

INVESTIGATION OF WASTE STABILIZATION POTENTIAL OF A MEDIUM AGED
SOLID WASTE IN A BIOREACTOR LANDFILL

by

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ABSTRACT

The production of solid waste is an inevitable consequence of human life. The tremendous increase in the solid waste generation makes the use of landfills, especially bioreactor landfills imminent. Research has shown that municipal solid waste can be rapidly degraded by enhancing and controlling the moisture within the landfill under aerobic and/or anaerobic conditions. Some studies indicate that bioreactors increase the feasibility for cost effective LFG recovery, which in turn would reduce fugitive emissions. This presents an opportunity for beneficial reuse of bioreactors in energy recovery projects. The most common method of creating a landfill bioreactor is the recirculation of leachate, which enhances the degradation of waste.

The objective of this study is to evaluate the waste degradation mechanisms of the stabilized waste applying Retrofit Bioreactor Concept. Determination of the further stabilization potential of stabilized solid waste is important for the development of the rehabilitation strategies. Moreover, the study using stabilized refuse provides better understanding of the rehabilitation of traditional landfills and the conversion of existing conventional landfills to operate as a bioreactor concept.

ÖZET

Katı atık üretimi insan hayatının vazgeçilmez bir sonucudur. Büyük bir artış gösteren katı atık üretimi depolama sahaları ve özellikle biyoreaktör depolama alanları kullanımını kaçınılmaz kılmıştır. Çalışmalar, evsel katı atıkların aerobik ve/veya anaerobik ortamdaki depolama sahası içerisindeki nem ihtivasının kontrolü ve arttırılması ile kolayca ayrışabildiğini göstermiştir. Yapılan bazı çalışmalar, biyoreaktör depolama sahalarının biyogazın geri kazanımında uygunluğunu ve maliyet açısından da verimliliğini arttırdığını ve bunun sonucunda da kaçak emisyonlarının azaltıldığını göstermiştir. Bu özellik de, enerji geri kazanımı projeleri için biyoreaktörlerin faydalı bir şekilde kullanımı için fırsat sağlamaktadır. En çok kullanılan metod ise biyoreaktör depolama sahalarını oluşturan ve atık ayrışmasını arttıran sızıntı suyunun geri devridir.

Bu çalışmanın amacı, depolama sahalarından alınan stabilize olmuş atığın ayrışma evrelerinin Retrofit Biyoreaktör kapsamında incelenmesidir. Stabilizasyona uğramış olan atığın kalan ayrışma potansiyelinin incelenmesi ile atık depolama sahalarının rehabilitasyonun geliştirilmesi hakkında önemli bir bilgiye ulaşılması açısından önemlidir. Depolama sahasından alınan belirli bir ayrışma evresinde olan atığın işletilmesi, atık içerisindeki atık ayrışma fazlarının özelliklerinin biyoreaktör kapsamındaki işleyişinin anlaşılması açısından önemlidir. Bu çalışma mevcut konvansiyonel sahaların biyoreaktör olarak işletilmesi ve vahşi depoların rehabilitasyonu açısından önemlidir.

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LIST OF SYMBOLS/ABBREVIATIONS

Symbol	Explanation	Units
MSW	Municipal Solid Waste	
M.C.	Moisture Content	(%)
CH ₄	Methane	(%)
CO ₂	Carbon dioxide	(%)
COD	Chemical Oxygen Demand	(mg/L)
BOD	Biochemical Oxygen Demand	(mg/L)
TS	Total Solids	(mg/L)
VS	Volatile Solids	(mg/L)
TOC	Total Organic Carbon	(mg/L)
VFA	Volatile Fatty Acids	(mg/L)
VOA	Volatile Organic Acids	
HA	Humic Acids	
FA	Fulvic Acids	
TKN	Total Kjeldahl Nitrogen	(mg/L-N)
NH ₃ -N	Ammonia Nitrogen	(mg/L)
SO ₄ ²⁻	Sulfate	(mg/L)
TP	Total Phosphorus	(mg/L-P)
Ortho-P	Orthophosphate	(mg/L-P)
C/N	Carbon /Nitrogen	

1. INTRODUCTION

Municipal solid waste generation has been tremendously increasing all over the world. The management of the municipal solid waste is a major worldwide challenge. Landfilling is the least desirable alternative management option for the solid waste disposal. However, landfills are still the most common methods of the waste management in many regions of the world. Improper leachate and gas management of solid waste has negative impacts on the environment. The long term environmental effects may last for centuries. The long term monitoring and maintenance have been applied to achieve better control over liquid and gas emissions resulting from landfills.

Sanitary landfills are designed to minimize health risk or ecological damage from the disposal of solid wastes. The concept of a sanitary landfill is developed because of the problems associated with open dumps, such as fires, rodents, flies, odors, leachate, and explosive gases. A new and emerging waste management trend in the world is to operate landfills as a bioreactor. Creation of biologically enhanced environment is accomplished by injecting leachate and air into the landfills. Today, the conversion of the existing landfills into bioreactors by retrofit concept is a new trend in the developed and developing countries. In order to operate such systems, the fate and behavior of the waste within the landfill should be investigated initially to understand the potential of waste stabilization.

The objective of this study is initially to evaluate and understand the behavior of the waste degradation potential of medium aged landfilled waste under “Retrofit Bioreactor Concept”. The effect of the leachate recirculation strategy on the further degradation of the initially landfilled waste in a conventional landfill was studied. The results of this study will address i) examination of the waste degradation potential ii) determination of the factors that affect the waste stabilization and iii) capability of conversion of existing conventional landfills into bioreactors. Laboratory scale lysimeter was operated to simulate anaerobic bioreactor landfills with leachate recirculation. For this purpose, 5 year old real solid waste sample retrieved from İZAYDAŞ sanitary landfill site was operated in the

bioreactor simulator for 114 days. The change in the degradation behavior of the waste sample was observed through leachate and gas indicator parameters.

The utilization of the retrofit bioreactor is a new concept in the solid waste management. Especially, in the U.S.A, there are a number of efforts trying to convert conventional landfill to bioreactor landfill for a more controlled and rapid waste stabilization with energy recovery from landfill gas. In out country, there are several raw disposal landfills posing important threats to the environment and human health with uncontrolled liquid and gas emissions. Their rehabilitation by converting them into bioreactor is a new and challenging research problem. This study will offer a better understanding for the rehabilitation of landfills by evaluating further waste stabilization potential necessary for the utilization of retrofit bioreactor.

2. LITERATURE REVIEW

The management of solid waste is a universal concern for both developed and developing countries. Landfills have a key role in the management of solid wastes and are an important component of the waste management system. This section will briefly discuss the types of landfills, leachate management, gas management, waste degradation phases in landfills, factors effecting the degradation phases and leachate quality.

2.1. Waste Management

Tremendous increase in the solid waste generation, parallel to the population growth, brings several environmental problems. The increasing consumption of resources has resulted in huge amounts of solid waste generation from industrial to domestic activities, which can pose significant threats to human health (Frosch, 1996). Several disposal methods are developed in response to solve problems related to solid waste.

Integrated solid waste management (ISWM) can be defined as the selection and application of suitable technique, best proper technologies and management programs to achieve the objective and goals. However, the development of such system requires reliable data on the characteristics of the waste stream, performance specifications for alternative technologies and cost information. According to the U.S. Environmental Protection Agency (EPA), the ISWM hierarchy is composed of source reduction, recycling, waste combustion and landfilling (Tchobanoglous et al., 1993).

The waste hierarchy is a tool which puts in order different waste management options according to their impact to the environment (Figure 2.1). Source reduction is the principle strategy of the waste hierarchy followed by reuse, recycling, resource recovery, incineration and finally landfilling. Waste minimization is the foundation of the waste hierarchy which can be achieved thorough source reduction, reuse and recycling. The main objective of the waste hierarchy is to obtain maximum practical benefits from products and generate minimum amount of waste. According to the European Union (EU) waste management policy, sanitary landfilling is the least desirable alternative management

option for the disposal of urban solid waste. However, sanitary landfilling is expected to be on the stage, at least for the disposal of non-recycled solid waste materials. For many years, since sanitary landfilling is the most economical option among other alternative waste disposal methods, the use of sanitary landfilling has wide acceptance around the world especially in developing countries (Tatsi and Zouboulis, 2002).



Figure 2.1. Solid waste management hierarchy (Earth 911, 2009).

The total waste production in the EU-27 and selected countries (Denmark, Germany, Greece, Spain, France, Italy, Turkey, Sweden and United Kingdom) reached to 2.62 billion tonnes in 2008 (Table 2.1). The total waste generation was lower than the value of the year 2004 and 2006 where total waste generation in the EU-27 was 2.68 billion tonnes and 2.73 billion tonnes, respectively. In 2008, 98 million tonnes or 3.7 % of the total generated waste was classified as hazardous waste in Europe. The decrease in the waste generation and the use can be explained by the introduction of cleaner technology in manufacturing. Municipal solid waste which is landfilled in the EU-27 and selected countries is given in Table 2.1.

Table 2.1. Total waste generated and MSW landfilled for The EU-27 and selected countries in 2008 (Eurostat, 2008).

Country	Waste Generation (1000 Tonnes)	MSW landfilled (kg/person-year)
European Union (27 countries)	2615220	186
Denmark	15155	23
Germany	372796	2
Greece	68644	374
Spain	149254	310
France	345002	166
Italy	179034	254
Turkey	64770	340
Sweden	86169	4
United Kingdom	334127	255

Technological measures have been applied to achieve a better control over liquid and gaseous emissions from landfills in order to prevent groundwater pollution and reduce greenhouse gases emissions, prevent fire hazards, odors and vegetation damages (Manfredi and Christensen, 2009). However, the long term environmental impacts caused by municipal solid waste (MSW) landfills may last for centuries (Kruempelbeck and Ehrig, 1999). Recent European regulations on waste management are primarily intended to reduce the use of landfilling which is the Landfill Directive adopted by the European Union (EU) requires that the amount of biodegradable MSW going to the landfill should be reduced by 25 % until 2002, 50 % by 2005 and 75 % by 2010 (Council Directive 1999/31/EC).

According to the waste management in the EU countries, less waste is landfilled and more is recycled or incinerated with energy recovery. Nevertheless, the percentage distribution of landfills for municipal solid waste disposal among other treatment options decreased steadily from 62 % in 1995 to 37 % in 2010 in the EU-27. The main decrease has been seen in Norway and Switzerland. However, Turkey and the Western Balkan countries have still deposited wastes in landfills which constitute 80–100% of total management options (Eurostat, 2008). Regional and country- specific data on waste composition in MSW are given in Table 2.2.

Table 2.2. MSW composition in different countries (IPPC, 2006).

Region	Food Waste*	Paper & Cardboard*	Wood*	Textiles*	Rubber & Leather*	Plastic*	Metal*	Glass*	Other*
Asia									
Eastern Asia	26.2	18.8	3.5	3.5	1.0	14.3	2.7	3.1	7.4
South Central Asia	40.3	11.3	7.9	2.5	0.8	6.4	3.8	3.5	21.9
South Eastern Asia	43.5	12.9	9.9	2.7	0.9	7.2	3.3	4.0	16.3
Western Asia & Middle East	41.1	18.0	9.8	2.9	0.6	6.3	1.3	2.2	5.4
Africa									
Eastern Africa	53.9	7.7	7.0	1.7	1.1	5.5	1.8	2.3	11.6
Middle Africa	43.4	16.8	6.5	2.5	-	4.5	3.5	2.0	1.5
Northern Africa	51.1	16.5	2	2.5	-	4.5	3.5	2	1.5
Southern Africa	23	25	15	-	-	-	-	-	-
Western Africa	40.4	9.8	4.4	1.0	-	3.0	1.0	-	-
Europe									
Eastern Europe	30.1	21.8	7.5	4.7	1.4	6.2	3.6	10.0	14.6
Northern Europe	23.8	30.6	10.0	2.0	-	13.0	7.0	8.0	-
Southern Europe	36.9	17.0	10.6	-	-	-	-	-	-
Western Europe	24.2	27.5	11.0	-	-	-	-	-	-
Oceania									
Australia and New Zealand	36.0	30.0	24.0	-	-	-	-	-	-
Rest of Oceania	67.5	6.0	2.5	-	-	-	-	-	-
America									
North America	33.9	23.2	6.2	3.9	1.4	8.5	4.6	6.5	9.8
Central America	43.8	13.7	13.5	2.6	1.8	6.7	2.6	3.7	12.3
South America	44.9	17.1	4.7	2.6	0.7	10.8	2.9	3.3	13.0
Caribbean	46.9	17.0	2.4	5.1	1.9	9.9	5.0	5.7	3.5

*These data are based on wet weight percentages

The municipal solid waste composition in Turkey is given in Figure 2.2. The percentage distributions are similar to those in the Western Asia and Middle East Regions as given in Table 2.2. The organic fraction of the MSW is relatively higher in Turkey compared to most developed countries.

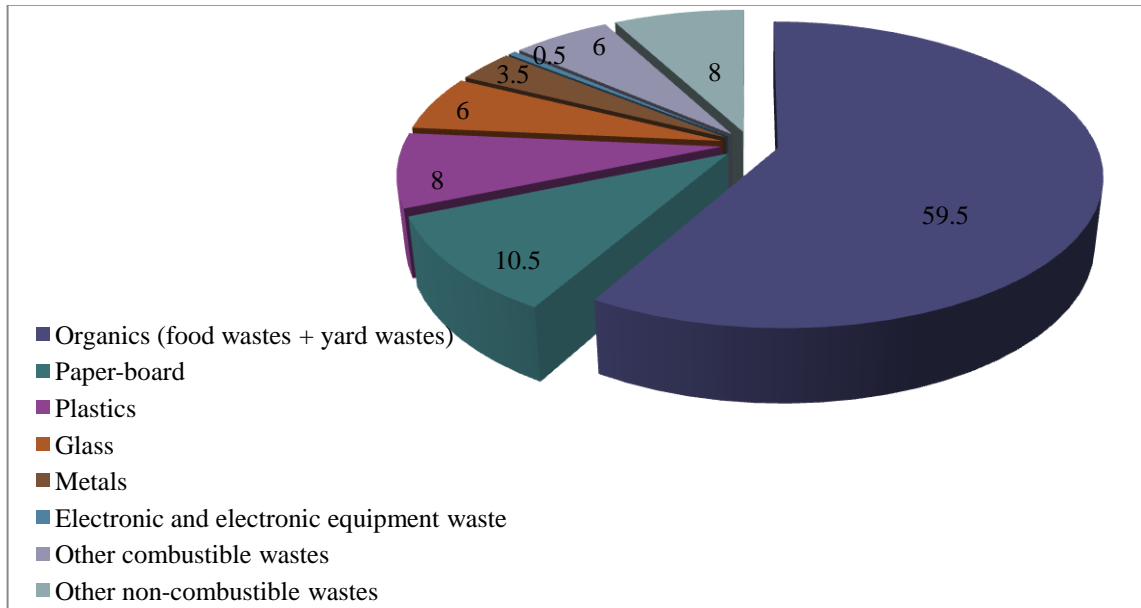


Figure 2.2. Municipal solid waste composition in Turkey (Adopted from Mimko, 2006).

According to the Turkish Statistical Institute's (TUIK) 2008 database, approximately 24.36 million tonnes of municipal waste was collected and daily amount of municipal waste per capita was calculated as 1.15 kg for yearly average in Turkey and only 10 million tonnes of these collected wastes were disposed of in controlled landfill sites. Turkey has still over 2000 open dumps (Turan et al., 2009). However, it has been estimated that the landfilling is going to be the major disposal technique for a long time even though landfill requires a certain time for stabilization period. Based on 2008 statistical data of TUIK, the properties of landfill sites in Turkey are given in Table 2.3.

Table 2.3. Properties of landfill sites in Turkey (Erdem, 2011).

Landfill Sites	Years			
	2008	2009	2010	2011
Number of Sanitary Landfill Sites	38	41	52	59
Capacity of Landfills (1000 ton)	390478	-	423142	-
Amount of Waste in Landfills (1000 ton)	11657	-	14377	-

2.2. Sanitary Landfill Types

Landfilling has been widely used and accepted method for municipal solid waste (MSW) disposal all over the world. Especially in developing countries, it is considered to be a reliable and cost effective method if adequate land is available. Many countries in Asia depend on landfill for waste disposal. However, improper management and operation of landfill could create severe environmental impacts such as groundwater pollution, fires, and air emissions. Currently, there are two sanitary landfill options adopted by many countries. These options are conventional and bioreactor landfill.

2.2.1. Conventional Landfills

Conventional landfills are also called “dry tomb”. The design of the conventional landfill depends on the option to store wastes in order to eliminate the exposure to human and the environment. This can be done by developing gas management and infiltration of surface water. Conventional landfills are designed with liners, drains, gas vents, leak detection systems, intermediate and final covers (Erses, 2008). The main drawback of this type of landfilling is that low moisture content result in the slower degradation and thereby extending the landfill life. The stabilization process of the decomposable organic waste within landfill takes 30 to 100 years in conventional landfills. In such landfills, stabilization of the waste, methane gas leachate generations take place over long periods of time (Chiemchaisri et al., 2002).

2.2.2. Bioreactor Landfills

Bioreactor landfill is a concept that the organic fraction of the waste can be stabilized in a short time compared to long decomposition time for conventional landfill (dry tomb). The use of bioreactor landfills gained popularity in the worldwide especially in the U.S.A and Japan.

Bioreactor landfills have many advantages compared to the conventional landfills. Sludge, nutrient, buffer and liquid can be added to enhance waste stabilization. The addition of moisture is a common practice in bioreactors to accelerate the microbially mediated waste transformation within the waster matrix (Pohland, 1980). Leachate recirculation provides an environment for the uniform distribution of nutrients and microorganisms (Bayard et al., 2005).

The advantages of leachate recirculation are the enhancement of biodegradation of organics which contributed the stabilization of wastes and thereby shorten waste degradation time, reduction in the amount of leachate to be treated externally, the removal of organics and inorganics in the leachate and finally increase in the methane production (Reinhart, 1996; El-Fadel, 1999; Pohland et al., 1992, 1998; Pohland and Kim, 1999; Onay and Pohland, 1998; Tittlebaum, 1982).

The recirculation of leachate provides well stabilized leachate containing low concentrations of biodegradable carbon compounds and thereby decreasing the BOD₅ and COD concentrations. However, the recirculation can cause increase in the ammonia concentration therefore the higher concentrations of ammonia will climb at the end of the stabilization period (Abdulhussain et al., 2009).

In the literature, it was reported that significant decrease in the leachate COD concentrations was observed when the recirculated leachate volume was 30 % of initial waste bed volume (Sponza and Agdag, 2004). Gould et al. (1989) found that leachate recirculation stimulated reducing conditions providing for the reduction of sulphate to sulphide, which moderated leachate metals to very low concentrations. Chian and DeWalle

(1976) reported that the formation of metal sulphides under anaerobic conditions effectively precipitated the majority of heavy metals in leachate.

There are five different operational conditions for bioreactor landfills;

- Aerobic Bioreactor Landfills
- Semi-aerobic Bioreactor Landfills
- Aerobic-anaerobic Bioreactor Landfills (Hybrid)
- Anaerobic Bioreactor Landfills
- Retrofit Bioreactor Landfills

2.2.2.1. Aerobic bioreactor landfills. Aerobic bioreactors are operated by the controlled injection of moisture and air into the waste mass through horizontal and vertical pipes. Waste degradation, oxidation process takes place naturally and pollutants-mainly carbohydrates, proteins and lipids are broken down into carbon dioxide, water, nitrates, and sulphates and stabilized humus remaining. Blowers typically are used to force air into the waste mass through a network of perforated wells that have been installed in the landfill. The rates of injection of air and leachate into the landfill are similar to the air and moisture application rates used in many composting systems. The aerobic process continues until most of the easily and moderately degradable compounds have been degraded (Reinhart and Townsend, 1996; Tchobanoglous et al., 1993).

2.2.2.2. Semi aerobic bioreactor landfills. Systems are also known as Fukuoka Method. In this system, leachate and gas are continuously removed from the waste matrix using leachate collection and gas venting with such application in which the ambient air flows into the waste body through leachate collection pipes and eventually enhance the microorganisms activity (Chong et al., 2005).

2.2.2.3. Hybrid bioreactor landfills. A sequence of aerobic and anerobic treatment applied to rapidly degrade organics in the upper section and collect gas from the lower sections. Aerobic conditions usually occur in the newly placed waste in the upper sections of the landfill, while anaerobic conditions occur in the lower sections. Because anaerobic

conditions exist in the older lower sections of the landfill, methane production still occurs. The onset of the methanogenesis occurred earlier in hybrid systems compared to aerobic systems.

2.2.2.4. Anaerobic bioreactor landfills. This is the most common type of bioreactors. Anaerobic bioreactor landfill is the modification of conventional landfill with leachate recirculation. Waste degradation occurs in the absence of oxygen and produces landfill gas rich in methane content which can be captured to minimize greenhouse gas emissions and used for energy project. The gas content of anaerobic bioreactors is similar to that of conventional landfills, with methane and carbon dioxide each making up approximately 50% of the total landfill gas volume (Tchobanoglous et al., 1993).

2.2.2.5. Retrofit bioreactor landfills. Bioreactor concept is divided into two major categories: “As-built” bioreactors and “retrofit” bioreactors. Retrofit landfills defined as a landfill that is not originally built as a bioreactor; the construction and operation of bioreactor components occurs after landfill operation is completed, or after wastes placed into the system. According to EPA (2008), there are approximately 2500 permitted Municipal Solid Waste Landfills (MSWLFs) currently in operation in the United States. Approximately 10 % of these facilities will involve retrofitting bioreactors and commence liquids recirculation on existing landfill infrastructures (Interstate Technology Regulatory Council, 2006). As-built bioreactor landfills differ from retrofit bioreactors in that leachate and air injection started as waste is disposed into the landfill site. The application of air addition and/or liquid injection system was accomplished at the time of temporary final closure in the retrofit bioreactor (Berge et al., 2009).

Open dumps still are the common method of waste disposal in developing countries. Open dumps leads to uncovered waste, insects and rodents at the site, open burning, polluted water generation. For this reason, it is essential to convert open dumps into a controlled waste disposal sites for public health and sustainability. The conversion of the open dumps into bioreactor is an important new approach for waste management.

2.3. Waste Degradation in Landfills

The fate and transport of compounds in a landfill is determined by conditions in the landfill and the physical and chemical properties of the compounds. Several natural processes can change compounds properties. These transformations can be physical/chemical (such as volatilization, dissolution/advection, precipitation, adsorption, reduction/oxidation, and hydrolysis) or they can be biological (such as mineralization, co-metabolism, accumulation, and polymerization).

2.3.1. In Situ Waste Degradation Mechanisms

Anaerobic process is a complex biochemical system covering and including a number of steps and several types of microorganisms. There are four stages of the organic transformations under anaerobic conditions as given in Figure 2.3.

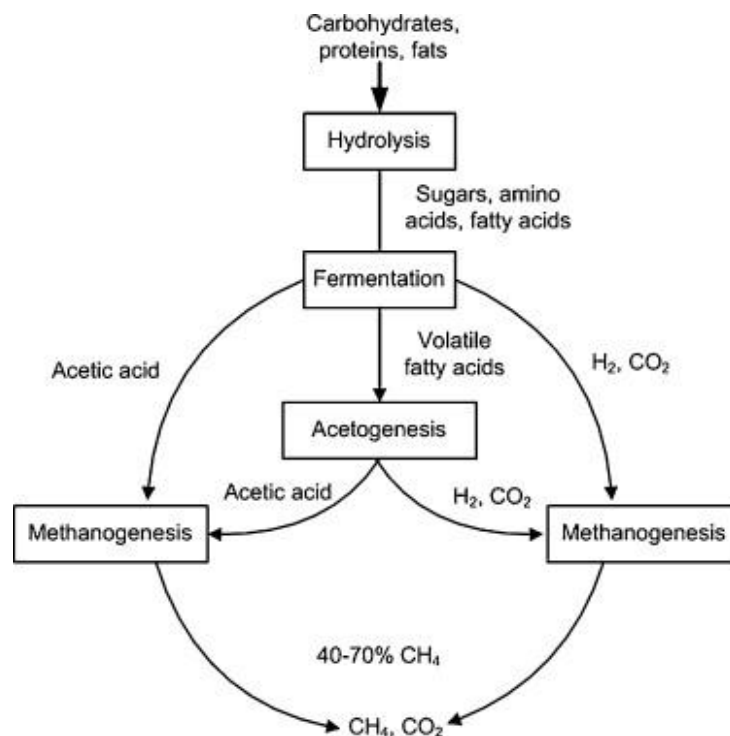


Figure 2.3. Four stages of organic transformation in anaerobic condition (Li et al., 2011).

In the first stage, namely hydrolysis stage, complex compounds are hydrolysed into dissolved compounds with a low molecular weight. Protein is degraded to amino acid, carbohydrate is transformed to monosaccharides and disaccharides and lipids are converted to long-chain fatty acid. Hydrolysis step controls the rate of organic decomposition processes. As the degradation of solid waste proceeds, the substrate volume decreases and the remaining organic material remains resistant to the attack of by microorganisms.

In the second stage dissolved compounds are extracted to simple organic compound such as volatile fatty acid, alcohol, lactic acid and mineral compounds such as carbon hydroxide, hydrogen, ammonia and hydrogen sulfide.

The third stage named as acetogenesis stage or fermentation in which the products from acidogenesis stage are converted to suitable substrate of methanogen microorganism such as acetate, hydrogen and carbon dioxide. Propionate converted to acetate, only achievable at low hydrogen pressure. Glucose and ethanol among others are also converted to acetate during the third stage of anaerobic fermentation (Ostrem, 2004).

In the fourth stage, called methanogenesis, is often the limiting step of anaerobic digestion. In this step, carbon dioxide and hydrogen are converted to methane by hydrogenotrophic bacteria and acetate is converted to methane by methanogen bacteria (Lettinga and Van Haandel, 1990).

2.3.2. Stabilization Phases of Landfills

Various studies have classified the stabilization of waste within landfill in five distinct phases (Pohland and Harper, 1986; Mertoğlu et al., 2007). According to the microbial activity within the landfill, the characteristics of leachate and biogas vary from one phase to another. The duration of each phase during the production of landfill gas depends on the distribution of organic compounds, nutrients, moisture content of waste and degree of compaction. The production of landfill gas may be hindered by insufficient moisture. For example, the increased density of waste matrix prevents the possibility of contact moisture with waste matrix resulting in the reduced biogas generation and bioconversion

(Tchobanoglous et al., 1993). The waste stabilization phases in landfills are given in Figure 2.4.

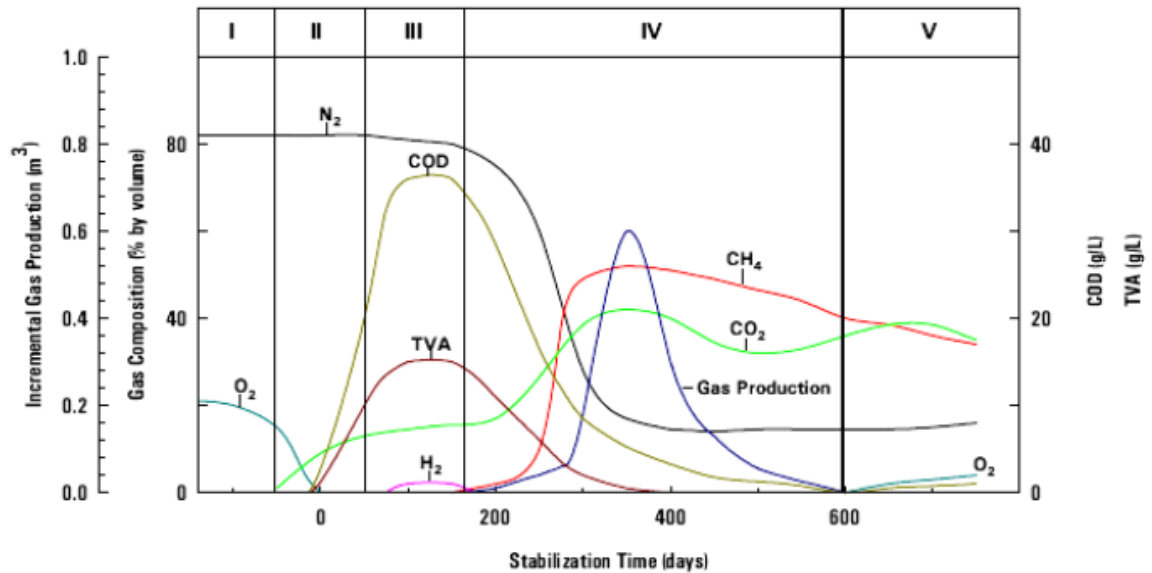


Figure 2.4. Phases of MSW degradation (Pohland and Harper, 1986).

In the first phase, initial adjustment phase, accumulation of moisture begins to develop with the initial placement of solid waste. An initial lag time is observed until sufficient moisture obtained in order to support microbial community (Tchobanoglous et al., 1993).

In the second phase, transition phase, oxygen is depleted and anaerobic conditions begin to develop. After that, reducing conditions is developed in accordance with shifting of electron acceptors from oxygen to nitrates and sulphates, and the displacement of oxygen by carbon dioxide. The oxidation reduction potential (ORP) of the waste is mainly the indicator of the onset of the anaerobic conditions. Mainly, ORP values within the range between -150 to -300 mV are indicator of the production of methane. However, nitrate and sulfate reductions occur at -50 to -100 mV (Tchobanoglous et al., 1993). In phase II, the pH of the waste decreases due to the presence of organic acids and the production of carbondioxide.

In the third phase, acid phase, the continuous solubilization and microbial conversion of biodegradable content result in the production of intermediate VOAs and thereby decreasing the pH value followed by metals mobilization. Biomass growth related with the activity of acidogenic bacteria and the rapid consumption of nutrients are the specific features of this phase. The principle gas produced during this stage is carbon dioxide and smaller amounts of H₂ are appeared. The microorganisms involved in this stage are specified as nonmethanogenic bacteria which are mainly identified as acidogens. The decreased pH values are mainly attributed to the elevated concentrations of carbon dioxide and the presence of organic acids. Due to the dissolution of organic acids COD, BOD₅ and the conductivity begin to increase. The additional moisture provides an ideal environment for the anaerobes, and the bacteria in the leachate provide an extra seeding of bacteria to degrade the organic matter (Tchobanoglous et al., 1993; Pohland and Harper, 1986).

In the fourth phase, methane fermentation phase, intermediate acids are converted into methane and carbondioxide by methane-forming consortia as they used up alternative electron acceptors (methanogens). Sulfate is reduced to sulfide. The pH increase and support the growth of methanogens. The pH within the landfill begins to rise to the neutral values of 6.8 to 8.0 (Tchobanoglous et al., 1993). Apart from the acid phase, the concentration of BOD₅, COD and the conductivity in leachate will be reduced during this stage. Metals are removed through precipitation. Increase in hydroxide concentration is coupled with the reduction of sulfate to sulfide. Both, sulfide and hydroxide form insoluble complexes with metals. Therefore, metal concentrations in the leachate are significantly reduced. Methanogenic bacteria use carbon dioxide as electron acceptor and consume hydrogen ions produced during acidogenesis phase to produce methane (Tchobanoglous et al., 1993).

In the final maturation phase, this phase appeared after the conversion of readily biodegradable material into methane and carbon dioxide. Most of the degradable materials are removed via leachate during the degradation period. The rate of biological activity decreases dramatically due to the limiting amount of nutrients and substrate. Additionally, gas production decreases and leachate strength reached to its lower concentrations. The presence of resistant organic substrates results in the production of humic like substances.

Oxygen concentrations begin to develop at the end of the stabilization period (Tchobanoglous et al., 1993; Pohland and Harper, 1986).

The duration of the five distinct phases are identified with certain parameters. COD is a chemical parameter which indicates the organic strength of the leachate. However, BOD₅/COD ratio indicates the biodegradability of the waste (Pohland and Harper, 1986). Oxidation reduction potential and pH are physical-chemical parameters and the indication of the oxidation-reduction and acid-base conditions, respectively. The presence of the volatile organic acids is an indication of the degree of the waste conversion as well as the potential amount of the methane and carbondioxidd which is produced. Leachate nitrogen and phosphorus concentrations are the reflective of the availability of the nutrients in the anaerobic system. Additionally, other parameters include alkalinity (buffer capacity), heavy metal concentration (potential inhibitory effects), conductivity (ionic strength/activity), chloride (migration potential), sulfate (oxidizing potential) and the bacteria or viruses (health hazards). The intensity of these parameters varies according to phase of the landfill stabilization.

2.3.3. Factors Affecting Landfill Stabilization

Major factors that influence MSW degradation in landfills are pH, temperature, nutrients, moisture content, alkalinity, inhibitory substances (Table 2.4).

Table 2.4. Summary of influencing factors on MSW degradation in landfills (Yuen et al., 1994).

Influencing factors	Criteria/Comments	Reference
Moisture	Optimum: 60% and above	Pohland (1986); Rees (1980)
Oxygen	Optimum redox potential for methanogens: -200 mv -300 mv < -100 mv	Farquhar & Rovers (1973) Christensen & Kjelden (1989) Pohland (1980)
pH	Optimum pH for methanogenesis: 6 to 8 6.4 to 7.2	Ehrig (1983) Farquhar & Rovers (1973)
Alkalinity	Optimum alkalinity for methanogenesis: 2000 mg/L. Maximum organic acid concentration for methanogenesis: 3000 mg/L Maximum acetic acid/alkalinity ratio for methanogenesis: 0.8	Farquhar & Rovers (1973) Farquhar & Rovers (1973) Ehrig (1983)
Temperature	Optimum temperature for methanogenesis; 40°C 41°C 45 (34 – 38°C)	Rees (1980) Hartz et al (1982) Mata-Alvarez et al (1986)
Hydrogen	Partial hydrogen pressure for acetogenesis: <10 ⁻⁶ atm	Barlaz et al (1987)
Nutrients	Generally adequate	Christensen & Kjelden (1989)
Sulphate	Increase in sulphate decrease in methanogenesis	Christensen & Kjelden (1989)
Inhibitors	Cation concentration producing moderate inhibition (ppm) Ammonium (Total) : 1500 – 3000 Sodium : 3500 - 5500 Potassium : 2500 – 4500 Calcium : 2500 – 4500 Magnesium : 1000 – 1500 Heavy metals: No significance influence Organic compounds: Inhibitory effect only in significant amount.	McCarty & McKinney (1961) Ehrig (1983) Christensen & Kjelden (1989)

2.4. Enhancement of Landfill Stabilization

The degradation of solid wastes in conventional landfills takes decades to achieve stabilization in conventional landfills. Therefore, due to the waste decomposition process, waste settlement and gas production continues for a long time, which requires a long-term post closure-monitoring period. To overcome these difficulties a new technology was

developed to accelerate the rate of waste decomposition and stabilization known as bioreactor landfill.

Leachate quality, gas quality and waste composition are the main indicators of the landfill stabilization. It is confirmed that complete stabilization is reached when leachate strength is sustained at a COD below 1000 mg/L and BOD₅/COD ratio less than 0.1 (Renou et al., 2008). Additionally, a blackish colored and sludge-like appearance is considered as an indicator of stabilization of solid waste in the landfill (Reinhart and Townsend, 1998). Leachate recirculation with shredding, compaction, pH control, buffer, sludge and nutrient addition, were reported to accelerate waste stabilization (Barlaz et al., 1989).

2.4.1. Leachate Recirculation

Leachate recirculation back into the waste matrix named bioreactor concept (Karthikeyan et al., 2007a). Increasing attention is being given to the leachate recirculation in landfills (Benson et al., 2007; El-Fadel, 1999; Erses and Onay, 2003; Erses et al, 2005; Reinhart, 1996; Reinhart and Townsend, 1998; San and Onay, 2001). The main purpose of the bioreactor concept is to enhance the biodegradation and promote the landfill stabilization of landfilled waste by distributing optimum moisture and transfer of nutrients, substrates and microbes throughout the waste body. Some of the studies on both pilot and laboratory scale simulated systems were summarized in terms of the dimensions of the simulations, the moisture content and density of the waste samples and recirculation ratio in Table 2.5.

2.4.2. Shredding

Shredded waste can increase waste degradation and contact between microbes and nutrients. However, Barlaz et al. (1990) reported that increased rate of shredding resulted in the accumulation of organic acids. The reduction in the pH value inhibits methanogenesis since a neutral pH range is optimum for the methane production. However, the period of hydrolysis in the transition phase last longer without shredding

2.4.3. Compaction

Compaction may affect the degree of anaerobic decomposition. Abdulhussain et al. (2009) stated in their study that the compaction reduces the filtration rate. For this reason, leachate formation has been found to be greater in less compacted refuse (Tatsi and Zouboulis, 2002). In the studies carried out using small columns (less than 50 cm height) and low quantities of waste, the results were not indicative of what happens on site. When the quantity of waste was great enough (approximately 10 kg), the evaluation was the same; nevertheless, it was not possible to make evaluation between the the results obtained from columns and that occurs on site (Francois et al., 2007).

2.4.4. pH Control

pH control is the most critical parameter in the stabilization phases of the landfilled waste. The pH control can be provided by adding buffer material. Stegman and Spendlin (1989) found the negative effects of sodium hydroxide (NaOH) addition. Nevertheless, the reactor having no buffer addition exhibited an active methanogenic environment whereas the reactor with NaOH additives inhibited methane formation by increased sodium content. Buffer addition may be advantageous when the acid phase is predominant.

2.4.5. Buffer Addition

The buffer addition increases pH and assists the CH₄ formation process. It has a positive effect on CH₄ formation (Christensen and Kjeldsen, 1989). Buffer addition is reasonable only when methanogens failed to produce methane due to the low pH values.

2.4.6. Sludge Addition

Sewage sludge addition has a positive effect which increases CH₄ formation if it added with neutral pH (Christensen et al., 1996). Potential positive effects of the sewage sludge are the increased water content, readily available nutrients and active anaerobic biomass which enhances the methanogenic phase of the degradation.

Table 2.5. Summary of the studies from different recirculation regimes.

Lab scale studies	Waste quantity (kg)	Moisture content (%)	Reactor volume (L)	Height (m)	Diameter (m)	Density (kg/m ³)	Recirculation (%)	Recirculation rate (L/d or L/week)	L/day/t _{DM}
Ağdağ and Sponza (2004)	24, 26, 29 (waste+sludge)	75-86	70.68 three reactors	1	0.3	-	13-30 % of reactor volume	9-21 L/day	
Benbelkacem et al. (2010)	410-415	26.5	1200 three reactors	1.3	0.96	500-540	-	17-4.25 L/week	8-2
Hao et al. (2008)	39	55	144	1.5	0.35	325	-	1 L/week & 10 L/week	
San and Onay (2001)	13	80	96 two reactors	1	0.35	178	-	1-2 L/week+ rainfall 0.5 L/week	-
Shalini et al. (2010) Flushing bioreactor	2327	28	3982 Six reactors	3	1.3	834	-	30 L/d - 50 L/week- 100L/week	-
Lubberding et al. (2010)	350-450	20	750	-	-	-	-	60 L/week	-
	300 mg	20	1	0.21	0.16	-	-	30 mL/week	-
Long et al. (2009)	27.4	38.2	62	1	0.287	680	-	-	-
	26.5	38.2	42	0.65	0.287	940	-	-	-
Long et al. (2010)	-	54	475	2	0.55	-	-	-	-
	-	54	14	1	0.15	-	-	-	-
Francois et al. (2007)	41	-	170	1.5	0.38	362.8	-	542+110 mL/d	38.6
Novella et al. (1997)	500	-	1200	4.25	0.6	-	-	15 L/week	-
	750	-	1920	3	0.8	-	-	31 L/week flushing	

Table 2.5. Summary of the studies from different recirculation regimes (continued).

Lab scale studies	Waste quantity (kg)	Moisture content (%)	Reactor volume (L)	Height (m)	Diameter (m)	Density (kg/m ³)	Recirculation (%)	Recirculation rate (L/d or L/week)	L/day/t _{DM}
Cossu et al. (2001)	9.32	-	26	1	0.18	-	-	1.5 L/week	-
	7.93	-	26	1	0.18	-	-	1.5 L/week	-
	8.12	-	26	1	0.18	-	-	4.13 L/week	-
Chiemchaisri et al. (2002)	16 kg	75.7-88.5	70.68	1	0.3	1147-1171	-	4-8-15 times/month (8-4-2.2 L)	-
	763	80	1718	2.7	0.9	621	-	-	-
Sun et al. (2009)	120	40-46	163	1.3	0.4	890	-	-	-
Bayard et al. (2005)	10	48-53	20	-	-	-	-	120 mL/kg DW/week	4.3
Sanphoti et al. (2006)	38.15	70.28	63.6	1.25	0.3	600	-	6L distilled water+ recycled (unknown)	17.04
Sun et al. (2011)	60	76.7-78.5	29.25	1.3	0.3	850	-	-	10-28-5 ml/kg.d
Sun et al. (2011)	60	21.0-34.0	29.25	1.3	0.3	770	-	-	-

2.5. Literature Review on Retrofit Bioreactor Landfills

Existing conventional landfills and open dumps need to be rehabilitated in order to eliminate the potential risk of the landfill site to the environment. Conversion of an existing landfill from conventional to bioreactor (retrofit) should evaluate existing leachate collection design since repair, removal or replacement of the system is cost prohibitive. Berge et al. (2009) developed an economic model to evaluate the impact of various operational (anaerobic, aerobic, or hybrid) and construction (retrofit and as-built) bioreactor landfill strategies on project economics. According to the model, the cost of retrofit bioreactor landfill was approximately 8.7 % more expensive than the traditional landfill, whereas as-built and aerobic bioreactor landfills were 20 % and 13 % less costly, respectively, than the traditional landfill (Berge et al., 2009).

There are several studies in the literature classifying landfills according to the waste disposal age. Tchobanoglous et al. (1993) classified young landfills as less than two years and mature landfills as more than 10 years. In another related study, Hang et al. (2002) monitored humic substances in leachate with different ages. In their study, they classified landfills as “young landfill” with an age of <5 years, “medium aged landfill” with an age of 5-10 years and “old landfill” with an age of >10 years. The classification of different landfill age and phases are given in Table 2.6 and 2.7.

Table 2.6. The classification of different landfill ages.

Reference	Landfill Age		
	Young	Medium aged	Old
Tchobanoglous et al. (1993)	<2 years	-	>10 years
K. Hang et al. (2002)	<5 years	5-10 years	>10 years
Renou et al. (2008)	<5 years	5-10 years	>10 years

Table 2.7. The classification of different landfill stabilization phases.

Reference	Landfill Phases			
	Transition phase	Acid-formation phase	Methane fermentation phase	Final maturation phase
Aziz et al. (2010); Kostova (2006)	0-5 years	5-10 years	10-20 years	>20 years

There are numerous studies conducted about the comparison of the stabilization potential of the fresh and aged refuse from taken real conventional landfill site and the operation of the waste samples as bioreactor concept in the literature (Swati et al., 2011; Sun et al., 2009; Sun et al., 2011; Long et al., 2009; Shalini et al., 2010; Kulikowska and Klimiuk, 2008; Chen et al., 2009).

Swati et al. (2011) studied pilot scale simulations of young and old landfills. The simulations were filled with two types of substrate; fresh Municipal Solid Waste (MSW) and excavated from open dumpsite. The reactors were operated with/without recirculation. Densities of 652-825 kg/m³ could be achieved initially due to higher levels of moisture (60 %) in fresh MSW and inerts (70 %) in stabilized MSW. It was found that bioreactor concept affects positively young landfills with percentage removal of, 86 % removal in COD, 82 % removal in BOD₅, 85 % removal in Dissolved organic carbon (DOC) and 75 % volatile solids in leachates. However, operation of old dumps as bioreactors seems to have no exceptional advantage. Comparison of waste degradation by applying different reactor configurations with different refuse ages is given in Table 2.8.

In another related study, the sequencing recirculation technology which recirculates leachate taken from aged refuse reactor into the fresh refuse reactor was investigated (Sun et al., 2009). It was found that the sequencing recirculation technology can accelerate the degradation of the refuse and improve the quality of leachate from fresh refuse reactor compared to self recirculation technology. The effluent ammonia and COD concentrations were below 15 mg/L and 150-400 mg/L, respectively in the aged refuse.

Sun et al. (2011) conducted a study to investigate the combined semi-aerobic and anaerobic fresh refuse bioreactor with the aged refuse bioreactor applying sequencing recirculation bioreactor. It was stated at the end of the study that the semi-aerobic recirculation process can improve the productivity and reduction of leachate, biodegradation of organics from refuse, and refuse settlement to enable acceleration of refuse stabilization compared with the anaerobic recirculation process.

In a related study, Karthikeyan et al. (2007) conducted a research on using two lysimeters filled with municipal solid waste excavated from dumpsite to simulate the

leaching of pollutant loads from controlled dumps and to assess the effect of leachate recirculation on waste stabilization. According to the data gathered at the end of the study, TKN and ammonia nitrogen in leachate reduced by 50 % in one year. It was found that the leachate recirculation in old dumps can leach out both organic and inorganic compounds from the partially degraded waste. The most promising result of that study was that methane recovery was possible with the bioreactor landfill operation in old dumps.

As landfill age increases, the organic concentration in leachate decreases whereas ammonia nitrogen concentration increases (Kulikowska and Klimiuk, 2008). Leachate recirculation results in the production of more stabilized leachate which has lower biodegradable organic compounds but higher amount of ammonia. The increase of ammonia in old landfill leachate is mainly attributed to the hydrolysis and fermentation of nitrogen containing fractions of biodegradable refuse (Abdulhussain et al., 2009).

Table 2.8. Comparison of waste degradation from different reactor configuration with different refuse ages.

Reactor type	Reactor		Substrate	Operation	Leachate recirculation	Density (kg/m ³)	M.C. (%)	COD removal (%)	NH ₃ -N (mg/L)	BOD ₅ /COD	Biogas methane (%)	Reference
	Diameter (m)	Length (m)										
Bioreactor	1.3	3	Young	Anaerobic	√	632	58-62	82-86	-	>0.5	34-59	Swati et al. (2011)
Retrofit	1.3	3	Old (10 years old)	Anaerobic	√	825	27-28	68	-	0.1-0.8	15-47	Swati et al. (2011)
Sequencing recirculation Bioreactor	0.40	1.30	Young (3 months)	Anaerobic	√	961	40-46	25	1200-1400	-	-	Sun et al. (2009)
Retrofit	0.40	1.30	Old (10 years old)	Anaerobic	√	892	21-34	90.5	<15	-	-	Sun et al. (2009)
Sequencing recirculation Bioreactor	1.3	3	Young	Anaerobic	√	850	77-79	75	1500-2900	-	-	Sun et al. (2011)
Sequencing recirculation Bioreactor	1.3	3	Old (10 years old)	Anaerobic	√	770	21-34	-	-	-	-	Sun et al. (2011)
Sequencing recirculation Bioreactor	0.29	1.00	Young	Anaerobic (hybrid)	√	680	70	-	929-359	-	-	Long et al. (2009)
Sequencing recirculation Bioreactor	0.29	0.65	Old (6-7 years old)	Anaerobic (hybrid)	√	940	38.2	-	411	-	62- 80% max. production	Long et al. (2009)

The quality of leachate generated from a landfill site gives information about the refuse age and its stabilization phases (Tchobanoglous et al., 1993). Generally, landfills are classified as young, medium and old (mature) according to the refuse ages. Ziyang et al. (2009) studied the attenuation of the contaminants in the leachate with different disposing ages. According to the results, it was found that the alkalinity concentration decreased significantly over ages, from 18,162 mg/L in 2 years old leachate to 1714 mg/L in 12 years old and where as 5573 mg/L in 6 years old leachate due to the decrease of carbonate and bicarbonate in leachate.

Tatsi and Zouboulis (2002) studied investigation of the quantity and quality of leachate from a municipal solid waste landfill in a Mediterranean climate. In their study, it was stated that 'Fresh' leachate samples showed a higher degree of metal solubilization due to lower pH values caused by the biological production of organic (fatty) acids. However, the increase in the pH of the leachate samples resulted in decrease in metal solubility. Moreover, the lower concentration of metals in stabilized leachates is mainly due to adsorption and precipitation reactions (by co-existing sulfide, carbonate or hydroxide anions), which, this accompanied by the gradual increase in ORP values with increasing age of the landfill (Irene and Lo, 1996). According to the study conducted by Martensson et al. (1999), a number of factors were identified that could affect metal's mobility in a well decomposed refuse that is undergoing a transition from anaerobic to aerobic. Working with samples of 20-year-old refuse excavated from a landfill, they showed that the concentrations of Zn, Cd, Cr, S roughly doubled when the refuse was decomposed under aerobic conditions relative to anaerobic conditions in reactors.

In young landfills, organic concentration (expressed in COD) is above 10000 mg/L while in old landfills COD value is below 4000 mg/L (Table 2.9). However, recent studies show that leachate generated from young landfills gives much lower COD values due to the recently adapted practice of bioreactor concept with leachate recirculation principles (Kulikowska and Klimjuk, 2008).

Table 2.9. Leachate characteristics during different phases.

Leachate constituents	Landfill Phases				Reference
	Transition phase 0-5 years	Acid-formation phase 5-10 years	Methane fermentation phase 10-20 years	Final maturation phase >20 years	
BOD ₅ /COD	0.2-0.5	0.66- 0.80	0.35-0.66	0.13	Kostova (2006)
	>0.3	0.1-0.3	<0.1	-	Renou et al. (2008)
COD (mg/L)	500-22000	1500-71000	150-10000	30-900	Kostova (2006)
	41507	5348	1367	-	Hang et al. (2002)
	>10000	4000-10000	<4000	-	Renou et al. (2008)
	1543-7125	1015-2424	695-1523	-	Ziyang et al. (2009)

In other related work, Ziyang et al. (2009) studied the leachate characteristics under different disposal ages. Leachate with different disposal ages were taken from a real landfill site and analyzed in a laboratory. The change in leachate parameters as the disposal time extended is given in Table 2.10.

Due to the natural attenuation process, it was found that the organic concentration (as COD) of leachate were 7125 mg/L and 695.2 mg/L for 2 and 10 year old waste, respectively (Ziyang et al., 2009). Irene and Lo (1996) conducted a study in order to provide a database for the leachate quality of Hong Kong landfills. Their study showed that even low concentrations of both COD and NH₃-N in younger landfills revealed that landfills become methanogenic very fast.

Table 2.10. The change in leachate parameters as refuse ages (Data obtained from Ziyang et al., 2009).

Parameters	Landfill Age							
	2	3	4	6	7	9	11	12
TN (mg/L)	4368.2	4156	1753.5	1489.8	873.5	1092	980.1	428.2
NH ₄ ⁺ N (mg/L)	4251	3821	1564.2	1273.6	733.1	807.4	715	238.2
OP (mg/L)	34.29	21.77	17.56	12.43	6.78	2.37	4.75	0.19
TP (mg/L)	34.9	23.2	17.97	14.83	9.58	3.4	7.21	0.62
Alkalinity (mg/L)	18162	18379	8049	5573	4365	5227	4649	1754
ORP (mV)	-277	-289	-307	-127	-229	-112	-127	-104
Conductivity (µs/cm)	41500	40500	17870	15030	10630	12270	12080	6380
Mineral oil (mg/L)	8505	5619	5638	5309	4595	5878	3007	2547

There are several studies conducted in order to monitor different components in leachate while refuse age extended. Hang et al. (2002) conducted a study to monitor humic substances in leachate with different age. Leachates were collected from different landfill ages and classified as young landfill” with landfilling age of <5 years (landfill-G), medium-aged landfill of 5–10 years (landfill- P), and old landfill of more than 10 years (landfill-N). The biodegradability rate which represented as BOD₅/COD ratio is reduced from 0.79 of landfill-G to 0.11 of landfill-N with respect to refuse age. This information given in the literature is important to understand the impact of landfilled waste age on the overall attenuation processes.

3. STATEMENT OF THE PROBLEM

The aim of this study is to evaluate and understand the waste degradation potential of a 5 year old waste sample taken from a real conventional landfill site when operated in a bioreactor. The effect of the leachate recirculation strategy on the potential degradation of the previously conventionally landfilled waste was investigated.

For this purpose, laboratory scale simulator was operated in temperature controlled room (35°C) according to the recirculation strategy. Prior to the placement of the solid waste, initial solid waste and seed sludge analyses were conducted. According to the characteristics of the solid waste, initial field capacity was determined and arranged at the beginning of the operation. Furthermore, the fate and behavior of the waste degradation mechanisms were observed by measuring and evaluating the leachate and gas analysis. The indicator parameters such as pH, ORP, conductivity, salinity, color, turbidity, COD, BOD₅, TKN, ammonia nitrogen, VFA, sulfate, orthophosphate, metals and alkalinity were monitored in leachate; daily and cumulative gas productions, and gas compositions were determined in the produced biogas in order to monitor the fate of the pollutants and behavior of the degradation.

The potential stabilization of solid waste under a more controlled reactor provides a basis for the utilization of retrofit bioreactor. The conversion of conventional landfills to bioreactors requires an extensive preliminary study to understand the nature and stabilization potential of existing waste matrix. Finally, the results of this study will be used to evaluate the suitability of this conversion and gives information about the rehabilitation potential of existing landfills especially for medium aged landfills by evaluating the remaining stabilization potential under bioreactor concept.

4. MATERIALS AND METHODS

Laboratory scale anaerobic bioreactor system was set up to simulate and understand waste degradation potential on an 5 year old waste sample taken from a conventional landfill. The operation of a conventional landfill as bioreactor landfill after necessary modifications will provide to get more controlled operations for a faster waste decomposition. The experimental part of the study consists of the monitoring of leachate indicative parameters and gas analysis.

4.1. Design of Simulated Landfill Reactor

A pre-constructed lysimeter reactor made from PVC columns was operated in closed constant temperature room (35°C). The reactor was designed with 1 m of length and 0.35 m of diameter. The available volume of the reactor was 96 L. PVC flanges were used both at the top and bottom of the reactors to provide support for the top and bottom lids. There are three ports mounted on the reactor; one was used for sampling of leachate while others used for gas sampling and liquid addition. Additionally, reactor was supported with the thermometer for monitoring.

Reactor was equipped with the PVC tee with 2 cm diameter at the center of the bottom lid for the leachate collection and at the center of the top lid in order to provide uniform leachate distribution onto the waste matrix. All joints were applied with silicon for the impermeability (Figure 4.1).

At the top of the reactor, 2 masterflex pipes 0.75 mm were attached to the end of the PVC tee placed; one was used for gas sampling by applying rubber stopper and another was for gas collection end up with wet gas meter and leachate collection container with a volume of 19 L. For the purpose of the leachate recirculation, one end was attached to the addition port and another was attached to the container. Selecta Percom –I peristaltic pump was used for leachate recirculation purposes.

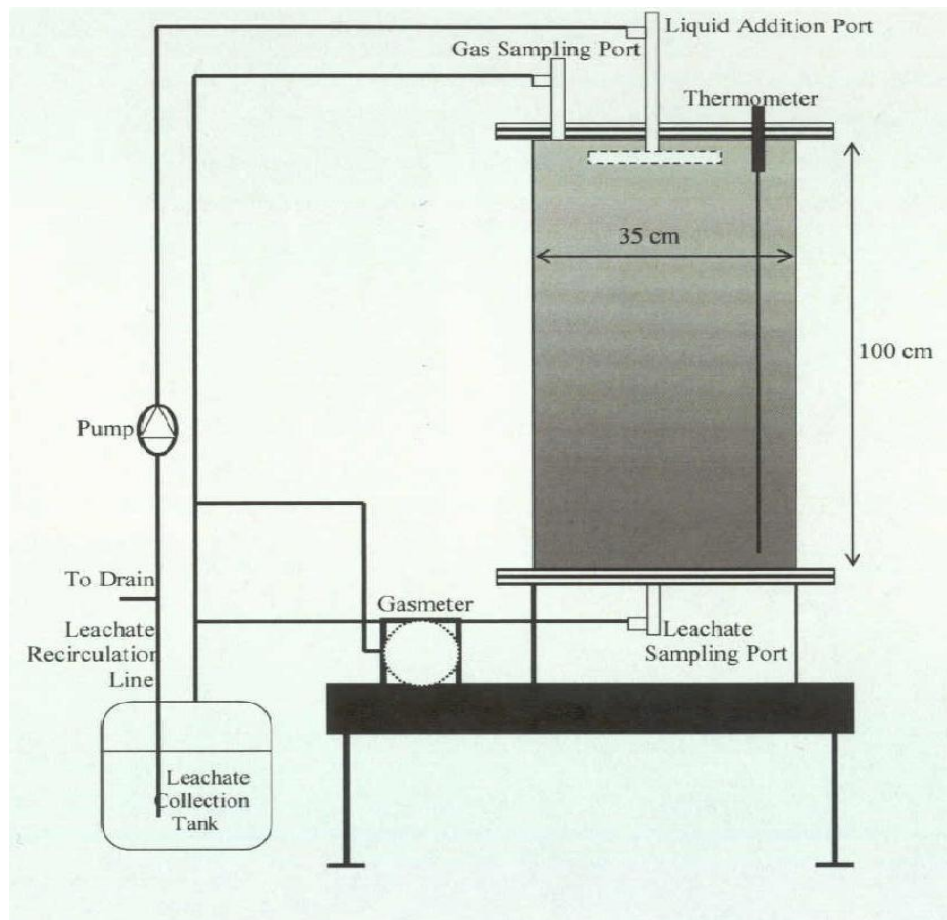


Figure 4.1. Simulated bioreactor landfill with leachate recirculation (Adopted from Erses and Onay, 2003).

Before loading, 1-2 cm thick layer of gravel and a nylon screen with 1-2 mm diameter holes were placed at the bottom of the each reactor in order to prevent the penetration of the particles from the waste matrix into the drainage system which can cause clogging.

4.2. Reactor Loading

In order to understand the main principles of operating conventional landfills as bioreactors and rehabilitation of existing landfills, a 5 year old waste sample was taken from a real landfill site of İZAYDAŞ in İzmit. The average waste composition is given in Figure 4.2.

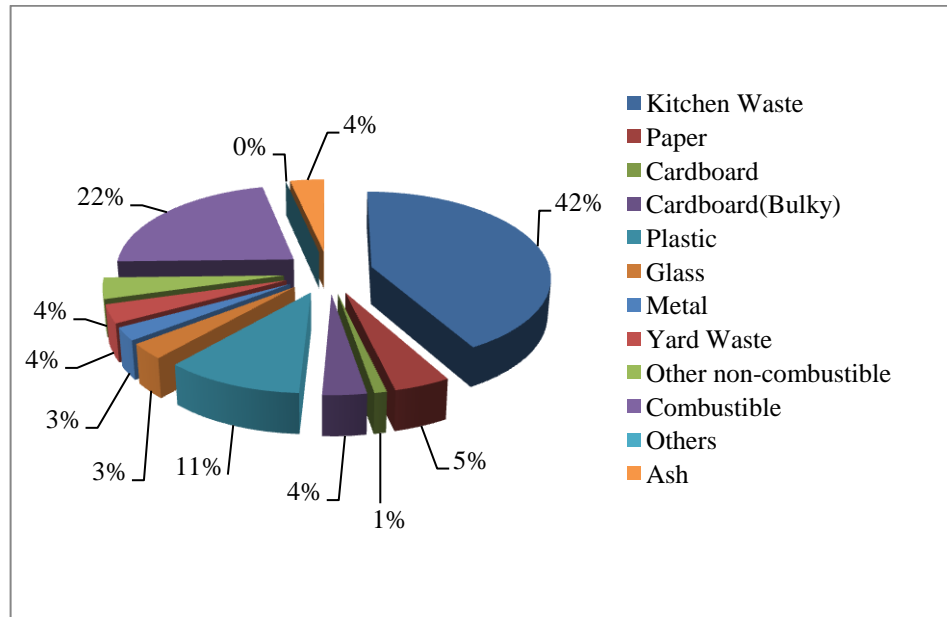


Figure 4.2. The average waste composition of solid waste (İZAYDAŞ, Personal Communication).

İZAYDAŞ established in 1996 and the municipal solid waste landfill site is the first waste disposal plant in Turkey. İZAYDAŞ, Solaklar Municipal Solid Waste Landfill Site consists of hospital and hazardous waste incineration plant and municipal landfill site. Between 1997-2011, 3,106,028 tons of domestic and household waste, 29,7485 tons of domestic industrial waste are accepted to the Solaklar Domestic Waste Landfill Area. The Solaklar Domestic and Hazardous Solid Waste Sanitary Landfill have been started to accept wastes in 1997 on a portion of 363,007 m² of total 800,000 m². There are 7 lots were constructed in the landfill site. There are six lots with a capacity of 3,163,000 m³ for domestic wastes and one lot with a capacity of 969,919 m³ for hazardous wastes (İZAYDAŞ, Annual Report, 2011).

5 year old waste sample was taken from lot 3 which covers a volume of 290,000 m³ with a depth of 10 m. The most homogenized form of waste sample was tried to be taken for the laboratory simulations in order to represent the real waste compositions. Reactor was fed with the real waste taken from the disposal site and seeded with the anaerobic digested sludge of Fritolay A.Ş. The amount of solid waste and sludge loaded to the reactor is given in Table 4.1.

Table 4.1. Loading conditions of the reactor.

	Operating condition	Landfill type	Solid waste (kg)	Seed sludge (L)	Moisture content (%)	Water added (L)
Reactor	Anaerobic	Retrofit	19.5	1	40	5.6

The amount of water added to the reactor prior to operation was calculated with regard to the moisture content of the waste sample by adjusting moisture content of the system to 40 %. Solid waste sample taken from the landfill site and sludge sample were stored in the cold room at 4°C until the loading. On the day of loading, solid waste and sludge sample were taken and cooled to ambient temperature. The amount of solid waste sample loaded to the reactor was selected based on the capacity of the reactor volume and headspace of the reactor. Simulated retrofit bioreactor was loaded with solid waste sample of 19.5 kg and mixed with sludge of 1 L. Sludge was used to enhance the microbial population in the solid waste mixture. After loading of the waste sample into the reactor, reactor and all joints sealed with silicon and flushed with nitrogen in order to ensure the presence of anaerobic conditions.

4.3. Reactor Operation

The anaerobic bioreactor was operated in temperature controlled room at 35°C to obtain mesophilic conditions for the growth of desired microbial populations. Solid waste sample taken from the conventional landfill site of the İZAYDAŞ was operated in a bioreactor to represent conditions supporting retrofit bioreactor concept.

Prior to leachate recirculation, field capacity should be reached in order to provide optimum moisture content for the microbial activity. Using the mass balance for the leachate generation, the amount of leachate introduced should be equal to the amount generated to reach to field capacity. The moisture content of solid waste was arranged to 40 % in the reactor. The day that field capacity reached was set as Day 0. Field capacity reached 4 days after the placement of solid waste in the reactor. Total volume of water applied to the reactor until field capacity reached was calculated as 2 L. In addition to the leachate recycling, 500 mL of distilled water was added to the simulated reactor to represent the 20 cm/year rainfall encountered in real landfill site. There was not any loss in

the leachate; only for sampling, recycling and moisture loss due to the gas production occurred. By using the mass balance, net water storage was determined. The anaerobic reactor fed with 5 year old waste sample was operated 114 days. Additionally, 1 L of collected leachate was recirculated once per week throughout the study.

4.4. Analytical Methods

Prior to loading and after the end of operation approximately 500 g of solid waste was allocated for initial and final elemental analysis. In order to represent the characteristics of the reactor, not only the solid wastes but also the mixture of seed sludge and solid waste were analyzed. The moisture content, TS (%), VS (%), TKN, trace metals (Fe, Mn, Cu, Ni, Cd, Zn, Cr) and elemental content (C, H, N) were determined and compared.

4.4.1. Leachate Analysis

Leachate samples were taken from the bottom of the reactor for analysis. About 100 ml of leachate samples were taken every week. Leachate samples were analyzed for chemical oxygen demand (COD), biochemical oxygen demand (BOD₅), volatile fatty acids (VFA), pH, oxidation-reduction potential (ORP), conductivity, salinity, turbidity, color, alkalinity, sulfate, orthophosphate, ammonia nitrogen, total kjeldahl nitrogen (TKN), total organic carbon (TOC) and heavy metals (Fe, Mn, Cu, Ni, Cd, Zn, Cr). Heavy metals were analysed using Perkin Elmer Analyst 300 AAS and Optima 2100 DV ICP-MS via liquid extracts of the substrates. The methods and parameters analyzed for both leachate and gas samples were summarized in Table 4.2. The volatile fatty acid (VFA) concentrations were measured using Perkin Elmer Clarus 600 Gas Chromatograph with a flame ionization detector (FID). The maximum column (30 m length and 0.32 mm I.D.) temperature of FID is 260°C. The set point of the oven and maximum temperature of inlet are 100°C and 240°C, respectively. Helium gas was used as a carrier gas at a rate of 0.8 ml/min. Air tight cell was used to store the sample and the injection volume 2 µL. The instrument uses H₂ (45.0 mL/min) and air (450.0 mL/min). All these analyses were performed according to Standard Methods for the Examination of Water and Wastewaters (APHA, AWWA-WEF, 1998).

Table 4.2. Experimental protocol.

Parameter	Frequency	Methods used	Instrument information
COD	2/week	5220 D Method Closed Reflux, Chlorimetric (APHA,AWWA-WEF-1998)	HACH COD digester; HACH DR/3 Spectrophotometer
BOD ₅	1/week	5210 D Method 5-day BOD Test (APHA,AWWA-WEF-1998)	Dissolved Oxygen meter HACH model 16046
TOC	1/month	5310 D Method (APHA,AWWA-WEF-1998)	Schimidzu TOC-V CSH Analyzer
VFA	1/month	Gas Chromatograph with FID Detector	Perkin Elmer Clarus 600 Gas Chromatograph
ORP	3/week	2580 B Method (APHA,AWWA-WEF-1998)	HANNA Instruments HI 221 Microprocessor pH meter
pH	Daily	4500-HB Method Electrometric (APHA,AWWA-WEF-1998)	HANNA Instruments HI 221 Microprocessor pH meter
Conductivity	1/week	2510 B Method (APHA,AWWA-WEF-1998)	WTW LF 320 Conductivity meter
Salinity	1/week	2520 B Method (APHA,AWWA-WEF-1998)	WTW LF 320 Conductivity meter
Turbidity	1/week	2130 B Method (APHA,AWWA-WEF-1998)	HACH 2100P Turbidimeter
Color	1/week	2120 C Method (APHA, AWWA-WEF-1998)	HACH DR/3 spectrophotometer
Alkalinity	1/week	2320 B Method Titration (APHA,AWWA-WEF-1998)	-
Ammonia-N	1/week	4500 C Method Titration (APHA,AWWA-WEF-1998)	Gerhardt Vapodest Distillation Apparatus
TKN	1/month	4500 Method (APHA,AWWA-WEF-1998)	HACH Digester
Orthophosphate	1/week	4500-P E Method Ascorbic Acid (APHA,AWWA-WEF-1998)	HACH DR/3 Spectrophotometer
Sulfate	1/week	4500-SO ₄ ⁻² E Method Turbidimetric (APHA,AWWA-WEF-1998)	HACH DR/3 Spectrophotometer
Heavy Metals	1/month	ASTM 3010	Perkin Elmer Analyst 300 AAS and Perkin Elmer Inductively Coupled Plasma (ICP-OES)
Gas analyses			
Gas Production	Daily	Wet Gas meter	Shinagawa Corporation Wet Gas meter
Gas Composition (O ₂ , N ₂ , CO ₂ and CH ₄)	1/week	Gas Chromatograph	Gas Chromatograph Agilent 6850

4.4.2. Gas Analysis

The gas generated from the reactor was collected by Shinagawa Corporation wet gas meter (Figure 4.3). The gas production from the reactor was recorded in 24 h period and corrected according to the standart temperature and pressure (STP). The cumulative biogas was determined as the sum of the daily biogas results.

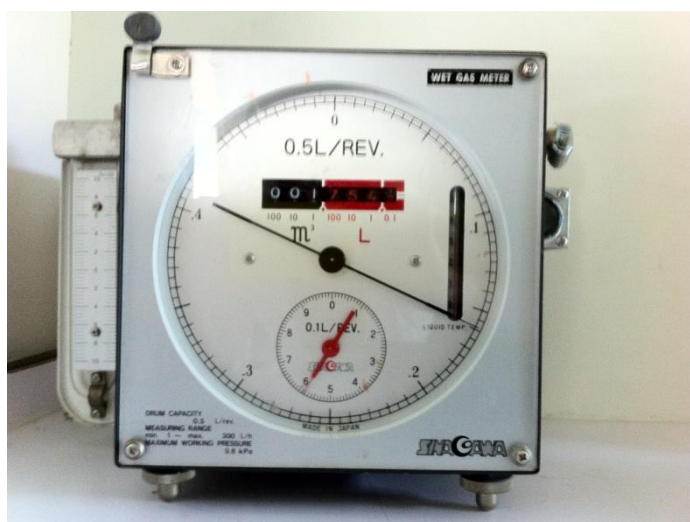


Figure 4.3. Wet gas meter used in the experiment.

The composition of the produced biogas was analyzed by Gas Chromatograph (GC) HP Agilent 6850 (Carboxen 1010 plot column 30 m x 0.53 mm) using thermal conductivity detector (TCD). As a carrier gas, helium was used at a range of 2ml/min. The final temperatures of detector and injection section were 160°C and 150°C, respectively. The oven temperature was programmed at 70°C. The three point calibration curves for the GC analyzer were determined prior to the study. Methane (4 %, 40 % and 99 %), carbondioxide (5 %) and 5 % gas mixtures were used to calibrate the instrument. The instrument gives peaks and curve for each present gases and calculated the composition of each gases in terms of percentage by plotting the areas under the peaks to the calibration curves. Air tight syringe (2.5 mL) was used to collect the sample accumulated in the headspace.

5. RESULTS AND DISCUSSION

All experiments including leachate, gas, initial and final solid waste analysis were evaluated in this section. Initial and final characterization of solid waste, leachate and gas produced from the simulated reactor were analyzed as the indicative parameters of waste stabilization.

5.1. Initial Waste Analysis

Municipal solid waste (MSW) and seed sludge samples were analyzed at the beginning of the experiments in order to understand the characteristics of the mixture prior to loading. The photography of the waste sample taken on the arrival day is given in Figure 5.1.



Figure 5.1. Solid waste samples.

Seed sludge was mixed with the solid waste in order to enhance the microbial activity within the waste matrix. The initial characteristics of MSW and seed sludge used in the reactor are given in Table 5.1.

Table 5.1. Initial characteristics of MSW and seed sludge used in the reactor.

Parameter	MSW	Sludge
TS (%)	79.50	6.29
VS (%)	51.70	57.65
Moisture Content (%)	20.50	93.71
TKN (mg/kg)	12000	41791
Carbon (%)	23.39	32.76
Nitrogen (%)	6.29	2.51
Hydrogen (%)	2.64	4.48
Carbon/Nitrogen	3.72	13.05
Wet density (kg/m ³)	342	-

The C/N ratio is the indicator of the nutrient balance in the waste matrix showing available carbon and nitrogen for the microbial activity. The C/N ratio was determined in initial and final waste to understand the degradation of readily available organic matter. The main reason of the reduction is the active decomposition of carbon to carbon dioxide and new cells and transformation of mineralisation of nitrogen.

Table 5.2. Initial heavy metal concentrations of MSW.

Heavy metals	Concentration (mg/kg)
Cr	108.30
Mn	376.83
Ni	179.82
Cu	463.83
Zn	210.25
Cd	1.41
Pb	108.31

The mobility of heavy metals inside landfills is low, and washout of metals may require hundreds of years. A significant part of the heavy metals in the waste will be in glass, plastics, slag, ceramics, steel, wood etc. The degradation process takes slowly in the landfills. Heavy metal analyses were conducted for seed sludge sample and the heavy metal concentrations showed no adverse effect on the microbial activity.

5.2. Water Balance

The results of the initial waste characterization indicated that the moisture content of solid waste sample was 20.50 %. According to the preliminary analysis, the initial amount of available moisture was calculated as 4.94 L. The moisture content of solid waste sample was insufficient in order to maintain optimum biodegradation. For this reason, 5.6 L of water was added to the reactor prior to loading in order to obtain about 40 % moisture content in the waste matrix. After loading, distilled water was used in order to sustain field capacity and leachate production. The amount of distilled water added to the system was 2 L. The start up of the system was set to Day 0 when the field capacity was reached after 4 days.

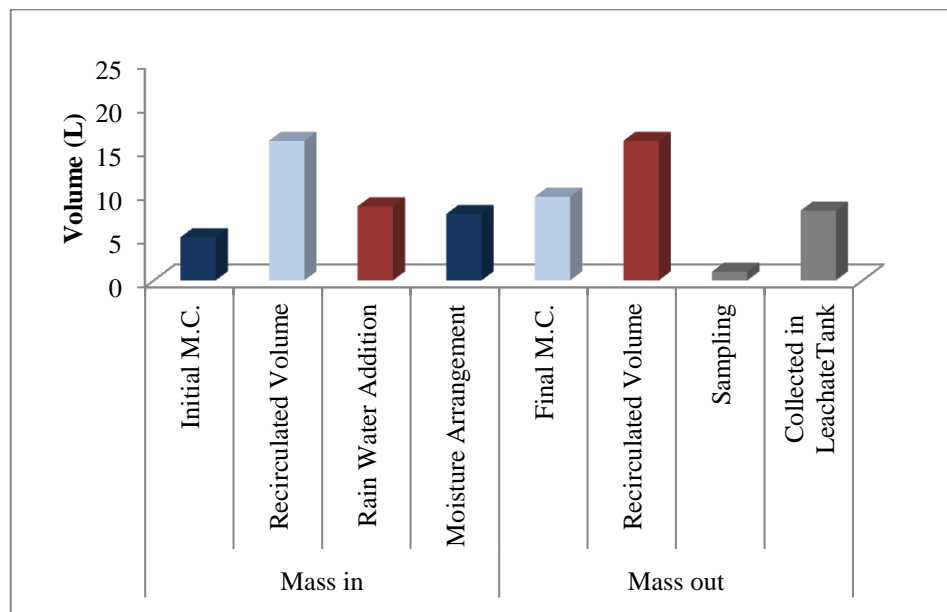


Figure 5.2. Water balance in the reactor.

In order to simulate the 20 cm/year rainfall, 500 mL of distilled water was added to reactor on a weekly basis. The total amount of distilled water applied to the reactor was calculated as 8.5 L. 1 L of the collected leachate was recirculated once per week period. The total amount of leachate recirculated in the reactor was calculated as 16 L (Figure 5.2 and 5.3).

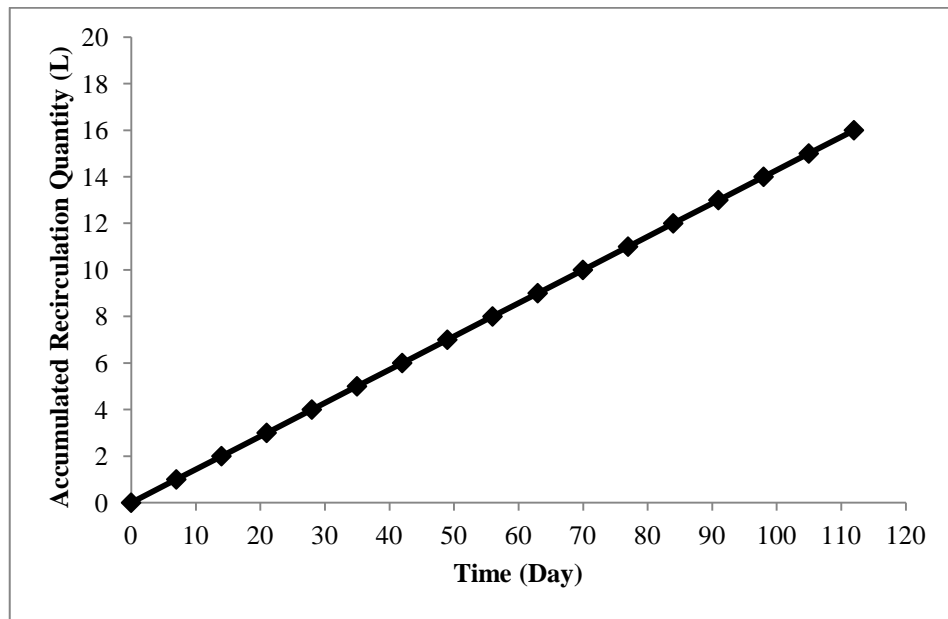


Figure 5.3. The quantity of recirculated leachate.

The water mass balance for the Reactor was calculated by taking into account the initial and final moisture content, water addition, and recirculation, sampling for analysis and collected volumes in the tank. The loss of moisture due to the gas production and reactions were ignored during the mass balance calculations. The mass balance equations were summarized in Equation 5.1.

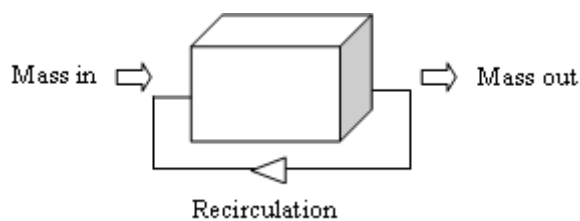


Figure 5.4. The mass balance in the reactor.

Mass Balance Equations;

$$M_{\text{net}} = M_{\text{in}} - M_{\text{out}} \quad (5.1)$$

Where;

M_{in} = initial waste moisture content + recirculation + water addition

$M_{out} = \text{final waste moisture content} + \text{recirculation} + \text{sampling} + \text{collection}$

Reactor 5;

$M_{in}: 4.94 + 16 + 8.5 + 7.6 = 37.04 \text{ L}$

$M_{out}: 9.6 + 16 + 1 + 8 = 34.6 \text{ L}$

$M_{net} = 2.44 \text{ L}$

The summary of the mass balance calculation is shown in Figure 5.4. According to the mass balance calculation, the mass in and mass out was calculated as 37.04 L and 34.60 L, respectively. The volume of water held in the reactor was calculated as 2.44 L. High amount of recirculation and rain water addition were accomplished in the reactor due to the long operational time. The results of the mass balance calculation indicated that the water holding capacity in reactor was high due to the low initial moisture content of solid waste matrix.

5.3. Leachate Analysis

Leachate provides nutrient and essential substrates for the biological activity within the system; served as a transport medium and represents the progression of landfill stabilization phases (Pohland, 1993). Therefore, certain parameters of leachate such as; pH, ORP, Salinity, Conductivity, Color, Turbidity, COD, BOD₅, NH₃-N, TKN, TOC Alkalinity, SO₄ and Ortho-P were measured on a weekly basis and interpreted in order to gain insight to the extent of the waste conversion. Other than that heavy metals and VFA were also measured once in a month. The results from the leachate samples were presented and discussed in the following sections.

5.3.1. pH

The pH of the anaerobic degradation is the indication of the intensity of the prevailing buffer system. The pH is depending on interactions between volatile organic acids, alkalinity, and also partial pressure of the produced carbon dioxide (Pohland et al., 1995; Onay, 1995). Leachate pH values vary according to the age of landfills. The range is given

as 4.5-7.5 for young landfills, 6.6.-7.5 for mature landfills (Tchobanoglous et al., 1993). pH was increased as the landfill is getting older in which the organic concentration was decreased. Monitoring the pH of the leachate samples routinely gives information about the stabilization phases of the solid waste.

Leachate pH from the reactor ranged between 6.34 and 8.0 throughout the study (Figure 5.5). It was found that the pH range obtained during the study was suitable for the methanogenic activity compared with the given pH ranges 6.0 to 8.23 in literature (Ehrig, 1983). The results showed that the pH of leachate increased in old landfills. When the available organic acids are converted to methane and carbon dioxide during the methane fermentation phase, pH tends to rise with the excess ammonia generation.

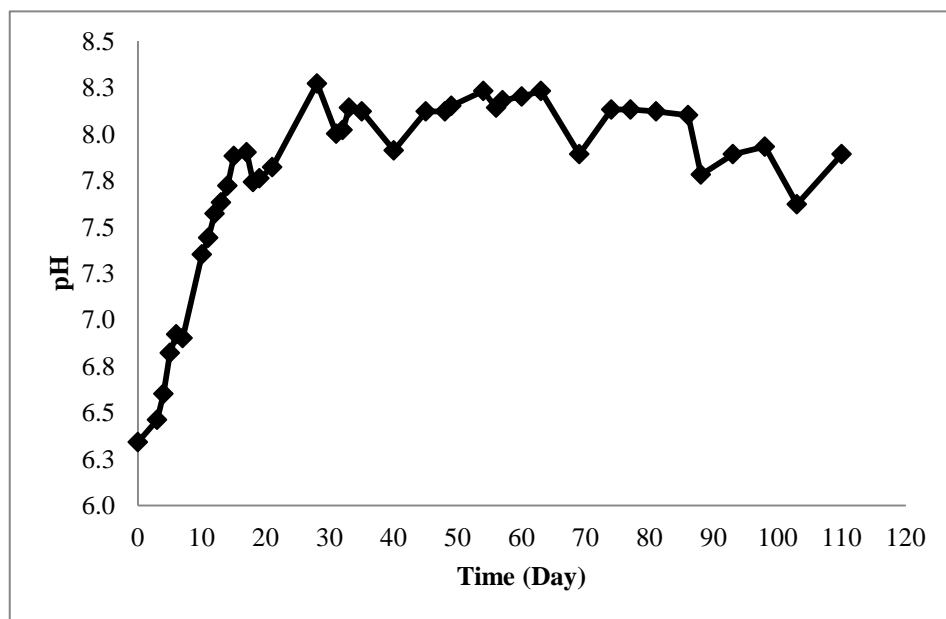


Figure 5.5. Leachate pH values.

Due to the presence of VFAs in leachate initially, the pH value was relatively low at the beginning of the experiment. However, the pH of the system tended to increase until Day 28 as volatile organic acids began to decrease. This increase was followed similar trend with alkalinity values. After that day, pH values stayed more or less constant until the end of the study.

5.3.2. ORP

Oxidation–reduction potential (ORP) is the indication of reducing and oxidizing strength of the leachate. Positive values of ORP indicate the existence of aerobic conditions whereas negative ORP values indicate the reducing anaerobic conditions. The ORP values of the anaerobic reactor were initially positive indicating the presence of aerobic conditions due to the initially high void spaces in the waste matrix. By the depletion of the oxygen and changes in the stabilization mechanisms, negative ORP values were observed in the reactor.

The ORP of the leachate samples ranged between 28.0 and -80.3 mV during 114 days of operation. After the placement of waste mixture into the reactor, the ORP values became positive due to the presence of small amount of oxygen which then removed from the system due to the onset of the methanogenic conditions. A decreasing trend in ORP was observed during the first 10 days indicating the onset of the methanogenic conditions (Figure 5.6). The minimum ORP value of -80.3 mV was achieved on Day 28. The methane concentration showed a sudden increase during that period. The ORP values remained constant and low throughout the study. According to the study conducted by Ziyang et al. (2009), the leachate samples taken from different age landfills indicated ORP values decreasing from -227 mV to -307 mV between the 2nd and 4th years of operation. However, ORP values showed a sudden increase after 4 years of operation reaching to -127 mV in the 6th year. In the following years, the ORP values continued to increase as landfill age is getting older reaching -104 mV by the 12th year. The results of the ORP values of the reactor were found to be compatible with the results of the Ziyang et al. (2009). According to the ORP values, the stabilization degree of the reactor indicated that solid waste sample had been undergone similar stabilization period with similar changes in the ORP value.

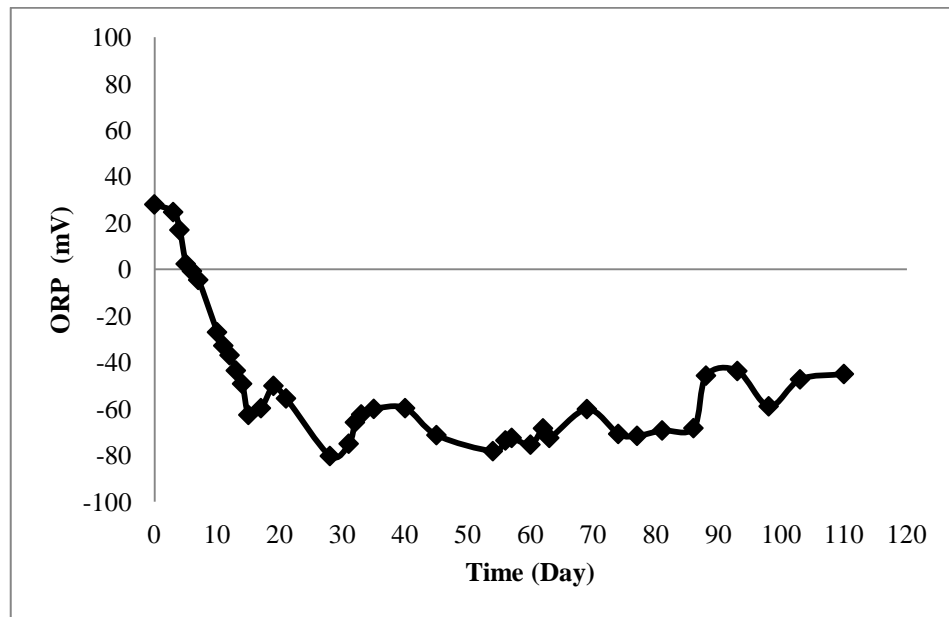


Figure 5.6. Leachate ORP.

Moreover, the ORP results were compatible with COD removal. A negative ORP is indicative of the presence of highly reducing environment. The reintroduction of the leachate to the system on Day 10 increases the amount of substrate required for the microbial community and then support the degradation as the conversion of the acid formation phases to methane fermentation phase continues. ORP levels become even more negative together with the onset of methane fermentation.

5.3.3. Conductivity

The conductivity of leachate samples represents the solution's current conduction ability and the total concentration of ionic solutes. In this study, the conductivity of leachate samples showed an unchanged trend (Figure 5.7). Additionally, higher conductivity values of the leachate samples reflect the presence of the high concentrations of soluble inorganics. In a study, it was detected that conductivity for 'old' landfill was ranged from 6.2 to 34.0 mS/cm while for 'fresh' landfill it was increased from 23.0 to 35.5 mS/cm (Tatsi and Zouboulis, 2002). Similar results were found by Chu et al. (1994) which showed that the conductivity for 3.5 year landfill leachate was ranged from 8.5 to 12.0 mS/cm and for 11 year landfill ranged from 2.5 to 8.4 mS/cm. According to the results of the studies in the literature, conductivity of leachate decreases as landfill ages. Since,

medium age waste sample used in this study, lower conductivity values were obtained which are similar to those given in the literature.

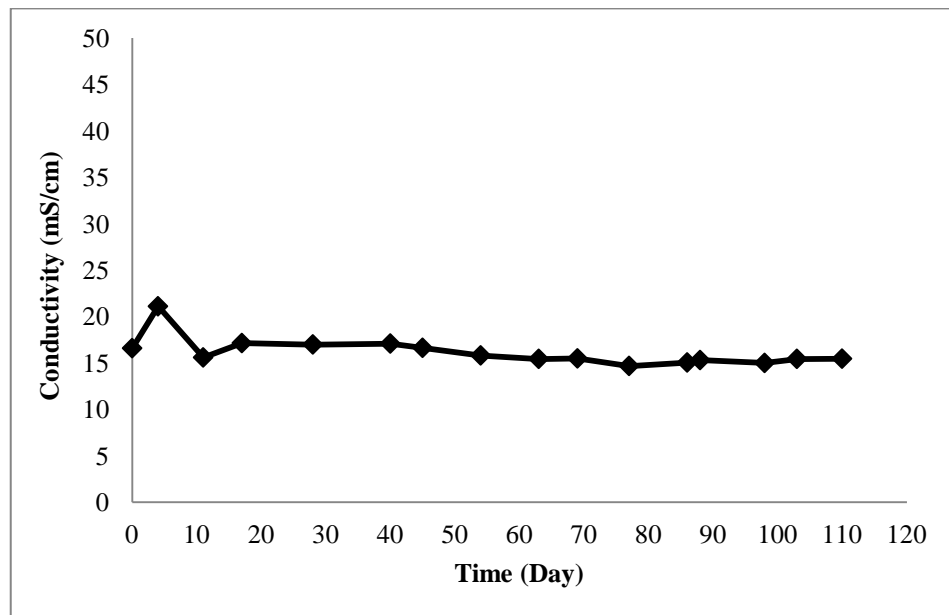


Figure 5.7. Leachate conductivity.

5.3.4. Salinity

Salinity is the measure of the mass of dissolved salts in the solution and expressed as ‰ (ppt) (Erses, 2008). The salinity values of the leachate samples are given in Figure 5.8. The initial salinity value in the reactor recorded as 9.5 ppt and the maximum value was 14.8 on Day 3.

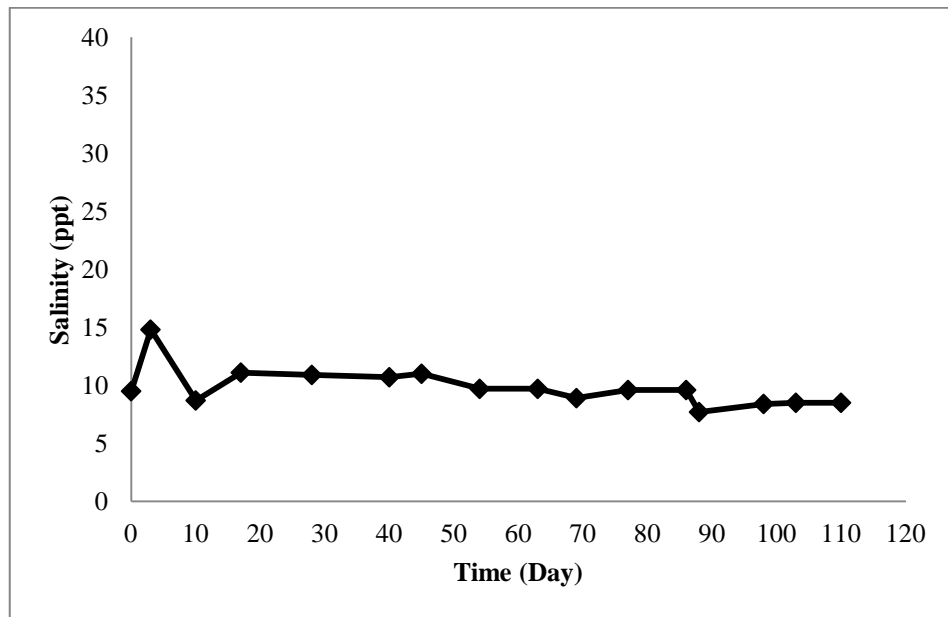


Figure 5.8. Leachate salinity.

Salinity decreased by time due to the washout from the system on Day 10. After that day, salinity value remained within the range 9.6-11.0 until the the Day 86 with the leachate recirculation. Finally, the salinity values gradually decreased to 8.5 at the end of the study. Salinity and conductivity values of the leachate sample showed similar trend.

5.3.5. Turbidity

Turbidity is a function of the presence of dissolved and suspended matter in a solution. The main contributors to the turbidity can be organic acids, microscobic organisms, finely divided organic matter and dyes (Erses, 2008). Turbidity unit was expressed as nephelometric turbidity units (NTUs). The time evaluations of turbidity values of the reactor are given in Figure 5.9.

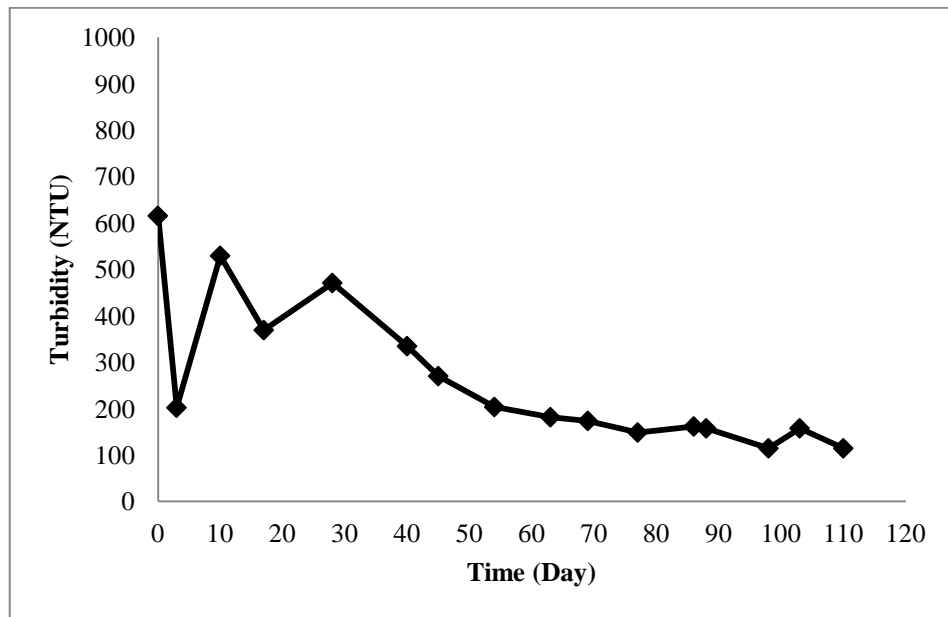


Figure 5.9. Leachate turbidity.

The initial turbidity of the reactor was measured as 615 NTU. The turbidity values fluctuated until Day 28 and reached 470.5 NTU. After that day, the turbidity value of the leachate samples showed a regular decreasing trend. The minimum turbidity of the reactor was recorded as 114.5 on Day 110.

5.3.6. Color

Color unit was expressed as Pt-Co. Generally, according to the stabilization phase of the solid waste mixture the color of the leachate varied from dark yellow to dark brown and the main reason of this color is the oxidation of ferrous ions to ferric form and the formation of ferric hydroxide colloids and complexes with fulvic/humic substances (Chu et al., 1994). Leachate color values of the Reactor are given in Figure 5.10.

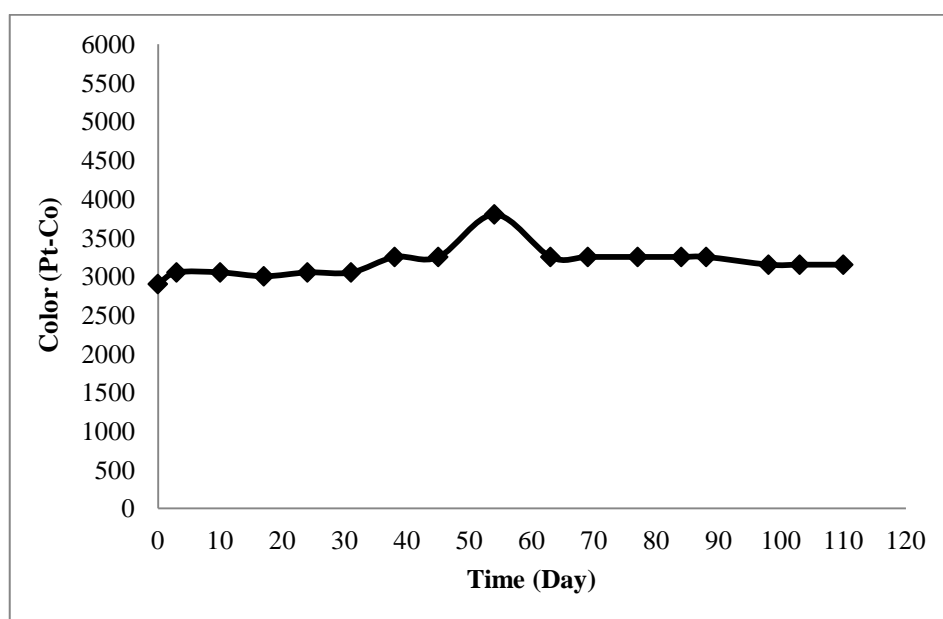


Figure 5.10. Leachate color.

The initial color values of the reactor were recorded as 2900 Pt-Co. The blackish color gives information about the maturity of the leachate sample. The color of the leachate samples were observed as blackish at the beginning of the study due to the seed sludge addition prior to loading. After Day 10, the visible color of the leachate sample started to fade. The color of the leachate samples apparently began to become blackish as the stabilized leachate reintroduced into the waste matrix. The color values stayed more or less constant during 114 days of operation.

5.3.7. COD

Organic strength of landfill leachate is generally expressed in terms of COD concentration. The change in the COD concentrations in the leachate samples is given in Figure 5.11. The COD concentrations of leachate decreased rapidly from 22218 mg/L to 2961 mg/L within 45 days of operation. Later leachate COD concentrations continued to decrease due to the active waste stabilization, and it reaches to 2929 mg/L by Day 55. After Day 55, the COD concentrations stayed constant in the range of 2649 mg/L -1995 mg/L which represent the organic materials resistant to biological decomposition in the waste matrix. Considering 22218 mg/L as the initial and 1995 mg/L as the final leachate COD concentrations at the end of the study, the COD removal efficiency was calculated as

91 %. The main reason of the rapid decrease in the COD concentration is attributed to the partially stabilized nature of a 5 year old waste sample and the presence of desired microbial community. Leachate recirculation provided a more uniform environment for the waste stabilization which also helped rapid waste decomposition.

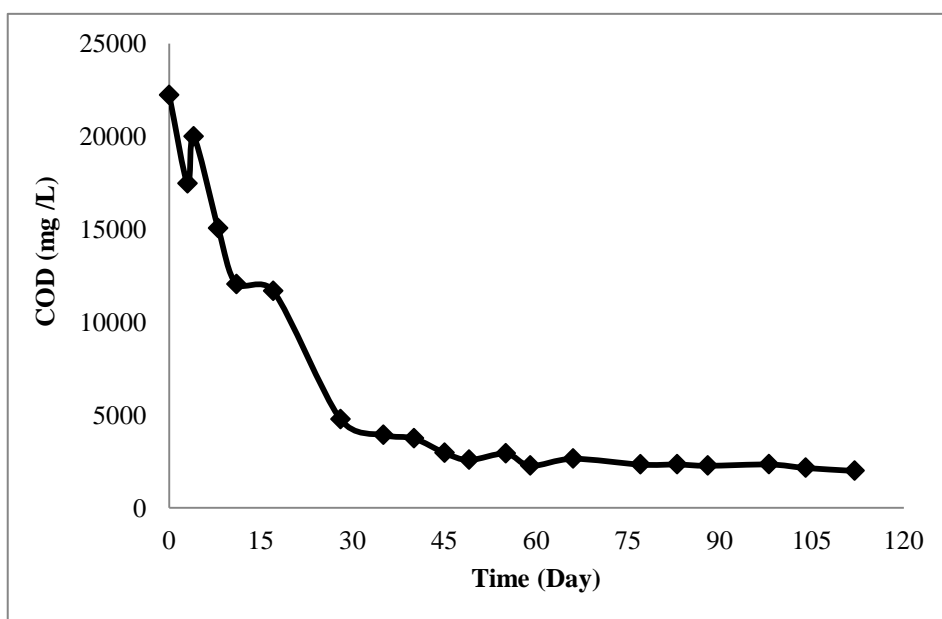


Figure 5.11. Leachate COD concentrations.

According to the various studies conducted on the leachate characteristics from different age of landfills (summarized in Table 2.11), the leachate COD concentration in the transition phase were given in the range 500- 41507 mg/L; the range for the acid formation phase is 1015-71000 mg/L. The conversion of the acidic conditions into the methanogenic conditions, the COD values reduced to the range of 150-10000 mg/L (Kostova, 2006; Renou et al., 2008; Ziyang et al., 2009, Hang et al., 2002). The COD value and the removal of the organics were compatible with the values in the literature with regard to the application of the leachate recirculation strategy.

5.3.8. Biochemical Oxygen Demand (BOD₅)

Both leachate COD and BOD₅ concentrations showed similar decreasing trend in the reactor. Initial BOD₅ concentration was 14775 mg/L as given in Figure 5.12. The BOD₅

concentration decreased to 238.5 mg/L on Day 104. A rapid decrease from 14775 mg/L to 300 mg/L was observed within first 56 days. Leachate recirculation resulted in faster degradation in waste matrix leading to faster reductions in BOD₅ and COD concentrations in leachate.

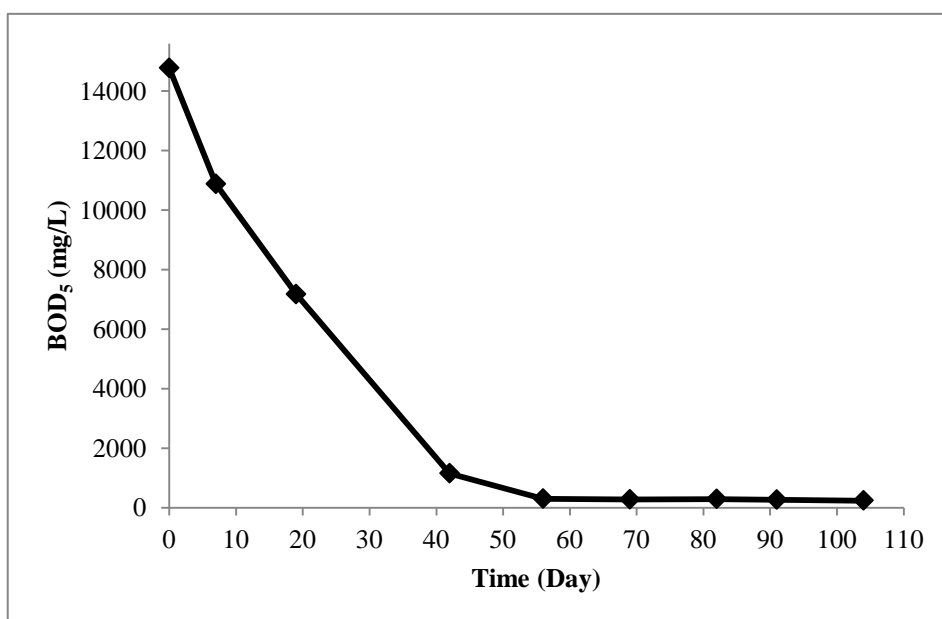


Figure 5.12. Leachate BOD₅ concentrations.

Generally, leachate from new landfills is high in terms of BOD₅ and COD concentrations afterwards they begin to steadily decline while waste decomposition is proceeding. The BOD₅ and COD concentrations appear to remain low due to stimulation of methanogenesis. The stimulation of methanogenesis is supported by high pH and low ORP values. Leachate recirculation resulted in enhanced waste degradation and consequently faster reduction in the BOD₅ and COD concentrations in leachate. The TOC, COD and BOD₅ concentrations are the critical parameters which are the indicator of pollution potential of leachates. The ratio of BOD₅/COD represents the age of leachate and gives information about the biodegradability of organic matter in the leachate. The change in leachate BOD₅/COD ratio for the reactor is given in Figure 5.13.

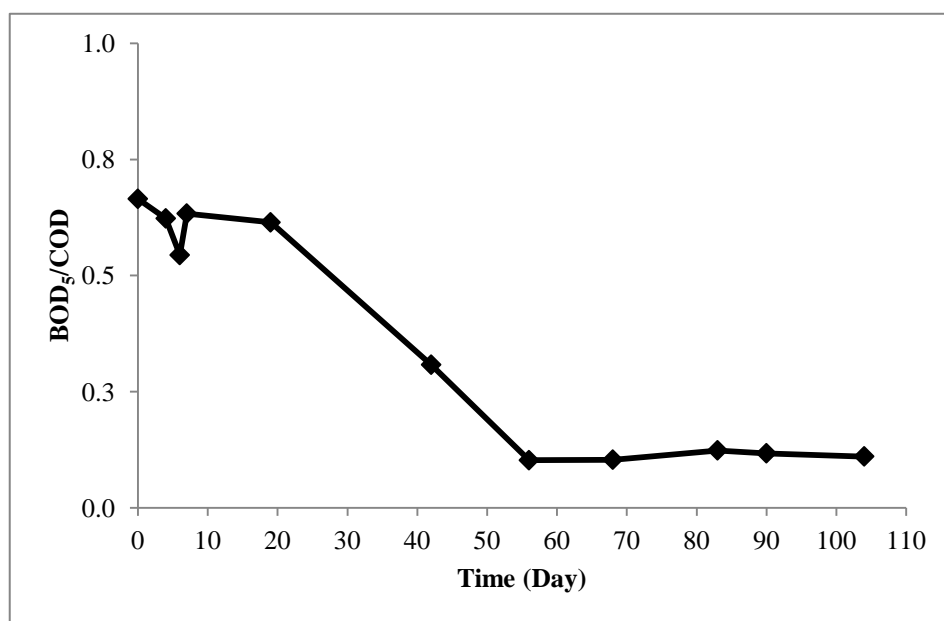


Figure 5.13. BOD₅ /COD ratio in leachate.

BOD₅/COD ratio decreased from 0.67 to 0.11 within 104 days. The biological processes have been shown to be very effective in removing organic matter when the BOD₅/COD ratio has higher values (>0.5). However, after a certain period of time elapsed, the major presence of refractory compounds (mainly humic and fulvic acids) tends to limit the effectiveness of processes.

In spite of short period of landfill exploitation, some physico-chemical parameters e.g. high pH (on average 7.84), low COD concentration (<2000 mg COD/l), low BOD₅/ COD ratio (<0.4) and low heavy metal concentration are indicatives of methanogenic landfill conditions (Kulikowska and Klimiuk, 2008). BOD₅/COD values given by Renou et al. (2008) are as follows: higher than 0.3 in young landfill; 0.1-0.3 in the medium aged landfill; and lower than 0.1 in mature landfill. A decrease in the ratio indicates that organic carbon becomes less readily available as an energy source for microbial growth. It can be concluded that the ratio measured in this study was representative of a stable methanogenic decomposition phase in the reactor. High BOD₅/COD ratio suggested that the leachate was highly biodegradable which is normal for young landfill. However, a decreasing trend in the BOD₅/COD ratio suggested that presence of biodegradable organic carbon tend to decrease by time and humic like compounds begin to appear as the landfill age getting

older. From this point of view, the initial stabilization phase of the reactor loaded with medium aged waste sample was acid formation phase which was then quickly converted into methane fermentation phase.

5.3.9. TOC

Like COD and BOD, after the onset of the operations TOC begins to appear as a result of the microbial solubilization of the organics. Leachate TOC concentrations increases in the acid formation phase whereas TOC concentrations tend to decrease during the methane fermentation phase due to the conversion of the VFA content to methane. The change in the TOC concentrations of leachate is given in Figure 5.14.

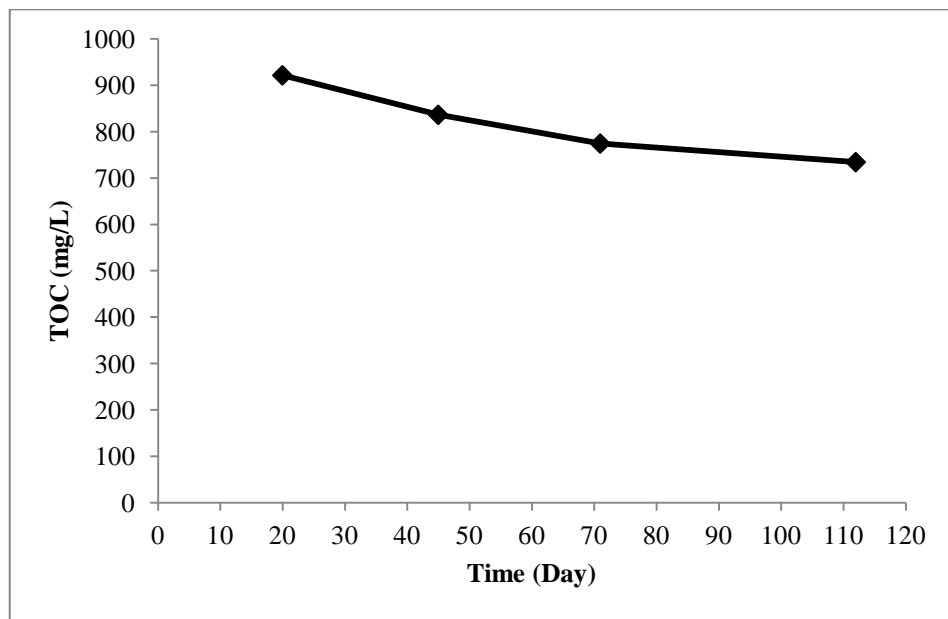


Figure 5.14. Leachate TOC concentrations.

The initial TOC concentration was 921 mg/L on Day 20. The TOC concentrations showed similarity with the COD concentrations. The final TOC concentration of leachate was 734 mg/L at the end of the study. Decrease in the COD and TOC concentrations as well as the VFA concentrations were consistent with the gas production.

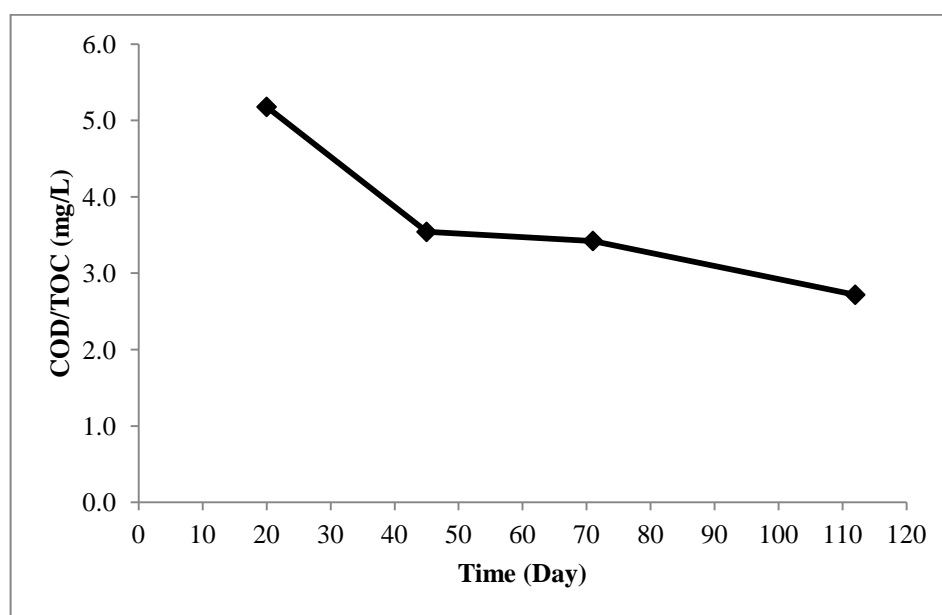


Figure 5.15. COD/TOC ratio in leachate.

COD/TOC ratio can be used as indicator of waste degradation. High COD concentrations (typically > 3000 mg/L), BOD₅/COD (typically > 0.3), and COD/TOC (typically > 3.0) characterizes young leachate. In contrast, mature leachate is characterized by low COD (typically < 3000 mg/L), BOD₅/COD (typically < 0.3), and COD/ TOC (typically 3.0) (Lehmann, 2007). The COD/TOC ratio tends to decrease as landfill ages because of strong proportion of nonoxydable organic compounds. Low COD/TOC means more oxidized state of the organic carbon less readily available as an energy source for microbial growth. The COD/TOC ratio was calculated to vary between 3 to 5, and this ratio decreased as the landfill aged. The calculated COD/TOC ratio found in this study was compatible with the ratio given in the literature and indicator of the biodegradability potential of the stabilized waste sample.

5.3.10. NH₃-N and TKN

Considering the nitrogenous compounds, ammonia nitrogen was initially present in high concentrations, probably due to the deamination of amino acids during destruction of waste organic compounds (Figure 5.16). The ammonia-nitrogen in leachate is derived from the organic nitrogen content of the waste matrix and is composed of proteins found in

refuse. For young landfill leachate $\text{NH}_3\text{-N}$ concentrations given by Abdulhussain et al. (2009) were below 400 mg/L, and it was around 400 mg/L in medium aged landfill.

Initial $\text{NH}_3\text{-N}$ concentration of the leachate sample was 1835 mg/L. Ammonia concentration decreased steadily within the reactor during 49 days. The final $\text{NH}_3\text{-N}$ concentration was recorded as 1030 mg/L at the end of the study. The leachate recirculation led the ammonia to be accumulated in the system even though some ammonia nitrogen was used by microorganisms during the active waste stabilization. The main disadvantage of anaerobic bioreactors with leachate recirculation is the accumulation of ammonia nitrogen. Callı et al. (2005) have reported that $\text{NH}_3\text{-N}$ concentrations up to 6000 mg/L could be tolerated in anaerobic bioreactors. According to the results from the study conducted by Long et al. (2009), the ammonia nitrogen concentrations were in the range of 359- 929 mg/L in young landfill leachate whereas 411 mg/L in 6 year old landfill leachate. The $\text{NH}_3\text{-N}$ concentrations of the leachate samples were found to be compatible with the anaerobic system.

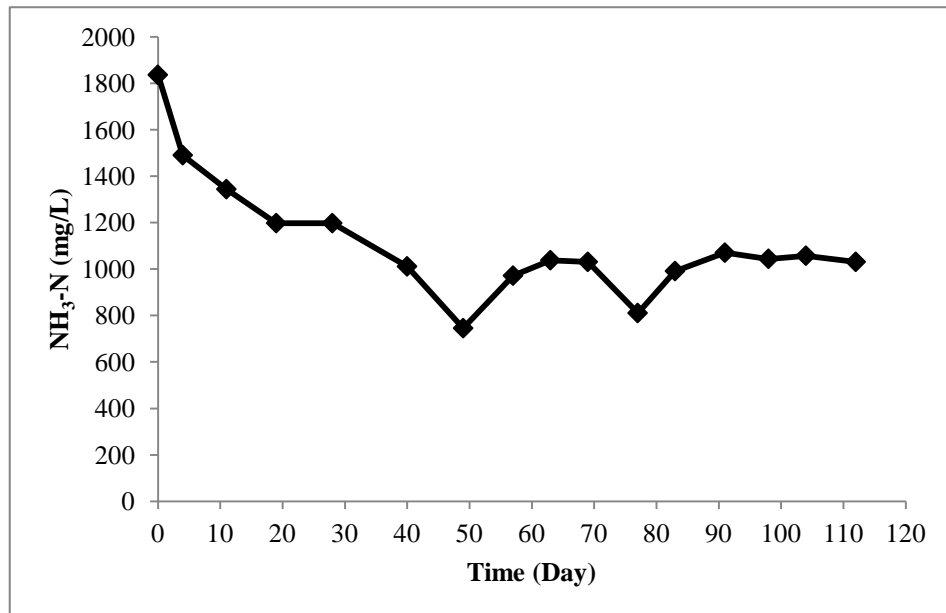


Figure 5.16. Leachate $\text{NH}_3\text{-N}$ concentrations.

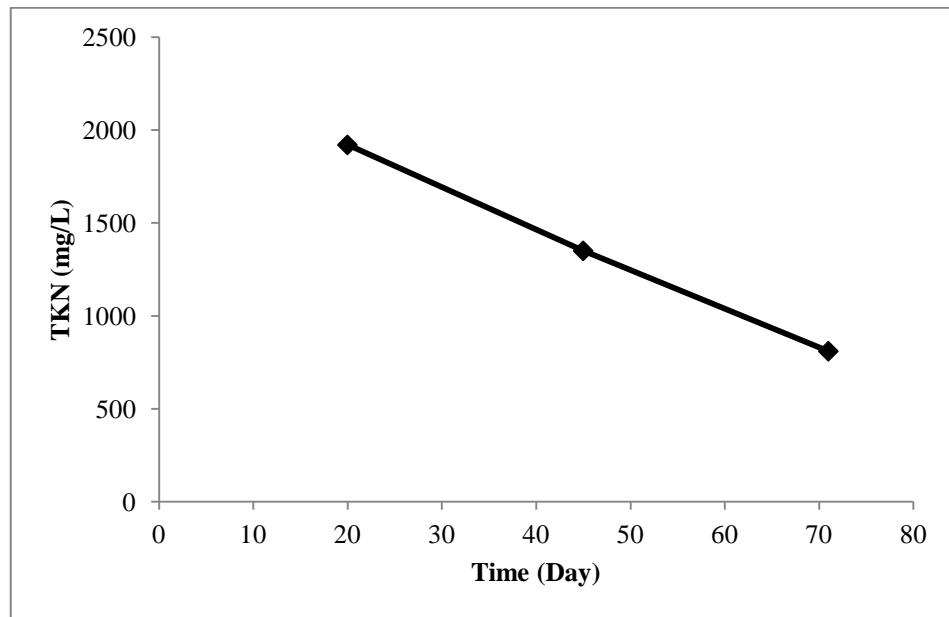


Figure 5.17. Leachate TKN concentrations.

Initial and final concentrations of TKN were calculated as 1920 and 842 mg/L. According to the study conducted by Sun et al. (2011), the ammonia and TKN concentrations in anaerobic reactors found 1500 mg/L and around 1000 mg/L. However, the TN concentration reached 4000 mg/L at the end of the experiment (Sun et al., 2011). The results of TKN concentrations of the leachate samples from the reactor resembled the values in the study conducted by Sun et al. (2011). The $\text{NH}_3\text{-N}:\text{TKN}$ ratio of leachate indicates the biodegradation state of landfill and the ratio increases to about 1 as the landfill ages. The range between $\text{NH}_3\text{-N}:\text{TKN}$ was found in the leachate samples from different studies was 0.78-0.99 in Jokela et al. (2002) and $\text{TKN}:\text{NH}_3\text{-N}$ was between 1.0-1.5 in the study of Durmaz (2005). The $\text{NH}_3\text{-N}:\text{TKN}$ ratio was calculated in the range of 0.6-0.97 which is normal as the landfill ages and compatible with the ratios in the literature.

5.3.11. Heavy Metals

A variety of heavy metals can be found in landfill leachates including zinc, copper, chromium, manganese, nickel, lead and cadmium. These are usually sourced from the waste matrix. The concentrations of heavy metals in leachate generally present especially in high concentrations at the initial phase. Additionally, the heavy metals concentrations

decreased rapidly with landfill age. Heavy metal release is a function of leachate characteristics such as pH and the concentration of available complexing agents. Factors that influence metals mobility are pH, ORP, functional groups on humic matter, and the sorptive capacity of the refuse mass. The increase in the pH of the leachate samples results in decrease in metal mobility (Tatsi and Zouboulis, 2002).

Several heavy metals were monitored throughout the study (Figure 5.18 and 5.19). The average concentration of copper was 0.06 mg/L in the leachate. No increase in the concentrations of heavy metals attributed to recirculation was observed throughout the study.

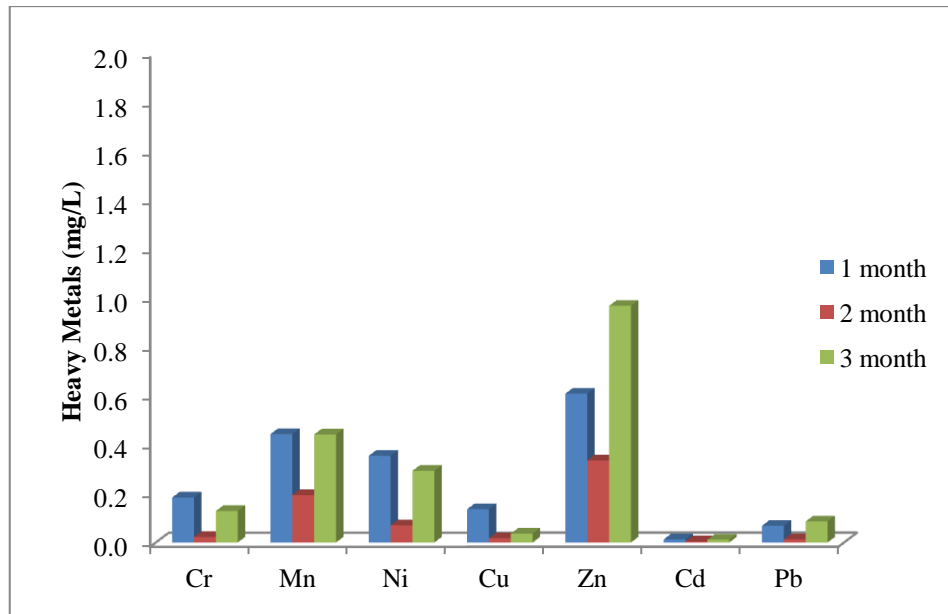


Figure 5.18. Leachate heavy metal concentrations.

The Cr, Mn, Ni, Cu, Zn and Pb concentrations decreased in the second month, then a rapid increase was observed in each metal concentration. The initial Mn concentration was 0.44 mg/L which decreased 0.19 mg/L on Day 46 and increased to the initial value of 0.44 mg/L on Day 78. The Mn concentration in the leachate samples were observed as high as the initial value. The Cd concentrations were observed more or less constant during the study. On the other hand, the initial Cr concentration was measured 0.18 mg/L and a slight decrease in the Cr concentration was observed at the end of the experiment. Establishment of highly reducing environment and the formation of sulfide from sulfate which was

providing heavy metal precipitation. The decrease in the heavy metal concentrations was confirmed with the highly reducing environment in the reactor in the second month. The measurements of ORP, sulfate and conductivity confirmed the removal of the heavy metals during this period. The onset of the reducing environment confirmed with the low ORP values, Fe^{3+} and sulfate were reduced to Fe^{2+} and sulfide, respectively (Erses and Onay, 2003). After that, metals formed insoluble metal sulfides. The initial values of the Ni, Zn, Cu and Pb obtained on Day 28 were 0.35, 0.61, 0.14 and 0.07 mg/L and the final values were measured as 0.29, 0.97, 0.04 and 0.09, respectively. Additionally, only the Zn and Pb was recorded as much higher than the initial value at the end of the experiment. This is the indication of the remobilization of the heavy metals in the waste matrix due to the change in the reactor environment (Campbell et al., 1983).

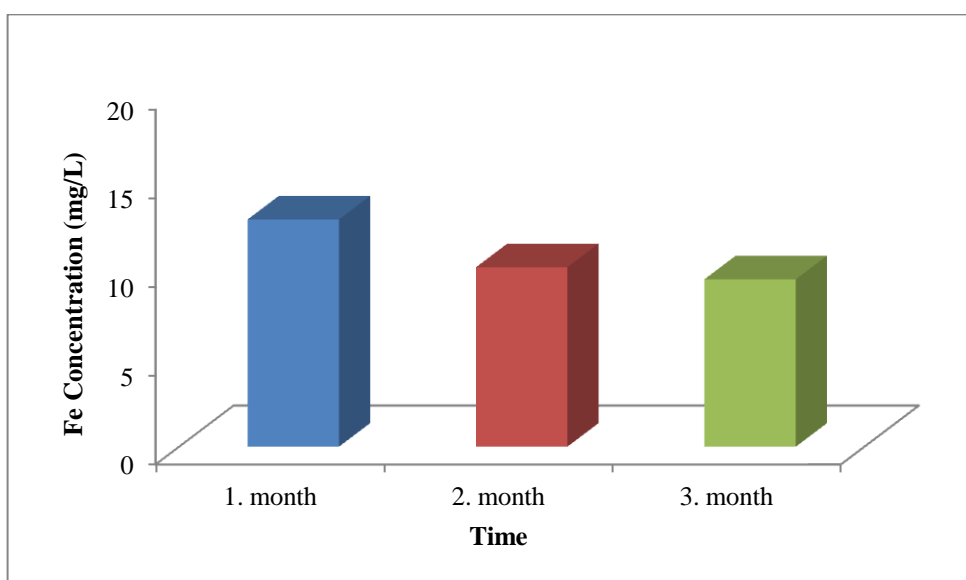


Figure 5.19. Leachate iron concentrations.

The iron was present in the form of Fe^{3+} in the acid formation phase whereas reduced more soluble form of Fe^{2+} in the methane fermentation phase (Pohland et al., 1992). This reduction was the indication of the onset of the reducing environment. This decrease in Fe is also confirmed with the decrease in the sulfate concentrations.

5.3.12. Alkalinity

Alkalinity is the measure of the buffering capacity of the system. If acid concentrations exceed the alkalinity of the system, the methanogenic activity could be inhibited. Due to the low alkalinity and high VFA accumulation, the methane production can be ceased (Ağdağ and Sponza, 2005). The alkalinity concentrations measured for the reactor are given in Figure 5.20.

The initial alkalinity values in the reactor were calculated as 6743 mg/L as CaCO₃. The alkalinity reached to its maximum value of 9000 mg/L as CaCO₃ on Day 69 and then this value decreased to 6293 mg/L as CaCO₃ at the end of the study.

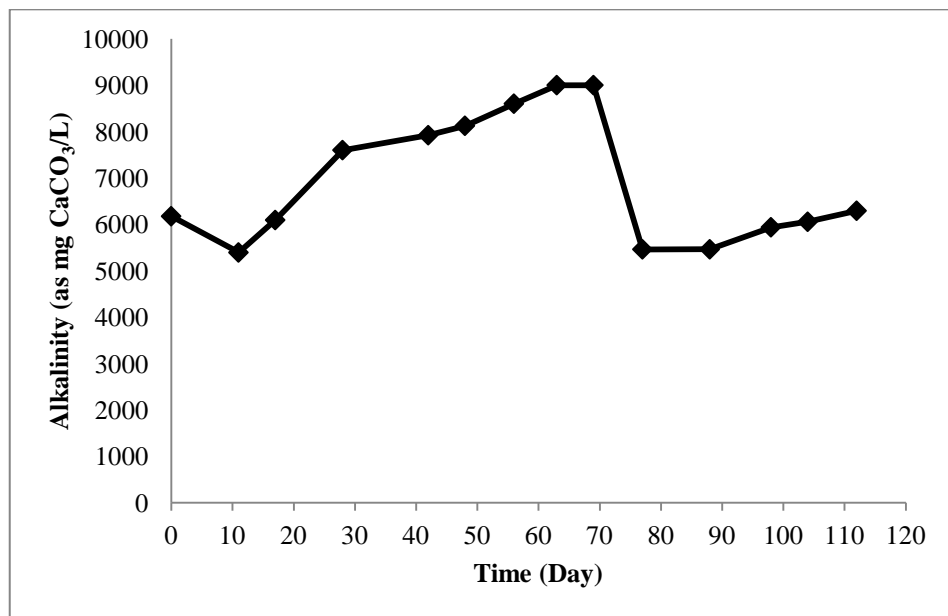


Figure 5.20. Leachate alkalinity concentrations.

At the beginning of the experiment, the increase in the alkalinity concentrations showed the generation of volatile organic acids, then the decrease is the indication of VFA consumption by methanogens as COD concentrations and pH value began to increase. The alkalinity levels observed throughout the study was sufficient for an active anaerobic waste stabilization.

5.3.13. Sulfate

The rapid decrease in the concentration of sulfate is a result of prevailing anaerobic conditions in the reactor, under which sulfate is reduced to sulfide. Decrease in the sulfate concentration is the indication of the reducing environment in the system also supported with the low ORP levels of the reactor. High sulfate concentration may inhibit methanogenesis which results in the high H₂S production and precipitation of metallic sulfides. The sulfate concentrations of the reactor is presented in Figure 5.21.

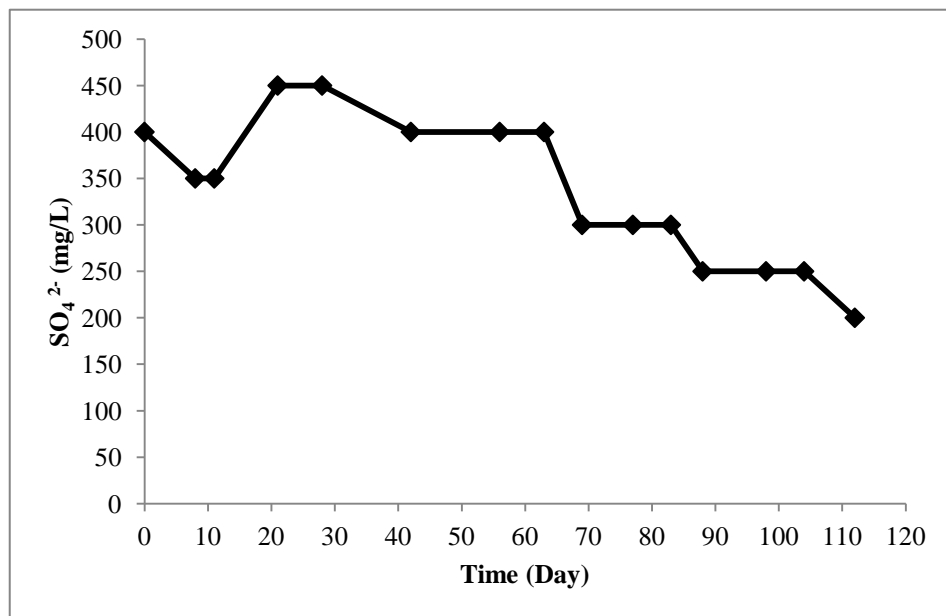


Figure 5.21. Leachate sulfate concentrations.

Initial sulfate concentration in the reactor was recorded as 400 mg/L. Leachate SO₄²⁻ concentrations were fluctuated within first 21 days and then the concentration increased to 450 mg/L. The final SO₄²⁻ concentration was recorded as 200 mg/L on Day 114.

5.3.14. Orthophosphate

Phosphate is the rate limiting micronutrient in landfills. The concentrations of ortho-P showed an upward trend in the reactor. The ortho-P concentration was 3.3 mg/L at the beginning of the experiment which then increased rapidly to 8.7 mg/L (Figure 5.22). The

increase in the ortho-P concentrations in the reactor was attributed to the hydrolysis of organic material and polyphosphates.

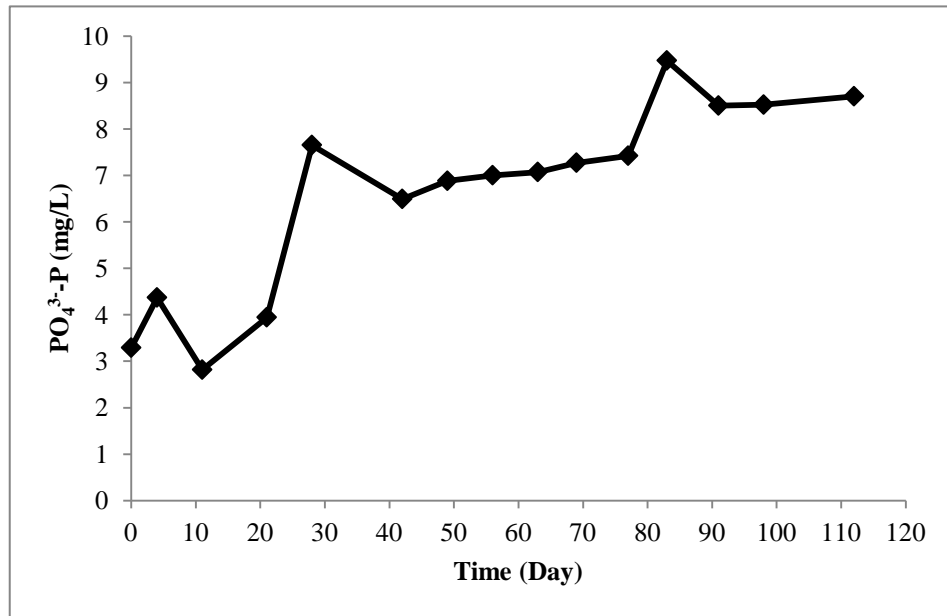


Figure 5.22. Leachate orthophosphate concentrations.

According to the study conducted by Ziyang et al. (2009), the PO_4^{3-} concentrations for young, semi mature and mature leachate were given as 20.20, 1.71 and 0.36 mg/L, respectively. An upward trend of the ortho-P concentration in the reactor can be attributed to the age of solid waste sample. Additionally, the higher amount of orthophosphate may be resulted from the anaerobic digested sludge degradation which was added to waste sample prior to loading to enhance the degradation. Most of orthophosphate are used during the microbial metabolism and some can be precipitated with various cation ions, such as Ca^{2+} and Mg^{2+} (Ziyang et al., 2009).

5.3.15. Volatile Fatty Acids

Leachate individual volatile fatty acids concentrations are given in Figure 5.23. Acetic acid, propionic, butyric, isobutyric, valeric, isovaleric, caproic, isocaproic and heptanoic were measured three times throughout the study. The acetic acid concentration in the

reactor was recorded as 3425 mg/L on Day 10, 645 mg/L on Day 48 and 199 mg/L on Day 71.

The total VFA concentration expressed in acetic acid showed also a rapid decrease from 11135 mg/L to 236 mg/L at the end of the experiment. This sharp decrease in the total VFA concentration observed in the reactor represented the presence of the methanogenic phase in which volatile organics are converted to methane and carbondioxide without any accumulation (Figure 5.23).

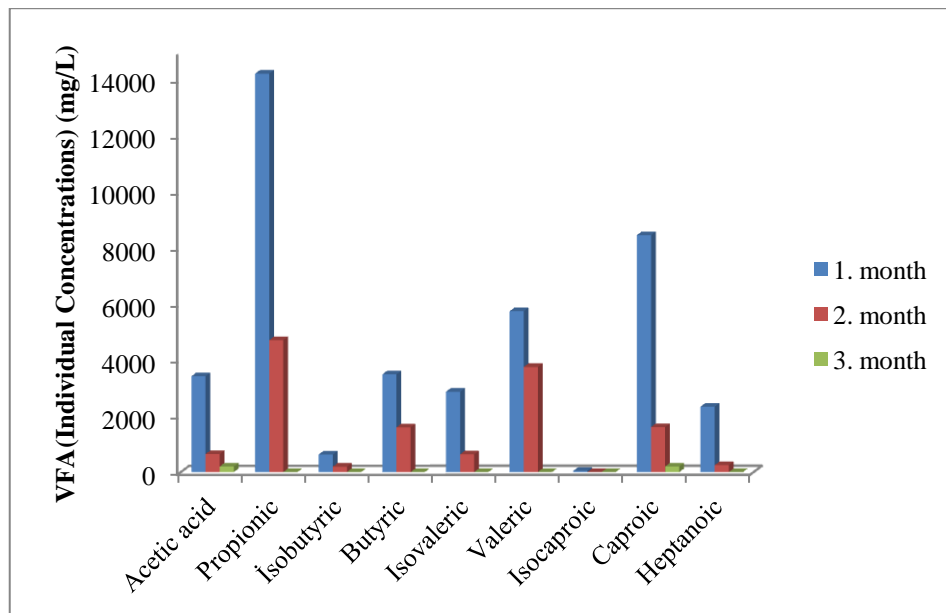


Figure 5.23. Leachate VFAs (individual) concentrations.

Initial presence of VFA in the reactor resulted in a decrease in leachate pH value. For example, pH value of the reactor at the beginning of the study was about 6.0- 7.0. due to the conversion of VFAs to methane, pH values increased at the end of the study. When VFA, COD and pH data are considered together, it can be said that the reactor environment was suitable for methanogenesis and fast and controlled anaerobic waste degradation.

5.4. Gas Analysis

Daily and cumulative gas production and gas composition of the reactor are monitored in the study. The daily and cumulative biogas production and biogas composition are given in Figures 5.24, 5.25 and 5.26, respectively.

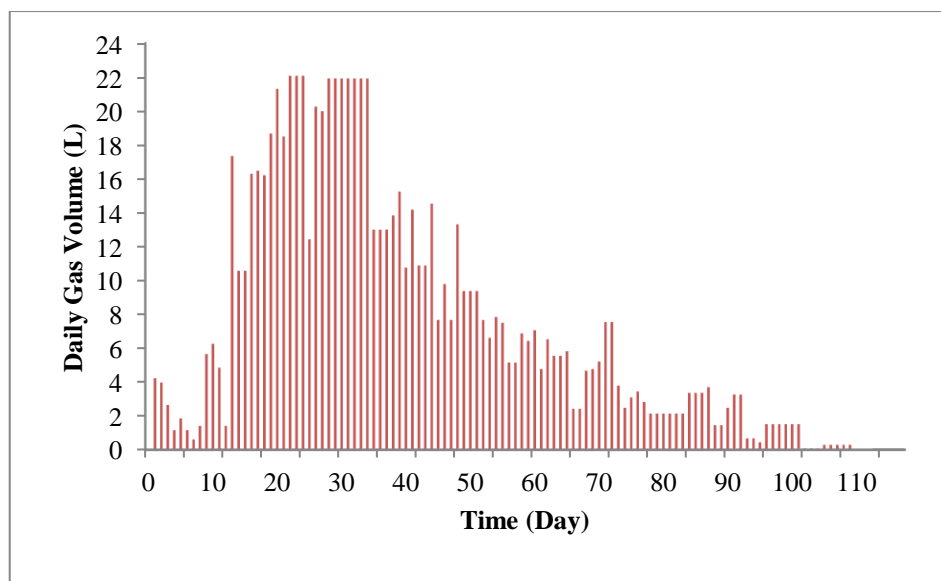


Figure 5.24. Daily biogas production.

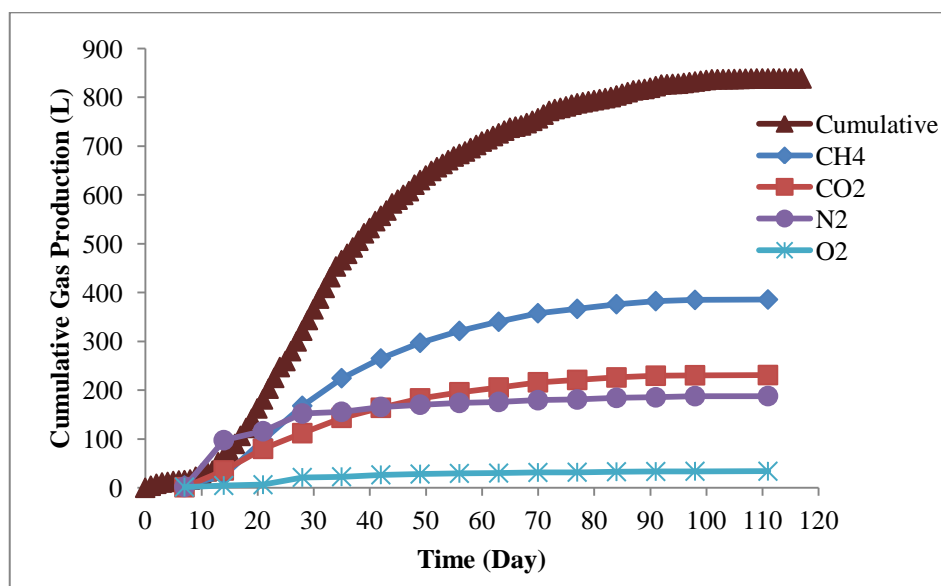


Figure 5.25. Cumulative biogas production.

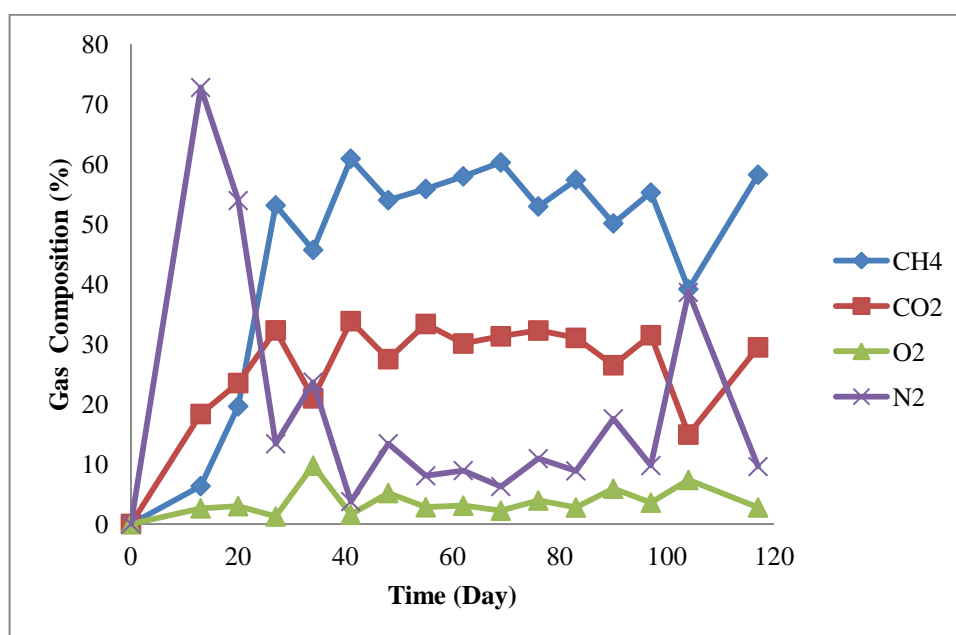


Figure 5.26. Biogas composition.

After the initiation of methanogenesis was observed at earlier stage, approximately by Day 10, daily gas productions increased rapidly and reached to its maximum value of 22 L/day. It was observed that the biogas production profile had similar progress with the leachate COD removal. The increase in the maximum methane and biogas generation on the first 40 days was confirmed with the highest COD removal of 87 %. The initiation of methanogenesis can be explained by redistribution of nutrients via leachate recirculation. The cumulative biogas production was calculated as 838.49 L at the end of the study. The highest methane percentage was recorded as 61 % on Day 41. The cumulative methane and carbon dioxide production for the reactor were calculated as 386 L and 231 L, respectively at the end of the study. After the conversion of easily degradable organic substances, gas production decreased slowly.

The initial high nitrogen composition of 73 % resulted by the nitrogen purge at the beginning of the study. However, after the initiation of the methanogenesis, methane began to appear accompanied by concomitant of carbon dioxide production which gradually purge N₂ from the system. The methane yield calculation is given in Table 5.3.

Table 5.3. Methane yield of the reactor on dry and wet weight basis.

	Dry weight (kg)	Methane yield (L)	Methane yield (L CH ₄ /kg dry waste)	Methane yield (L CH ₄ /kg wet weight)
Reactor	15.50	385.71	24.88	19.78

The theoretical methane yield was calculated as 0.018 kg CH₄/kg dry waste in the reactor. However, the literature values from various studies confirmed the methane yield such as 0.18 kg CH₄/kg dry waste, 0.07-0.13 kg CH₄/kg dry waste (Kura and Lee, 1995; Li et al., 1999). The methane yield of the reactor with medium aged refuse was lower than the proposed values in the literature. Nevertheless, the results confirmed that the enhanced stabilization of medium aged refuse with retrofit bioreactor concept resulted in the increased biogas production rich in methane content which means aged refuse has the potential for further degradation.

5.5. Final Waste Analysis

At the end of the operation, the reactor was opened and small amount of solid waste sample was taken for final analyses. The final depth of solid waste mixture in the reactor was measured in order to calculate the settlement ratio. All analyses conducted for initial waste characterization were repeated to determine final conditions of the discarded waste in order to gather information about the degradation in the reactor. Table 5.4. shows the results of the final analysis conducted for the waste.

According to the physical appearance of the waste, the blackish color of the solid waste sample represents the stabilized solid waste samples. The difference between the initial and final image showed an apparent degradation occurred in the reactor. Figure 5.27. shows the solid waste sample collected at the end of the operation in the reactor.



Figure 5.27. Discarded solid waste sample.

Table 5.4. Final analysis of waste sample.

Parameter	MSW
Wet Weight (kg)	17.95
Dry Weight (kg)	8.32
Moisture Content (%)	53.67
Volatile Solids (%)	40,81
TKN (mg/g)	1400
Carbon (%)	18.80
Nitrogen (%)	6.17
Hydrogen (%)	2.31
Carbon/Nitrogen	3.04
Wet Density (kg/m ³)	339

The COD mass concentration of the waste sample was reduced from 101.74 mg/g to 11.55 mg/g owing to the degradation within the reactor. The other waste constituents reduced during the study, including C/N ratio, carbon, hydrogen, nitrogen. The decrease in these compounds indicated waste stabilization during the operation of the reactor.

Table 5.5. The comparison of the initial and final analysis.

MSW characteristics		
Parameter	Initial	Final
Volatile Solids (%)	51.70	40,81
Carbon (%)	23.39	18.80
Nitrogen (%)	6.29	6.17
Carbon/Nitrogen	3.71	3.04

The reduction in the VS content of the waste sample is the indication of the more stabilized waste matrix at the end of the experiment. The initial and final carbon content of waste sample in Reactor 5 was measured as 23 % and 19 %, respectively. The initial and final C/N ratios were calculated as 3.71 and 3.04, respectively. Beaven and Walker (1997) carried out six lysimeter tests to evaluate the total pollution in leachate. The C/N ratio was 10 in the acid phase, and after active formation of methane gas, C/N decreased to a proximity of 1. Since the stabilization phase of the reactor was initially found to be at the end of the acid formation phase which then suddenly changes into methane fermentation phase, the C/N ratio of 3.71 was compatible with the biodegradability of the waste sample. The final density and settlement calculations for the reactor are given in Table 5.6.

Table 5.6. Final density and volume calculations.

	Initial wet density (kg/m³)	Final wet density (kg/m³)	Settlement (%)
Reactor	342	339	6.78

Higher waste settlement observed in the reactor, this result can be attributable to the the degree of degradation. The settlement was measured as 6.78% in the reactor at the end of the 114 days of operation.

5.6. Comparison of the Medium Aged Bioreactor with Literature

Determination of the further stabilization potential of landfilled solid waste is important in terms of understanding the capability of its rehabilitation. Moreover, prediction of the remaining stabilization capacity of a waste can be made by monitoring

leachate and gas generation. The comparison of the findings from the leachate and gas analysis of the reactor experiment was evaluated with the data given in the literature.

Moisture content of various waste ages vary significantly and it is one of the important parameters for the waste decomposition. Moisture content of the waste samples with different ages were compared in Table 5.7 along with the other indicative parameters for leachate and waste samples used in the studies.

Table 5.7. The comparison of the MSW and leachate characteristics of lysimeters with partially degraded waste.

Age	Operation	MSW analysis		Leachate parameters					Reference
		M.C. (%)	VS (%)	pH	COD (mg/L)	BOD (mg/L)	BOD ₅ /COD	VFA (g/L)	
5 year old	Retrofit Bioreactor	20	52		22218	14775	0.67-0.11	11-0.2	Reactor 5 used in this study
3 year old	Retrofit Bioreactor	27	30	-	-	-	-	-	Shalini et al. (2010)
6 year old	Retrofit Bioreactor	32	-	6.8-7.3	880-850	-	-	-	Chen et al. (2009)
10 year old	Retrofit Bioreactor	27-28	30	5.6-8.5	<14000	<6000	0.30-0.80	1-2	Swati et al. (2011)
11 year old	Retrofit Bioreactor	28	-	6.8-7.4	490-420	-	-	-	Chen et al. (2009)
Excavated waste unknown	Retrofit Bioreactor	28-30	20-30	5.8-8.4	1472-4373	10-118	0.22-0.26	1-2	Karthikeyan et al. (2007a)

The moisture content of the fresh refuse was expected to be higher in comparison to medium aged refuse (Swati et al., 2011; Sun et al., 2009; Sun et al., 2011; Long et al., 2009). The moisture and volatile solids content of the 3 year old waste sample were 27 % and 30 %, respectively. However, the moisture content and volatile solid content of the

reactor in this study were 20 % and 52 %, respectively. The moisture content of both simulator landfills found to be similar.

According to the study conducted Swati et al. (2011), the pH value of old landfill leachate was measured as 7.5 in alkaline conditions. However later in the operation, a drop in pH to a value of 6.5 was observed and that followed by an increase up to 8.23. Although stabilized MSW produces leachates with alkaline nature after full maturation, leachate recirculation and rainwater addition stimulated the acidogenic activity leading pH below 7.0. Therefore, the leachate pH values from the reactor showed an increasing trend during the first 28 days of operation. This increase was attributed to the decrease in the organic acid concentrations which indicates the transition from acid formation to methane fermentation phase. After Day 28, pH values stayed more or less constant until the end of the study.

The VFA concentrations were higher in the reactor compared to the leachate sample from the old landfill simulation. The maximum levels of VFA at the beginning of the experiment confirmed the transition phase from acid formation to methane fermentation phase. Gradual removal of residual BOD₅ to levels below 100 mg/L and a COD reduction of 68 % indicate that a complete degradation achieved in the simulator with old waste (Swati et al., 2011). This suggested that the total amount of organic material in the landfill was decreasing with increasing age. The decrease of COD over time was consistent with several literatures.

The pH of the leachate varied widely within the range of 4.9 – 8.1 in fresh waste lysimeter. In a study conducted by Karthikeyan et al. (2007a), fresh leachate sample were found to be acidic during the initial stages of study period. Then pH values shifted to neutral and slightly alkaline range within the operating period of 560 days (Karthikeyan et al., 2007a). Chian and DeWalle (1976) reported that the pH of leachate increased with time due to the decrease of the concentration of the partially ionized free volatile fatty acids. The comparison of the some MSW and leachate characteristics of lysimeters with fresh waste and medium aged waste in the reactor is given in Table 5.8.

Table 5.8. The comparison of the MSW and leachate characteristics of lysimeters with fresh waste.

Age	Operation	MSW analysis		Leachate parameters					Reference
		M.C. (%)	VS (%)	pH	COD (mg/L)	BOD (mg/L)	BOD ₅ /COD	VFA (g/L)	
5 year old	Retrofit Bioreactor	20	52	6.34-8.0	22218	14775	0.67-0.11	11-0.2	Reactor 5 used in this study
Fresh	Single pass	58	52	5.5-6.5	58424-87882	30512-67000	-	21-31	Swati et al. (2007)
Fresh	Bioreactor	58	52	5.5-8.0	52052-12866	29362-5800	-	24-16	Swati et al. (2007)
Fresh	Bioreactor	51	82	5.80-7.5	38022-900	40800-55	0.93-0.05	27	Erses (2008)
Fresh	Single pass	80	-	5.5	5000-45000	-	-	-	San and Onay (2001)
Fresh	Bioreactor	80	-	5.5-7.3	5000-39000	-	-	-	San and Onay (2001)

San and Onay (2001) evaluated the impact of various leachate recirculation regimes on municipal solid waste degradation. The reactors operated with single pass and recycle produced 70 and 269 L of biogas with 13 kg of fed waste matrix, respectively. The volume of the reactor used in the study of San and Onay was the same with the used in the reactor. It was stated in that study that the increase in the recirculation frequency has a positive effect on the methanogenic population. The maximum observed methane concentrations were 51 % for recycle reactor and 10 % for single pass reactor. Low methane concentrations confirmed the inability of the system to enhance the waste stabilization.

According to the study conducted by Karthikeyan et al. (2007b), the control reactor fed with the excavated waste sample was operated under single pass and anaerobic conditions. The reactor volume was 3982 L and the amount of waste fed to the system was 2327 kg of excavated MSW. About 50 % of the waste was fine fraction consisting of partially degraded MSW. Biogas showed a maximum of 22 % of methane content in gas samples collected from controlled lysimeters. However, the methane percentage was

measured between 6-61 % in the reactor. The cumulative methane production was calculated as 385.71 L at the end of the study.

Finally, it can be said that the reactor had the potential for further degradation and biogas production. Leachate recirculation strategy stimulated the microbial population and enhanced the degradation mechanisms in the reactor. Although the stabilization phases differs from the waste to waste, it can be concluded for the medium aged waste sample used in this study have further waste degradation potential and biogas generation potential.

6. SUMMARY AND CONCLUSIONS

The rehabilitation of old landfills and conversion of the conventional systems into bioreactor (Retrofit) has drawn attention in later years. Understanding the waste degradation stage within the waste matrix is important to determine the rehabilitation potential of landfills since the conventional landfill applications pose significant risks to human health and the environment, especially as MSW become more complex in industrializing countries.

In this study, leachate recirculation was applied to the landfilled waste (5 year old) in order to evaluate further waste degradation mechanisms within the waste matrix and the effect of the leachate recirculation strategy on its potential degradation. Next, the capability of stabilized MSW to produce methane, suitability of the rehabilitation of a conventional system (approximately 5 year old) and further degradation potential were tested and evaluated. Finally, the results of this study were compared with the degradation behavior of the fresh and stabilized refuse from the literature. These results can be summarized as follows;

The waste degradation mechanisms were observed in the reactor by monitoring changes in the leachate and gas productions. The most critical indicator parameters pH, ORP, COD, BOD₅, sulfate, VFA, and ammonia nitrogen were monitored to understand in situ waste degradation and the stabilization phases.

The pH value of the reactor exhibited a range of 6.34 and 8.23 that is optimum for the methanogenic activity. The increase in the pH value at the beginning of the operation was directly related to the conversion of VFAs into methane and carbon dioxide by the methanogenic activity.

Additionally, the ORP values were measured around -80 mV which is the indicator of the reducing conditions in the leachate. Furthermore, significant decrease in the ORP value confirmed the onset of the methanogenic activity in the reactor.

Since COD concentration is the indicator of organic strength in leachate, the rapid reduction in the COD concentrations in the leachate sample was directly related to the partial stabilized nature of the waste sample. Importantly, the COD removal of the leachate sample in the reactor found as 91 %. In addition, the rapid decrease in the COD concentrations also attributed to the leachate recirculation, which enhances the waste biodegradation. The biodegradability expressed in terms of BOD₅/COD was between 0.67-0.11 which was consistent with the methanogenic decomposition phase and representative of medium age waste characteristics in the reactor.

Moreover, the initial ammonia concentrations were recorded as 1835 mg/L. The ammonia concentrations found in the leachate samples were within the acceptable limits of anaerobic bioreactors. Besides, the onset of methanogenesis in early stages of the waste degradation supported by the reduction in the sulfate and low ORP values.

The VFA concentrations were also decreased over time. The maximum level of concentrations was recorded at the beginning of the operation indicated the end of the acid formation phase along with the onset of the methane fermentation phase. This rapid transition of initial acid formation into methane fermentation phase was accomplished with the help of the conversion of VFAs into methane and carbon dioxide which resulted in the increase in the pH values.

Finally, the cumulative biogas production was 838.49 L. However the amount of methane produced was calculated as 385.71 L which made up 46 % of the total biogas productions. According to the total methane generation, the theoretical methane yield was calculated as 0.018 kg CH₄/ kg dry waste in the reactor. The theoretical methane yield for the reactor was lower than the proposed values given in the literature which was attributed to the stabilized nature of the medium age solid waste sample.

At the end of the study, final decision process was developed based on the waste degradation and stabilization phases in the reactor. The schematic distribution of the final decision process was presented in Figure 6.1.

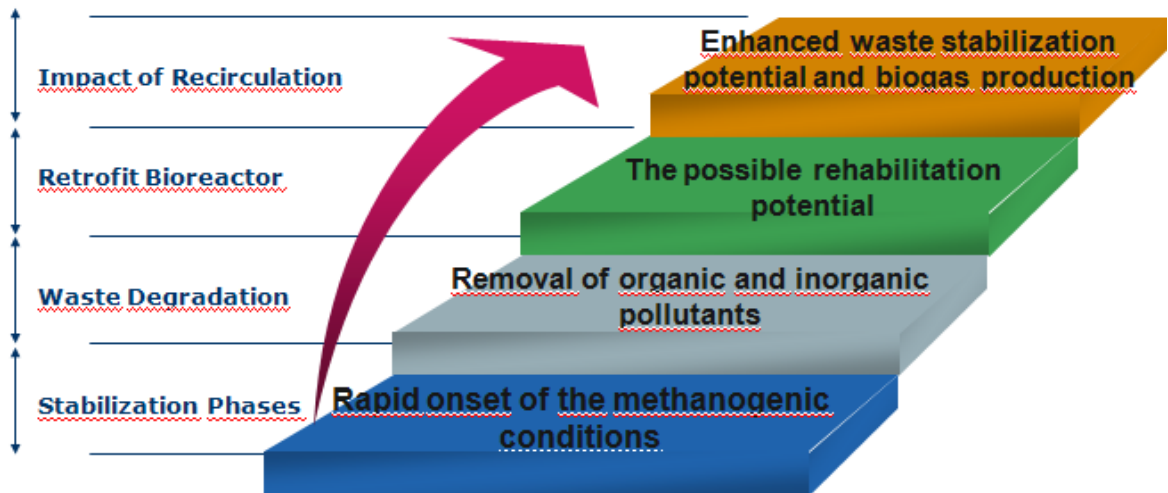


Figure 6.1. Final decision process.

The rapid waste degradation was attributed to the nature of the stabilized waste sample, seed sludge addition as a stimulator, and additionally, leachate recirculation which enhanced the waste decomposition. The stabilized waste used in this study had a potential degradation and capability to produce biogas rich in methane composition. The positive effect of the leachate recirculation on the stabilized (5 year old) waste degradation provided an insight for the future studies. Results found in medium age waste sample suggested that the evaluation of the waste degradation phases provided the possible rehabilitation potential of the conventional landfill sites. However, future studies on the waste degradation mechanisms under bioreactor concept with different waste ages will give more detailed information about the conversion of existing landfills to bioreactor.

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