus, landfill management needs to be improved in order to become more cost-effective and environmentally efficient. The aftercare period is a potential target period to be improved because at least 30 years of monitoring are required before the landfill to be considered stable. Leachate treatment is another aspect to be improved because is known that is one of the most costly processes in the landfill operation (Berge *et al*., 2006).

With this regard several studies were taking place in the last two decades, firstly with simple water or leachate recirculation to keep the moisture content as well as improve the methane production and carbon content depletion (Warith *et al*., 2005). However, this technique comes with a problem, the ammonium nitrogen accumulation in the leachate and the difficulty to treat it (Pohland, 1995).

To deal with this problem another research subject has taken place, *in situ* aeration. This technique is pointed out as an effective nitrogen removal option, because leachate is nitrified and denitrified inside landfill waste body (Onay and Pohland, 1998).

The present study aims to achieve some knowledge to help the field-scale implementation and decision making in the way of manage a bioreactor landfill with *in situ* aeration system. Denitrification in the old portions of a landfill had been studied but further knowledge is needed to understand the behaviour in well decomposed waste, characterized by the low biodegradable carbon content. Under such conditions denitrification could be limited by the lack of carbon as electron donor (Price *et al*., 2003). Thus, autotrophic denitrification has been found to be a possible pathway to remove nitrate from the leachate (Onay and Pohland, 2001). In this experiment denitrification as well as nitrification processes were tested and nitrogen removal was assessed with resource to six reactors filled with well decomposed waste.

Thus the questions to be answered by this dissertation are: i) Is ammonium nitrogen removed in well decomposed waste, and which is the removal rate? ii) Is nitrate removed in well decomposed waste and which is the removal rate? iii) Did the addition of an external carbon source improve the nitrate removal from the landfill leachate? iv) Did autotrophic denitrification play an important role in denitrification in well decomposed waste?

1.1 Dissertation organization

The document is divided in five chapters. The first one, Introduction, establishes the scope of the dissertation, the relevance of the problem and the objectives to achieve with the study.

In chapter 2, Literature revision, the state of the art in bioreactor landfill technique is presented. As well as a review of the nitrogen transformation processes that can possibly occur in a landfill environment. Relevant examples of bioreactor landfill aeration implementation in field scale and laboratory scale are described in order to understand better the possibilities and weaknesses of manage a landfill as an aerated bioreactor.

In chapter 3, Methodology, the experimental methodology describes the materials, the analytical techniques and the experimental chronology. Calculations and assumptions are also developed in this chapter.

In chapter 4, Results and discussion, the results are shown by reactor in order to understand the evolution of the leachate characteristics on each individual reactor. Leachate characterization and carbon content are revealed along with off-gas sampling values. Discussion of each subject is made in the same section where the respective results are presented in order to achieve an answer for the study objectives.

In chapter 5, Conclusion and future perspectives, based on chapter 4 evaluations, a conclusion of the study is made, pointing some recommendations and strategies for landfill management. The accomplishment of the objectives is evaluated and limitations are identified. Some future recommendations and perspectives are advanced.

2 Literature revision

2.1 Literature revision approach

Literature revision was elaborated starting with the description of bioreactor techniques applied until now. The several variants of aeration technique are described as well. Following, the traditional treatments of leachate are listed, and then several nitrogen transformation processes that possibly occur in a bioreactor landfill body are exposed. In the end, laboratory and field scale studies are presented in order to identify the processes and the efficiency of nitrogen removal that are known until today.

2.2 Bioreactor landfills: the concept

There are several methods and technologies available to manage a landfill. In the past decades anaerobic model has been the most used worldwide. However, landfill management techniques have been modified to create more sustainable ways, in economically and environmentally aspects. Thus, managing landfills as bioreactors has becoming a promising technique (Ritzkowsi *et al*., 2006; Read *et al*., 2001).

Bioreactor landfill is a sanitary landfill site that uses enhanced microbiological processes to transform and stabilize the readily and moderately decomposable organic waste constituents within 5 or 8 years of bioreactor process implementation. The bioreactor landfill increases significantly the extent of organic waste decomposition, conversion rates and process effectiveness over those that otherwise occur within the traditional landfill sites (Warith *et al*., 2003).

Stabilization means that the environmental performance measurement parameters (landfill gas (LFG) composition and generation rate, and the leachate constituent concentrations) remain at steady levels, and should not increase in the event of any partial containment system failures beyond the lifetime of the bioreactor (Warith *et al*., 2003). Barlaz *et al.* (2002) also refers that the leachate safety criteria should be:

- The leachate should not contain high concentrations of organics, ammonia, or heavy metals;
- The leachate should not exhibit toxicity to the organisms in the ecosystem;
- The landfill should not be releasing gas that may cause contamination of ground water supplies, odor nuisances, or explosions.

A bioreactor landfill site requires specific management activities and operational modifications to enhance and accelerate microbial decomposition processes. The single most important aspect for effective operation is liquid addition and management. Other strategies, including waste shredding, pH adjustment, nutrient addition and balance, waste pre-disposal and post-disposal conditioning, and temperature management, may also contribute to optimize the bioreactor process (Warith *et al*., 2003). The successful operation of bioreactor landfill also requires the development and implementation of focused operational and development plans to ensure that optimal conditions for bioprocesses exist and to allow the system to function effectively (Warith *et al*., 2003).

Odour emission is one of the aspects that the stakeholders often point as negative. However, according to Read *et al*. (2001), minimal NH_3 and H_2S odours were detected in aerobic bioreactors. In fact, compared with conventional landfill less pungent, organic odours indicative of composted waste were detected. From a public acceptance perspective, this benefit can be important to solid waste planners during the sitting of new landfills or to address odour complaints at existing ones.

Bioreactor landfills have been explored in four different configurations: anaerobic bioreactor landfills, aerobic bioreactor landfills, facultative and hybrid bioreactor landfills (Berge *et al*., 2005).

2.2.1 Anaerobic bioreactor landfills

Anaerobic bioreactor landfills are those in which moisture addition is practiced. Sources of liquid addition may include groundwater, storm water, infiltrating rainfall, or leachate. By leachate recirculation the time required for waste degradation is reduced, the quality is improved and the gas rate production is enhanced (San and Onay, 2001). Bioreactor landfill systems as a modification of conventional landfill with the addition of leachate recirculation were developed to minimize environment impacts through optimizing waste degradation. Here, leachate is collected, stored and reinjected back into the landfill to promote *in situ* anaerobic biological degradation (Erses *et al*., 2008).

In anaerobic bioreactors waste degradation is enhanced and organic material is returned to the landfill via leachate recirculation, methane is produced at a much faster rate. 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, allowing a more efficient capture and subsequent use (Francois *et al*., 2007).

Anaerobic bioreactor landfills are more effective at degrading the solid waste than conventional landfills. However, when compared to other types of bioreactor landfills, anaerobic systems tend to have lower temperatures and slower degradation rates (Ritzkowski *et al*., 2006; Cossu *et al*., 2003).

A disadvantage to operating the landfill as an anaerobic bioreactor is the accumulation of ammonia nitrogen. In anaerobic environment the ammonia nitrogen present in the leachate is continually returned to the landfill where there is no degradation pathway for it (Francois *et al*., 2007; Price *et al*., 2003; Cossu *et al*., 2003; Onay and Pohland, 1998).

An advantage of operating the bioreactor anaerobically when compared to other bioreactor landfill types is that air is not added. Therefore, the potential costs are less than what would be incurred aerobically and methane can be captured and reused (Berge *et al*., 2005).

2.2.2 Aerobic bioreactor landfills

The basic technical concept of the aeration of the landfill body consists on a system of gas wells, through which atmospheric oxygen is led into the landfill body via active aeration in such a way that an accelerated aerobic stabilization of deposited waste is realized. Simultaneously, the low-contaminated waste gas is collected and treated in a controlled manner by means of further gas wells. Aeration is achieved using low pressures and is continuously adjusted to meet the oxygen demand so that energy consumption is low and constantly optimized (Heyer *et al*., 2005).

Aeration on landfills has two major advantages comparing with anaerobic or conventional landfills: the nitrogen removal as well as the shorter period of organic degradation process (Ritzkowski *et al*., 2006; Berge *et al*., 2005; Warith *et al*., 2003).

Another important advantages of aeration comparing with anaerobic landfills are the increased settlement, decreased metal mobility, reduced ex-situ leachate treatment required, lower costs in leachate management and methane control, and reduced environmental liability (Warith *et al*., 2003; Read *et al*., 2001).

During aerobic degradation of MSW, biodegradable materials are converted mostly to carbon dioxide and water. Low methane levels are produced which may be viewed as either an advantage or disadvantage, depending on whether methane collection and used as an energy source is desired or required. Methane is a potent green-house gas, thus, if it cannot be efficiently controlled in anaerobic landfills, its production can be a local environmental concern. Furthermore, the solid waste environment during aerobic degradation has a fairly neutral pH (Berge *et al*., 2006; Read *et al*., 2001), which decreases metal mobility.

Volatile organic acid production is decreased in aerobic bioreactors because the anaerobic fermentation processes are limited. However, volatile acid and methane production may still occur in anaerobic pockets within the landfill (Berge *et al.*, 2005).

The aerobic process generates a considerable amount of heat, leading to elevated *in situ* temperatures as high as 66ºC (Raga and Cossu, 2013; Rich *et al*, 2008). The elevated temperatures increase evaporation, which results in a significant loss of leachate. As a consequence, there is less leachate to manage (Read *et al*., 2001). Additionally, the combination of the high temperatures and presence of air may create a fire potential. However, by minimizing methane production and ensuring moisture contents, fire potential is lessened (Berge *et al*., 2005).

Aerobic bioreactor landfills favours nitrogen transformation processes including nitrification, ammonia stripping and volatilization. Air stripping and volatilization may be favoured in aerobic bioreactor landfills than in anaerobic ones due to 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).

Both laboratory and field-scale studies have been conducted showing the effectiveness of the aerobic bioreactor landfill system (Hrad *et al*., 2013). Some examples of practical applications of the technique are presented in section 2.6.

Ritzkowski and Stegmann, (2012) summarizes the existing types and concepts of aeration mechanisms performed in aerobic bioreactor landfills:

2.2.2.1.1 High pressure aeration

High pressure aeration is a technique mostly used in landfill mining projects, due to the requirement of a widely bio-stabilization treatment in a range of several years. Aeration is realised by shock pressure releases, with pressures up to 6 bars, from lances using air which might be enriched by additional oxygen (up to 20%) and potentially by nutrients. The air is distributed by a compressed air distribution network. Each lance features a quick-release valve which is intermittently opened once a specified positive pressure has been built-up. The released aeration gas is capable of penetrating both highly and weakly compacted waste materials (Ritzkowski and Stegmann, 2012).

In figure 2.1 is represented the conceptual scheme of pressured aeration. In order to minimize the uncontrolled release of off-gases an extraction system of suction lances is installed. The extraction system is operated in parallel with the aeration and has an increased extraction capacity of 30%, in comparison to the inlet gas volumes. It collects the off-gases and conducts them to a treatment that could be achieved by means of biofilters and/or activated carbon (Ritzkowski and Stegmann, 2012).

The disadvantage of this technique is the intensive supply of energy and materials such as the industrial air.

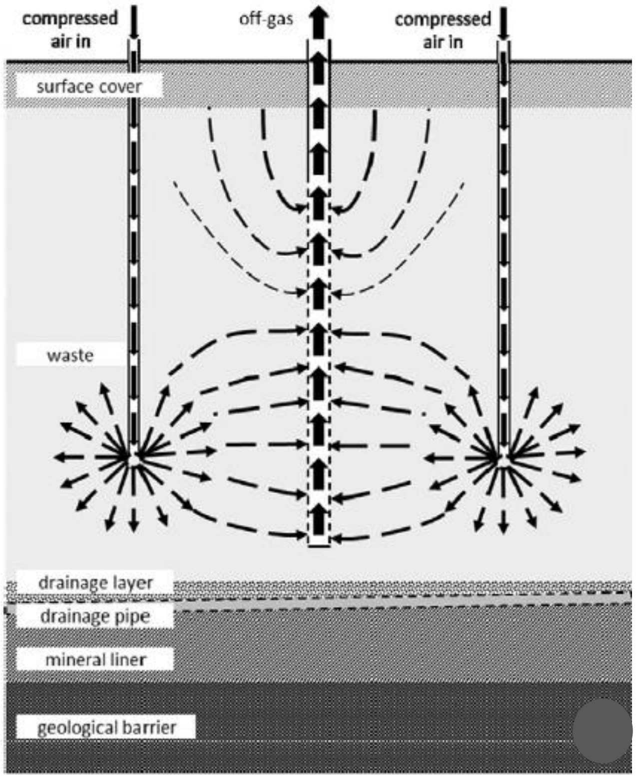

Figure 2.1 High pressure aeration. Adapted from: Ritzkowski *et al.* 2012)

2.2.2.1.2 Low pressure aeration

Low pressure aeration is characterized by a range of positive pressures of 20 to 80 mbar. This technique is the mostly applied in the landfill aeration cases with the goal of accelerate *in situ* biological waste stabilization. In figure 2.2 a., b. and 2.3. some variants of the low pressure technique are schematized, the main differences are in the off-gas systems. These variants are (Ritzkowski and Stegmann, 2012):

- Active aeration with off-gas extraction:

This concept was design with simultaneous air supply and extraction operation. It works using a system of vertical gas wells where ambient air is continuously introduced into the landfill waste body (Fig. 2.2 a.). Convection and diffusion are the air distributing processes, and then air is simultaneously directed through the extraction system. The extraction system as well as the aeration system consists in gas wells connected to an air compressor and the final off-gas purification stage. This simultaneous supply and extraction operation offers advantages in terms of flexibility because air can be targeted to be introduced in areas where there is a deficient oxygen supply. At the same time the air flow inside the waste mass can be manipulated through the selection of the air supply and extraction wells location.

- Active aeration without off-gas extraction

In this concept the landfill cover acts like a biological filter layer, the cover can be enhanced on its biological methane oxidation capacity. Additionally, air supply is executed without an off-gas extraction system, thus it can result in a significantly lowered emission reduction compared with the combined systems (Fig. 2.2 b.). The aeration can be done by two methods: through gas wells in the waste body or through air injection in the unsaturated soil zone beneath the wastes. For the latter case, the soil functions as an air distribution layer aiming at an even aeration of the wastes from bottom to top.

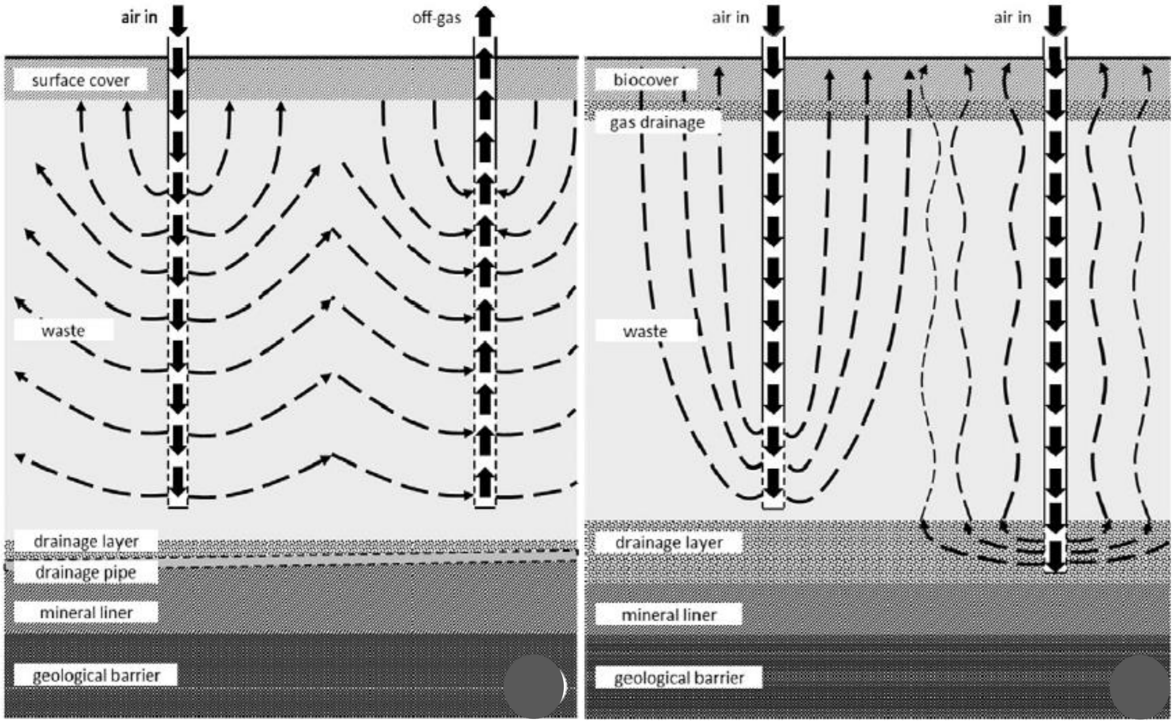

Figure 2.2 a) Active aeration with off-gas extraction; b) Active aeration without off-gas extraction. (Adapted from: Ritzkowski *et al*. 2012)

- Air venting

Passive aeration concepts follow the basic approach of air venting (*i.e.*, the introduction of ambient air into the landfill through its surface or eventually through open gas wells) driven by a negative pressure induced inside the landfill body (fig. 2.3). The gas wells are perforated only in the deeper waste layers in order to increase the waste volume to be reached by the aeration and to avoid short circuits near the landfill surface. To ensure a gradual aeration, starting at the surface before shifting into the deeper layers, extracted gas volumes are significantly higher than the gas production rate of the landfilled waste (Ritzkowski and Stegmann, 2012).

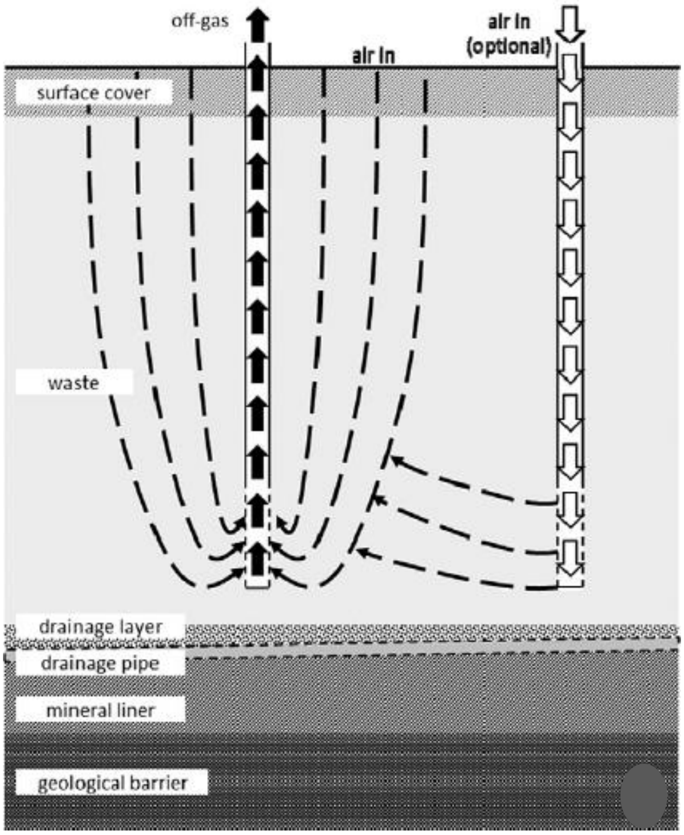

Figure 2.3 Air venting. (Adapted from: Ritzkowski *et al*. 2012)

2.2.2.1.3 Semi-aerobic concept

The concept of semi-aerobic landfills is actually the oldest in regard to landfill aeration. Back in 1975, the first semi-aerobic landfill was developed in Japan. In these, the leachate collection system consists of a central perforated pipe (main collection pipe) with perforated branch pipes on either side laid at a suitable interval. The pipes are embedded in graded gravel (5–15 cm) and installed with adequate slope. The main collection pipe ends in an open leachate collection pond. The pipes are designed in a way that only one-third of the section is filled with liquid. At each intersection of the main collection pipe with the branch pipes, and at the end of each branch pipe, vertical gas ventilation wells enclosed in graded gravel (eventually packed inside a wire netting) are erected. The air will be able to flow into the waste layer through these pipes when the leachate head is low. Since the two piping systems are connected, ambient air and landfill gas flows through the leachate collection pipes and the gas ventilation wells, thus, enhancing the intrusion of the air into the inner part of the landfilled wastes occasionally (Fig. 2.4).

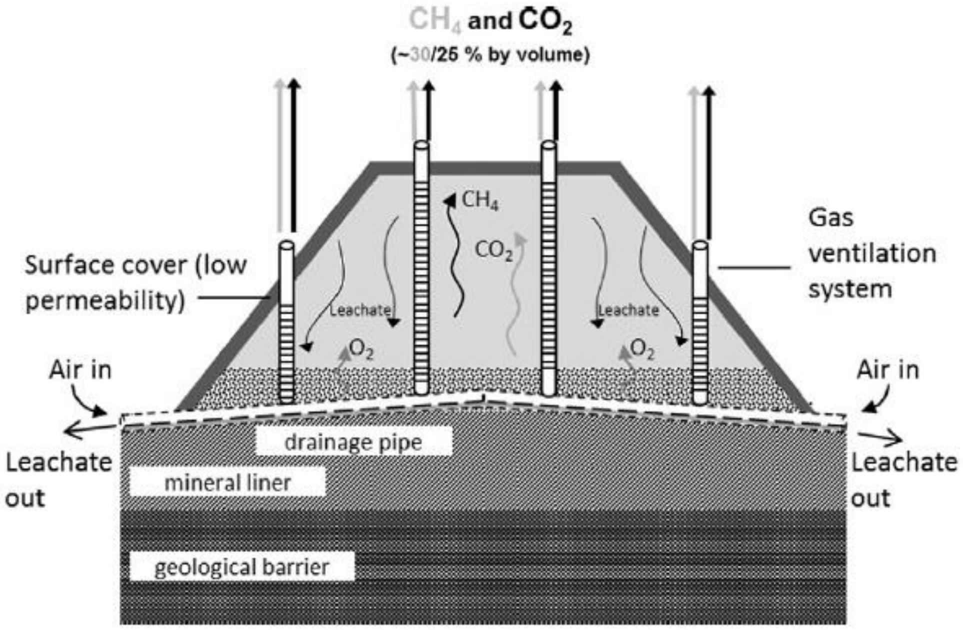

Figure 2.4 Semi-aerobic bioreactor landfill technique (adapted from: Ritzkowski and Stegman, 2012).

Due to higher temperatures in the waste (compared to the ambient air), the gas inside the waste tends to rise and gets vented through the gas wells, thus, generating a negative pressure siphoning effect that draws more air into the leachate collection pipes (Ritzkowski and Stegmann, 2012).

2.2.3 Facultative bioreactor landfills

Facultative bioreactor landfills are operated with the intent of actively degrading the waste mass and, at the same time, controlling high ammonia nitrogen concentrations typically found in the leachate from bioreactor landfills (Ritzkowski and Stegmann, 2012; Berge *et al*., 2005).

In facultative systems, leachate is removed from the bioreactor landfill and nitrified in an external treatment system prior to recirculation. Thus, the ammonia nitrogen concentrations of the treated leachate are low to non-existent, while the nitrate levels are high. As the nitrate-rich leachate is recirculated and passes through the landfill the denitrification occurs (Price *et al*., 2003).

A disadvantage of this method 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 (Berge *et al*., 2009). Additionally, while denitrification of the leachate is occurring, methane production may be ceased until the nitrate is consumed. It has been shown that methane production quickly resumes after nitrate is depleted (Price *et al*., 2003).

2.2.4 Hybrid bioreactor landfills

This type of bioreactor landfill is still in the early stages of development. Hybrid bioreactor landfills involve the combination of both aerobic and anaerobic conditions. Two types of these systems have been explored: short term cycling of air injection into landfill and sequencing of aerobic and anaerobic conditions (Berge *et al*., 2005).

The first, cycling of air injection into the landfill, is defined as a pattern of alternating *in situ* aerobic and anaerobic conditions that is repeated throughout the life-cycle of the landfill, while sequencing of air-injection into landfill involves an initial aerobic phase, followed by a final anaerobic phase. Because there are many advantages associated with both aerobic and anaerobic degradation processes, researchers admit combining the process as a valid way to maximize the potential of a bioreactor landfill (Rich *et al.*, 2008; Berge *et al*., 2005).

For example hard degradable components like lignin and aromatic compounds are recalcitrant under anaerobic conditions but degradable in aerobic conditions. The combination between these two environments could increase the leachate treatment quality. Hybrid systems could also be combined to complete nitrogen removal allowing processes as nitrification and denitrification (Berge *et al*., 2005; Onay and Pohland, 1998).

2.3 Aerobic bioreactor landfill technique: field application

In a landfill management situation the application of *in situ* aeration should be an available option. There are some evident objectives during the lifetime of a landfill or even in a situation of remediation of an old waste deposit where aeration is a clear answer for the problem. The presented situations are considered by Heyer *et al.* (2005) as field problems where aeration is applicable, they could be divided by both bottom and top boundaries:

Bottom sealing:

- Landfills with bottom sealing: if the objective is decreasing leachate contamination which, in a long term, still exceeds the requirements for direct discharge;
- Landfills without bottom sealing: where a potential risk of water contamination exists, aeration is a subject of protection.
- Old deposits: where technical barriers would be too cost-intensive or technically unfeasible.

Surface sealing:

- Aeration should be an option before the installation of a surface sealing in order to prevent concentration and gas migration at low landfill gas production, and to anticipate the landfill settlement.

- In landfills where gas collection and treatment is still necessary but economic utilization of methane as an energy source is no longer possible, aeration comes with the aim of avoid a long-term and cost-intensive poor gas treatment.
- In surrounding areas where landfill gas must be kept free, aeration should be an option before any measures were taken.

2.4 Nitrogen in landfill leachate

Ammonium nitrogen is originated by biological decomposition of nitrogen content in MSW, *i.e.* organic waste, green wastes etc. Protein hydrolyses and fermentation produce ammonium nitrogen (Burton and Watson-Craik, 1998). It concentration could range from almost inexistent to 5 000 mg/l (Reinhart and Townsend, 1998; Qasim and Chiang, 1994). Leachate composition is quite variable, depending highly on waste composition, moisture content of the waste, and age of landfill (Berge *et al*., 2005).

Removal of ammonium nitrogen from leachate is necessary because of its aquatic toxicity and oxygen demand in receiving waters. Barlaz *et al*. (2002) have concluded that ammonium nitrogen significantly contributes to the toxic nature of the leachate. In landfill leachate, the vast majority of the ammonium nitrogen species will be in the form of ammonium ion (NH_4^+) because pH levels are generally less than 8,0 (Read *et al*., 2001; Reinhart and Townsend, 1998).

2.4.1 Nitrogen removal processes

The conventional methods based on physical, chemical and biological processes are (Tchobanoglus *et al.*, 1993):

- Activated sludge, responsible for the removal of organics;
- Nitrification, responsible for the removal of nitrogen;
- Neutralization, responsible for pH control;
- Chemical Precipitation, responsible for the removal of metals and some anions;
- Ion exchange, responsible for the removal of dissolved inorganics;
- Filtration and/or flotation/sedimentation, responsible for suspended matter removal;
- Air stripping, responsible for ammonia or VOC;
- Evaporation, responsible for leachate concentration.

Those treatments require a dedicated wastewater plant, or can be pumped to municipal waste water facilities if the leachate criteria are according to what is required by the municipal authorities. Thus, leachate treatment is costly in the initial capital as well as in its operation during the landfill lifetime.

According to Cossu *et al*. (2003), Bilgili *et al*. (2006) and Berge *et al*. (2005), in bioreactor landfills the nitrogen removal is possible. However, there are several issues that can limit the nitrogen removal processes. The heterogeneous nature of solid waste complicates the nitrogen cycle in bioreactor landfills. Because of this, portions of the landfill may contain different amounts of nutrients, be at different temperatures, have different moisture content, and may be at different oxy-reduction potential. Environmental conditions greatly affect the transformation and removal of nitrogen. Thus, within one landfill cell, there may be many nitrogen transformation processes occurring simultaneously or sequentially.

2.5 Nitrogen transformation processes

According to the different chemical, physical and biological characteristics of a specific area, nitrogen has diverse transformations pathways. The most significant nitrogen transformations that can occur in bioreactor landfills are presented in the following sections.

2.5.1 Ammonification

Proteins present in the waste are the main source of ammonia nitrogen. This conversion of organic nitrogen to ammonia-nitrogen by heterotrophic bacteria is termed ammonification. Ammonification is a two-step process consisting of the enzymatic hydrolysis of proteins by aerobic and anaerobic microorganisms releasing amino acids and the subsequent deamination or fermentation (depending on aerobic vs. anaerobic conditions) of the acids to carbon dioxide, ammonia-nitrogen, and volatile fatty acids (Burton and Watson-Craik, 1998). During deamination, amine groups are liberated to form ammonia or ammonium, depending on the pH, and alkalinity is slightly elevated (Burton and Watson-Craik, 1998).

Once ammonification occurs, the ammonia nitrogen is dissolved in the leachate and is ready to be transformed and/or removed via volatilization, sorption, or biological processes when in an aerobic environment (Berge *et al*., 2005).

2.5.2 Nitrification

Nitrification is a two-step aerobic process in which ammonia nitrogen/ammonium is microbially oxidized to nitrite and nitrate via obligate aerobe, autotrophic microorganisms. Because nitrification is an aerobic process, it is almost non-existent in conventional landfills and in bioreactor landfills in which air is not added (Jiang *et al*., 2007; Cossu *et al*., 2003). In those systems, nitrification is restricted to upper portions of the landfill or the cover where air may infiltrate (Onay and Pohland, 1998). In landfills in which air is purposely added, nitrification can be a significant nitrogen removal pathway (Raga and Cossu, 2013).

During the first step of nitrification, *Nitrosomonas* bacteria oxidize ammonia nitrogen to nitrite, according to the following reaction (Rittman and McCarty, 2001):

$$NH_4^+ + 1{,}5\ O_2 \text{ -> } NO_2^- + 2H^+ + H_2O \qquad \text{(eq. 1)}$$

The second step of the nitrification process is the oxidation of nitrite to nitrate by *Nitrobacter* bacteria according to the following reaction (Rittman and McCarty, 2001):

$$NO_2^- + 0{,}50\ O_2 \text{ -> } NO_3^- \qquad \text{(eq. 2)}$$

Nitrifiers must fix and reduce inorganic carbon to use as their carbon source (Rittman and McCarty, 2001), resulting in low cell yields and thus small maximum specific growth rates. Additionally, nitrification results in the consumption of alkalinity as nitrous acid is formed. Additionally, 7,14 g of alkalinity, expressed as $CaCO_3$, are consumed for each gram of oxidized $N\text{-}NH_4^+$ (Tchobanoglous *et al.*, 2003). The first step of nitrification is often the limiting step, as the *Nitrosomonas* bacteria grow more slowly than *Nitrobacter* or *Nitrospira* (Tchobanoglous *et al.*, 2003).

Nitrification may occur in bioreactor landfills in which air is added. Although the metabolic processes associated with nitrification may be essentially the same in landfills and wastewater treatment processes, the operation, control, and potential extent of such processes is not the same. Nitrification in landfill environments is complicated by oxygen and temperature limitations, heterotrophic bacteria competition, and potentially pH inhibition (Jun *et al.*, 2007; Berge *et al*., 2005).

Oxygen is a required element for nitrification. Adding air to a landfill would be dual-purpose: to nitrify, removing the ammonium nitrogen, and to enhance the degradation of solid waste (Erses *et al*., 2008). However, maintaining and controlling sufficient oxygen levels within the landfill, especially considering the heterogeneous nature of solid waste and the high temperatures characteristic of aerobic landfills, may be difficult and may result in oxygen limitations (dissolved oxygen concentration declines with temperature increases) and thus reduced nitrification rates (Berge *et al*., 2005). Additionally, oxygen may become limiting to nitrifiers in areas within the landfill containing large amounts of organic carbon (newly placed waste) due to competition with heterotrophs.

In well decomposed waste, more recalcitrant organics, such as humic acids, are present. In leachate collected during the methanogenic stage of degradation, almost 60% of the dissolved organics present were in the form of high molecular weight compounds (*i.e.* humic and fulvic acids) (Kjeldsen *et al*., 2002). Humic acid has been shown to inhibit nitrification, resulting in the accumulation of nitrite concentrations. However, since well decomposed waste had a low concentration of biodegradable organic matter, the development of heterotrophic bacteria is apparently low making well decomposed waste indicated as a good ability to nitrify (Hoilijoki *et al.*, 2000).

Alkalinity consumption in nitrification process may be a limitation since typical leachate alkalinity has a range of 1 000 to 10 000 mg $CaCO_3$/l (Tchobanoglous *et al*., 1993) and may not be enough. Thus, is possible that alkalinity need to be added to the landfill to buffer the leachate, otherwise alkalinity consumption could cause a drop in pH levels.

2.5.3 Denitrification

Denitrification is the conversion of nitrate to N_2 by heterotrophic and autotrophic bacteria, depending on the nature of the electron donor (Vigneron *et al*., 2007).

In situ denitrification is also complicated in solid waste systems, although it may be easier to implement than nitrification. Denitrifiers are more robust than nitrifiers, however, they require a sufficient organic carbon source for high nitrate removal rates (Price *et al*., 2003). Because of the carbon needs, denitrification may occur most efficiently in young waste, rather than in older, partially oxidized waste. Price *et al*. (2003) evaluated the potential need for an external carbon source in the laboratory and noted that a fresh layer of refuse contained sufficient carbon to stimulate significant nitrate consumption. If a sufficient organic carbon source is not readily available, partial denitrification may occur which may lead to the production of harmful intermediates (N_2O and NO), which are potent greenhouse gases (Khalil *et al*., 2004).

Typically, *in situ* denitrification occurs in anaerobic bioreactor landfills. However, because of the potential for anoxic pockets to be present in aerobic systems, denitrification may also occur in portions of aerobic bioreactor landfills that air does not reach (Raga and Cossu, 2013; Berge *et al*., 2005).

2.5.3.1 Heterotrophic denitrification

Denitrification is an anoxic process that reduces nitrate to nitrite, nitric oxide, nitrous oxide, and finally nitrogen gas, as shown in reactions (Rittman and McCarty, 2001):

$$NO_3^- + 2\,e^- + 2H^+ \rightarrow NO_2^- + H_2O \qquad \text{(eq. 3)}$$

$$NO_2^- + e^- + 2H^+ \rightarrow NO + H_2O \qquad \text{(eq. 4)}$$

$$2NO + 2e^- + 2H^+ \rightarrow N_2O + H_2O \qquad \text{(eq. 5)}$$

$$N_2O + 2e^- + 2H^+ \rightarrow N_{2\,(g)} + H_2O \qquad \text{(eq. 6)}$$

Typically, denitrifying bacteria are heterotrophic, facultative aerobes, which use nitrate as an electron acceptor when oxygen is absent or limiting (Tchobanoglous *et al.*, 2003). A potential advantage of denitrification is the simultaneous carbon and nitrate destruction without requiring oxygen supply. It is important to note that processes in which nitrate is used as a terminal electron acceptor are energetically favoured over acetogenic, sulphate reduction, and methanogenic processes. Thus in landfills in anaerobic/anoxic environments in which nitrate reduction occurs, inhibition of such processes may occur (Price *et al*., 2003).

pH is a main parameter in heterotrophic denitrification, Oh *et al*. (2001) suggests that the optimal range of pH for this type of denitrification is from 7 to 8. In heterotrophic denitrification bicarbonate alkalinity is produced and carbonic acid concentrations are reduced during denitrification. Thus, theoretical alkalinity production is 3,57 mg $CaCO_3$ per mg of nitrate nitrogen reduced to nitrogen gas (Oh *et al*., 2001).

2.5.3.2 Autotrophic denitrification

Nitrate removal in wastewaters containing high sulphur concentrations or reduced sulphur sources, such as hydrogen sulphide, may occur via autotrophic denitrification. *Thiobacillus denitrificans* use an inorganic sulphur source (*i.e.* H_2S, S, SO_3^{2-}) rather than an organic carbon source when reducing nitrate to nitrogen gas according to reaction (Koenig and Liu, 2001):

$$1{,}06\ NO_3^- + 1{,}11\ S + 0{,}3\ CO_2 + 0{,}785\ H_2O \text{ -> } 0{,}5\ N_2 + 1{,}11\ SO_4^{2-} + 1{,}16\ H^+ + 0{,}006\ C_5H_7O_2N \qquad \text{(eq. 7)}$$

Autotrophic denitrification may occur in landfills, especially in older landfills or older portions of landfills where the carbon to nitrogen ratio may be low. According to Sun *et al.* (2012), autotrophic denitrification was the main process for nitrate removal, when the biodegradable COD/N-NO_3^- ratio in the leachate was lower than the stoichiometric ratio of heterotrophic denitrification. In their study, using cloning and genetic analyses, the autotrophic *T. denitrificans* group had the main role in nitrate removal in the absence of easily biodegradable organic compounds.

The increased sulphate concentrations may have an adverse effect on methane production rates by limiting the amount of organic carbon available to the methanogens due to competition with sulfidogenic bacteria. Additionally, it was stated that autotrophic denitrification is advantageous, as it converts nitrate to nitrogen gas in the absence of an organic carbon source and can utilize inorganic sulphur compounds (Onay and Pohland, 2001). According to Onay and Pohland (2001), autotrophic denitrification could represent a range of 15 to 55% of total denitrification.

pH in autotrophic denitrification have a range from 6 to 9 and alkalinity is consumed (Oh *et al*., 2001). According to eq. 7 when 1 mg of nitrate nitrogen is reduced to N_2 4,57 mg $CaCO_3$ are consumed (Moon *et al*., 2004). Thus, likewise nitrification, a buffer capacity is required in order to maintain a pH in the optimal range.

2.5.4 Volatilization

Volatilization only occurs when free ammonia is present. At pH levels above 10,5 to 11,5, the majority of the ammonia nitrogen present in solution is in the form of free ammonia gas (NH_3). As temperature increases, more of the ammonia is converted to free ammonia gas because of temperature dependence of the acid dissociation constant. At a pH level of 7, under standard conditions, 0,56 % of ammonia present is in the form of free ammonia. When the temperature increases to 60º C, a temperature commonly found in aerobic landfills, the percentage of free ammonia present at pH 7 increases to 4,90 % (Berge *et al*., 2005).

Airflow also plays an important role in ammonia nitrogen volatilization. As air is introduced, it interacts with the leachate creating a removal pathway for dissolved free ammonia to volatilize and leave the landfill. Airflow also dilutes the concentration of gas-phase ammonia nitrogen above the leachate, increasing the driving force for dissolved ammonia nitrogen to partition to the gaseous phase (He *et al*., 2011).

Ritzkowski and Stegmann (2003) conducted a laboratory-scale study in which the amount of ammonia nitrogen volatilized from the waste mass was measured. All gas emissions from a simulated aerobic bioreactor landfill exited through an acid scrubber to capture any ammonia nitrogen that may have been volatilized. It was found that at a pH of 7,4 and a temperature of 35^{o}C, 50% of the ammonia nitrogen initially present in the leachate was volatilized.

2.5.5 Flushing

The mass of ammonium nitrogen that can be leached from the waste is controlled by the volume of water passed through the landfill, the nitrogen content of the waste, and the ammonium nitrogen concentration in the bulk liquid. Reducing ammonium nitrogen concentrations by washout and dilution to acceptable levels within a landfill requires the addition of large volumes of water. The effectiveness of flushing will be dependent on hydraulic conductivity of the waste, as it will be harder to introduce liquid in areas of lower permeability. As the hydraulic conductivity decreases, the time required for leaching to occur increases, as well as the ammonification process (Berge *et al*., 2005).

In conventional landfills flushing results in the removal of ammonium nitrogen from landfills by adding large volumes of water, which must be treated externally. When operating the landfill as a bioreactor, leachate is recycled, and hence ammonium nitrogen is continually reintroduced to the landfill while additional ammonia is solubilized into the leachate (Berge *et al*., 2005).

2.5.6 Sorption

Sorption of ammonium nitrogen to waste may be significant in bioreactor landfills because of the high ammonium concentrations present. Ammonium is known to sorb onto various inorganic and organic compounds. Sorption of ammonium to the waste will allow a temporary storage of ammonium before 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 is dependent on pH, temperature, ammonium concentration and ionic strength of the bulk liquid. For ammonia to sorb to waste particles, it must be in the form of ammonium (NH_4^+). At pH levels expected in a landfill, the dominant form of the ammonia species is the ammonium ion (Tchobanoglous *et al.*, 2003). As ionic strength of the bulk liquid increases, sorption of ammonium tends to decrease due to ion exchange effects (Heavey, 2003). The sorbed ammonium is released and exchanged with other ions present in the bulk liquid, especially those with higher selectivity or concentration. A common procedure used to extract sorbed ammonium from solid particles involves the addition of a sodium or potassium sulphate solution. The sodium or potassium ions exchange with the ammonium, allowing for the ammonium to desorb from the waste. The conductivity of landfill leachate is generally high (approximately 7,000 umhos/cm) (Kjeldsen *et al*., 2002) and thus may influence ammonium sorption.

It seems probable that more sorption occurs in older solid waste than in younger waste because older waste has a smaller particle size and thus a larger surface area yielding more available reactive sites for sorption. Additionally, older waste contains more recalcitrant organic particles (predominantly humic and fulvic acids) to which ammonium may sorb. Further, as waste ages, there may be changes in the surface charges of the waste, resulting in higher levels of sorption. The presence of complex organics has been shown to influence ammonium sorption; the ammonium ions may fix irreversibly to these molecules (Heavey, 2003).

2.6 Aerobic bioreactor landfill technique practical application

In the past decade several laboratory scale experiments tried to improve and understand the aeration effects in the waste decomposition, gas emissions and leachate production and treatment. The following two sections illustrate some *in situ* aeration studies that had been done. As well as field scale implementations of the bioreactor *in situ* aeration technique and the results of these experiments.

2.6.1 Examples of laboratory scale applications

Berge *et al*. (2006) had conducted a laboratory scale study where ammonia removal rates in old waste were evaluated. For that, a 133l reactor was designed to allow leachate draining and recirculation, air addition and gas sampling. The reactor was loaded with 14kg of digested MSW. Wood chips were added to the reactor to promote air distribution throughout the matrix. Air was added in a total rate of 2,77 l/min, air was saturated with moisture prior to introduction to the reactor to replenish any water lost due to evaporation and it was added continuously throughout the duration of the study. The aerobic reactor was operated for 717 days and it was periodically spiked with small concentrations of N-NH_3 to ensure the compost was populated with nitrifying bacteria.

The main results were:

- After each spike of ammonia, an initial decline of ammonia followed by an increase in both nitrate and sulphate was observed. However, the concentration of nitrate and nitrite was never as high as it would have been stoichiometrically expected if only nitrification had occurred, suggesting that both nitrification and denitrification were occurring within the system;
- Because of the presence of anoxic pockets coupled with a lower production of nitrate and nitrite than expected, a spike of nitrate was added to the leachate recirculation stream to confirm whether or not denitrification was occurring *in situ*. After the nitrate spike a subsequent disappearance of nitrate from the leachate stream was observed;

- The nitrate decrease was coupled with an increase in sulphate concentration suggesting a portion of nitrate removal may be attributed to autotrophic denitrification;
- During the nitrate spikes period, denitrification was coupled with a sulphate increasing, which suggests that a portion of nitrate removal was due to autotrophic denitrification.
- 1000 mg/l ammonium nitrogen spikes were added and followed by an increase in nitrate and, at times, nitrite, indicating nitrification was proceeding. The sulphate concentrations continued to increase as the reactor was spiked. On average, during each spike, the sulphate concentrations measured suggest conversion of 10–15% of the nitrate via autotrophic denitrification. Both the COD and BOD remained fairly constant throughout each spike;
- Ammonium removal efficiencies achieved a range of 95 to 99 %.

The main conclusions were:

- When examining the data from the aerobic reactor, the time for each ammonium spike to be removed is approximately 30 days, a short period when considering the lifetime of a landfill;
- Ammonium removal via nitrification and denitrification is feasible in bioreactor landfills, readily occurring in decomposed solid waste environments;
- Results suggest that nitrification and denitrification may occur simultaneously in one aerobic landfill cell (even under low biodegradable C:N conditions);
- Denitrification can occur in older portions of the landfill (via both heterotrophic and autotrophic denitrification) provides valuable insight concerning to where nitrification and denitrification can occur in landfills.

Erses *et al*. (2008), had done a laboratory scale study with the aim of evaluate the operational parameters and attenuation mechanisms of carbon, nitrogen and other constituents and their removal rates in conventional aerobic bioreactor landfills. For that a 96l reactor was used. The bioreactor was filled with a shredded and compacted 19,5kg solid waste mixture. 1l of collected leachate in storage bottles was recycled to reactors once per week. The aeration rate was 2,2 l/min for 5h in a day.

The main results were:

- Aeration of the waste mass produces a rapid oxidation of organics and nitrogen when compared to the anaerobic bioreactor landfill. More than 90% of COD was decomposed within 70 days in the aerobic bioreactor compared to 462 days in the anaerobic bioreactor;
- The waste settlement in the aerobic reactors occurred faster than the waste settlement in the anaerobic reactors. A higher degree of settlement was achieved in the aerobic bioreactor where settlement was about 37% at 374 days. Anaerobic bioreactor exhibited settlement about 5% after 630 days;

- Under aerobic conditions the initial concentration of ammonia-nitrogen (399 mg N/l) decreased to 132 mg/l on day 116 and 14 mg N/l on day 175 and continued to decline slightly until reaching to 5mg N/l at the end of the study.

Giannis *et al*. (2008) had conducted a study where leachate characteristics were investigated in terms of BOD_5, COD, nitrate, ammonium, sulphate and heavy metals. For that, a cubic 343l reactor was used and filled with 68kg of MSW and it was monitored for 17 months in a temperature controlled room maintained at 22 ºC. The leachate recirculation had a rate of 8 l/d. The average flow rate throughout the experiment was 18 l/min.

The main results and conclusions were:

- In the early stages of MSW decomposition, the influent COD and BOD_5 in the leachate increased reaching a maximum of 4150 and 1320 mg/l, respectively, after 15 days of treatment. This indicates that recirculation was insufficient in removing the organic load in pace with its production during the initial stage. Then, COD and BOD_5 decreased sharply over the next 35 days and remained almost constant for the rest of the experiment, this suggests that the decomposition of the organic matter of MSW occurred in a relatively short period of time and for the remainder of the experiment the COD did not change significantly. At the end of the experiment, the COD was 352 mg/l and the BOD_5 was 6 mg/l, giving a BOD_5/COD ratio of 0,017. By these criteria, the aerobic reactor had reached a stable state. By the end, the removal efficiency of COD and BOD_5 was 90,6% and 99%, respectively;
- NH_4^+ concentration initially increased and, after 15 days, it was 740 mg/l. It then started decreasing gradually and, after 250 days, almost 100% removal was achieved. The NO_3^- concentration increased periodically and took 240 days to reach the maximum 33,5 mg/l. Thereafter it started decreasing and, at the end of the experiment, it was 10 mg/l. All these results indicate that an aerobic landfill bioreactor with leachate recirculation could effectively remove almost all nitrogen content;
- With the degradation of MSW organic matter, the influent sulphate increased gradually at the early stages and reached the maximum value of 1696,4 mg/l on day 360, and having then decreased to 1312,2 mg/l by the end of the experiment. The sulphate concentrations reached their maximum value when almost all organic matter had been degraded and it was in a stable condition;
- The nitrate decrease was coupled with an increase in the sulphate concentration, suggesting that a portion of nitrate removal may be attributed to autotrophic denitrification. Autotrophic denitrification is favoured whenever there is a low biodegradable environment in the presence of inorganic sulphur compounds, such as hydrogen sulphide;

- By the end of the experiment the MSW settlement had reached 26%. It must be noted that the highest rate of MSW settlement occurred during the first period when MSW contained the maximum biodegradable organic matter.

2.6.2 Examples of field scale applications

Heyer *et al.* (2005) had studied aeration processes with the aim of aerobic *in situ* stabilization. The technique was applied in Germany and the case of Kuhstedt landfill, in the Rotenburg district, is described in the following lines.

The main goal of this application is the controlled reduction of emissions and the resultant potential risk within a relatively short period of time in order to be able to carry an economic site closure, aftercare or securing measures.

The specific aeration mechanism was the low pressure aeration. The system used the 25 gas wells and each of them was connected to a distribution station by means of separate mains. There, the mains may be connected to the distribution system for aeration or to the system for the collection of waste gas.

The whole aeration system main characteristics were:

- Aeration via the gas wells;
- Waste gas collection via the gas wells;
- Three distribution stations;
- Distribution network for aeration;
- The gas collection for the collection of waste gas;
- Compressing unit for aeration and collection of waste gas;
- Waste gas cleaning.

The main achievements and conclusions of this system were:

- In the leachate, accelerated decrease of the parameters of COD and, above all, BOD_5 as well as ammonium nitrogen occurs with the aerobic degradation of organic compounds and their release into gas phase (mainly as carbon dioxide) as a result of aeration;
- Avoidance, respectively, reduction of the methane content in the exhaust air, thereby reduced risk of explosion, for example, and lower costs with concern to long-term waste air treatment;
- The increased carbon conversion during *in situ* aeration therefore leads to a faster stabilization of organic substances;
- At the end of the stabilization process, organic compounds only consist of hardly or non-degradable compounds with a very low residual gas potential;

- As a result of the accelerated biodegradation processes, the anticipation of the main settlements is also accelerated;
- Changes in the consistency of the aquifer may be detected, *e.g*., enhancement of the redox potential, oxygen content and pH value as a first step towards the reduction of the contamination with organic compounds and nitrogen;
- From the beginning of aeration, a considerable decrease in the nitrogen contamination may be achieved after one year of stabilization instead of in several decades;
- After an aeration period of just under 2 years at the old Kuhstedt landfill, settlements or subsidence between 15 and 70 cm respectively, 2% and 10% regarding the landfill height took place;
- Aerobic *in situ* stabilization leads to temperatures in the landfill body in a range of 35 to 50 °C;
- Considerable cost-saving potentials must be set off against the costs for aeration measures so that cost reduction may be expected in the medium and long term; Calculations show that by means of stabilization, total cost reductions of at least 10–25% are possible as regards closure and aftercare measures.

Hrad *et al*. (2013) had conducted a study in the old MSW landfill site, located south-east of Vienna. The total landfill site has an area of 2,6ha, where 200 000 Mg (fresh matter) of untreated municipal and commercial waste were deposited in two different sections (VA01 and VA02) between 1976 and 1995. The first part of the old landfill (VA01), closed in 1985 after 9 years of operation, was installed on a natural clay-liner without an artificial impermeable bottom seal and leachate collection system. The second landfill section (VA02), which was built with a base seal as well as a base drainage system, started operation in 1986. The depth of disposed solid waste was between 3 and 18m.

The *in situ* aeration plant was installed in autumn 2007 and consists of 37 gas wells for aeration and collection of exhausts as well as a biofilter for off-gas purification. Each of the gas wells is connected via pipes to a distribution system either for low pressure aeration or gas extraction. The air injection and extraction system includes six distribution networks, which are connected to the operating unit by three main aeration and extraction pipes. These pipes are in turn connected to one main line each. The gas wells (outer diameter 13cm) are fully perforated over their entire length except for 1m blank covering below the surface. The operating unit, installed in a mobile container, comprises side channel blowers for either low pressure aeration (approx. 20mbar) or, by administering negative pressure, exhaust air extraction as well as a condensate separator.

The initial aeration and extraction capacity of the plant was 600m^3/h, which was increased to 1000m^3/h in autumn 2010 by installing a second aeration and extraction aggregate.

The main results in this study in terms of leachate quality were:

- Leachate pH remained alkaline in a range of 7,5 to 8,2;
- During the aeration period of 3 years ammonium nitrogen reduced from approx. 580 mg/l to 100–350 mg/l, whereas nitrate nitrogen reached values up to 100–200 mg/l;
- The BOD_5 (initial value 60mg O_2/l) under field conditions depreciated significantly to very low values (<3 mg O_2/l) within 10 weeks of aeration;
- COD concentration remained rather stable between 800 and 1200mg O_2/l.

The main results in the solid phase were:

- Only ammonium nitrogen and nitrate nitrogen in the eluate showed a noticeable influence by the aeration measures. Ammonium nitrogen was reduced by approx. 100 mg/kg DM in both sections (VA01 and VA02), while nitrate nitrogen was increased by a factor of six. In general, the high variability of individual parameters is a first indication of the difficulties of solid waste sampling;
- Settlements were measured in the range of 10–50 mm per year in the older section VA01, while in the younger section up to 100–170 mm per year could be detected;
- The highest temperatures (up to 41–48 °C in summer 2009) were observed in the younger section of the landfill (VA02) in the surrounding of the distribution network for aeration, in a depth of 2–4 m, indicating the greatest activity of aerobic biodegradation.

3 Methodology

3.1 Material

The reactors for the experiment consist in 48l columns made of Plexiglas with an intern diameter of 24cm and a height of 106cm. In the top flange are accommodated the air introduction valve, the recirculated leachate input and water introduction valve and the off-gas sampling (connected to a sample bag) and extraction valve (Annex II).

The lower flange is made to collect the leachate from the waste into a recipient (fig. 3.1). From this recipient the leachate is pumped, by peristaltic pumps Heidolph PD 5001 in a rate of 8l/h, back to the top flange. An analogical timer was set to pump 15 minutes at 6h, 12h and 18h every day. This rate allows the recirculation of all the leachate volume in the recipient at least once a day.

The aeration system was set with two air pumps Prodac Air Professional 360 connected to six flow meters Sho-Rate GT1335 flow meter (Brooks Instruments). Each flow meter was calibrated to supply 2l of air per hour. Before enter in the columns the air flux passes by a bottle with water in order to saturate the air preventing any water loss due to evaporation. Air was supplied continuously during the experimental period. The air was channelled into each column by a side perforated and bottom-sealed PVC tube guaranteeing the homogeneous air distribution. The air circuit ends with the off-gas passing by an acid scrubber in order to collect the eventual free ammonia released from the system.

The temperature was set in 35ºC for every reactor. The temperature control is made by a thermo-regulated insulation system that covers the lateral column surface. Temperature was monitored with a temperature probe that was installed inside of each reactor.

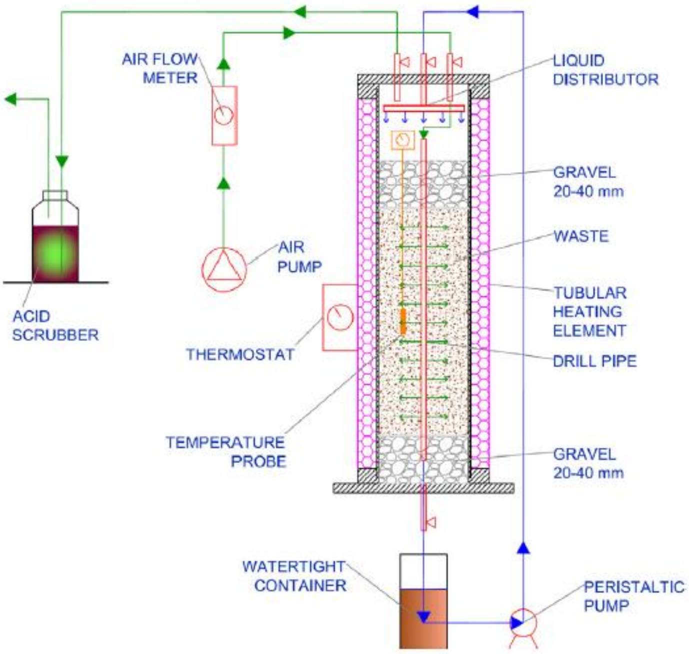

Figure 3.1 Sketch of the test reactors (Adapted from: Raga and Cossu, 2013).

3.2 Experimental set-up

The experimental period had 108 days since the first leachate sample was taken after the set-up of the reactors. The waste used to fill the columns was collected to previous experiments, at the time, the waste samples were collected from a landfill by drilling at depths which correspond to ages of 5, 10 and 15 years. Those samples were distributed by pairs of reactor, *i.e.* reactors 1 and 2 received waste with 5 years old, reactors 3 and 4 received waste with 10 years old and reactors 5 and 6 received waste with 15 years old. The column filling material was composed by two main fractions, fines (0 – 20 mm fraction) and plastic (20 – 50 mm fraction) in a ratio of plastic/fines of 0,16. By the time of the current study the waste was similarly degraded as shown by the carbon content revealed by the leachate analyses.

The liquid used for the experiment was the leachate stored from the previous experiment as well and no water was added. Before the leachate characterization, the air and leachate systems were turned on. Since the beginning all columns were under aerobic conditions. The sampling consists in an approximate 100ml leachate collected directly from the bottom exit valve in the columns.

Characterization phase started after the recirculation of the remaining leachate in order to achieve the field capacity of the waste mass in all reactors. New water has not been added in order to maintain the original characteristics in the leachate.

After the characterization phase, the injection phase started and it followed the schedule and injections presented on table 3.1 and 3.2.

Table 3.1 Summary of the injections objectives, compounds and respective reactors. Reactor 3 initially was a control reactor until the addition of Na_2S.

Reactor	**System Environment**	**Injected Compound**	**Objective**
R1	Autotrophic	KNO_3	Evaluate autotrophic denitrification
R2	Heterotrophic	KNO_3 + CH_3COONa	Evaluate heterotrophic denitrification
R3	Control*	Na_2S	Verify if sulphur was a limiting element for nitrate depletion
R4	Autotrophic	NH_4Cl	Evaluate nitrification and autotrophic denitrification
R5	Heterotrophic	CH_3COONH_4	Evaluate nitrification and heterotrophic denitrification
R6	Control	-	-

Table 3.2 Injections plan.

Reactor	**Injection day**						
	35	**63**	**65**	**70**	**76**	**77**	**84**
R1	57g KNO_3 50g Buffer	-	37g KNO3	-	-	-	-
R2	6g Buffer	18g KNO_3 13g CH_3COONa	-	-	-	30g CH_3COONa	20g CH_3COONa
R3	33g Buffer	-		30g Na_2S	40g Buffer	-	-
R4	4g Buffer	18g NH_4CL 25g Buffer	-	30g Buffer	-		-
R5	46g CH_3COONH_4	-	48g CH_3COONH_4	-	-	-	-
R6	-	-	-	-	-	-	-

In reactor 1 a nitrate source was injected (KNO_3) on days 35 and 65. This reactor was selected due to the initial low nitrate content in the leachate. Also a buffer solution (sodium bicarbonate) was added on day 35 in order to prevent the pH drop caused by the autotrophic denitrification.

In reactor 2, also with lower levels of nitrate, it was chosen to assess the heterotrophic denitrification. In order to do it, nitrate (KNO_3) and acetate (CH_3COONa) were injected. Acetate had to be injected because the biodegradable carbon available in the waste was low as showed by a low BOD_5/COD ratio. Injections were performed on day 63. On days 77 and 84 additional acetate injections were performed due to the carbon consumption.

Reactor 3 was initially taken as a control reactor due to the highest levels of nitrate. A buffer injection has been performed on day 35 in order to assess if the alkalinity lack was the reason to denitrification not happen. On day 70 the reactor was open and a sulphur source (Na_2S) was added in order to see if the sulphur was the limitative factor of the denitrification reaction. On day 76 a buffer solution was added to prevent the eventual pH drop caused by the autotrophic denitrification.

In reactor 4 was injected ammonium chloride (NH_4Cl) on day 63 with the aim of evaluate nitrification and autotrophic denitrification. It was injected as well a buffer solution of sodium bicarbonate at the same day and on 70th day to prevent the pH drop.

Reactor 5 was prepared to evaluate the leachate nitrification, as well as to stimulate heterotrophic denitrification due to have a high content of carbon in the system (comparing with the other reactors). Ammonium acetate (CH_3COONH_4) was the injected substance to study the nitrification and denitrification.

Reactor 6 was selected to be the control due to the average levels of the main parameters as NH_4^+, NO_3^- and SO_4^{2-}. As a control, no injections have been performed on this reactor.

All the nitrogen content injections were calculated in order to achieve a concentration of 1000mg N/l.

Since the beginning of the experiment six scrubbers were filled with 100ml of boric acid in order to capture the eventual releasing of free ammonia from the reactors. Theoretically those 100ml were capable of retain 800mg of free ammonia. Colorimetric indicators were used, namely methyl red and blue methylene.

3.3 Calculations

3.3.1 Free ammonia calculations

Free ammonia is likely to occur in systems where pH is elevated and high temperatures are achieved as explained on section 2.5.4. In this experiment it is not likely that those conditions to occur. However, the system was set up to capture free ammonia eventually released. Thus, when the off-gas passes by the scrubber, which is filled with boric acid, the reaction (eq. 8) that occurs inside the scrubber is the following one:

$$NH_3 + H_3BO_3 \rightarrow (NH_4^+ + H_2BO_3^-) + H_3BO_3 \qquad \text{(eq. 8)}$$

The principle of this reaction consists in a known quantity of boric acid and a known ability to form the complex ammonia-borate ($NH_4^+ + H_2BO_3^-$). When the gas that contains ammonia passes by the scrubber this complex is formed and an excess of boric acid is left, simultaneously the colour change happens (from purple to green). This excess of boric acid is determined with a titration that respects the next equation (eq. 9):

$$(NH_4^+ + H_2BO_3^-) + H_3BO_3 + H_2SO_4 \rightarrow NH_4^+ + H_3BO_3 + HSO_4^- \qquad \text{(eq. 9)}$$

In this experiment the scrubbers were filled, initially, with 100ml of boric acid that can contain 800mg of ammonia (each liter of boric acid can contain 8000mg of NH_3). This amount of boric acid can be adjusted if the volatilization of NH_3 increases.

Berge *et al*. (2006) suggests a formula to evaluate the potential of ammonia volatilization (eq. 10):

$$[\mathrm{N-NH_3}] = \frac{[N-NH_4^+]\ \mathrm{x}\ 10^{pH}}{\frac{Ka}{Kw}+10^{pH}} \qquad \text{(eq.10)}$$

Where:

$[N\text{-}NH_3]$ is the free ammonia concentration (mg/l);

$[N\text{-}NH_4^+]$ is the ammonium concentration (mg/l);

Ka is the acid dissociation constant;

Kw is the water ionization fraction (10^{-14})

3.3.2 Calculations for the amount of NH_4Cl to be injected

Ammonium chloride was injected in reactor 4 in order to study the nitrification process. The following steps are the calculations made to find the right amount of NH_4Cl based on the present amounts of ammonium nitrogen in the leachate as well as the reagents ratios.

1. Select the wanted concentration of ammonium nitrogen inside the system, in this experiment it was always 1000mg N/l.

2. Determine the mass of $N\text{-}NH_4^+$ present in the system multiplying the concentration of ammonium nitrogen by the liters of water in the system.

3. Determine the quantity of ammonium to add by calculating the difference between the wanted and the present amounts of ammonium nitrogen in the system.

4. Determine the quantity of reagent (ammonium chloride) to add to the system by the next formula:

$$\frac{N-NH4\ needed\ amount}{N\ atomic\ weight} \times \mathrm{NH_4Cl\ molecular\ weight} \qquad \text{(eq. 11)}$$

3.3.3 Calculations for the amount of KNO_3 to be injected

Potassium nitrate was injected in reactor 1 and 2 in order to study the denitrification process. The following steps are the calculations made to find the right amount of KNO_3 based on the present amounts of nitrate nitrogen in the leachate as well as the reagents ratios.

1. Select the wanted concentration of nitrate nitrogen inside the system (1000mg N/l).

2. Determine the mass of $N\text{-}NO_3^-$ present in the system multiplying the concentration of nitrate by the liters of water in the system.

3. Determined the quantity of nitrate nitrogen to add by calculating the difference between the wanted and the present amounts of nitrate nitrogen in the system.

4. Determine the quantity of reagent (potassium nitrate) to add to the system by the next formula:

$$\frac{N\!-\!NO_3^-\ needed\ amount}{N\ atomic\ weight} \times \mathrm{KNO_3\ molecular\ weight} \qquad \text{(eq. 12)}$$

3.3.4 Calculations for the amount of CH_3COONH_4 to be injected

Ammonium acetate was injected in reactor 5 in order to study the nitrification process. The following steps are the calculations made to find the right amount of NH_4Cl based on the present amounts of ammonium nitrogen in the leachate as well as the reagents ratios.

1. Select the wanted concentration of ammonium inside the system (1000mg N/l).

2. Determine the mass of $N\text{-}NH_4^+$ present in the system multiplying the concentration of ammonium nitrogen by the liters of water in the system.

3. Determined the quantity of ammonium nitrogen to add by calculating the difference between the wanted and the present amounts of ammonium nitrogen in the system.

4. Determine the quantity of reagent (ammonium acetate) to add to the system by the next formula:

$$\frac{N\!-\!NH4\ needed\ amount}{N\ atomic\ weight} \times \mathrm{CH_3COONH_4\ molecular\ weight} \qquad \text{(eq. 13)}$$

3.3.5 Calculations for the amount of CH_3COONa to be injected

Sodium acetate was injected in reactor 2 in order to supply a carbon source. The following steps are the calculations made to find the right amount of CH_3COONa based on the carbon stoichiometric needs to denitrify the leachate.

1. Determine the amount of nitrate to deplete in moles by dividing the amount of nitrate by the molecular weight.

2. Determine the amount of acetate (mol) required by multiplying the nitrate to deplete (mol) with the stoichiometric ratio 0,625 (acetate/nitrate).

3. Determine the quantity of acetate (g) to add by multiplying the moles needed with the molecular weight of acetate.

4. Calculate the grams of sodium acetate to add in the system by multiplying the amount of acetate needed by the ratio (1,39) sodium acetate/acetate.

3.3.6 Denitrification stoichiometric assumptions

Stoichiometric calculations, in order to understand the range of autotrophic denitrification, whenever nitrate nitrogen in depleted, are based on the stoichiometric equation advanced by Koenig and Liu (2001):

$1{,}06\ NO_3^- + 1{,}11\ S + 0{,}3\ CO_2 + 0{,}785\ H_2O \text{ -> } 0{,}5\ N_2 + 1{,}11\ SO_4^{2-} + 1{,}16\ H^+ + 0{,}006\ C_5H_7O_2N$ (eq.7)

Thus, sulphate/nitrate nitrogen ratio is 4,64. The measured amount of nitrate removed is proportional to the theoretical 100% sulphate production. Therefore, the sulphate measured is related to the theoretical 100% sulphate and the percentage of autotrophic denitrification is assessed.

3.4 Analytical methods

The following laboratorial methods were based in the Italian environmental agency (APAT and IRSA-CNR, 2003) and were used in the laboratorial determinations in this study.

3.4.1 Sulphate determination

The method used for measure the sulphate in the leachate samples was the turbidimetric determination. The homogeneous suspension of barium sulphate is stabilized by means of a solution of glycerine and sodium chloride. With a spectrophotometer (UV-1601 Shimadzu) the absorbance of the suspension is measured and the concentration is achieved with a calibration curve. The wave length used was 309nm. The method is described in: IRSA-CNR 29/2003 vol. 2 n. 4140 B.

3.4.2 pH determination

The leachate pH was determined by the potentiometric method by means of a pH analyser. The method is described in: IRSA-CNR 29/2003 vol. 1 n. 2060.

3.4.3 Ammonium nitrogen determination

Leachate ammonium nitrogen measurements used the method of spectrophotometric determination with Nessler’s reagent. The ammonium present in the water reacts with an alkaline solution of potassium iodomercurate to form a coloured complex. The absorbance of this complex is measured with a wave length of 400 nm. The spectrophotometer used was the UV-1601 Shimadzu. The method is described in: IRSA-CNR 29/2003 vol. 2 n. 4030 A2.

3.4.4 Nitrate nitrogen determination

Leachate nitrate nitrogen was measured using the method of spectrophotometric determination with sodium salicylate. It is based on the reaction between the nitrate and the sodium salicylate in an acid solution by sulphuric acid. The obtained compost has, in alkaline solution, a stable yellow colour measurable by spectrophotometry in a wave length of 420 nm. The spectrophotometer used was the UV-1601 Shimadzu. The method is described in: IRSA-CNR 29/2003 vol. 2 n. 4040 A1.

3.4.5 Alkalinity determination

The method used for the leachate alkalinity determination was the titration with indicator. The determination is based on the addition of a quantity of mineral acid diluted in the sample, after two equivalence points evidenced by the turn of the indicators (bromocresol green and methyl red). The method is described in: IRSA-CNR 29/2003 vol. 1 n. 2010 B.

3.4.6 TOC determination

TOC was determined by high temperature catalytic oxidation. The leachate sample is injected in the oxygen stream in the combustion tube where the sample is vaporized and the organic carbon oxidized to CO_2 and H_2O. The CO_2 (g) is determined in the end of the tube by an infra-red detector. By the measure of the produced CO_2 infra-red absorption peak area, correct by the blank contribution, the TOC concentration is determined by means of a calibration curve. The equipment used was TOC-VCSN Shimadzu Analyser. The method is described in: IRSA-CNR 29/2003 vol. 2 n. 5040.

3.4.7 BOD_5 determination

The method used to determine the biochemical oxygen demand was the direct determination. It is based on the determination of dissolved oxygen in the sample before and after five days, at conditions of darkness and a temperature of 20ºC. The difference between both determinations is the BOD_5 of the sample, expressed in mg O_2/l. the expressions to calculate the concentration are (the method is described in: IRSA-CNR 29/2003 vol. 2 n. 5120 A1):

$$C = \frac{a\,.N\,.f\,.8\,.1000}{V} \qquad \text{(eq. 14)}$$

Where:

C = Concentration (mg/l) of dissolved oxygen;

a = Volume (ml) of solution of sodium thiosulphate used on titration;

N = normality of the solution of sodium thiosulphate;

8 = Oxygen equivalent weight;

V = Volume (ml) of sample used in titration;

f = correction factor for the volume of the introduced reagents in the incubation bottle.

The f value comes from:

$$f = \frac{B}{B-b} \qquad \text{(eq. 15)}$$

Where:

B = Volume (ml) of the used bottle;

b = Total volume (ml) of the reagents used for the precipitation.

Whether X and Y values are the concentrations of dissolved oxygen in the sample, respectively before and after the incubation of the sample, the value of BOD_5 (mg O_2/l) is calculated by:

$$BOD_5 = (X - Y) \qquad \text{(eq. 16)}$$

3.4.8 COD determination

The method to determine COD of the leachate was the oxidation of the organic and inorganic substances, present in the leachate sample, by means of a solution of potassium dichromate in a presence of concentrated sulphuric acid and silver sulphate as a catalyst. The excess of dichromate is titrated with a solution of ammonium and iron (II) sulphate. The concentration of the oxidizing organic and inorganic substances in the method conditions, it is proportional to the quantity of consumed potassium dichromate. The method calculations are (the method is described in: the method is described in: IRSA-CNR 29/2003 vol. 2 n. 5130):

$$C = \frac{(m1-m2).N\,.8000}{V} \qquad \text{(eq. 17)}$$

Where:

C = Chemical oxygen demand (mg/l)

m1 = ml of ammonium and iron (II) sulphate solution consumed in the blank test;

m2 = ml of ammonium and iron (II) sulphate solution consumed by the sample;

N = normality of the ammonium and iron (II) solution;

8000 = equivalent weight of oxygen multiplied by 1000, to match the value with the volume of one liter;

V = Volume (ml) of the sample analysed.

3.4.9 Off-gas samples

CO_2, O_2 and CH_4 (% volume) were determined from the gas released from the reactors by a portable analyser Eco-Control LFG 20.

4 Results and discussion

4.1 Leachate characterization

The characterization phase was done with the aim of evaluate the key parameters of the experiment in each reactor. The experiment injection strategy was designed based on these values which are displayed in table 4.1.

Table 4.1 Characterization of leachate parameters in all reactors before the experimental injections.

Reactor	initial carbon parameters (day 23)			Initial average parameters (from day 0 to day 35)				
	BOD_5 (mg O_2/L)	COD (mgO_2/L)	TOC (mg/L)	$N\text{-}NH_4^+$ (mg N/L)	$N\text{-}NO_3^-$ (mg N/L)	SO_4^{2-} (mg/L)	pH	Alkalinity (mg $CaCO_3$/L)
R1	1,6	1822	841	4,9	221	1466	6,97	201
R2	0,5	2008	784	6,8	837	1482	6,82	184
R3	0,8	1027	748	6,1	1827	1329	6,77	65
R4	2,2	1588	1107	6,5	719	1546	6,82	120
R5	10,1	388	2934	11,9	11	815	7,36	849
R6	0,8	420	621	5,2	1133	1591	6,87	103

Firstly, the low biodegradability was evident due to the low BOD_5 content, at least reactors 1, 2, 3, 4 and 6 were able to simulate well decomposed waste environment. Thus, reactor 5, due to its higher carbon content and low ammonium nitrogen and nitrate nitrogen concentrations, was established as the reactor to evaluate nitrification and subsequent denitrification always in the presence of available carbon source.

Nitrate nitrogen values were an important decision factor due to the significance of the possible results because denitrification was the evaluation goal for two of the reactors. Reactor 1 and 2 were established to perform the denitrification evaluation reactors mainly due to the lower sulphate concentration than in reactor 4, and the lower nitrate nitrogen concentration than in reactors 3 and 6.

Reactor 6, due to the stability of the parameters and also because of its elevated concentration of nitrate nitrogen and sulphate, was kept as the control during all the experimental time. Reactor 3 was kept as an experimental reactor, *i.e.* some limitative parameters (alkalinity and sulphur source) were tested in order to achieve nitrate depletion.

4.2 Leachate carbon content

Before the experimental injections, a leachate carbon characterization was made and it is represented on table 4.2. The results reveal a low biodegradable carbon content, characteristic of well decomposed waste. The samples were taken on day 23.

Table 4.2 Leachate initial and final carbon content.

Reactor	Initial carbon leachate parameters (day 23)				Final carbon leachate parameters (day 76)
	BOD (mg O_2/l)	COD (mg O_2/l)	BOD/COD	TOC (mg/l)	TOC (mg/l)
R1	1,6	1822	0,00086	841	381
R2	0,5	2008	0,00026	784	396
R3	0,8	1027	0,00074	748	563
R4	2,2	1588	0,00140	1107	687
R5	10,1	388	0,02610	2934	620
R6	0,8	420	0,00181	621	448

The results obtained on day 23 have shown that BOD was negligible which was expected due to the age of the waste making the BOD/COD ratio only indicative. Additionally, the COD results of the reactors R5 and R6 were lower than the results obtained for the TOC it is explained by the chloride interference in the laboratorial determination, for that reason the COD values were not repeated again on day 76.

On day 76 another sample was taken to assess the TOC levels in order to understand whether the carbon content in leachate had decreased. The results of final TOC leachate values show a decrease in all reactors. In the control reactors (R3 and R6) a reduction on carbon content was observed (25% and 28% respectively). While on reactors R1, R2, R4 and R5 a reduction of 55, 49, 38 and 79 %, respectively, was measured. Such reduction on TOC content was expected since aerobic microorganisms are able to decompose organic compounds, which are resistant to anaerobic fermentation processes (Prantl *et al*., 2006).

R1 and R5, because they had two injections instead of one, like R2 and R4, the carbon removal was higher possibly due to heterotrophic denitrification which consumes carbon present in the system (see 4.3.1, 4.3.5). Since aeration, recirculation rate and temperature were the same for all reactors, it seems that heterotrophic denitrification also plays an important role in the consumption of hardly degradable carbon.

On the other hand, R2 and R5 were injected with acetate together with the nitrogen source in order to stimulate heterotrophic denitrification. Denitrification clearly occurs in these two reactors (see 4.3.2 and 4.3.5) and CO_2 gas levels were higher in those reactors (with an average of 3,49% and 4,71% of CO_2, respectively), so heterotrophic denitrification could be an explanation to the higher carbon removal. In fact, despite the acetate was enough to promote total nitrate denitrification, it appears that denitrifying bacteria were able to use the hardly biodegradable carbon.

4.3 Nitrogen fate in the reactors

In the following sections the laboratorial results are presented and discussed. The collected laboratorial data for each reactor is show in Annex I.

4.3.1 Reactor 1

In reactor 1, potassium nitrate (KNO_3) was injected on days 35 and 65 with a target concentration of 1000mg N-NO_3/l. A buffer solution was also added in order to prevent the pH drop. pH average in each injection period was 6,98 and 6,99 respectively.

According to figure 4.1, before the first injection, the parameters were stable, specially nitrate, alkalinity and sulphate, with average concentrations of 221mg N/l, 201mg $CaCO_3$/l and 1466mg/l respectively.

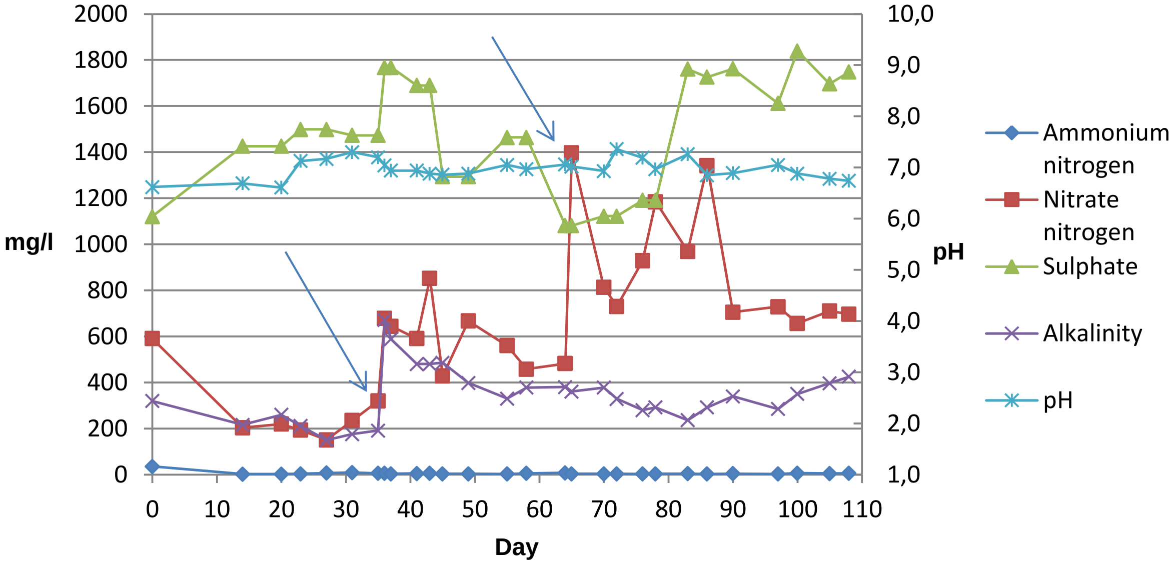

Figure 4.1 Reactor 1 leachate parameters. Values of pH, Alkalinity ($CaCO_3$/l), Sulphate (mg/l), Ammonium nitrogen (mg N/l) and Nitrate nitrogen (mg N/l). Injections of potassium nitrate (KNO_3) on days 35 and 65.

After each injection, nitrate nitrogen tends to never decrease from the initial phase values, *i.e.* from day 0 to day 35, the average nitrate concentration was 221mg/l and in the two injection periods that value was never crossed. However, 48,8% and 56,6% of nitrate nitrogen removal were achieved in each nitrate injection.

In the first injection, the highest nitrate nitrogen concentration was 852mg N/l and the lowest, on day 58, 458mg N/l that indicates a nitrate removal rate of 235mg N/d within a period of 15 days. In the same injection period, sulphate values, which were expected to increase due to autotrophic denitrification according to eq. 7, had only a little peak from day 35 to day 43. By applying the stoichiometric calculations to this sulphate peak the result is approximately 27% of the autotrophic denitrification and 73% of the heterotrophic denitrification (table 4.3). Those calculations were made according to the stoichiometric ratio between the produced sulphate and the reduced nitrate nitrogen of 4,64 mg of SO_4^{2-} per mg of N-NO_3^- reduced to N_2 (eq. 7).

It was expected a higher contribution from the autotrophic denitrification because of the low carbon content, COD/N-NO_3^- was 1,74 (g/g). According to Sun *et al.* (2012), with COD/N-NO_3^- ratio below 5,03 (g/g) autotrophic denitrification is the dominant reaction of nitrate nitrogen removal. However, aspects like the carbon released from the waste (Jun *et al*., 2007) by the action of recirculation and the consequent competition with heterotrophic bacteria for the nitrate available could limit autotrophic denitrification. Another limitative aspect could be the sulphur source availability. Sulphate levels in both injection period seem to reach the same higher value (1768 and 1839mg/l; approx. 1800mg/l) which means that all the available sulphur was used. Thus, without a carbon source and a limited sulphur source, nitrate levels will not decrease from a certain level due to the nonexistence of another pathway to degrade nitrate (Berge *et al*., 2005). Furthermore, autotrophic denitrification stays limited to the capacity of sulphate reduction to sulphide (Vigneron *et al*., 2007; Onay and Pohland, 2001).

Table 4.3 Autotrophic denitrification estimative for reactor 1.

Injection	Autotrophic denitrification estimative					Heterotrophic denitrification estimative %
	Nitrate removed (mg N)	SO_4^{2-}/N-NO_3^- ratio	theoretical sulphate produced (mg)	Measured sulphate production (mg)	Autotrophic denitrification %	
1st	3532	4,64	16389	4349	26,5	73,5
2nd	7120	4,64	33036	5535	16,8	83,2

In this case, due to the addition of a nitrate source and the restricted denitrification capacity, nitrate nitrogen minimum levels had increased injection after injection. The accumulation of nitrate could be explained by the low BOD_5 content as well as an eventual elevated redox potential as advanced by Mertoglu *et al.* (2006), unfortunately in this study redox potential was not measured.

On the second injection denitrification occurs from day 65 until day 100 (35 days). In this period nitrate removal rate was 203mg N/day. In this second injection the same behaviour occurs with a lower sulphate production taking into account the expected stoichiometric amount. Calculating a direct relation with the stoichiometric ratio (4,64mg of SO_4^{2-} per mg of N-NO_3^- reduced to N_2), denitrification outcome approximately17% of autotrophic and 83% of heterotrophic denitrification (table 4.3). Additionally, denitrification stops as evidenced by the stable level observed on days 90 until 108. Likewise on first injection, reduced sulphur sources seem to be the main reason because sulphate level did not increase more than 1800mg/l as explained above.

Alkalinity levels are unlikely the reason why denitrification is limited in this case because denitrification occurs and alkalinity did not decrease sharply, instead it is available for the reaction. Additionally, heterotrophic denitrification produces alkalinity (3,57mg $CaCO_3$/mg N-NO_3^- reduced) (Oh *et al*., 2001) and if heterotrophic denitrification seems to be the dominant nitrate removal process, alkalinity is not likely to be the limitative factor.

pH levels never decrease from 6,74 in both injection periods making pH to be in the optimal range, according to literature, pH must be between 7,0 and 8,0 (Koenig and Liu, 2001).

4.3.2 Reactor 2

Characterization phase results show a leachate with a nitrate nitrogen average concentration of 837mg N/l and an alkalinity stable level of 184mg $CaCO_3$/l. On day 63 a potassium nitrate and acetate injections were performed in order to stimulate denitrification with an available carbon source, *i.e.* simulating the option of a new layer of waste addition over a well decomposed landfill cell, or fresh leachate (high BOD content) added to the older parts of a landfill (Price *et al*., 2003).

As observed in figure 4.2, denitrification clearly occurs and 89,9 % of nitrate removal was achieved. Comparing with reactor 1, where readily biodegradable carbon was not present (BOD/COD= 0,00086), nitrate removal was more effective. The removal rate achieved was 220mg N/day within a period of 44 days. However, due to the extra carbon source additions, it was slower than the expected. Extra carbon additions were made due to the natural conversion of acetate to CO_2, which makes the initial stoichiometric amount of acetate insufficient to complete the denitrification. Additionally, it is evident that the initial phase of denitrification was faster, *i.e*. from day 64 until day 90 (26 days), approximately 85% of nitrate had been removed which represents a removal rate of 352mg N/day. Thus, as expected, denitrification was faster with available carbon than without it (Price *et al*., 2003).

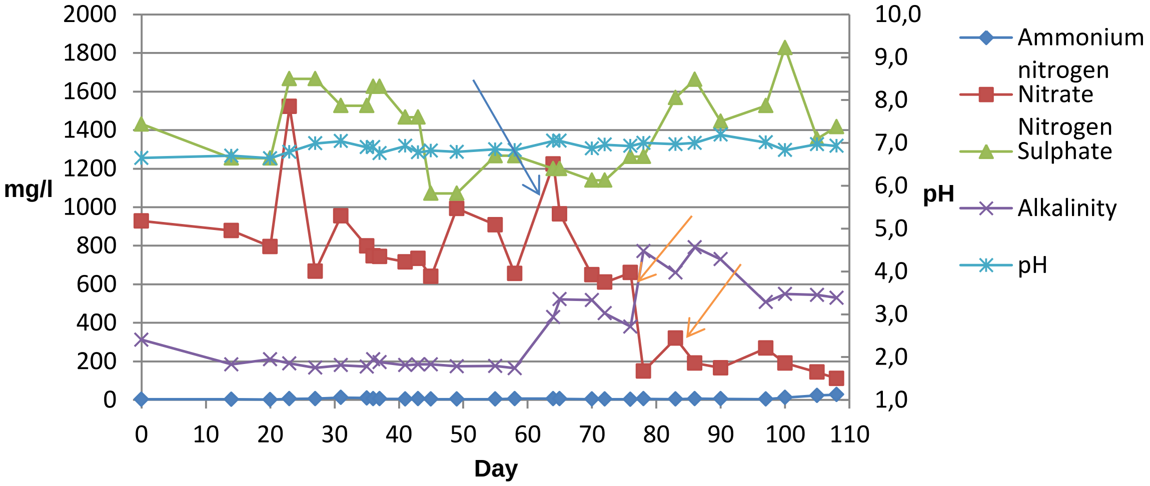

Figure 4.2 Reactor 2 leachate parameters. Values of pH, Alkalinity ($CaCO_3$/l), Sulphate (mg/l), Ammonium nitrogen (mg N/l) and Nitrate nitrogen (mg N/l). Injection of KNO_3 on day 63 and sodium acetate on days 63, 77 and 84.

Even in the presence of biodegradable carbon, sulphate concentration increased during the denitrification process. It could mean that autotrophic denitrification occurs. By stoichiometric calculations, according to eq. 7, approximately 18% of denitrification was executed by autotrophic bacteria (table 4.4). As expected, the higher concentration of sulphate was coincident with the final phase of denitrification due to the slower development of the autotrophic bacteria (Koenig and Liu, 2001). Another evidence of the dominant heterotrophic denitrification process is the increase of alkalinity in the system. As it is known, heterotrophic denitrification produces 3,5mg $CaCO_3$/mg $N\text{-}NO_3^-$ reduced to N_2 (Oh *et al*., 2001). pH average during all denitrification period was 6,98, which is between the pH 7 and 8, the optimal range for denitrification reaction (Tchobanoglous *et al.*, 2003).

Table 4.4 Autotrophic denitrification estimative for reactor 2.

Injection	Autotrophic denitrification estimative					Heterotrophic denitrification estimative %
	Nitrate removed (mg N)	SO_4^{2-}/$N\text{-}NO_3^-$ ratio	theoretical sulphate produced (mg)	Measured sulphate production (mg)	Autotrophic denitrification %	
1st	9683	4,64	44931	8110	18,1	81,9

4.3.3 Reactor 3

Reactor 3 was kept as a control reactor, due to high $N\text{-}NO_3$ concentration, in order to understand if nitrate concentration starts to decrease with the recirculation action. Autotrophic denitrification was expected to occur because of the initial leachate low biodegradable carbon content (BOD_5 0,8mg O_2/l) (Sun *et al*., 2012).

However, nitrate did not decrease, as it is observable in Fig. 4.3, and an eventual lack of sulphur source in the waste mass was hypothesized because reduced forms of sulphur such as S^{2-}, $S_2O_3^{2-}$ and SO_3^{2-} are used as electron donors by the autotrophic bacteria as shown on eq.7 (Keonig and Liu, 2001; Onay and Pohland, 1998).

On day 70, 30g of Na_2S were added to the waste mass.

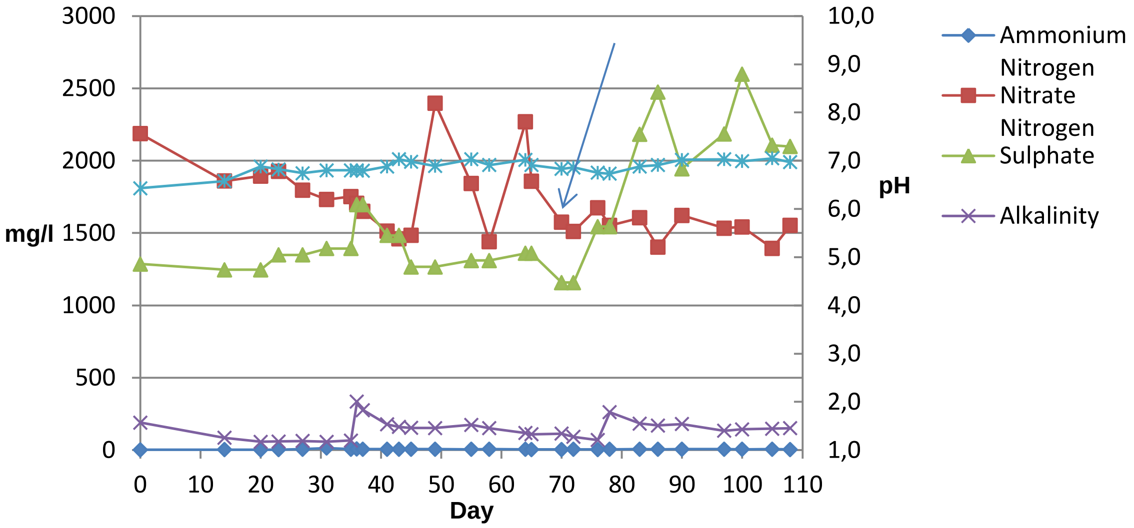

Figure 4.3 Reactor 3 leachate parameters. Values of pH, Alkalinity ($CaCO_3$/l), Sulphate (mg/l), Ammonium nitrogen (mg N/l) and Nitrate nitrogen (mg N/l). Na_2S addition on day 70.

The results reveal an immediate increase of sulphate, however, nitrate nitrogen remains stable on 1539mg N/l instead of suffering a decrease. The increasing of sulphate concentration suggests the oxidation of sulphur because the system had been aerated for 70 days. In fact, off-gas analysis suggest this immediate oxidation because, before sulphur source addition, the average oxygen percentage on reactor 3 was 17,2% and dropped to 16,0% after the sulphur source addition, with a minimum value of 15,4%.

Those facts evidence a weakness of the sulphate method to assess the denitrification origin because of the sulphate concentration increase could be due to sulphur chemical oxidation, like the reactions that occur on reactor 3 and 5, or it could be due to effective autotrophic denitrification.

However, the bacteria adaptation to the added sulphur particles could be slower, Koenig and Liu (2001) have made an experiment with sulphur packed-bed reactors and the nitrate removal was achieved with the development of a biofilm around the sulphur particles. Denitrification occurs inside the biofilm where sulphur was transformed into sulphate by autotrophic bacteria. In the current experiment, in one hand the biofilm possibly had no time to be formed in the other hand, as proposed by the same authors, the limiting factor of autotrophic denitrification is the slow dissolution of elemental sulphur making it hardly available for denitrification process.

4.3.4 Reactor 4

On the characterization phase, reactor 4 leachate had stable values in alkalinity, ammonium nitrogen, pH and nitrate nitrogen. On the other hand, sulphate values were not so stable and it was unlikely that denitrification was responsible for them. It is most probably that it was due to sulphate reduction and subsequent oxidation of that reduced forms (Christensen *et al*., 2001).

On day 63 the injection of ammonium chloride was performed in order to assess nitrification process and the consequent ammonium removal rate. Nitrate production and removal were assessed as well. At the same time, a buffer solution was injected in order to prevent a pH drop caused by nitrification.

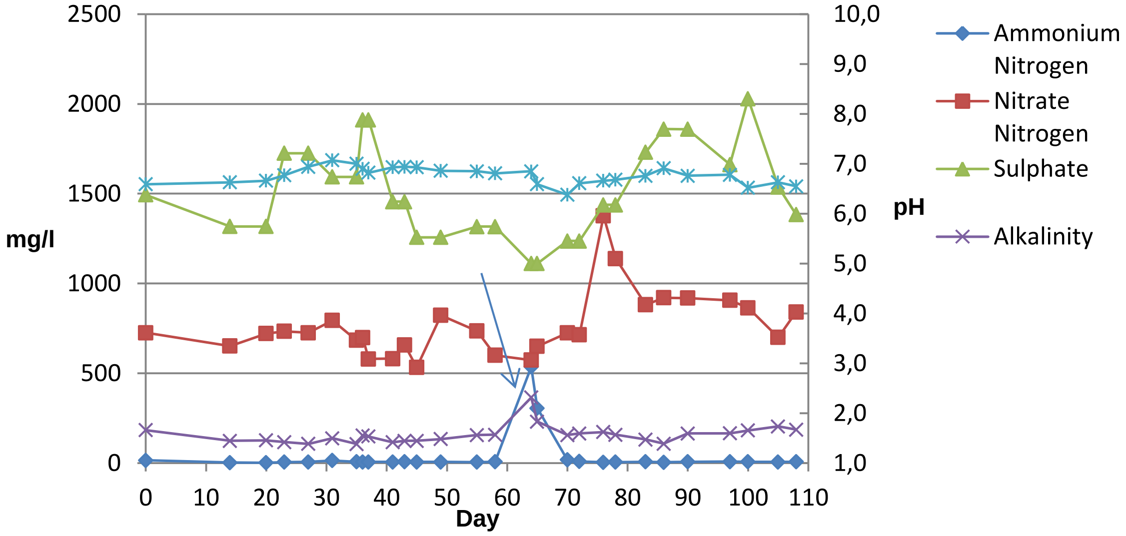

Figure 4.4 Reactor 4 leachate parameters. Values of pH, Alkalinity ($CaCO_3$/l), Sulphate (mg/l), Ammonium nitrogen (mg N/l) and Nitrate nitrogen (mg N/l). Ammonium chloride injection on day 63.

As displayed on figure 4.4, nitrification occurs in a range of 99,0% with an ammonium nitrogen removal rate of 270mg N/day within a period of 12 days. A nitrate nitrogen peak appears days after nitrification. Stoichiometric amounts are close to the amounts measured in terms of nitrate nitrogen produced from the amount of ammonium injected. That could indicate that the sorption or volatilization processes were negligible in ammonium transformation. Additionally, the scrubber connected to reactor 4 did not detect any free ammonia during all the experimental period.

Nitrate removal was incomplete, like in reactor 1, achieving only 40,8% of nitrate nitrogen removal and a removal rate of 111mg N/day within a period of 32 days. A sulphate peak was recorded during the denitrification period and applying the stoichiometric sulphate/nitrate ratio from eq.7 it was possible to determine that approximately 34% of autotrophic denitrification occurs (table 4.5).

Table 4.5 Autotrophic denitrification estimative for reactor 4.

Injection	Autotrophic denitrification estimative					Heterotrophic denitrification estimative %
	Nitrate removed (mg N)	SO_4^{2-}/N-NO_3^- ratio	theoretical sulphate produced (mg)	Sulphate produced (mg)	Autotrophic denitrification %	
1st	3539	4,64	16420	5594	34,1	65,9

Comparing reactor 4 with reactor 1, which was run under similar conditions, the last obtained a faster nitrate nitrogen removal rate and a higher percentage of removal as well. However, the estimated percentage of autotrophic denitrification was lower in reactor 1 than in reactor 4, which indicates a slower nitrate removal rate as higher the percentage of autotrophic bacteria is. That is expected because heterotrophic denitrification bacteria have a faster reaction than autotrophic denitrification bacteria (Koenig and Liu, 2001).

In reactors 1 and 4, nitrate was not totally removed which indicates some limitations in autotrophic denitrification process. In both cases, pH was near 7 in the optimal pH range. Alkalinity levels were different, in reactor 1 alkalinity was 466 and 330mg $CaCO_3$/l (in each injection) and reactor 4 had an average of 184mg $CaCO_3$/l. However, because heterotrophic denitrification produces alkalinity and it is the dominant process is not plausible that a lack of alkalinity could be a limitative factor. An evident limitative factor could be the electron donor problem, *i.e.* in both cases readily biodegradable carbon source was not available and reduced sulphur sources were needed to supply autotrophic denitrification. Thus, because sulphate levels were high in both reactors a reduction to sulphide was a critical reaction for the availableness of reduced sulphur forms (Vigneron *et al*., 2007).

According to Christensen *et al*. (2001) sulphate reduction kinetics are slow and the migration of sulphate in the leachate could limit the reduction in the anaerobic pockets, causing further reduced sulphur forms to stay unavailable to autotrophic denitrification process.

4.3.5 Reactor 5

Reactor 5 characterization samples evidenced stable parameters and on day 35 an injection of ammonium acetate was performed in order to assess nitrification process and ammonium nitrogen removal rates, as well as the subsequent denitrification process.

As observed in figure 4.5, on the first injection nitrification occurred successfully once 99,7% of ammonium nitrogen was removed within a period of 18 days. The ammonium nitrogen removal rate was 465mg N/day. In the same injection period, *i.e.* before day 65, nitrate did not increase which could be explained by simultaneous nitrification and denitrification, due to the presence of anoxic pockets (Raga and Cossu, 2013; Berge *et al*., 2006). However, two nitrate peaks were measured on days 37 and 49 with nitrate nitrogen concentrations of 21 and 34mg/l respectively. Those two peaks coincided with the two sulphate peaks, these coincidences could mean that autotrophic denitrification occurs even with a carbon source available. The estimative of autotrophic denitrification by the stoichiometric sulphate/nitrate method is not clear, in this case, due to the assumptions that need to be made and also because the total amount of nitrate was not possible to measure due to the simultaneous denitrification.

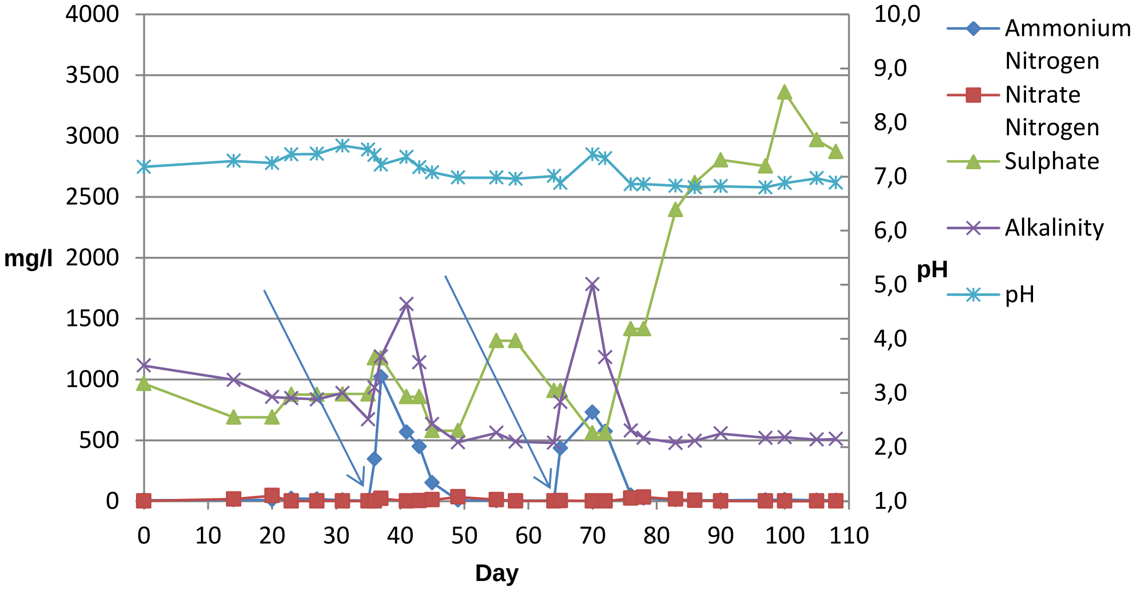

Figure 4.5 Reactor 5 leachate parameters. Values of pH, Alkalinity ($CaCO_3$/l), Sulphate (mg/l), Ammonium nitrogen (mg N/l) and Nitrate nitrogen (mg N/l). Ammonium acetate was injected on days 35 and 65.

In the second injection, another amount of ammonium acetate was added to the reactor and, again, nitrification was successfully achieved with 99,2% of ammonium nitrogen removal. Ammonium nitrogen removal rate was 381mg N/day within a period of 16 days. As in the first injection, nitrate nitrogen was not accumulated which means that denitrification occurred. A low peak of 33mg N/l of nitrate was recorded on day 78.

During this second injection, sulphate concentration sharply increases to a concentration of 3361mg/l. This concentration was definitely not due to autotrophic denitrification because it goes far beyond stoichiometric sulphate production amount, including the hypothesis of an accumulation of the ammonium amount of both injections.

According to the values of table 4.2, TOC had been removed by 79%, on the sulphate peak beginning day, and it remained at the level of the other reactors. This possibly means that the initial elevated carbon content has been definitely reduced to CO_2. Off-gas samples also demonstrate lower O_2 and higher CO_2 percentages than in the other reactors due to the carbon reduction to CO_2 (table 4.8). Thus, when carbon was reduced, O_2 became available for other oxidation processes such as sulphate production.

Additionally, in the previous studies, reactor 5 also had carbon injections, meaning that sulphur sources were not used for denitrification as occurred in the other five reactors. So, with the carbon extinction, sulphur had the opportunity to be oxidized due to the higher availability of oxygen. The same reaction happens on reactor 3 where a sulphur source was added to the reactor and it immediately starts to be oxidized due to the high availability of oxygen.

Alkalinity remained with high concentrations as consequence of the prevalence of heterotrophic denitrification. As it is known, heterotrophic denitrification produces 3,5mg $CaCO_3$/l (Oh *et al.*, 2001), which ensures that the consumption of alkalinity by nitrification process (7,14mg $CaCO_3$/l) does not affect pH in the system. Additionally, in both injections, when the nitrate peaks were recorded, alkalinity kept the level or increased a little. That evidences the predominance of heterotrophic denitrification process.

Ammonium nitrogen volatilization was not detected in the scrubber in this reactor, similarly to reactor 4, volatilization was not expected to occur due to the levels of pH and temperature.

4.3.6 Reactor 6

Reactor 6 was the control reactor where no injections were performed. As observed on figure 4.6, the evolution of the parameters shows that no meaningful denitrification occurs, remaining nitrate nitrogen at an average level of 1137mg N/l. In fact, those were equilibrium conditions similar to those found on reactors 1, 2, 3 and 4. From this equilibrium none nitrate was depleted and sulphate remains at elevated concentrations. Ammonium nitrogen was always on negligible concentrations. Sulphate seems to be reduced and oxidized continuously but always in the average axel of 1514mg/l.

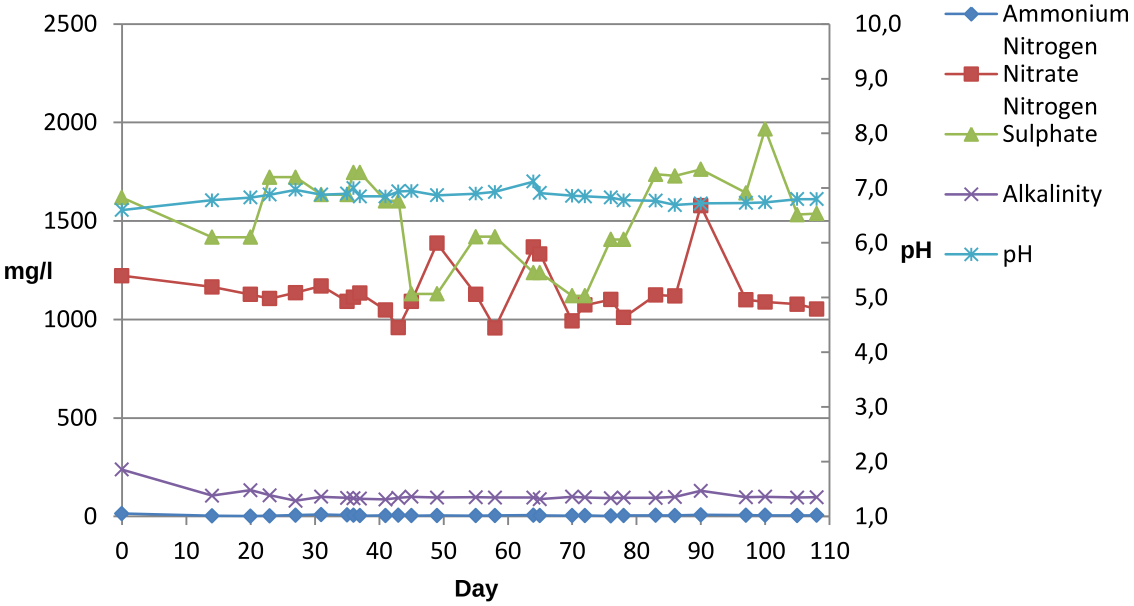

Figure 4.6 Reactor 6 leachate parameters. Values of pH, Alkalinity ($CaCO_3$/l), Sulphate (mg/l), Ammonium nitrogen (mg N/l) and Nitrate nitrogen (mg N/l). No injections were performed due to be the control reactor.

4.4 Nitrogen removal: results summary

With the presented results in table 4.6 it is possible to analyse some implications of them in the *in situ* aeration method applied in well decomposed MSW.

Table 4.6 Summary of the nitrogen removal performance.

Reactors	**N-NH$_4^+$ removal %**	**N-NH$_4^+$ removal rate (mg N/d)**	**N-NH$_4^+$ removal period (d)**	**N-NO$_3^-$ removal %**	**N-NO$_3^-$ removal rate (mg N/d)**	**N-NO$_3^-$ removal period (d)**	**MSW Conditions**
R1	-	-	-	48,8 - 56,6	203 - 235	15 - 35	**Low carbon**
R2	-	-	-	89,9	352	26-44	**Available carbon**
R4	99,0	270	12	40,8	111	32	**Low carbon**
R5	99,2 - 99,7	381 - 465	16-18	-	-	-	**Available carbon**

In the reactors 2 and 5, which have the presence of biodegradable carbon, was registered the highest nitrogen removal efficiency, once both nitrification and denitrification have removed 99,2 to 99,7% of ammonium nitrogen respectively and 89,9% of nitrate nitrogen in R2.

In contrast, in the systems with low concentration of readily biodegradable carbon the overall nitrogen efficiency was lower. In this case, the nitrification achieved was 99,0% of ammonium nitrogen removal and the denitrification obtained was between 40,8 and 56,6% of nitrate nitrogen removal.

As expected in both conditions ammonia nitrogen removal was satisfactory, since another researchers had reached similar conclusions, as Youcai *et al*. (2002) had reported a nitrification of 99,5% in aged refuse. In well decomposed MSW systems the addition of a carbon source might improve the results of the leachate quality in terms of nitrogen content. Comparing the removal rates, both nitrification and denitrification reactions were faster in the presence of a carbon source resulting in a better leachate quality in terms of nitrogen content.

4.5 Off-gas analyses

The off-gas analyses were different between reactors, however the presence or absence of readily biodegradable carbon have influenced the off-gas samples values. In tables 4.7, 4.8 and 4.9 the measured values of oxygen, carbon dioxide and methane are presented.

O_2

Oxygen levels are critical to nitrification process, in this regard the aeration rate is an important criteria to achieve an economical cost-effective aeration. Sekman *et al.* (2011) had concluded that an aeration rate of 0,10 $l/min.Kg^{-1}$ of waste is enough to promote nitrogen removal from landfill leachate on fresh MSW, however they admit that an optimal aeration rate was below that value. In the current experiment the aeration rate was 0,0012 $l/min.Kg^{-1}$ of waste and the removal of ammonium nitrogen was achieved as well. It can be explained, according to Long *et al*. (2008), by the high efficiency of oxygen utility because of the porous characteristic of aged refuse.

In fact on nitrification reactors (R4 and R5) have successfully nitrify the respective leachate, the oxygen measured in the off-gas is different in both reactors due to the higher available carbon content in reactor 5 than in reactor 4. Observing reactor 4 off-gas oxygen values (table 4.9) it is evident the utilization of oxygen in nitrification process, since the minimum values were recorded from day 63 to day 72, the same period of nitrification.

In reactor 5 off-gas oxygen values (table 4.9) the utilization peak is not so evident as in reactor 4 due to the utilization of O_2 in the carbon degradation process, however in the nitrification periods (from day 35 to 48 and from day 64 to 76) the minimum values of O_2 are observed.

Prantl *et al.* (2006) advanced that as the carbon is degraded a smaller part of the injected oxygen is used and its concentration increases to 15%. This is coherent with the average oxygen levels recorded in this study particularly in the reactor where available carbon source was not present (R1, R3, R4 and R6).

In the beginning, in reactors 1 and 2, oxygen levels could have represented a problem due to the excess of oxygen that could affect denitrification, despite the anoxic pockets. However, denitrification occurred in both reactors even with average O_2 percentage of 15,24 and 14,07

CO_2

CO_2 levels present interesting trends. For instance, in reactor 5, which starts with the higher BOD_5 concentration, CO_2 percentage was always the highest due to the carbon degradation during the experimental time.

Reactor 2 had the second higher average in CO_2 production, it is clearly due to acetate addition and its consequent conversion to CO_2. Such is confirmed by the CO_2 levels registered since day 63, in which the first acetate injection was performed.

Reactors 1 and 4 had similar CO_2 average productions since both produced 2,77 and 2,16% during the experimental time (Table 4.7). Coincidently, in both reactors, the CO_2 highest levels were recorded when the buffer solutions (sodium bicarbonate) were injected and during the few following days. The same happens on reactor 3, the only two peaks of CO_2 were a reflection of the buffer solution added in that specific period. Furthermore, those two reactors presented the highest BOD_5 concentrations, next to reactor 5, and both had a TOC reduction of 55 and 38%, respectively.

Table 4.7 Average off-gas values (% of volume), measured during the experimental period.

Reactor	Average off-gas values		
	O_2 %	CO_2 %	CH_4 %
R1	15,24	2,77	0,04
R2	14,07	3,49	0,04
R3	16,70	1,26	0,06
R4	15,43	2,16	0,04
R5	11,94	4,71	0,05
R6	17,01	0,60	0,02

CH_4

Prantl *et al.* (2006) described the aeration period in a MSW column test and report that methane production almost completely stopped with the aeration, also report that oxygen concentration is low in the presence of biodegradable carbon due to the microorganism’s respiration.

On tables 4.8 and 4.9 are represented the air sample values. It is possible to verify that methane levels were always very low. This was expected since there were not enough biodegradable carbon to permit a large production of methane and the supplied oxygen did not allow the methane production. Additionally, in the reactors where nitrate is present and/or in those where denitrification occurs methanogenesis ceases, as proved by Price *et al*. (2003).

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Table 4.8 Off-gas sampling values (O_2, CO_2 and CH_4) expressed in % of volume for reactor 1, 2 and 3.

Day	**R1**			**R2**			**R3**		
	O_2	**CO_2**	**CH_4**	**O_2**	**CO_2**	**CH_4**	**O_2**	**CO_2**	**CH_4**
35	16,6	3,45	0,01	16,7	2,13	0,05	17,3	1,6	0,14
36	15,7	6,81	0,1	16,7	2,6	0,1	17,3	1,41	0,1
37	16	4,9	0,15	16,8	2,09	0,1	17	2,91	0,05
41	14	5,25	0,1	15,4	2,7	0,1	17,2	1,57	0,1
42	14,5	4,46	0,12	16,4	1,9	0,09	17,3	1,57	0,13
46	13,5	5,5	0,12	15,6	2,54	0,2	17,2	1,57	0,09
48	12,2	4,9	0	15,85	2,19	0,1	16,8	1,05	0
49	15,9	2,69	0	16,1	1,85	0	16,9	1,09	0,01
55	16,7	1,81	0	15,9	1,85	0,01	16,4	1,57	0,05
58	15,4	2,82	0,01	16,5	1,69	0,03	17,5	1,01	0,05
59	15	3,13	0,01	16,5	1,85	0,08	17,7	0,81	0,01
63	14,8	3,29	0,01	15,7	2,01	0,01	17,5	0,81	0,02
64	14,6	3,74	0,01	13,6	2,69	0,01	17,5	0,81	0,05
66	13,5	3,89	0	12,5	3,82	0	17,2	0,61	0,01
70	12,3	4,21	0	12,6	3,82	0	17	0,53	0,01
71	15,6	2,17	0	14,4	2,97	0	16,9	0,53	0,01
72	16,7	1,33	0	14,6	2,94	0	15,5	0	0
76	16,8	0,93	0	16,2	1,33	0	15,9	4,37	0
78	15,8	1,25	0	12,1	3,33	0	16,4	1,77	0
83	16,2	0,85	0	13,9	3,17	0	16,2	1,05	0,01
85	15,9	1,05	0	14,5	2,53	0	15,9	1,05	0,05
89	16	0,85	0,01	15,3	1,65	0,01	15,9	0,93	0,05
95	16,4	0,36	0,12	12,4	4,05	0,18	15,9	1,29	0,22
98	16,5	0,28	0,1	9	8,46	0,05	16,2	0,93	0,18
102	15,2	1,05	0,05	3,9	14,5	0,01	16,1	0,97	0,18
105	14,5	1,01	0	6,6	10,1	0	15,4	0,85	0

Table 4.9 Off-gas sampling values (O_2, CO_2 and CH_4) expressed in % of volume for reactors 4, 5 and 6.

Day	**R4**			**R5**			**R6**		
	O_2	**CO_2**	**CH_4**	**O_2**	**CO_2**	**CH_4**	**O_2**	**CO_2**	**CH_4**
35	17,4	1,05	0,05	11	3,53	0,05	17,4	0,93	0,01
36	16,9	3,13	0,18	10,7	4,18	0,15	17,2	0,89	0,06
37	17,7	0,6	0,05	8,2	6,01	0,14	17,3	0,89	0,06
41	17,4	1,17	0,1	10,4	7,6	0,1	17,6	0,77	0,09
42	17,7	0,85	0,11	11,6	6,9	0,14	17,5	1,05	0,05
46	17,4	1,21	0,06	12,5	5,8	0,1	17,7	0,85	0,14
48	17	0,97	0	14,1	3,45	0	17,6	0,45	0
49	16,9	1,05	0	10,1	5,66	0	17,5	0,57	0
55	16	1,69	0	8,5	7,5	0,02	17,6	0,69	0
58	16,7	1,5	0,05	13,7	4,54	0,05	17,4	0,89	0,02
59	17,2	1,13	0,01	13,6	4,42	0,05	17,5	0,81	0,03
63	17	1	0,01	13,7	4,22	0	17	0,69	0
64	16,5	2,81	0,02	13,6	4,29	0,01	17,5	0,54	0,01
66	11,1	5,06	0	6,7	7,42	0,01	16,9	0,57	0,01
70	12	3,37	0	9,1	6,9	0,01	17	0,25	0
71	13,5	5,1	0	11	5,5	0	16	0,45	0
72	14,8	3,85	0	12	4,66	0	16,7	0,57	0
76	16,7	0,85	0	12,5	4,1	0	16,9	0,49	0
78	16,5	0,77	0	12,4	3,91	0	16,6	0,53	0
83	16,6	0,49	0	12,7	3,85	0	16,6	0,49	0
85	16,5	0,53	0,01	12,4	4,09	0	16,7	0,24	0
89	15,9	0,61	0,05	12,5	3,93	0,01	16,4	0,24	0,01
95	16,8	0,25	0,18	12,6	4,58	0,15	16,8	0,24	0,05
98	13	3,58	0,13	12	4,98	0,1	16,5	0,41	0,01
102	9,5	6,02	0,05	16,9	0,24	0,09	16,5	0,69	0,05
105	6,56	7,6	0,01	15,9	0,24	0	15,9	0,32	0

5 Conclusions and future perspectives

Laboratory scale experiments show that ammonium nitrogen accumulation on anaerobic landfills is treatable when the landfill becomes aerobic and it is operated as a bioreactor. On this study, ammonium removal was achieved from 99,0 to 99,7% and the removal rates registered were from 111mg N/day to 465mg N/day, suggesting a fast reduction of ammonium nitrogen accumulated in landfill leachate.

Nitrate removal was also achieved, however it was only reduced efficiently when there were available carbon sources, with a removal of nitrate nitrogen of 89,9%. In environments with well degraded waste, *i.e.* with low biodegradable carbon available, nitrate nitrogen removal was only achieved from 40,8% to 56,6%.

On field scale, these results could implicate an addition of an external carbon source when the leachate presents a high concentration of nitrate to denitrify. This external carbon source could come from a fresh waste layer, a mix of fresh landfill leachate, etc. By the evaluation of the removal rates, it is possible to support that this addition could lead to a better quality leachate in terms of nitrogen content in a shorter period of time.

The recirculation of leachate could lead to nitrate accumulation if nitrification continue to occur under aerobic and in well decomposed waste conditions due to the low efficiency of nitrate removal and of the autotrophic denitrification in such conditions, as is evidenced in reactor 1.

The attempt to assess the denitrification origin it is a tricky point due to the oxidation of the reduced sulphur sources. On the other hand, when the sulphur source is exhausted and only sulphate remains in the leachate it is difficult to quantify the sulphate produced by autotrophic bacteria because sulphate is being reduced at the same time as it is used to denitrify. Thus, the stoichiometric approach could be used despite it should be complemented with some other parameters.

In this experiment even in dedicated autotrophic environments, *i.e.* with low biodegradable carbon concentrations, by applying stoichiometric calculations it was possible to verify that autotrophic denitrification could represent from 16,8% to 34,1% in denitrification process.

In future research it should be tested intermittent aeration in well decomposed MSW in order to solve the problem of the nitrate accumulation and try to evaluate the needed time of aeration to nitrify and denitrify the leachate. In the same type of test, to study if the elevated values of sulphate obtained in the aerobic bioreactor landfills are reduced under anaerobic conditions, and whether the stoichiometric amount of sulphate is produced when denitrification process occurs, in order to evaluate if this method is reliable to assess the autotrophic denitrification or not. Additionally solid sample analyses should be done to measure the sulphur content in the waste, prior to denitrification, to have a clear idea of the autotrophic denitrification influence and the respective role in the landfill management. At a field scale, more experiments should be done in order to test the laboratorial data collected until now, to evaluate the real benefits of aerobic bioreactor landfills.

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Annex I – Leachate laboratorial results

Table I.1 Reactor 1 experimental measurements.

Date	**Day**	**Column Leachate Volume (l)**	**pH**	**Alkalinity (mg $CaCO_3$/l)**	**$N\text{-}NH_4^+$ (mg N/l)**	**$N\text{-}NO_3^-$ (mg N/l)**	**SO_4^{2-} (mg/l)**
23-Abr	**0**	7,0	6,6	320	35,4	591	1121
07-Mai	**14**	7,0	6,7	216	2,1	204	1426
13-Mai	**20**	7,0	6,6	260	2	220	1426
16-Mai	**23**	7,0	7,1	211	3,5	193	1499
20-Mai	**27**	7,0	7,2	150	6,9	151	1499
24-Mai	**31**	6,9	7,3	176	9,2	235	1473
28-Mai	**35**	6,8	7,2	191	5,4	320	1473
29-Mai	**36**	8,8	7,0	672	5,9	679	1768
30-Mai	**37**	8,7	6,9	588	3,7	644	1768
03-Jun	**41**	8,6	6,9	480	5,3	591	1690
05-Jun	**43**	8,5	6,9	480	6,2	852	1690
07-Jun	**45**	8,4	6,9	486	3,9	428	1294
11-Jun	**49**	8,3	6,9	398	3,9	667	1294
17-Jun	**55**	8,2	7,1	330	3,0	560	1464
20-Jun	**58**	8,1	7,0	378	5,5	458	1464
26-Jun	**64**	8	7,1	380	7,6	482	1081
27-Jun	**65**	9	7,0	361	3,4	1397	1081
02-Jul	**70**	8,9	6,9	378	3,6	814	1122
04-Jul	**72**	8,8	7,4	329	3,9	730	1122
08-Jul	**76**	8,7	7,2	280	3	928	1191
10-Jul	**78**	8,6	7,0	292	3,4	1185	1191
15-Jul	**83**	8,5	7,3	236	4,6	969	1761
18-Jul	**86**	8,4	6,9	292	2,9	1342	1726
22-Jul	**90**	8,3	6,9	340	4,2	705	1762
29-Jul	**97**	8,3	7,1	285	3,2	729	1612
01-Ago	**100**	8,3	6,9	350	6,2	657	1839
05-Ago	**105**	8,3	6,8	397	4,7	710	1697
08-Ago	**108**	8,3	6,7	425	5,4	697	1748

Table I.2 Reactor 2 experimental measurements.

Date	**Day**	**Column Leachate Volume (l)**	**pH**	**Alkalinity (mg $CaCO_3$/l)**	**N-NH_4^+ (mg N/l)**	**N-NO_3^- (mg N/l)**	**SO_4^{2-} (mg/l)**
23-Abr	**0**	7,6	6,7	312	3,0	928	1431
07-Mai	**14**	7,6	6,7	184	3,0	878	1254
13-Mai	**20**	7,6	6,6	211	2,0	795	1254
16-Mai	**23**	7,6	6,8	189	6,1	1522	1666
20-Mai	**27**	7,6	7,0	167	6,9	667	1666
24-Mai	**31**	7,6	7,0	180	12,8	955	1527
28-Mai	**35**	7,6	6,9	173	9,9	798	1527
29-Mai	**36**	8,1	6,9	210	5,5	747	1627
30-Mai	**37**	8,0	6,8	196	5,9	743	1627
03-Jun	**41**	7,9	6,9	180	4,9	716	1467
05-Jun	**43**	7,8	6,8	184	6,7	734	1467
07-Jun	**45**	7,7	6,8	184	4,3	640	1072
11-Jun	**49**	7,6	6,8	174	4,5	993	1072
17-Jun	**55**	7,9	6,9	176	3,8	908	1267
20-Jun	**58**	7,8	6,8	164	6,5	655	1267
26-Jun	**64**	8,8	7,1	430	6,6	1224	1200
27-Jun	**65**	8,7	7,1	522	5,6	965	1200
02-Jul	**70**	8,6	6,9	518	4,5	648	1140
04-Jul	**72**	8,5	7,0	449	4,2	610	1140
08-Jul	**76**	8,4	6,9	380	3,1	660	1263
10-Jul	**78**	9,4	7,0	772	5,9	149	1263
15-Jul	**83**	9,3	7,0	660	4,6	320	1569
18-Jul	**86**	9,8	7,0	792	6,4	191	1663
22-Jul	**90**	9,8	7,2	730	5,5	166	1445
29-Jul	**97**	9,8	7,0	507	4,1	268	1527
01-Ago	**100**	9,8	6,8	550	12,6	191	1828
05-Ago	**105**	9,8	7,0	545	23,7	144	1355
08-Ago	**108**	9,8	6,9	530	27,5	111	1417

Table I.3 Reactor 3 experimental measurements.

Date	Day	Column Leachate Volume (l)	pH	Alkalinity (mg $CaCO_3$/l)	N-NH_4^+ (mg N/l)	N-NO_3^- (mg N/l)	SO_4^{2-} (mg/l)
23-Abr	**0**	6,9	6,4	190	2,3	2187	1286
07-Mai	**14**	6,9	6,6	84,8	3,0	1860	1246
13-Mai	**20**	6,9	6,9	57,8	2,0	1894	1246
16-Mai	**23**	6,9	6,8	60	3,0	1927	1349
20-Mai	**27**	6,9	6,7	63	6,9	1795	1349
24-Mai	**31**	6,9	6,8	58	14,6	1731	1393
28-Mai	**35**	6,9	6,8	66	7,0	1752	1393
29-Mai	**36**	7,9	6,8	335	7,5	1706	1697
30-Mai	**37**	7,8	6,8	276	6,2	1650	1697
03-Jun	**41**	7,7	6,9	178	6,4	1514	1484
05-Jun	**43**	7,6	7,0	160	7,0	1460	1484
07-Jun	**45**	7,5	7,0	154	6,4	1484	1266
11-Jun	**49**	7,4	6,9	153	6,6	2397	1266
17-Jun	**55**	7,3	7,0	175	5,9	1842	1311
20-Jun	**58**	7,2	6,9	152	6,8	1441	1311
26-Jun	**64**	7,1	7,0	118	6,0	2270	1360
27-Jun	**65**	7,0	6,9	110	4,5	1859	1360
02-Jul	**70**	6,9	6,8	114	4,0	1575	1158
04-Jul	**72**	6,8	6,9	92	6,0	1512	1158
08-Jul	**76**	7,8	6,8	70	4,0	1675	1545
10-Jul	**78**	7,7	6,7	262	5,8	1552	1545
15-Jul	**83**	7,6	6,9	183	7,0	1606	2182
18-Jul	**86**	7,5	6,9	170	5,5	1402	2475
22-Jul	**90**	7,4	7,0	180	6,6	1622	1945
29-Jul	**97**	7,3	7,0	134	6,5	1534	2186
01-Ago	**100**	7,3	7,0	144	5,6	1542	2598
05-Ago	**105**	7,3	7,1	148	6,2	1394	2107
08-Ago	**108**	7,3	7,0	152	4,4	1552	2098

Table I.4 Reactor 4 experimental measurements.

Date	Day	Column Leachate Volume (l)	pH	Alkalinity (mg $CaCO_3$/l)	N-NH_4^+ (mg N/l)	N-NO_3^- (mg N/l)	SO_4^{2-} (mg/l)
23-Abr	**0**	4,8	6,6	184	15,1	726	1494
07-Mai	**14**	4,8	6,6	124	2,6	652	1318
13-Mai	**20**	4,8	6,7	127	2,0	721	1318
16-Mai	**23**	4,8	6,8	117	5,8	734	1726
20-Mai	**27**	4,8	6,9	107	6,9	726	1726
24-Mai	**31**	4,8	7,1	138	14,6	794	1594
28-Mai	**35**	4,8	7,0	106	7,0	684	1594
29-Mai	**36**	5,3	6,9	154	6,7	699	1911
30-Mai	**37**	5,2	6,8	148	6,2	580	1911
03-Jun	**41**	5,1	6,9	116	6,4	582	1456
05-Jun	**43**	5,0	6,9	124	7,0	657	1456
07-Jun	**45**	4,9	6,9	124	6,4	533	1257
11-Jun	**49**	4,8	6,9	134	6,6	823	1257
17-Jun	**55**	4,7	6,9	156	5,9	736	1317
20-Jun	**58**	4,6	6,8	158	7,1	600	1317
26-Jun	**64**	6,1	6,9	365	536	574	1111
27-Jun	**65**	6,0	6,6	231	306	650	1111
02-Jul	**70**	6,5	6,4	156	17,9	725	1237
04-Jul	**72**	6,4	6,6	165	9,1	715	1237
08-Jul	**76**	6,3	6,7	173	5,0	1377	1438
10-Jul	**78**	6,2	6,7	158	5,3	1139	1438
15-Jul	**83**	6,1	6,8	131	7,2	882	1731
18-Jul	**86**	6,1	6,9	108	4,5	921	1860
22-Jul	**90**	6,1	6,8	165	7,1	919	1859
29-Jul	**97**	6,1	6,8	166	8,4	907	1662
01-Ago	**100**	6,1	6,5	182	7,1	865	2028
05-Ago	**105**	6,1	6,6	204	6,8	700	1538
08-Ago	**108**	6,1	6,6	186	7,8	842	1384

Table I.5 Reactor 5 experimental measurements.

Date	**Day**	**Column Leachate Volume (l)**	**pH**	**Alkalinity (mg $CaCO_3$/l)**	**$N\text{-}NH_4^+$ (mg N/l)**	**$N\text{-}NO_3^-$ (mg N/l)**	**SO_4^{2-} (mg/l)**
23-Abr	**0**	7,5	7,2	1113	6,6	1,3	966
07-Mai	**14**	7,5	7,3	996	10,5	17	689
13-Mai	**20**	7,5	7,3	855	10,5	45	689
16-Mai	**23**	7,5	7,4	846	22,2	-	876
20-Mai	**27**	7,5	7,4	836	17,2	0,6	876
24-Mai	**31**	7,4	7,6	888	7,8	0,7	880
28-Mai	**35**	7,3	7,5	672	3,4	0,1	880
29-Mai	**36**	8,3	7,4	932	345	2,2	1177
30-Mai	**37**	8,2	7,2	1188	1021	21	1177
03-Jun	**41**	8,1	7,4	1620	567	0,7	858
05-Jun	**43**	8,0	7,2	1140	447	3,2	858
07-Jun	**45**	7,9	7,1	633	151	11	579
11-Jun	**49**	7,8	7,0	483	7,9	34	579
17-Jun	**55**	7,7	7,0	560	3,6	12	1319
20-Jun	**58**	7,6	7,0	488	3,5	0,9	1319
26-Jun	**64**	7,5	7,0	479	5,7	1,2	908
27-Jun	**65**	8,5	6,9	815	434	3,7	908
02-Jul	**70**	8,4	7,4	1783	729	1,9	560
04-Jul	**72**	8,3	7,3	1182	573	0,7	560
08-Jul	**76**	8,2	6,9	580	48	24	1416
10-Jul	**78**	8,1	6,9	518	24	33	1416
15-Jul	**83**	8,0	6,8	478	9,9	16	2396
18-Jul	**86**	8,0	6,8	496	6,3	5,0	2617
22-Jul	**90**	8,0	6,8	555	8,4	1,0	2804
29-Jul	**97**	8,0	6,8	520	9,1	1,0	2753
01-Ago	**100**	8,0	6,9	525	11,7	0,7	3361
05-Ago	**105**	8,0	7,0	505	6,1	0,7	2969
08-Ago	**108**	8,0	6,9	510	6,4	1,0	2873

Table I.6 Reactor 6 experimental measurements.

Date	Day	Column Leachate Volume (l)	pH	Alkalinity (mg $CaCO_3$/l)	N-NH_4^+ (mg N/l)	N-NO_3^- (mg N/l)	SO_4^{2-} (mg/l)
23-Abr	**0**	7,0	6,6	238	15,1	1222	1619
07-Mai	**14**	7,0	6,8	106	3,0	1165	1418
13-Mai	**20**	7,0	6,8	133	2,0	1127	1418
16-Mai	**23**	7,0	6,9	107	3,0	1106	1722
20-Mai	**27**	7,0	7,0	80	6,3	1136	1722
24-Mai	**31**	7,0	6,9	100	9,8	1170	1634
28-Mai	**35**	7,0	6,9	94	7,3	1092	1634
29-Mai	**36**	7,0	7,0	92	5,7	1113	1746
30-Mai	**37**	6,9	6,9	90	4,2	1133	1746
03-Jun	**41**	6,8	6,9	86	4,9	1047	1602
05-Jun	**43**	6,7	6,9	94	5,6	959	1602
07-Jun	**45**	6,6	7,0	100	4,5	1091	1130
11-Jun	**49**	6,5	6,9	96	5,3	1387	1130
17-Jun	**55**	6,4	6,9	98	4,1	1128	1420
20-Jun	**58**	6,3	6,9	96	4,7	956	1420
26-Jun	**64**	6,2	7,1	96	6,5	1367	1237
27-Jun	**65**	6,1	6,9	88	4,7	1332	1237
02-Jul	**70**	6,0	6,9	100	3,8	992	1120
04-Jul	**72**	5,9	6,9	97	5,1	1073	1120
08-Jul	**76**	5,8	6,8	93	2,9	1101	1406
10-Jul	**78**	5,7	6,8	95	5,1	1010	1406
15-Jul	**83**	5,6	6,8	94	6,1	1124	1737
18-Jul	**86**	5,5	6,7	99	5,1	1119	1729
22-Jul	**90**	5,5	6,7	130	8,1	1577	1762
29-Jul	**97**	5,5	6,7	98	6,6	1100	1643
01-Ago	**100**	5,5	6,7	100	5,6	1089	1967
05-Ago	**105**	5,5	6,8	96	5,2	1077	1532
08-Ago	**108**	5,5	6,8	98	5,6	1053	1538

Annex II – Reactors photos

Figure II.1 Picture of the reactors.

Figure II.2 Picture of leachate exit valves, two leachate collection bottles and a leachate peristaltic pump.

Figure II.3 Picture of a top flange with the leachate inlet valve, the air inlet valve and the off-gas exit valve.

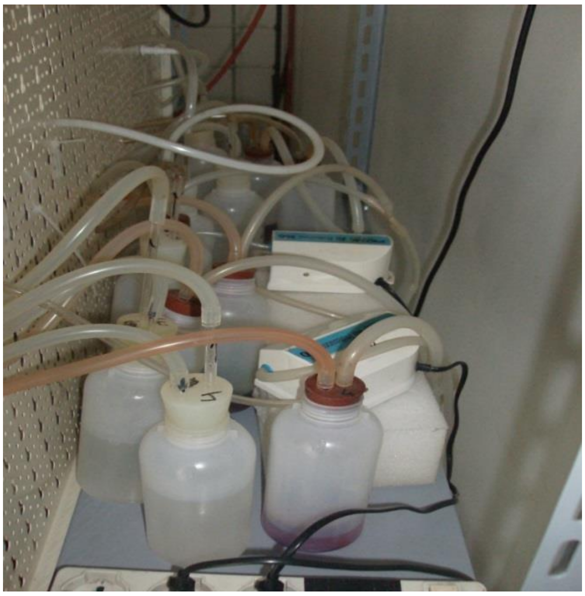

Figure II.4 Picture of some air saturation bottles, a scrubber and the two air pumps.

Figure II.5 Picture of a thermo-regulator from an insulation system.

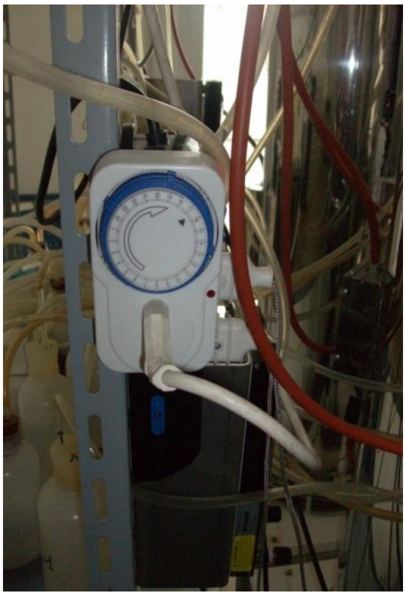

Figure II.6 Picture of the timer used for control the recirculation periods.

Figure II.7 Picture of three flow meters used to regulate the air flow.