UNIVERSITY OF PADOVA

Master of Science
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Analytical Study for the assessment of bioreactor leachate for landfills

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Abstract

Lab scale bioreactors can provide valuable information on the characteristics of a leachate over a simulated period of time. By analysing the materials produced from a bioreactor, the trends in the different parameters like TOC, Nitrogen, BOD5, Chlorides. Using four lab scale bioreactors, the parameters have been measured over an extended period of 603 days thereby permitting us to form an extensive picture on the long-term fate of landfills. The results showed that all of the parameters measured fell within the acceptable concentrations. They also indicated a downward trend in all of the parameters excluding chlorides.

Keywords: landfill, leachate, bioreactors

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Table of Contents

Chapter 1 – Introduction

1.1. Motivation

The creation of a system of integrated municipal solid waste management leads to recycling, composting, incineration and landfilling. Landfills are engineered methods of solid waste disposal aimed towards the protection of the environment.

Rapid increases in the production of municipal and industrial solid waste have occurred over the past years in many nations as a result of rising standards of living, ongoing industrial and commercial development, and expanding lifestyles. The production of municipal solid waste (MSW) is still increasing globally and per person.

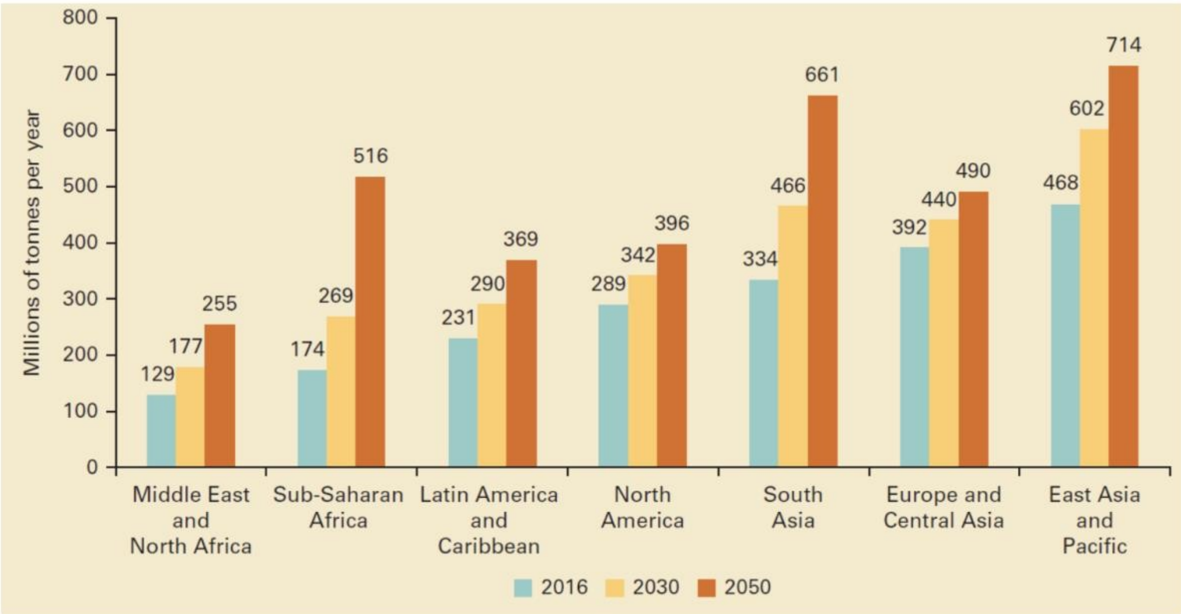

Figure 1.0.1 Projected waste generation, by region (millions of tonnes/year) (World Bank, 2019)

The constant rise in the level of waste generation calls for continued research in different areas of waste management. A particular area would be in terms of the disposal of Municipal Solid Waste (MSW) and landfilling encompasses a very important part of MSW disposal. Bioreactor landfills in which liquids and air are added in order to enhance microbial processes have aided in the process of waste degradation and stabilization

Lab-scale bioreactors have become an increasingly popular method for studying the dynamics between microbial populations and environmental conditions at landfills. By using these systems, scientists can study how different environmental factors affect the performance of bioreactors during long-term operation and evaluate different strategies for managing leachate quality. Lab-scale bioreactors provide a valuable source of data about microbial community structure and dynamics, which can be used in landfill aftercare studies to better understand how landfills behave over time and develop effective remediation strategies.

The leachate produced from a bioreactor can be analyzed over time in order to find the trends in different parameters. These parameters can range from dissolved organic compounds to inorganic macro components and heavy metals (Renou et al., 2008)

The aim of this dissertation is to analyze parameters that have been collected from a laboratory and analyze the efficacy of the results.

1.1. Objectives

There will be two primary objectives in this dissertation which have a direct relationship to the domain of application.

1. Analyse existing parameters from a functional lab scale bioreactor and provide a detailed description on the patterns followed by the components found within a leachate.
2. Assess how well the current results generalize in the long-term fate of leachate parameters.

1.2. Dissertation Outline

Chapter 1 (this chapter) provides an overview of the motivation and objectives for the thesis. Chapter 2 focuses on the prior research that is relevant to the lab scale bioreactors. Chapter 3 discusses the method that has been followed for the experiment that has been conducted. Chapter 4 evaluates the results that have been obtained and Chapter 5 summarizes the findings of the paper and takes into account the limitations of the methods used and suggests paths for further research.

Chapter 2 – Background

2.1. The current state of landfills

The increase in world population has led to a greater necessity for the treatment and disposal of municipal solid waste. Conventional methods have become outdated because of the advent of engineered landfill bioreactors.

2.2. Conventional landfills & Bioreactor landfills

MSW is mostly composed of organic waste (food waste, yard waste, grass clippings, wood, paper residue, etc.) and inorganic waste (ashes, soil, glass debris, plastics, metal waste, etc.), which is formed as a result of excessive use of resources. Compostable organic fractions can also be used for bio-methanation. (Chakma, Vaishya, 2013). However, after recycling and energy recovery, the final residual waste is sent to a landfill. Sanitary landfilling and incineration are the conventional techniques of MSW treatment and disposal worldwide. When it comes to waste from developing and lower-middle-income countries, incineration is extremely uneconomical because more than 50% of the waste's weight is moist. Incineration is a costly technique that is only recommended for nations producing waste with a significant heating value (>2400 kcals) (Mukherjee et al., 2020).

Landfills fall as one of the last alternatives of the waste management hierarchy. Proper engineering practices and standards differentiate “open dumps” from “landfills”. When waste has been confined between an appropriate liner and a cover, the landfill is said to be a “dry tomb” landfill. The risk of leachate being released from the cover cracks in the liners is high with these types of landfills (Srivastava et al., 2022). Although, the waste material undergoes stabilization in a dry tomb landfill, there is an associated environmental risk with these types of landfills. The confined disposal of waste into these landfills can result in anaerobic respiration taking place within the landfill. Anaerobic digestion follows a consecutive degradation process in the form of hydrolysis, acidogenesis, acetogenesis and methanogenesis (Grossule et al., 2018).

Bioreactor landfills offer a modern solution to the problem of landfilling by enhancing the rate of degradation of water along with the improvement of leachate treatment and disposal (Mathur, Chakma, 2002). Bioreactors have benefits over dry tomb landfills in terms of decreased landfilling detention time, an improved leachate quality, higher levels of LFG production (as indicated in Figure 2.1) and energy recovery. Furthermore, it also enhances the level of microbial activity and it allows for the possibility of implementing a hybrid system involving both aerobic and anaerobic stabilization (Srivastava et al., 2022). Overall, this can lead to cleaner surroundings while providing a clean and energy efficient option when discarding municipal solid waste.

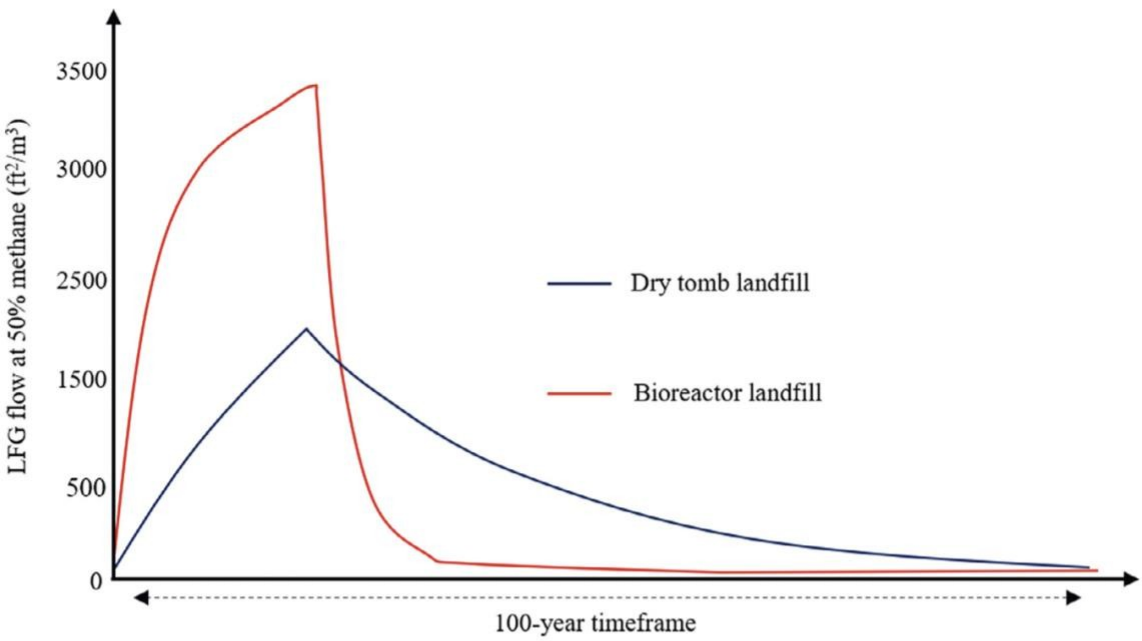

Figure 2.1. A comparison of the gas production from dry tomb and bioreactor landfills (Srivastava et al., 2022)

A major factor involved in bioreactors is the process of leachate recirculation. By adding moisture into a landfill, the level of microbial degradation can be enhanced. The process of recirculation allows waste to stabilize at a higher rate (Grossule et al., 2018)

A bioreactor landfill is considered a sustainable option for MSW disposal when compared to conventional landfilling systems because of the rate at which it stabilizes waste. This is done through a process of speeded distribution of water and moisture around a system (Tesseme, Chakma, 2020). Conventional landfills do not provide the sufficient conditions that satisfy a sustainable economy as they tend to create an increased level of groundwater contamination. Moreover, conventional landfills can also tend to be counterproductive because of its release of Green House Gases (GHGs), the loss of resources and the amount of time taken for the stabilization of waste (the process can take from 50 – 120 years) (Srivastava et al., 2022). Overall, bioreactors provide an alternative to the problem of landfilling by lowering the amount of time taken for waste stabilization and by providing an improved level of aeration, enhanced microbial degradation and a higher level of overall LFG generation.

2.3. The phases of a landfill

A landfill is a carefully engineered structure built to contain and manage waste. Landfills are designed in such a way that the waste that is stored there can eventually be stabilized and the harmful substances contained in it can be rendered harmless. This process of stabilization takes place in four distinct phases: aerobic, anaerobic, methanogenic, and post-methanogenic.

The initial phase of landfill stabilization is aerobic decomposition. During this stage, organic material present in the landfill undergoes breakdown due to the action of bacteria that use oxygen as part of their metabolic pathways (Dai & Chynoweth, 2001). As this process proceeds, carbon dioxide, water vapor, heat, and other byproducts are generated. The heat produced during this stage contributes significantly to the temperature increase within the landfill itself.

The second phase of stabilization is anaerobic decomposition which occurs once all available oxygen has been consumed within the landfill (Hao et al., 2018). During this period, bacteria utilizing anaerobic metabolism come into play and generate methane gas as well as other byproducts including carbon dioxide and sulfides (Dai & Chynoweth, 2001). This phase can take up to several years depending on the conditions within the landfill itself.

The third stage of stabilization is methanogenic which involves further breakdown of organic matter by methanogenic organisms. These organisms utilize methane as part of their metabolic pathways and produce carbon dioxide as one of their byproducts (Hao et al., 2018). This stage can last until all remaining organic matter has been broken down or oxidized.

Finally, after all stages have been completed landfill stabilization enters a post-methanogenic period where gases such as carbon dioxide are released more slowly than during earlier stages (Dai & Chynoweth, 2001). During this period temperatures begin to stabilize while hazardous materials leach out at slower rates than during earlier stages (Hao et al., 2018). Eventually these hazardous materials will also become rendered harmless though it should be noted that this process can take many years depending on the size and composition of the landfill itself.

Landfills are complex engineering structures carefully designed to contain and manage waste material safely over time. Stabilization occurs through four distinct steps: aerobic decomposition; anaerobic decomposition; methanogenic breakdown; and finally post-methanogenic release of hazardous materials over time until they become harmless.

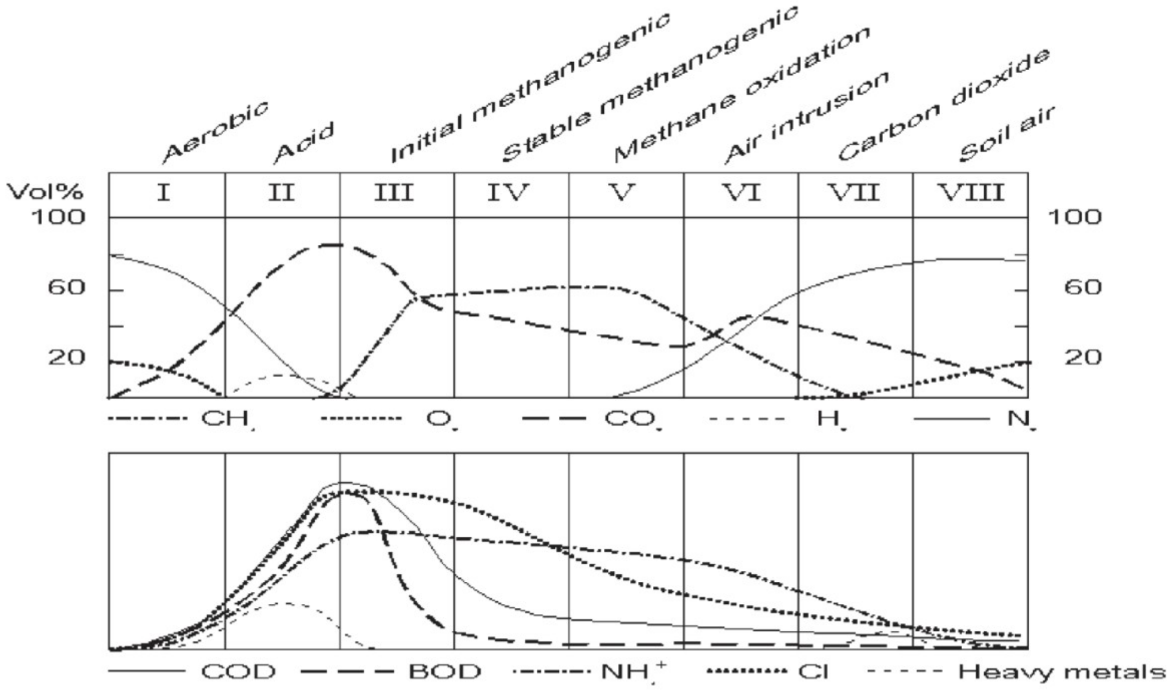

Figure 2.2. The phases of a landfill and the quality of leachate (Kjeldsen et al., 2002)

2.4. The components of landfill leachates

Landfill leachates are made up of a mixture of organic and inorganic pollutants. Some of these pollutants can be harmful to the environment. This effect is intensified when waste segregation is not practiced in a country (Salam et al., 2021).

In general, landfill leachates contain very high concentrations of organic compounds. These organic compounds are referred to as dissolved organic matter. This would be made up of sugars, acids, alcohols and aldehydes. There would also be inorganic compounds such as chlorides, nitrogen, magnesium and calcium. Ammonium, phosphorus, sulfate, and heavy metals are examples of inorganic contaminants present in leachates. Young leachates are mostly composed of volatile fatty acids, which gradually diminish in older landfills. Old landfills and leachate plumes frequently contain humic and fulvic acids as well. The most prevalent heavy metals are Fe, Pb, Ni, Cd, As, Cr, Cu, and Hg. The aromatic hydrocarbons (benzene, toluene, ethylbenzene, and xylene), phenols, insecticides, polyethylene, plasticizers, and halogenated organic compounds like PCBs and dioxins are among the other harmful contaminants found in landfill leachates. Pathogenic microorganisms, primarily coliform bacteria and a few viruses, can also be found in landfills. Yet, the pH and temperature fluctuations may render these microbes inactive (Salam et al., 2021)

The pollutants found in leachates can be divided into four categories namely:

• Dissolved organic matter, which can be measured as Total Organic Carbon (TOC) or Chemical Oxygen Demand (COD), volatile fatty acids and more refractory compounds like fulvic-like and humic-like compounds. (Kjeldsen et al., 2002)

• Inorganic macrocomponents include iron (Fe^{2+}), manganese (Mn^{2+}), calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}), potassium (K^{+}), ammonium (NH_4^{+}), chloride (Cl^{-}), sulfate (SO_4^{-}), and hydrogen carbonate (HCO_3^{-}). (Kjeldsen et al., 2002)

• Heavy metals, include copper (Cu^{2+}), lead (Pb^{2+}), nickel (Ni^{2+}), zinc (Zn^{2+}), cadmium (Cd^{2+}), chromium (Cr^{3+}), and nickel (Kjeldsen et al., 2002)

Leachate from landfills may also contain other substances, such as borate, sulfide, arsenate, selenate, barium, lithium, mercury, and cobalt. Nonetheless, these substances are typically detected in incredibly low amounts and are only marginally significant. Several toxicological tests can be used to define the composition of leachate and provide information about the pollutants that may be detrimental to organisms.

2.4.1. Dissolved Organic Compounds

Dissolved organic compounds (DOCs) are a major component of landfill leachate and can pose considerable environmental risks when not managed properly. DOCs are the result of complex biochemical processes that occur within the landfill, leading to the release of various organic compounds into surrounding groundwater or surface water systems. As these compounds accumulate over time, they can lead to various water quality issues such as eutrophication, taste and odor problems, and contamination of drinking water supplies. Advanced oxidation processes (AOPs) have been found to be an effective means of reducing DOC concentrations in landfill leachate before it is discharged into local waterways. This sectionprovides an overview of the most common methods used for monitoring and measuring DOC levels in landfill leachate, as well as how AOPs may be utilized to effectively reduce their concentrations.

DOCs are composed of a variety of different chemical compounds which are formed through microbial activity within landfills. These compounds can range from simple molecules such as carbon dioxide and methane, to more complex organics like fats, proteins, carbohydrates, lipids, hormones, and pharmaceuticals. The amount and composition of these dissolved organic compounds vary greatly depending on factors such as age of the landfill waste material and climate conditions at the time of deposition. It is important to understand the makeup of these DOCs in order to identify sources upstream which may be contributing pollutants downstream.

Monitoring dissolved organic compound levels in landfill leachate is essential for ensuring proper management practices are being employed which minimize environmental injury from discharges into local waterways. There are a number of different analytical techniques available for this purpose ranging from total organic carbon (TOC) measurement to chromatography-mass spectrometry (GCMS). TOC is a widely used method for determining DOC levels that involves passing a sample through an oxygenated chamber where its concentration can be inferred based on how long it takes for all oxygen within the chamber to become depleted. The results obtained with this technique provide general information about overall contaminant levels but do not provide any insight into their specific compositions or structures.

Spectrophotometry and GCMS offer more detailed information regarding the types and structures of dissolved organics present in samples while also providing reliable quantification data due to their high sensitivity thresholds. Spectrophotometry works by measuring light absorbance at various wavelengths by each type molecule present in a sample while GCMS involves analyzing samples using gas chromatograms coupled with mass spectra detectors which allow for identification and quantification purposes even at trace levels within samples (Ayres-Santiago et al., 2019). While both techniques require advanced instrumentation and training for accurate results, they offer greater confidence when working with unknown contaminants or when lower detection limits are desired (Kim et al., 2020).

AOPs offer several advantages over traditional wastewater treatment options such as sand filtration or activated carbon adsorption because they enable more rapid removal rates without sacrificing efficiency (Wang et al., 2017). They involve exposing wastewater containing contaminants to a variety oxygenated conditions created via either chemical or physical methods so that microorganisms present in the system can breakdown any organics present into simpler components that can then be removed using downstream treatment processes such as flocculation or membrane filtration (Robertson et al., 2015). Bioreactor systems represent one elaborate form AOPs where wastewater flows through reaction chambers containing air bubbles allowing microbes contained therein access to abundant amounts oxygen needed break down stubborn organics into simpler forms which can then be easily removed during later

processes(Kim et al., 2020). Research has shown bioreactors capable reducing DOC concentrations up 50% under ideal operating conditions (Ayres-Santiago et al., 2019).
Overall, AOPs represent an effective tool managing DOC concentrations within landfill leachates while simultaneously providing additional benefits such as improved air quality due odorous emissions reduction nutrient loading prevention receiving waters To ensure proper functioning these systems regular monitoring maintenance must conducted order identify potential issues before they result significant environmental damage Further research needed better understand how these technologies interact other forms wastewater treatment utilization become more widespread across industrial applications Moreover further studies should conducted optimize performance without sacrificing safety efficacy standards set forth regulatory agencies worldwide .

2.4.2. Inorganic compounds

Inorganic macrocomponents refer to elements or compounds that are not composed of carbon or hydrogen atoms. Common examples include metals such as lead, arsenic, chromium, mercury, cadmium, zinc, copper, and nickel; as well as nitrates and sulfates (Liu et al., 2017). These components can enter leachate from a variety of sources such as industrial wastewater disposal sites or hazardous waste sites (Liu et al., 2017).

The presence of these inorganic macrocomponents in leachate has been studied extensively due to their potential impacts on human health and the environment. For instance, high concentrations of certain metals such as lead can cause neurological disorders (Jha et al., 2019). Nitrate contamination can result in water-borne illnesses such as blue baby syndrome (BBS) (Kumar & Mishra 2018). The presence of sulfates can increase acidity levels which can be damaging to aquatic life (Ahmad et al., 2020).

These findings demonstrate the need for improved management strategies for landfill leachate and more research into ways to reduce its negative effects on human health and the environment. To do this effectively requires an understanding of what types of components are present in landfill leachate and how they interact with each other. Further research should focus on developing comprehensive environmental monitoring protocols to track changes in leachate composition over time so that any necessary steps can be taken quickly to protect public health.

Overall, landfill leachates contain numerous potentially dangerous components that must be monitored carefully if their effects on humans and ecosystems are to be minimized. Inorganic macrocomponents such as metals, nitrates, and sulfates represent some of the main contaminants present in these solutions which must be tracked carefully through proper environmental monitoring protocols so that any adverse effects can be identified quickly and appropriately addressed.

Table 2.1. Typical Landfill leachate characteristics (Alvarez-Vasquez et al., 2004; Chian et al., 1976)

No.	Parameter	Unit	Type of landfill leachate		
			Young (< 5 years)	Intermediate (5–10years)	Stabilized (> 10 years)
1	pH		<6.5	6.5–7.5	>7.5
2	COD	mg/L	>10000	4000–10000	<4000
3	BOD_5/COD		0.5–1.0	0.1–0.5	<0.1
4	Organic compound		80% VFA[a]	5–30% VFA[a] + HFA[b]	HFA[b]
5	NH_3-N	mg/L	<400	NA[c]	>400
6	TOC/COD		<0.3	0.3 –0.5	>0.5
7	Kjeldahl nitrogen	g/L	0.1–0.2	NA[c]	NA[c]
8	Heavy metals	mg/L	Low to medium	Low	Low
9	Biodegradability		Important	Medium	Low

[a]= Volatile fatty acids, [b]=Humic and fulvic acids, and [c]= Not available

Table 2.2. Leachate concentrations based on the time of landfill stabilization (Kostova, 2006)

Parameters	Phases			
	Transition	Acid-formation	Methane formation	Final maturation
	(0-5 years)	(5-10 years)	(10-20 years)	(>20 years)
BOD_5	100-11000	1000-57000	100-3500	4-120
COD	500-22000	1500-71000	150-10000	30-900
TOC	100-3000	500-28000	50-2200	70-260
NH_3-N	0-190	30-3000	6-430	6-430
NO_2^--N	0.1-500	0.1-20	0.1-1.5	0.5-0.6
TDS	2500-14000	4000-55000	1100-6400	1460-4640

2.5. Leachate parameters

2.5.1. TOC

Total organic carbon (TOC) is an important component of the leachates produced by landfills and their impacts on the environment. TOC measurements are used to assess the potential of landfill leachates to pollute surface waters, deplete oxygen in aquifers and contaminate drinking water supplies.

TOC is an acronym for Total Organic Carbon, which refers to organic compounds present in a sample of liquid or solid materials such as soil or water. TOC consists mostly of carbon-containing compounds from natural sources such as plant material, animal waste products, and decaying organic matter. Synthetic compounds such as industrial chemicals can also be included in the TOC measurement. In landfill leachates, TOC is primarily derived from organic material that has been disposed of in landfills. As this material decomposes under anaerobic conditions, it produces liquid wastes that contain high concentrations of dissolved organics. These leachates can contain high levels of proteins, carbohydrates, lipids and other macromolecules that have significant environmental effects when discharged into aquatic systems or drinking water supplies.

The presence of high concentrations of TOC in landfill leachate can lead to eutrophication (excessive nutrient loading), hypoxia (low oxygen levels), toxic substances development and algal blooms in surface waters downstream from landfills. Other possible implications include increased BOD (biochemical oxygen demand) levels leading to increased energy consumption for wastewater treatment processes; increased corrosion rates of pipes; and reduced water clarity due to suspended solids resulting from biodegradation processes associated with decomposition reactions (Cai & Zhang 2007).

Total organic carbon (TOC) plays an important role in assessing the potential impact of landfill leachate discharge on surface waters and drinking water resources. Measurements of TOC can be used for identifying sources of contamination and developing effective remediation strategies that minimize environmental risks associated with these landfills' operations.

2.5.2. Ammonia Nitrogen (NH4+)

Landfill leachate typically contains high levels of pollutants, including ammonia nitrogen (NH4+). Excessive NH4+ in landfill leachates can have detrimental effects on the environment, such as contaminating nearby surface and groundwater sources. Furthermore, the presence of NH4+ in leachates may cause excessive algal growth which can lead to a decrease in dissolved oxygen levels and resultant eutrophication of aquatic ecosystems (Carma et al., 2018).

NH4+ is found in landfills due to various organic matter decomposition processes taking place within them (Dai et al., 2016). The most common source of NH4+ is from food waste and animal manure present within municipal solid wastes. As these organic materials break down, they release NH4+, causing it to become highly concentrated within landfill leachates (Ge, 2017). In addition, the presence of ammonium salts within industrial wastes can also contribute to increasing NH4+ concentrations in landfill leachate (Gharabaghi & Rahmani-Nia, 2019).

Scientific research has demonstrated that an effective way to reduce the amount of NH4+ in landfill leachates is by applying chemical treatments to reduce its bioavailability. The most widely used method for this purpose is lime treatment which helps form insoluble calcium ammonium compounds that are unable to be utilized by microorganisms (Vesely et al., 2007).

Additionally, biotechnological solutions such as bioaugmentation or biofilm processes are also effective for reducing NH4+ levels in leachates (Sato et al., 2014). Bioaugmentation involves introducing specific microbial strains into landfill systems which can be specially adapted for metabolizing ammonia-nitrogen into less toxic compounds.

Scientific research has demonstrated that NH4+ can be a major pollutant in landfills and its presence in leachate poses an environmental hazard. Various techniques have been developed for controlling and reducing its concentration including chemical treatments and biotechnological solutions such as bioaugmentation or biofilm processes.

Table 2.3. Ammonia concentrations for landfills in their methanogenic phase (Kjeldsen et al., 2002)

Ammonia-N (mg/l)	Reference
110	Average ammonia concentration from 104 old, Danish landfills (Kjeldsen and Christophersen, 2001)
233	Composite results at Sandsfarm Landfill, (Robinson, 1995)
282	Composite results at Bishop Middleham Landfill, (Robinson, 1995)
399	Composite results at Odsal Wood Landfill, (Robinson, 1995)
43	Composition results at East Park Drive Landfill, (Robinson, 1995)
30	Composition results at Marton Mere Landfill, (Robinson, 1995)
12-1571	Range of concentrations from 21-30 year old, German landfills (Krumpelbeck and Ehrig, 1999)
445	Average concentration from 21-30 year old, German landfills (Krumpelbeck and Ehrig, 1999)
740	Average concentration (Ehrig, 1988)

2.5.3. Nitrities (NO2-)

Nitrates and nitrites (NO2-) are common components of landfill leachate due to the decomposition of organic waste materials. Nitrogen-containing compounds present in landfill leachate have been identified as major environmental pollutants and have been linked to eutrophication, reduced biodiversity, and the development of certain types of cancer (Voulvoulis et al., 2005). It is therefore important to monitor and manage their concentration in leachate produced by landfills.

Various scientific studies have reported that nitrate concentrations in landfill leachates range from 0 to 500 mg/L, with most values falling between 5 - 150 mg/L (Nyamugafata & Lottermoser, 2008; Goyal & Saini, 2012). Similarly, nitrite concentrations were typically low (<1mg/L), except for some sites that reported values up to 10mg/L (Nyamugafata & Lottermoser, 2008). However, these values can vary significantly depending on the type of waste deposited at the landfill site. For instance, higher concentrations of nitrogen-containing compounds were observed for landfills accepting industrial or agricultural wastes (Goyal & Saini, 2012).

2.5.4. Nitrates (NO3-)

Nitrates (NO3-) are a common component of landfill leachate, which is the liquid that forms when water passes through solid waste in landfills. Scientific research has found that nitrate concentrations in landfill leachates can range from 0.02 to 2 mg/L (McGurk & Gschwend, 1999). This is significant compared to nitrate levels found in other environments such as rivers and streams, which usually exhibit much lower concentrations. Nitrates in landfill leachates can be attributed to organic nitrogen sources like food scraps and sewage as well as industrial sources like fertilizers and septic tanks (Tchobanoglous et al., 2002).

The presence of high nitrate levels in landfill leachates can pose a potential environmental hazard if it contaminates the groundwater or nearby surface water resources. Nitrate pollution has been known to cause eutrophication of aquatic ecosystems due to its ability to stimulate algae growth (Wang et al., 2018). In addition, nitrates have been linked to adverse health outcomes such as methemoglobinemia, also known as “blue baby syndrome” (U.S Environmental Protection Agency, 2021).

Given these risks, it is important for landfill operators to take precautionary measures when it comes to managing their leachate. Common practices include using constructed wetlands and aerated lagoons for treatment prior to release into the environment (Kumari et al., 2019). Proper management of leachates will help ensure that local water resources are safe from contamination by nitrate pollutants.

Studies have shown that there is a wide range of nitrate concentrations found in landfill leachate. These values can vary depending on the types of waste disposed at the site, but they usually exceed what is seen in most natural environments. It is important for landfill managers and other stakeholders involved with solid waste disposal sites to be aware of these potential risks so they can take necessary steps towards preventing contamination of nearby surface or groundwaters with nitrates.

2.5.5. BOD5

Biological Oxygen Demand (BOD5) is a measure of the amount of oxygen consumed by microorganisms to break down organic matter in water. In landfill leachate, BOD5 is an important indicator of the environmental impact caused by this waste-water. High BOD5 levels indicate a higher level of organic pollution and can lead to negative impacts on water quality, such as eutrophication, sedimentation and reduced oxygen availability in receiving water bodies.

Scientific literature has been used to better understand the impact of BOD5 in landfill leachates and its common values for landfills. According to a study published in the Water Environment Research journal (Lian et al., 2017), the average BOD5 value for leachate from urban landfills is between 10 and 25 mg/L. This range can vary depending on factors such as type of waste being disposed, age of landfill, leachate treatment practices or rainfall conditions among others (Beck et al., 2014).

Another study conducted by researchers from Spain's University of Zaragoza focused on different types of landfills found around the world (Vicente et al., 2019). The results showed that significant variations in BOD5 concentrations may exist among landfills, with some having levels below 5 mg/L while others had values up to 50 mg/L or higher. The authors also found that modern sanitary landfills typically have lower BOD5 concentration compared to older ones, even when they receive similar amounts and types of wastes.

Table 2.4. BOD & COD values for landfills in the methanogenic phase (Kjeldsen et al., 2002)

BOD (mg/l)	COD (mg/l)	BOD/COD	Reference
5.7-1100	76-6997	---	Concentration ranges from 21-30 year old German landfills (Krumpelbeck and Ehrig, 1999)
290	1225	0.24	Average concentrations from 21-30 year old German landfills (Krumpelbeck and Ehrig, 1999)
44	320	0.11	Average concentrations from old, Danish landfills (Kjeldsen and Christophersen, 2001)
39	398	0.10	Composite results at Sandsfarm Landfill, (Robinson, 1995)
11	190	0.06	Composite results at Bishop Middleham Landfill, (Robinson, 1995)
38	517	0.07	Composite results at Odsal Wood Landfill, (Robinson, 1995)
1.0	53	0.02	Composite results at East Park Drive Landfill, (Robinson, 1995)
2.5	64	0.04	Composite results at Marton Mere Landfill, (Robinson, 1995)
180	3000	0.06	Average concentrations in methanogenic leachate (Ehrig, 1988)

2.5.6. Chlorides

Chlorides are salts composed of chlorine, and are commonly found in leachates from landfills due to the presence of industrial wastes, domestic sewage, agricultural runoff, and other sources (Baker & Novoa-Garrido, 2017). As such, chlorides present in landfill leachate can pose a health risk to the environment if they reach drinking water or surface water resources (Singh & Ghoshal, 2012).

The concentration of chlorides in landfill leachates varies significantly depending on the type and quantity of material disposed of in the landfill. Generally speaking, concentrations range from 10 mg/L to 4500 mg/L (Kosmulski et al., 2018; Singh & Ghoshal, 2012). Landfills located near bodies of water typically have higher concentrations of chlorides as increased leaching may occur due to the presence of groundwater and rainfall (Saravanakumar et al., 2016). Ultimately, the specific chloride content will depend on both the inputs into a landfill as well as environmental factors such as precipitation levels.

Given their potential for contamination of groundwaters and other resources, it is important to understand how chlorides behave within landfill environments. Research has found that their concentrations tend to increase with time due to their solubility in water (Baker & Novoa-Garrido, 2017; Sadeghi et al., 2015). Other research has explored techniques for managing chloride concentrations in landfills such as using clay-based materials which can reduce leaching rates (Aguado et al., 2019; Torii et al., 2013). This demonstrates the importance of understanding how chlorides behave in different systems so that effective methods can be employed for reducing contamination levels.

2.5.7. pH values

The pH values of leachates have been studied extensively. Generally, these values can vary depending on both the type of landfill and its operational phase. In terms of aerobic, anaerobic and methanogenic phases, the respective pH levels tend to be relatively low in aerobic phase (pH level 6-7), slightly higher during anaerobic phase (pH level 7-8) and highest during methanogenic phase (pH level 8-9) (Kanelis et al., 2005)

Studies have also shown that pH levels may vary based on factors such as temperature, substrate composition and hydraulic retention time. For example, research has suggested that higher temperatures can lead to elevated pH levels due to increased microbial activity, while lower temperatures can result in a decrease in pH levels. Similarly, the presence of high concentrations of biodegradable substrates such as carbohydrates or proteins can lead to an increase in pH levels due to increased microbial respiration. Moreover, longer hydraulic retention times have also been associated with higher pH values due to increased mineralization rates (Gilliam et al., 2006).

Landfill leachate pH values vary significantly according to the landfill's biological status and operational conditions; for instance, it tends to be relatively low in aerobic phase (pH level 6-7), slightly higher during anaerobic phase (pH level 7-8) and highest during methanogenic phase (pH level 8-9). Factors such as temperature, substrate composition and hydraulic retention time can also influence these values.

Table 2.5. Leachate composition & ranges for acid & methanogenic phase (Kjeldsen et al., 2002)

Parameter	Acid phase		Methanogenic phase		Average
	Average	Range	Average	Range	
pH	6.1	4.5-7.5	8	7.5-9	
Biological Oxygen Demand (BOD_5)	13000	4000-40000	180	20-550	
Chemical Oxygen Demand (COD)	22000	6000-60000	3000	500-4500	
BOD_5/COD (ratio)	0.58		0.06		
Sulfate	500	70-1750	80	10-420	
Calcium	1200	10-2500	60	20-600	
Magnesium	470	50-1150	180	40-350	
Iron	780	20-2100	15	3-280	
Manganese	25	0.3-65	0.7	0.03-45	
Ammonia-N					740
Chloride					2120
Potassium					1085
Sodium					1340
Total phosphorus					6
Cadmium					0.005
Chromium					0.28
Cobalt					0.05
Copper					0.065
Lead					0.09
Nickel					0.17
Zinc	5	0.1-120	0.6	0.03-4	

2.5.8. Methane

Research conducted on the methane values in landfill leachates has revealed that the levels of methane can differ greatly depending on which phase is being studied. During the aerobic phase, the concentrations of methane are typically low due to the presence of oxygen and high levels of microbial activity. As a result, methanogenesis and other sources of methane production are limited in this phase. In contrast, during anaerobic conditions, methanogens can proliferate and produce high amounts of methane. Finally, during the methanogenic phase, there are often very high amounts of methane present due to intense activity by a specialized group of microorganisms known as methanotrophs.

Recent studies have provided further evidence that different phases will show drastically different levels of methane production. For example, a study by Bey et al. (2020) found that when comparing aerobic to anaerobic conditions, the concentrations of methane were nearly five times higher under anaerobic conditions than aerobic conditions. Additionally, another study by Maxon et al. (2019) found that while under normal anaerobic conditions there was still significant levels of CH4 produced, when methanotrophic bacteria were introduced, it led to significantly increased rates of CH4 production compared to non-methanotroph environments.

Research on landfill leachates has demonstrated how important environmental factors such as oxygen availability are for controlling and predicting methane production from landfills.

2.5.9. Oxygen

In aerobic conditions, where oxygen is present, leachate oxygen concentrations are typically greater than those found in anaerobic conditions. In these scenarios, microorganisms can metabolize organic matter and utilize oxygen to do so. This process results in the formation of carbon dioxide (CO_2) as a byproduct, resulting in reduced oxygen levels in the leachate. However, if there is no available source of electron acceptors such as nitrogen or sulfur compounds, then the microorganisms will be unable to utilize oxygen and reduce its concentration even further.

In anaerobic conditions, where there is no available source of electron acceptors, microorganisms will utilize alternative sources such as sulfates or nitrates to break down organic matter. This process produces methane (CH_4) as a byproduct resulting in lower oxygen concentrations. Methanogenic phases occur when there are high methane levels present, resulting in even lower oxygen concentrations due to the fact that methane does not require any electron acceptors for its production (Schaefer et al., 2018).

2.5.10. Carbon Dioxide

The presence of carbon dioxide (CO_2) in landfill leachate is an important indicator of the performance and stability of landfills. Carbon dioxide is generated from organic matter decomposition, and its concentration can vary depending on the stage of leachate degradation.

In the aerobic phase, CO_2 concentrations are usually high due to the breakdown of organic material within the landfill. As oxygen levels decrease in the anaerobic phase, methane production increases resulting in a decrease in CO_2 concentrations. In the methanogenic phase, CO_2 concentrations are typically lower due to higher levels of methane production and as a result, the overall gas composition changes substantially (Fang et al., 2017).

Overall, the concentration of CO_2 in landfill leachates will vary depending on the stage of leachate degradation; with higher concentrations during aerobic stages and lower concentrations during anaerobic and methanogenic phases (Li et al., 2019). Furthermore, different types of organic matter can produce different amounts of CO_2 when degraded (Gutiérrez-Sánchez et al., 2018). Thus, it is important to consider these factors when evaluating leachates for CO_2 levels.

Chapter 3 – Methodology & Analytical Methods

3.1. Methodology

In order to observe the impacts that a bioreactor landfill would have on the quality and the different parameters regarding leachates, we carry out lab scale bioreactor tests. The experimental setup for this is shown in Figure 3.1.

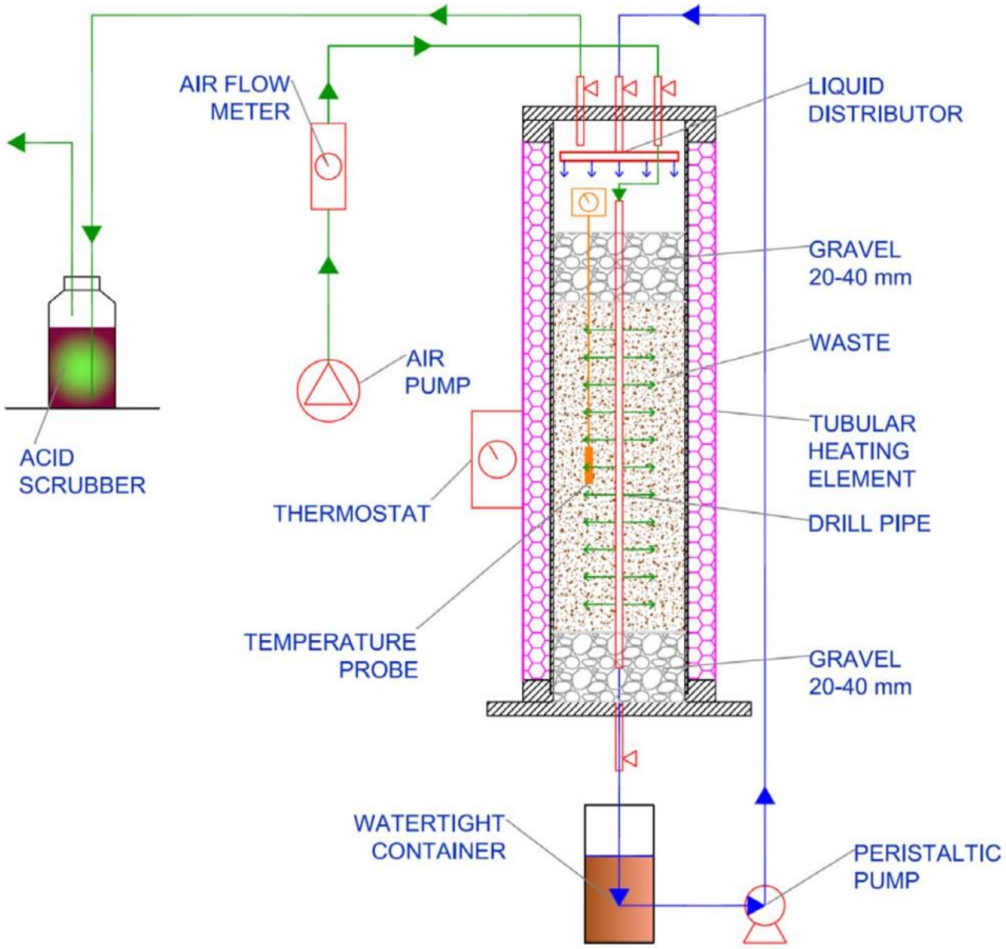

Figure 3.1. Schematic of a lab-scale reactor under aerobic conditions (Raga, Cossu, 2013)

For the lab-scale bioreactors, four reactors OC, OI, MC & MI are used. The first letter represents the name of the reactor and the final letter represents whether aeration is done continuously or intermittently.

The aeration of the system is carried out by using an air pump. The leachate would be recirculated through the system every week. Approximately 21 leachate samples have been collected in order to obtain readings for the values of ammonia-nitrogen, nitrates, TOC, BOD5 Chlorides and pH values.

In all of the reactors, the temperature is maintained at 45 ° C.

For the reactors with continuous aeration, the setup would initially be anaerobic. After 149 days of anaerobic conditions, air would be pumped in continuously. For the reactors with intermittent aeration, the system would initially be setup under anaerobic conditions with mid-intervals of air being pumped in.

3.2. Analytical Methods

3.2.1. Reactor setup

For the bioreactors, three plexiglass columns are filled with equal masses of waste. The columns have been properly isolated and sealed in order to ensure that there is no leakage of biogas. The collected gas is collected in bags in order to obtain a measurement of the volume of gas. A drainage valve at the bottom of the reactor is used in order to extract leachate. During the entirety of the experiment, the temperature of the reactors was monitored by probes.

3.2.2. Analytical Methods

International standard procedures have been followed for the analysis of solid samples, leachate and biogas.

Solids analysis is carried out by removing waste from the bioreactors. This waste would then be mixed in a tank in order to increase its homogeneity. A waste sample of a fixed mass (500g) is taken from the column. This waste sample has to be milled in order to determine parameters like Total Solids (TS), Volatile Solids (VS), Total Kjeldahl Nitrogen (TKN), Ammonia Nitrogen ($N\text{-}NH_4^+$), Total Organic Carbon (TOC) and the Respiration Index (RI_4). The RI_4 value is determined by using a Sapromat Apparatus. A leaching test would be carried out on the initial waste sample. This is done by bringing the Liquid to Solid Ratio (L/S ratio) to 10L/kgTS and it is then mixed for 24 hours and filtered at 0.45 µm. The resulting eluate would be analysed to identify the different parameters considered in the leachate (pH, TOC, COD, alkalinity, TKN, BOD_5, $N\text{-}NH_4^+$, SO_4^{2-} & Cl^-).

The leachate is collected for sampling on a weekly basis in order to analyze the aforementioned parameters.

The biogas that is produced is collected in bags attached to the reactor. The frequency of analysis ranges from once daily for hybrid reactors and weekly for anaerobic reactors. The composition of the bag would then be categorized in terms of oxygen, methane and carbon dioxide. A portable analyzer is used in order to analsye the composition of the gases and distinguish between them.

In the bioreactors, the gas is bubbled through a boric acid scrubber as shown in Figure 3.1. This process is carried out in order to trap the ammonia into the acid from the gas. This solution would then be titrated periodically with H_2SO_4 (0.1M) in order to find the exact amount of ammonia emanating from the gas. Methylene blue and Methyl Red would be used as indicators to verify changes in the pH value of the scrubber. If a color change from purple to green was observed, it indicated that NH_3 gas was emitted.

Chapter 4 – Results & Discussion

4.1. Ammonia Nitrogen

The results obtained for ammonia nitrogen for the bioreactors with continuous and intermittent aeration has been highlighted in Table 4.1.

Table 4.1. The results for Ammonia-Nitrogen over time

	AMMONIA NITROGEN (mg/L)				
Day #	**Sampling date**	**Reactor OC**	**Reactor OI**	**Reactor MC**	**Reactor MI**
16	16/12/2020	1073	956	1699	841
44	13/01/2021	1076	1215	1616	790
79	17/02/2021	1437	932	2246	857
107	17/03/2021	1428	902	2068	799
128	07/04/2021	834	386	1099	727
142	21/04/2021	1266	792	1072	782
149	28/04/2021	985	593	2074	668
156	05/05/2021	495	378	2107	666
163	12/05/2021	275	169	1454	236
170	19/05/2021	256	46	1267	180
178	27/05/2021	68.6	23.7	970	115
185	03/06/2021	8.23	17.4	889	289
191	09/06/2021	22.7	3.7	685	47.7
198	16/06/2021	9.01	5.74	523	24.7
205	23/06/2021	9.01	5.74	560	23.8
212	30/06/2021	9.01	5.74	416	19.4
219	07/07/2021	9.01	5.74	190	19.6
226	14/07/2021	9.81	15.8	214	32.8
298	24/09/2021	22.4	15.6	138.6	66.2
531	16/05/2022	13	9	15	17
603	27/07/2022	4.9	2.5	10	9.9

Separate graphs have been obtained for Reactors O & M to show how the amount of ammonia nitrogen changes over time for continuous and intermittent intervals of aeration.

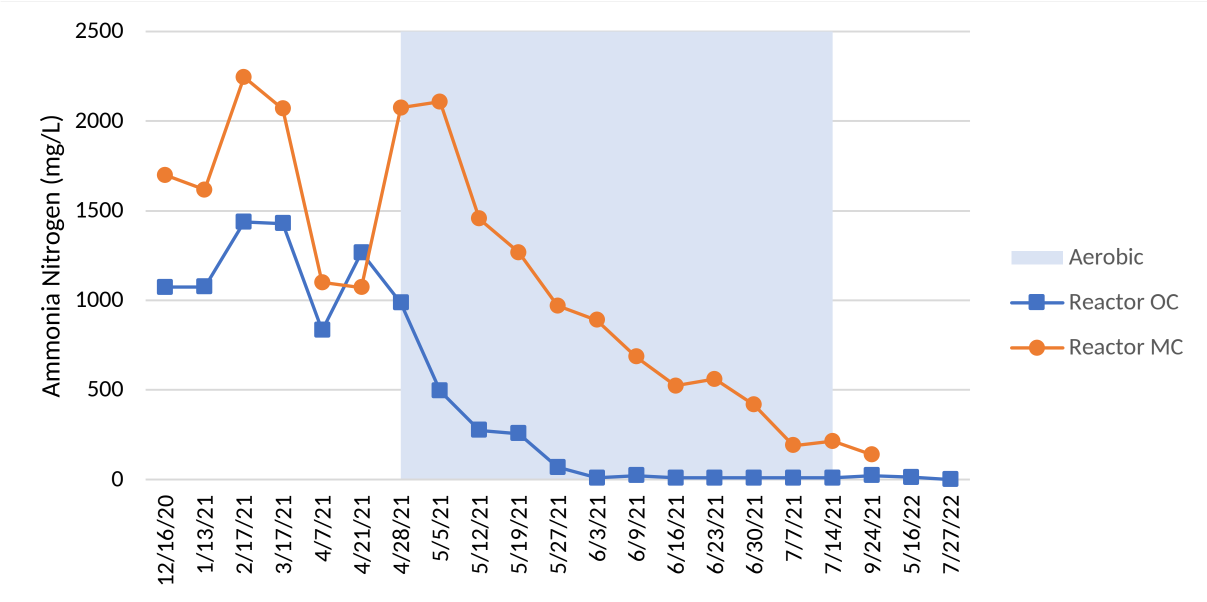

Figure 4.1. The change in Ammonia-Nitrogen in mg/L over time for continuous aeration

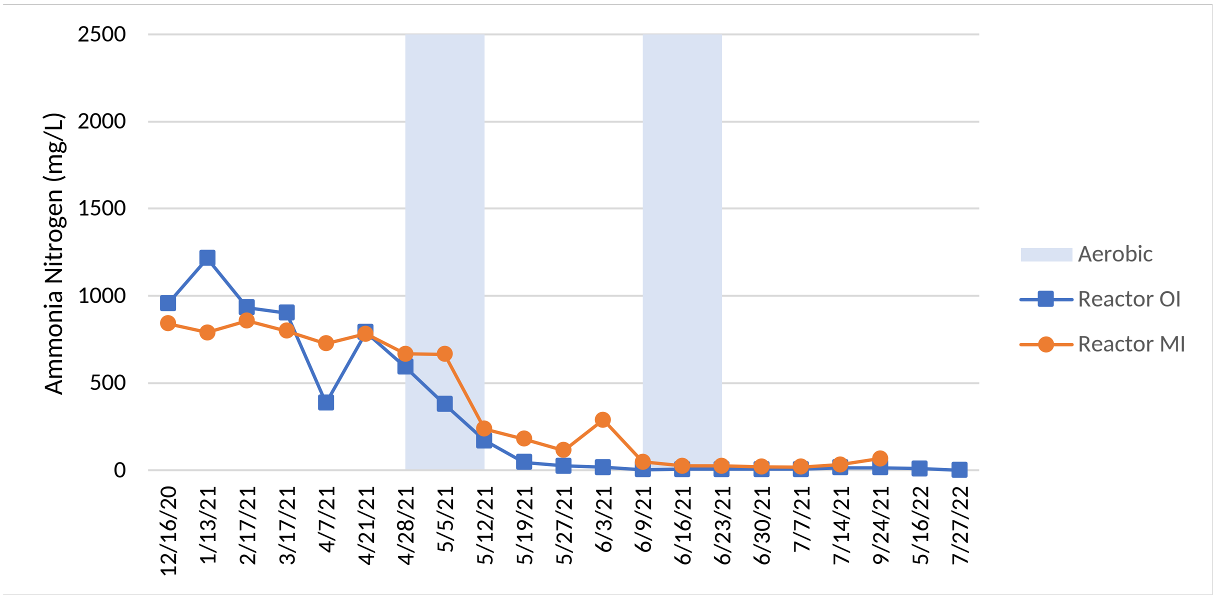

Figure 4.2. The change in Ammonia-Nitrogen in mg/L over time for intermittent aeration

The graphs indicate how over an extended period of time, the values for the ammonia-nitrogen tends to drop. It has to be noticed from Table 4.2 that the average values for the ammonia-nitrogen values tend to be much lower than the ammonia concentrations obtained for real landfills.

Table 4.2. Ammonia concentrations for landfills in their methanogenic phase (Kjeldsen et al., 2002)

Ammonia-N (mg/l)	Reference
110	Average ammonia concentration from 104 old, Danish landfills (Kjeldsen and Christophersen, 2001)
233	Composite results at Sandsfarm Landfill, (Robinson, 1995)
282	Composite results at Bishop Middleham Landfill, (Robinson, 1995)
399	Composite results at Odsal Wood Landfill, (Robinson, 1995)
43	Composition results at East Park Drive Landfill, (Robinson, 1995)
30	Composition results at Marton Mere Landfill, (Robinson, 1995)
12-1571	Range of concentrations from 21-30 year old, German landfills (Krumpelbeck and Ehrig, 1999)
445	Average concentration from 21-30 year old, German landfills (Krumpelbeck and Ehrig, 1999)
740	Average concentration (Ehrig, 1988)

The differences in the values obtained in graphs can be attributed to how lab-scale bioreactors. A review on leachate concentrations for landfills show that the relative concentrations of ammonia tend to be generally higher. The fact that the bioreactor indicates a big drop in the value of Ammonia-N has to be taken into account when compared to existing literature.

The concentrations of ammonia that were measured would be affected by nitrification and denitrification which would contribute towards nitrogen removal.

4.2. Nitrites

Table 4.3 shows the results for the change in nitrite concentration with continuous and intermittent aeration.

Table 4.2. The results for nitrites over time

	NITRITES N-NO2- (mgN-NO_2-/L)				
Day #	**Sampling date**	**Reactor OC**	**Reactor OI**	**Reactor MC**	**Reactor MI**
16	16/12/2020				
44	13/01/2021				
79	17/02/2021				
107	17/03/2021				
128	07/04/2021	0.47	8.24	0.4	8.66
142	21/04/2021	1.51	19	0.4	3.84
149	28/04/2021	84.6	106	5.2	64.4
156	05/05/2021	75.3	52.5	59.1	42.4
163	12/05/2021	1415	870	3105	269.5
170	19/05/2021	3085	26.2	433.5	18.35
178	27/05/2021	320	8.25	705	4
185	03/06/2021	0.55	1.46	1104	1.9
191	09/06/2021	0.17	2.52	960	6.45
198	16/06/2021	0.765	5.093	791	2.41
205	23/06/2021	2.03	1.27	952	2.16
212	30/06/2021	0.32	0.31	1043	0.73
219	07/07/2021	0.32	0.31	770	0.73
226	14/07/2021	0.385	0.205	466.5	1.85
298	24/09/2021	0.02	0.05	37.1	0.29
531	16/05/2022	<0.1	0.11	0.98	<1
603	27/07/2022	<0.04	<0.04	0.9	<0.5

The graphs are obtained for the reactors O & M for when continuous and intermittent aeration has been carried out. The collection of data started from day 107 and this shows the blank region indicated in the table.

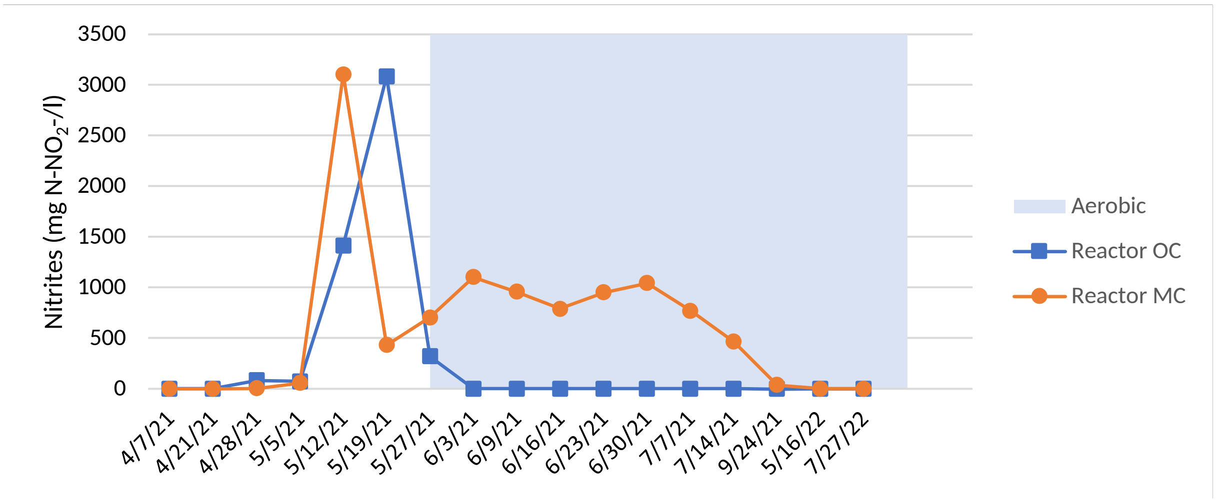

Figure 4.3. The change in nitrites in mg/L over time for continuous aeration

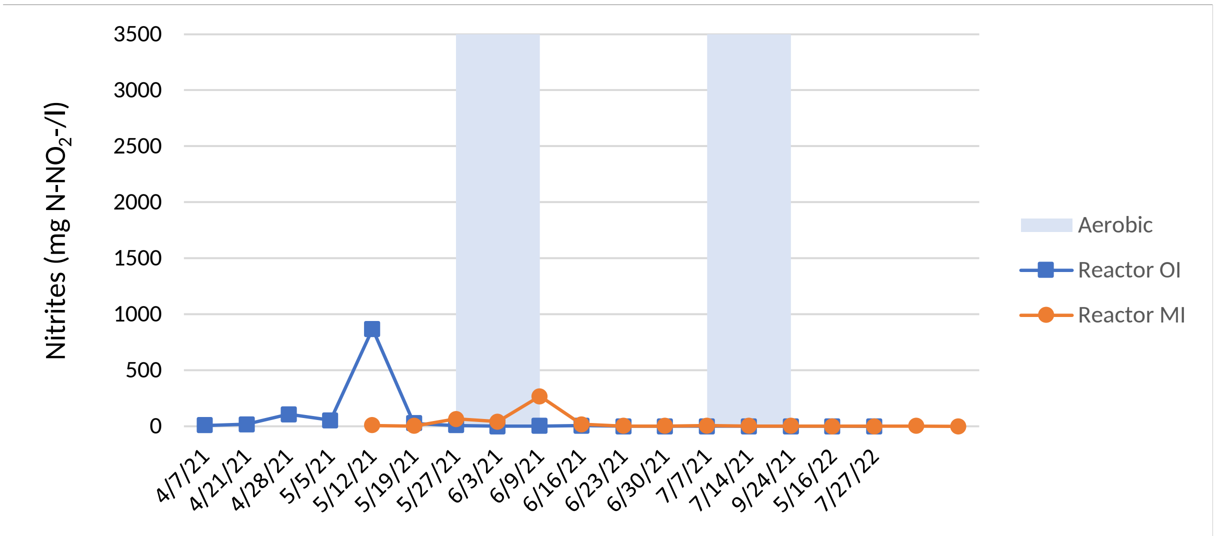

Figure 4.4. The change in nitrites in mg/L over time for continuous aeration

The trend for nitrites would also follow a similar pattern where in the long term, their concentration of leachate drops. In large scale landfills, the concentration of nitrites tend to drop and this is thought to be due primarily to two processes: biological denitrification and chemical precipitation (Xu et al., 2015).

Biological denitrification is the process by which bacteria convert nitrate and nitrite ions into nitrogen gas (N2) or diatomic nitrogen gas (N2O) (Friedman, 2014). In this process, bacteria obtain energy from organic material, such as plant matter or sewage sludge, allowing them to reduce the concentration of these compounds over time. The second process for reducing nitrate and nitrite levels is chemical precipitation. This occurs when calcium and magnesium ions bind with these anions in a reaction known as neutralization. These reactions form insoluble salts that can no longer be taken up by organisms, thus reducing their concentration over time (Yin et al., 2019).

The rate at which the concentration of nitrates and nitrites decreases depends both on the amount of organic matter available for denitrification as well as on environmental factors such as pH. Studies have found that pH values above 8 results in faster denitrification rates due to increased microbial activity while lower pH values tend to slow down denitrification rates (Zhan et al., 2016).

4.3. Nitrates

Table 4.3 shows the results for how the concentration of nitrates change within the leachate over time.

Table 4.3. The results for nitrates over time

	NITRATES N-NO3- (mgN-NO3-/l)				
Day #	**Sampling date**	**REACTOR OC**	**REACTOR OI**	**REACTOR MC**	**REACTOR MI**
16	16/12/2020				
44	13/01/2021				
79	17/02/2021				
107	17/03/2021				
128	07/04/2021	0.778	37.6		38.6
142	21/04/2021	1.254	36.4		35.8
149	28/04/2021	9.664	29.7	10	19.3
156	05/05/2021	8.64	20.6	10	48.6
163	12/05/2021	29.7	80.4	35.7	108.4
170	19/05/2021	323	221	117	50.9
178	27/05/2021	232	199	129	4.6
185	03/06/2021	248	122	57.4	2.91
191	09/06/2021	233	259	90.1	20
198	16/06/2021	229	171	158	33.9
205	23/06/2021	204	193	145	2.49
212	30/06/2021	179	173	267	4.31
219	07/07/2021	179	173	514	4.31
226	14/07/2021	116	84.7	789	2.64
298	24/09/2021	4	4.83	615	4
531	16/05/2022	<1.0	<1.0	62	<5.0
603	27/07/2022	<0.5	<0.5	587	< 2.5

The graphs are obtained for the reactors O & M for when continuous and intermittent aeration has been carried out. The collection of data started from day 128 and this shows the blank region indicated in the table.

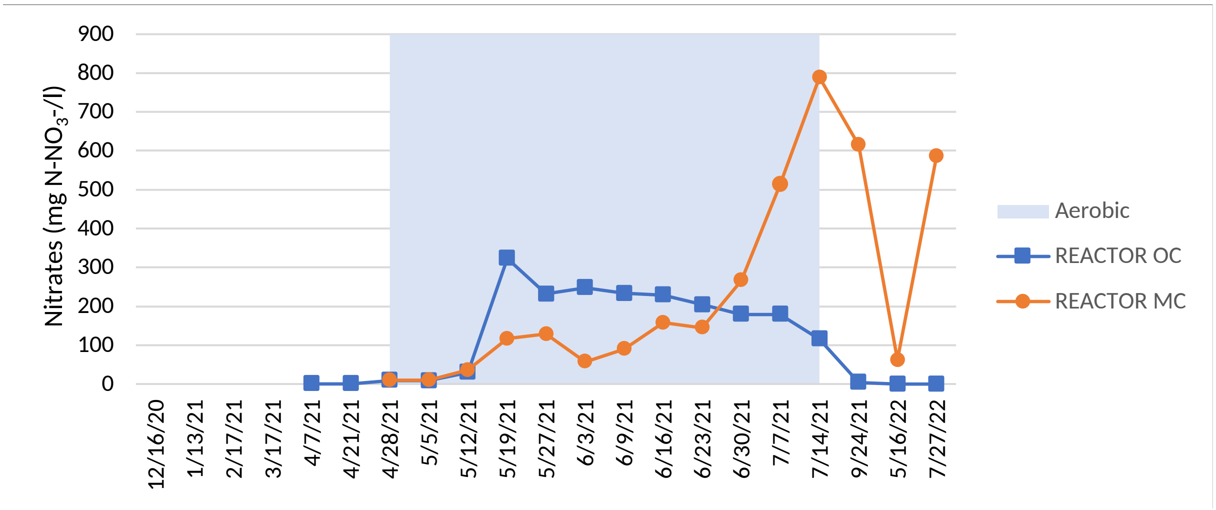

Figure 4.5. The change in nitrates in mg/L over time for continuous aeration

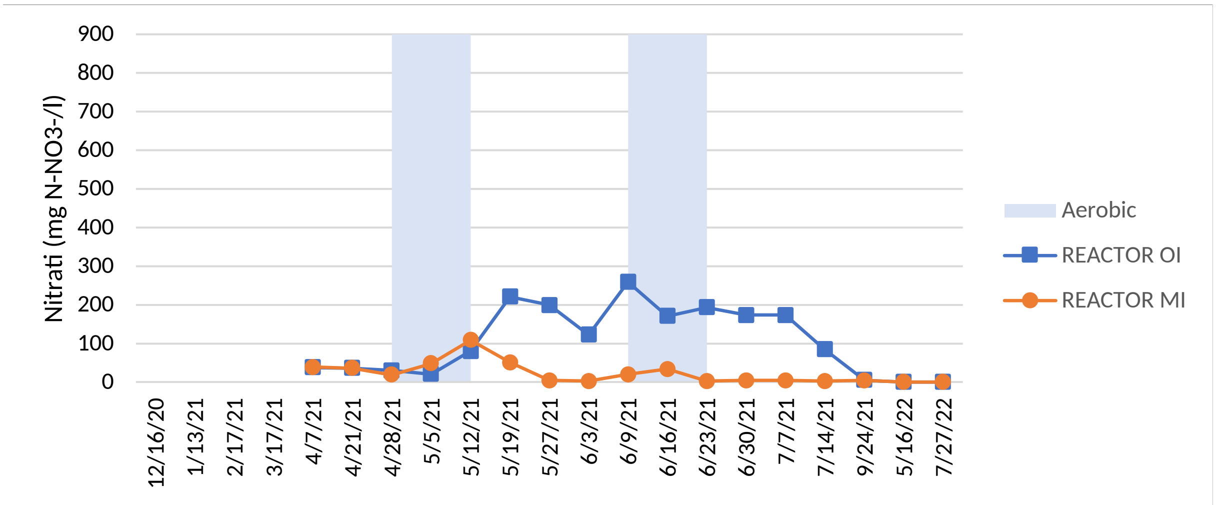

Figure 4.6. The change in nitrates in mg/L over time for intermittent aeration

The values obtained for nitrates follow a similar pattern to that of nitrites. However, it is important to notice that there is an anomalous value in reactor MC where there is a sudden spike in the nitrate concentrations. However, this does not seem to fit in with the regular pattern and is considered an anomaly.

4.4. TOC

Table 4.4 shows how the TOC values would change over time for the leachate that has been obtained.

Table 4.4. The results for TOC over time

	TOC (mgC/l)				
Day #	**Sampling date**	**Reactor OC**	**Reactor OI**	**Reactor MC**	**Reactor MI**
16	16/12/2020	1200	956	7200	6920
44	13/01/2021	880	1135	3610	3450
79	17/02/2021	1030	774	2750	1890
107	17/03/2021	640	377	1070	645
114	24/03/2021	229	100	925	487
128	07/04/2021	433	153	1090	555
149	28/04/2021	314	132	1100	510
156	05/05/2021	168	86.7	738	522
163	12/05/2021	170	106	619	627
170	19/05/2021	137	95.3	817	426
178	27/05/2021	119	86.5	1125	377
185	03/06/2021	121	225	1040	456
191	09/06/2021	104	103	1170	770
198	16/06/2021	113	173	805	670
205	23/06/2021	101	135	779	430
212	30/06/2021	92.6	181	665	645
219	07/07/2021			648	718
226	14/07/2021	110	124	556	482
298	24/09/2021	91.9	263	638	660
531	16/05/2022	315	55.3	316	297
603	27/07/2022	65.5	79.2	332	329

The graphs for reactors O & M for continuous and intermittent air flow have been shown in the following page.

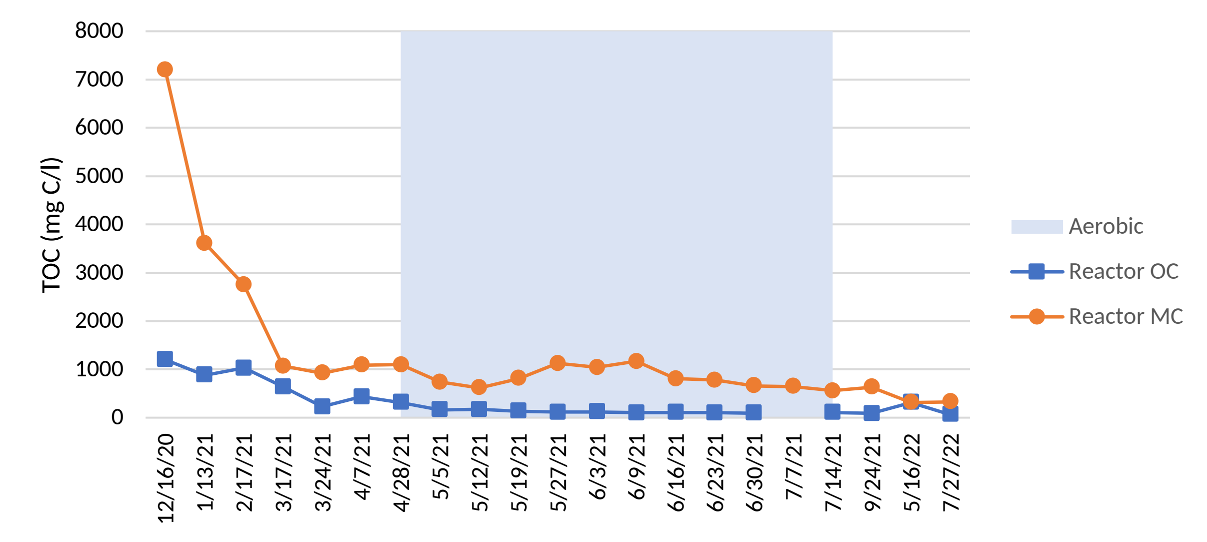

Figure 4.7. The change in TOC in mg/L over time for continuous aeration

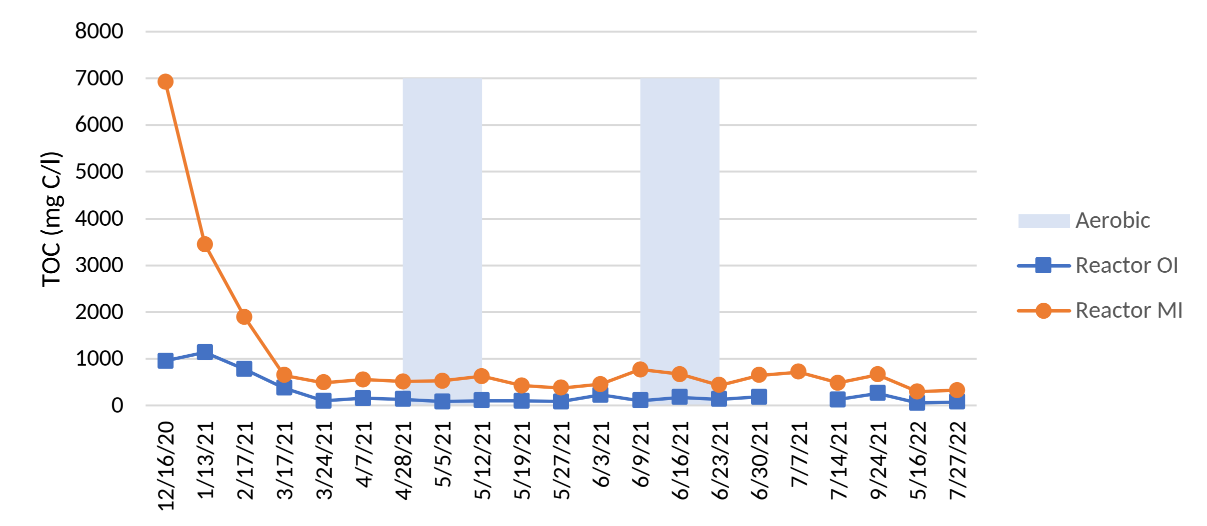

Figure 4.8. The change in TOC in mg/L over time for continuous aeration

The trend in the change in Total Organic Carbon follows an expected pattern. When an anaerobic system has been introduced.

The decrease in TOC in bioreactor landfill leachate over time is primarily due to microbial action. Microbes present in leachates, such as bacteria and fungi, break down complex organic substances into simpler components, releasing carbon dioxide into the atmosphere. During this process, TOC decreases as it is converted into other forms of carbon or released as carbon dioxide (Chen et al., 2015).

In addition to microbial activity, chemical oxidation can also contribute to the decline of TOC in leachates. Abiotic oxidation of organic compounds occurs through chemical reactions between reactive oxygen species generated during aerobic respiration and organic compounds present in leachates (Uppal et al., 2017). Oxidation processes lead to the progressive transformation of larger organic molecules into smaller ones which can then be used for further metabolic processes or released as gaseous CO2 (Su et al., 2019).

Lastly, volatilization is another important process that contributes to the long-term decrease in TOC concentrations found in bioreactor landfill leachates. Volatilization refers to the transfer of volatile organic compounds from aqueous solutions into the atmosphere (Gibson & Murphy, 2018). These volatile compounds include methane and other hydrocarbons which are produced during anaerobic degradation processes and can escape from liquids either by gas-liquid transfer or diffusion into a gas phase (D'Adamo et al., 2019).

4.5. BOD5

Table 4.6 shows how the BOD5 values would change over time for the leachate in question.

Table 4.5. The results for BOD5 over time

	BOD5 (mgO_2/l)				
Day #	**Sampling Date**	**Reactor OC**	**Reactor OI**	**Reactor MC**	**Reactor MI**
16	16/12/2020	208	124	10487	7022
44	13/01/2021	29	121	2844	4963
79	17/02/2021	107	89.8	5338	1969
114	24/03/2021	136	164	657	2480
163	12/05/2021	61.9	49.4	351	140
185	03/06/2021	23.3	25.4	226	246
205	23/06/2021	14.3	9.65	113	28.4
226	14/07/2021	10	10	14.2	42.2
298	24/09/2021	10	10	10	14.2

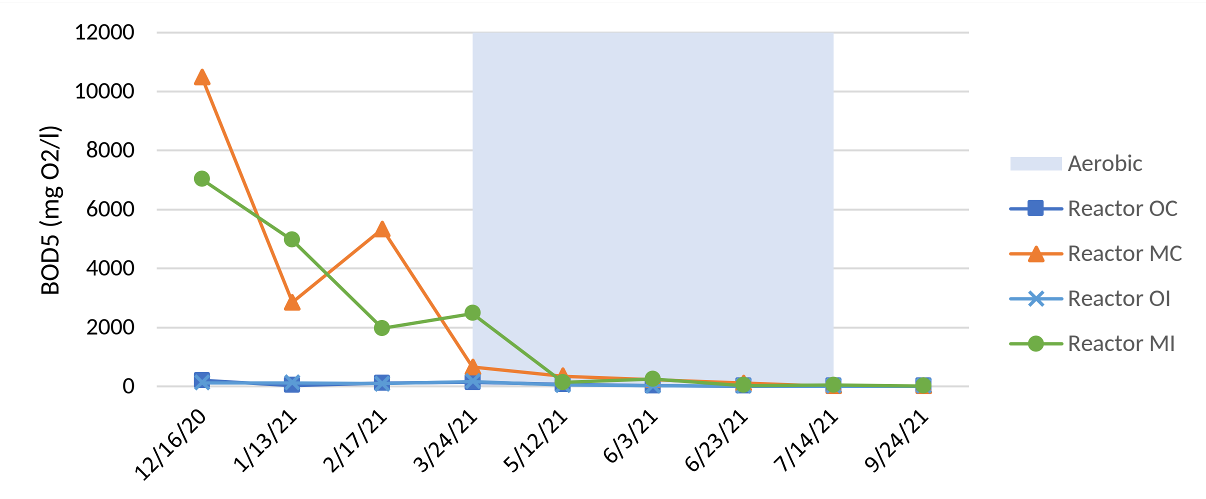

Figure 4.9. The change in BOD5 in mg/L over time for continuous aeration

The trend for decreasing BOD5 values is expected. This is because bioreactor landfills are designed to optimize energy recovery and pollutant removal through the use of anaerobic technologies. As a result, when leachate is generated in bioreactor landfills, its biochemical oxygen demand (BOD5) is expected to decrease in the long run. This process is due to several factors, all of which contribute to the overall reduction of BOD5 levels.

Bioreactor landfill leachate has been found to contain higher concentrations of organic compounds than traditional landfills (Muñoz-Carpena et al., 2008). This organic matter serves as a food source for naturally occurring microorganisms present in the leachate. These microbes consume organic material through biological processes such as hydrolysis and fermentation

(Ike & Osoro, 2018). As a result, the amount of BOD5 present in the leachate reduces over time due to microbial respiration.

Anaerobic digestion plays a key role in reducing BOD5 levels in bioreactor landfill leachates. In this process, bacteria such as methanogens consume organic material while producing methane gas as a by-product (Al sawalha & Abu-Qudais 2012). As these bacteria feed on the organic material present in leachate, less BOD5 remains and its concentration decreases over time.

Chemical oxidation can also reduce BOD5 levels in bioreactor landfill leachates (Tijani et al., 2017). When chemicals like hydrogen peroxide are added to leachate, they react with pollutants and break them down into simpler compounds that are easier for microbial organisms to consume (Yaghmaeian & Rahimi 2010). This process reduces pollutants from the leachate and decreases its overall BOD5 level.

4.6. pH levels

Table 4.6 shows how the pH values vary in the tested leachate over the chosen time interval.

Table 4.6. The results for pH over time

	pH				
Day #	**Sampling date**	**Reactor OC**	**Reactor OI**	**Reactor MC**	**Reactor MI**
16	16/12/2020	7.51	7.56	6.83	6.46
44	13/01/2021	7.61	7.91	8.12	7.55
79	17/02/2021	7.55	7.68	7.98	7.6
107	17/03/2021	7.86	7.9	7.98	7.79
128	07/04/2021	7.91	7.6	7.89	7.93
142	21/04/2021	7.71	7.58	8.04	7.55
149	28/04/2021	7.95	7.76	8.73	7.93
156	05/05/2021	8.09	7.73	8.74	7.81
163	12/05/2021	8.09	7.64	8.7	7.88
170	19/05/2021	7.62	6.74	8.47	7.61
178	27/05/2021	7.34	6.76	8.26	7.25
185	03/06/2021	7.27	6.83	7.96	7.64
191	09/06/2021	7.36	7.52	7.6	7.89
198	16/06/2021	7.27	7.36	7.38	7.76
205	23/06/2021	7.21	7.28	7.38	7.6
212	30/06/2021	7.44	7.16	7.29	7.64
219	07/07/2021	7.44	7.44	7.26	7.93
226	14/07/2021	7.43	7.32	7.19	7.37
298	24/09/2021	7	6.94	7.38	7.59
531	16/05/2022	7.56	7.5	7.49	7.9
603	27/07/2022	7.21	7.35	7.37	7.63

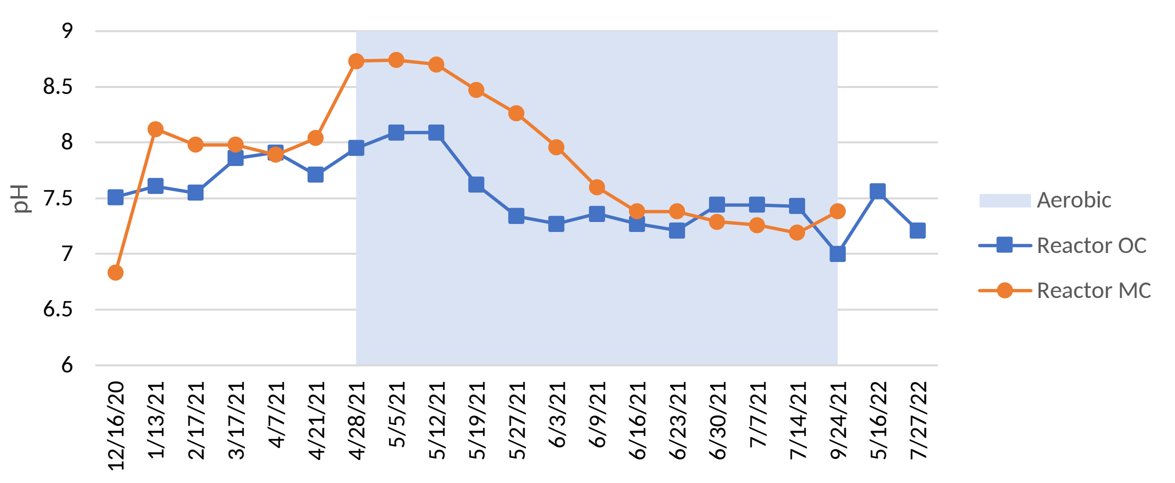

Figure 4.10. The change in pH over time for continuous aeration

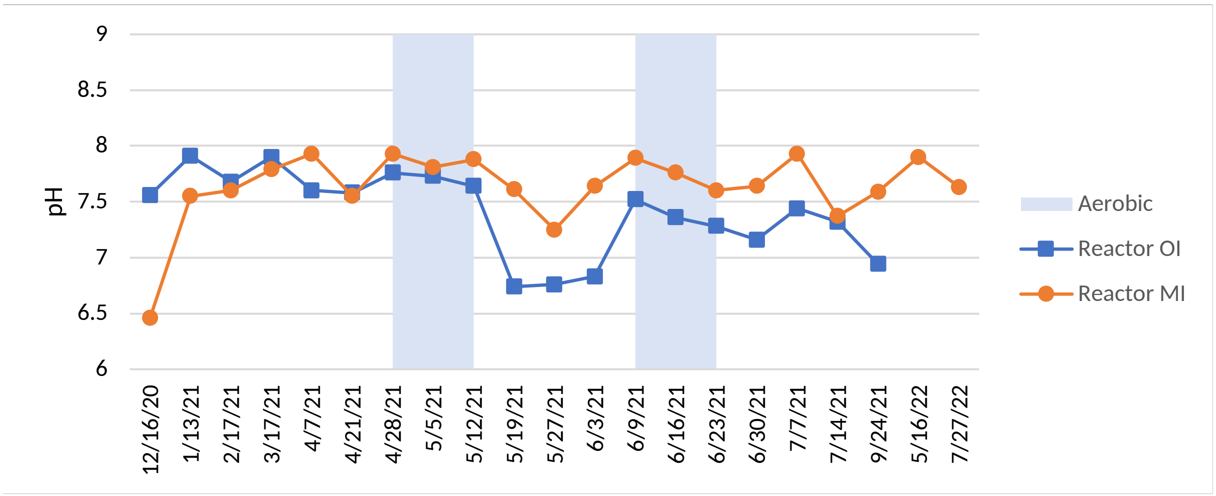

Figure 4.11. The change in pH over time for continuous aeration

The trends in pH that are noticeable have some slight deviations from the expected behaviour. Aerobically, the pH of leachate tends to be slightly basic due to the presence of dissolved oxygen, which undergoes oxidation with organic material in the leachate. This increases the abundance of alkaline compounds such as ammonia and hydroxide ions (Johnson et al., 2019). Additionally, nitrification processes can increase alkalinity as nitrifying bacteria convert ammonia into nitrate (Novak et al., 2018). Over the long run, these factors will raise the overall pH of a bioreactor landfill leachate.

In contrast, anaerobic conditions can lead to acidic environments in bioreactor landfills. This is due to fermentation processes that produce low-molecular-weight organic acids such as acetic acid (Cechnerova et al., 2016). As these acids accumulate over time, they lower the pH of a landfill leachate. Anaerobic processes also produce other substances such as hydrogen sulfide that further lower the pH level (Lee et al., 2020). Thus, over long-term anaerobic conditions, there should be a decrease in overall pH in a bioreactor landfill leachate.

4.7. Chlorides

Table 4.7 shows how chlorides would change over time in the lab-scale bioreactor for the leachate that has been analysed.

Table 4.7. The results for chloride concentrations in mg/l over time

	CHLORIDES (mg/l)				
Day #	**Sampling date**	**Reactor OC**	**Reactor OI**	**Reactor MC**	**Reactor MI**
16	16/12/2020	1191	510	2032	1262
44	13/01/2021	539	602	1812	1229
79	17/02/2021	721	427	1719	1105
107	17/03/2021	802	375	1689	1022
128	07/04/2021	355	217	1549	1008
142	21/04/2021	824	382	1994	1055
170	19/05/2021	758	446	2078	1096
185	03/06/2021	958	570	2039	1144
205	23/06/2021	721	575	1402	1151
226	14/07/2021	992	714	2012	1198
298	24/09/2021	1081	738	2074	1161

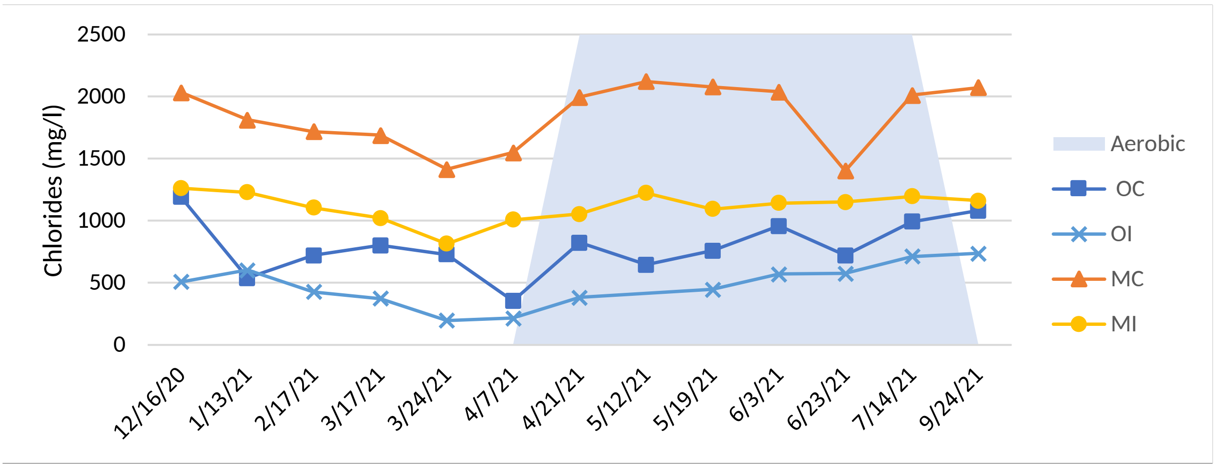

Figure 4.12. The change in chlorides over time for continuous aeration

The chloride values fall within the 4500 mg/l range as discussed in Chapter 2. There seems to be no particular trend to chlorides in the bioreactor.

Chloride levels in landfill leachate can be affected by a variety of factors. Bioreactor landfills are designed to reduce many of the environmental risks associated with typical landfills, and this includes the leachate released from them. In bioreactor landfills, leachate is actively managed through the addition of oxygen and frequent recirculation (Razaghi et al., 2018). This creates an environment which encourages microbial activity, resulting in higher oxygen levels;

thus allowing for more efficient degradation of organic pollutants (Gao et al., 2019). As such, it has been suggested that bioreactor landfill leachate may contain lower concentrations of chlorides than those seen in traditional landfills (Nasr et al., 2016).

While there have been numerous studies looking at chloride levels in landfill leachate over various time periods, changes in chloride concentrations over longer periods are still largely unknown. A study conducted by Razaghi et al. (2018) looked at chloride concentrations in bioreactor landfill leachates over an 18-month period. Results showed that chloride concentration decreased significantly over this time period, from 4600 to 890 mg/L. It was also found that this decrease was due to both natural microbial degradation processes as well as dilution caused by water entering the system through precipitation or surface runoff (Razaghi et al., 2018). This indicates that if left unmanaged, chloride concentrations could continue to decrease in bioreactor landfill leachate over long periods of time.

However, other studies suggest that the presence of certain compounds such as nitrates or sulfates can impact the rate at which chlorides degrade in landfill leachates. For example, a study conducted by Gao et al. (2019) found that nitrate addition had a significant effect on total dissolved solid (TDS) reduction but had no effect on chloride concentration reduction. They concluded that nitrate addition inhibited chloride degradation due to competition between chlorine and nitrate ions for electron acceptors (Gao et al., 2019). This suggests that if additional compounds are present within the system they may limit or inhibit the rate of natural degradation processes occurring within a bioreactor landfill leachate system and could thus affect its overall long-term chloride levels.

Overall, current research suggests that when left unmanaged and without additional compounds present within it, bioreactor landfill leachates will generally show decreasing trends in chloride concentration over long-term periods due to natural microbial activities combined with dilution from external sources such as precipitation or surface runoff. However, if additional compounds are present within the system, then their presence may limit or inhibit natural degradation processes affecting overall long-term trends in chloride concentration within a bioreactor landfill leachate system.

Chapter 5 – Conclusion

The use of lab scale bioreactors shows a good range of results for the parameters discusses. A simulated environment provides results that show ranges that are applicable to literature that is currently available.

The long-term fate of leachate parameters in a bioreactor landfill is an important area of research. Not only does it allow us to understand the potential environmental impacts of waste disposal, but also provides insight into the effectiveness of bioreactor landfills as a method for mitigating negative environmental effects associated with traditional landfill design. Long-term leachate parameters such as pH, COD, TOC and nitrogen species must be monitored over time to gain an understanding of the changes that occur in these parameters due to microbial activity within the landfill. Studies have suggested that bioreactor landfills can reduce leachate volumes and pollutant concentrations more quickly than conventional landfills; however, further research is needed to better understand their long-term performance. Additionally, it is important to consider other factors such as climate and soil type that may influence the leachate parameters over time. By understanding the long-term fate of leachate parameters in bioreactor landfills, researchers can develop more effective strategies for mitigating environmental impacts associated with waste disposal.

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