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FACTORS AFFECTING THE TREATMENT EFFICIENCY OF MUNICIPAL SOLID WASTES IN SIMULATED LANDFILL BIOREACTORS

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by

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ABSTRACT

Millions tons of solid wastes are generated each year from municipal, industrial and agricultural sources. Municipal solid wastes (MSWs) are major sources of air, water and soil contamination and they must be treated. Anaerobic digestion has been up to now essentially applied to wastewater. However, in recent years, there is increasing interest in using anaerobic digestion as a means of generating biogas from, and the reducing the volume of, the organic fraction of municipal solid waste (OFMSW). In addition, bioreactor landfill technology instead of traditional landfilling has been used for the treatment of MSW, recently.

In the frame work of this Ph.D. thesis, factors affecting the treatment efficiency of MSWs in simulated landfill bioreactors were investigated. OFMSWs were collected from the kitchen of Engineering Faculty in Dokuz Eylul University Campus. These investigated factors are leachate recirculation, recirculation volume, waste shredding, waste compaction, aeration and additions of alkalinity, industrial and sewage sludge to MSWs. The bioreactors were operated at eight different modes. During the study; chemical oxygen demand (COD), inert COD, Biological oxygen demand (BOD), volatile fatty acids (VFA), pH, ammonium nitrogen (NH_4-N), total nitrogen (TN), nitrate nitrogen (NO_3-N), total phosphorus (TP), total organic carbon (TOC), anaerobic toxicity assay (ATA), *Lumistox* toxicity test were carried out in leachate samples produced from the solid waste in simulated bioreactors. Water content, organic matters, C percentage, waste quantity, TN, TP analysis were carried out in solid waste before and after anaerobic incubation period. In addition, the quantities of total and methane gas and methane percentages were measured.

A leachate recirculation volume of 13 % of the reactor volume was found suitable for the anaerobic degradation and methane gas productions of MSWs in simulated bioreactors. The leachate quality was improved in this recirculation volume. The anaerobic landfilling bioreactors operated without leachate recirculation and high recirculation volume were found unsuitable for the anaerobic biodegradation of solid waste and methane gas productions.

Shredding of MSWs contributed to stabilization of solid waste, increase the treatment characteristics of leachate and methane gas production, while the waste compaction increased the stabilization time due to high quantity of compressed waste.

Addition of alkalinity reduced the waste quantity, the organic matter content of the solid waste and the biodegradation time in simulated solid waste bioreactors. Methane quantity and methane percentage also increased in alkalinity added reactors due to suitable pH for growth of methanogenic bacteria through the anaerobic incubation period. Between alkalinity added reactors, 6 g/l $NaHCO_3$ alkalinity added reactor was better than 3 g/l $NaHCO_3$ alkalinity added reactor in terms of leachate quality, methane production and solid waste characteristics.

Intermittent aeration (one day in a week during one hour) decreased the COD and VFA concentrations of leachate samples. Methane gas production and methane gas percentage significantly decreased in aerated bioreactors (especially three days in a week during one hour). Leachate quantity, waste quantity and organic matter content of the solid waste in aerated reactors were lower than the non-aerated reactor from the strictly anaerobic conditions. In addition, partial denitrification carried out in aerated reactor. Furthermore, aeration has no positive effect on reduction of leachate toxicity.

Co-digestion of industrial sludge (the weight ratio of the OFMSW to industrial sludge was 1:2 dry solid basis) with OFMSW has a positive effect in terms of COD and VFA reduction and pH adjustment in leachate samples. However, methane gas production and methane percentage were lower in industrial sludge added MSW bioreactor due to toxicity of heavy metal to methane genesis. ATA test showed that methane inhibition was occurred in industrial sludge added reactors.

Co-digestion of sewage sludge (the weight ratio of the OFMSW to sewage sludge was 1:3 dry solid basis) and OFMSW has a positive effect in terms of COD, VFA reduction and pH adjustment in leachate samples. Organic matter, C reduction, methane gas production, methane percentage, in reduction of waste quantity and waste settlement was better in sewage sludge amended landfilling bioreactors.

ÖZET

Her yıl kentsel, endüstriyel ve tarımsal faaliyetlerden kaynaklanan milyonlarca ton katı atık üretilmektedir. Kentsel katı atıklar havanın, suyun ve toprağın kirlenmesine sebep olan başlıca kirletici kaynaklardan biridir ve mutlaka arıtılmalıdırlar. Anaerobik arıtma şimdiye kadar genellikle atıksuların arıtımında kullanılmaktaydı. Ancak son yıllarda, katı atıklardan biyogaz oluşumu ve yüksek hacim azalması sağlaması nedeniyle anaerobik arıtmanın organik kökenli katı atıkların arıtılmasında kullanımına olan ilgi artmaktadır. Buna ilaveten son zamanlarda kentsel katı atıkların arıtımında, geleneksel katı atık depolaması yerine biyoreaktör depolama tekniği kullanılmaktadır.

Bu doktora tezi kapsamında, ketsel katı atıkların simüle biyoreaktörlerde arıtma verimini etkileyen faktörler incelenmiştir. Çalışmada Dokuz Eylül Üniversitesi, Mühendislik Fakültesi mutfağından alınan organik kökenli katı atıklar kullanılmıştır. İncelenen faktörler; sızıntı suyu geri devri, geri devir hacmi, atık parçalaması, sıkıştırma, havalandırma, alkalinite ilavesi, endüstriyel ve kentsel arıtma çamuru ilavesidir. Anaerobik biyoreaktörler 8 farklı çalışma periyodunda işletilmiştir. Çalışma boyunca simüle biyoreaktörlerde oluşan sızıntı sularında kimyasal oksijen ihtiyacı (KOİ), inert KOİ, biyolojik oksijen ihtiyacı (BOİ), uçucu yağ asitleri (UYA), pH, amonyum azotu (NH_4-N), toplam azot, nitrat azotu (NO_3-N), toplam fosfor, toplam organik karbon (TOK), anaerobik toksisite (ATA), *Lumistox* toksisite testi yapılmıştır. Katı atıklarda ise su muhtevası, organik madde, % karbon, atık ağırlığı, toplam azot ve toplam fosfor analizleri çalışma periyodunun başlangıç ve sonunda yapılmıştır. Buna ilaveten toplam ve metan gazı miktarları ile metan yüzdeleri ölçülmüştür.

Reaktör hacminin % 13'ü mertebesinde bir sızıntı suyu geri devri uygulamasının anaerobik reaktör verimini ve sızıntı suyu arıtma verimini artırdığı gözlenmiştir. Sızıntı suyu geri devri yapılmaması ve yüksek geri devir hacimleri katı atıkların biyolojik ayrışmasına ve metan gazı üretimlerine önemli bir katkı sağlamadıkları gözlenmiştir.

Atıkların parçalanması katı atıkların ayrışmasına, sızıntı suyu özelliklerinin iyileştirilmesine ve metan gazı oluşumuna önemli katkılar sağlarken, atıkların sıkıştırılması atık miktarını artırdığından ayrışma zamanını uzatmaktadır.

Simüle katı atık biyoreaktörlerine alkalinite ilave edilmesi katı atık miktarını, organik madde içeriğini ve biyolojik ayrışma zamanını azaltmaktadır. Alkalinite ilavesi yapılan reaktörlerde pH metan bakterileri için uygun aralığa geldiğinden metan miktarı ve metan yüzdesinin arttığı gözlenmiştir. Alkalinite ilave edilen reaktörler arasında 6 g/l $NaHCO_3$ alkalinitesi eklenen reaktörün sızıntı suyu kalitesi metan üretimi ve katı atık özellikleri bakımından 3 g/l $NaHCO_3$ alkalinitesi eklenen reaktörden daha iyi olduğu gözlemlenmiştir.

Simüle katı atık biyoreaktörlerinin kesikli havalandırılması (haftada bir gün bir saat havalandırma) sızıntı sularının KOİ ve UYA konsantrasyonlarında azalma sağlarken, metan miktarı ve yüzdesi (özellikle haftada 3 gün birer saat havalandırma yapılan reaktörde) önemli seviyelerde düşmüştür. Sızıntı suyu miktarı, atık miktarı ve organik madde içeriği havalandırmalı reaktörlerde havalandırılma yapılmayana kıyasla daha düşüktür. Buna ilaveten havalandırmalı reaktörlerde kısmi denitrifikasyon gerçekleşmiştir. Havalandırmanın sızıntı suyu toksisitesine olumlu bir etkisi olmamıştır.

Endüstriyel çamurlarla (organik kökenli katı atık endüstriyel çamur oranı ağırlık olarak 1:2) organik kökenli katı atıkların birlikte arıtılmaları, sızıntı suyu KOİ ve UYA azalması ile pH düzenlemesi bakımından olumlu bir katkı sağlamıştır. Fakat endüstriyel çamurlardaki ağır metal konsantrasyonu nedeniyle katı atık reaktöründeki metan miktarı ve metan yüzdesinin daha düşük olduğu gözlenmiştir. ATA testi endüstriyel çamur ilave edilen reaktörlerde metan inhibisyonu olduğu sonucunu vermektedir.

Kanalizasyon çamurları (organik kökenli katı atık kanalizasyon çamuru oranı ağırlık olarak 1:3) ile organik kökenli katı atıkların birlikte arıtılmaları, sızıntı suyu KOİ, UYA azalması, pH ayarlanması ile katı atık reaktörlerinde metan miktarı, metan yüzdesi, organik madde, karbon içeriğinin azaltılması, atık miktarında azalma ve atık çökelmesi bakımından olumlu bir katkı sağlamıştır.

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CHAPTER ONE
INTRODUCTION

1.1 Introduction

1.1.1 Removal of municipal solid wastes

Millions tons of solid wastes are generated each year from municipal, industrial and agricultural sources. Municipal solid wastes (MSW) are major sources of air, water and soil contamination. There is a need for alternative waste management techniques to better utilize the waste and minimize its adverse environmental impacts (Yu et al., 2002). Development of integrated solid waste management program which include recycling and in some cases, combustion, has led to a decrease in the use of landfills. However, there is a limit to the types of waste that can be recycled, and incineration is not the solid waste management alternative of choice for many communities (Wang et al., 1997). Within the range of management options, there are four level hierarchies for decision makers to consider when planning and implementing integrated waste management. The first level of the hierarchy is source reduction. Individuals, government, commercial establishments and industries are expected to participate in source reduction by reducing the quantity of solid and toxic wastes. The second level of the hierarchy is recycling. The third level hierarchy is waste combustion. Combustion can be used to reduce the volume of the waste stream and to recover energy. Finally, the fourth level of hierarchy is landfilling (Quasim & Chiang, 1994).

In many countries the current trend in solid waste management is waste minimization through recycling, reuse and selection of raw materials (Kettunen et al., 1996). Waste components such as paper, plastics, glass and metals can be recovered from MSW for remanufacturing into new products. The recycling of the organic fraction of MSW is the preferred concept in waste management in Europe (Veeken & Hamelers, 2000). Composting is coming increasingly under consideration in many municipalities throughout the world because it has several advantages over current disposal strategies. Firstly, composting can reduce the waste volume by 40-50 % and thus require less landfill space for disposal. Secondly, pathogens can be killed by the heat generated during the thermophilic phase. Finally, composting has been well established and it is currently used to provide a final product, which can act as a soil conditioner or fertilizer (Zorpas et al., 2000). If yard waste dominates within the all wastes, aerobic composting is preferred (Braber, 1995).

Another treatment method of MSW is combustion. The thermal processing of solid waste, used both for volume reduction and energy recovery, is an important element in many integrated waste management systems. It can be defined as the conversion of solid wastes into gaseous, liquid and solid conversion products, with the concurrent or subsequent release of heat energy. Thermal processing systems can be categorized on the basis of their air requirements. Combustion with exactly the amount of oxygen (or air) needed for complete combustion is known as stoichiometric combustion. Combustion with oxygen in excess of the stoichiometric requirements is termed excess-air combustion. Gasification is the partial combustion of solid waste under substoichiometric conditions to generate a combustible gas containing carbon monoxide, hydrogen and gaseous hydrocarbon. Pyrolysis is the thermal processing of waste in the complete absence of oxygen (Tchobanoglous et al., 1993).

Of all the different alternatives for the elimination or treatment of MSW, sanitary landfilling is probably the one that is most widely employed due to its economic advantages (Iglesias et al., 2000). Even with implementation of waste reduction, recycling and transformation technologies, the disposal of residual solid waste in landfills still remains an unavoidable component of an integrated solid waste management strategy (Chugh et al., 1999). Landfill design and construction is a continuous activity that is completed only when all of the available or permitted capacity of the site has been filled with solid waste. Once that happens, the landfill must be closed, the final action of a facility that is to receive no more solid wastes. The closure plan must show all futures of the completed site and identify the agencies responsible for implementing closure of facilities. The closure elements are final cover design, surface water and drainage control systems, control of landfill gases, control and treatment of leachate and environmental monitoring systems (Tchobanoglous et al., 1993). With increased use and public awareness of this method of disposal, there is much concern with respect to the pollution potential of the landfill leachate. Depending on the composition and extent of decomposition of the refuse and hydrological factors, the leachate may become highly contaminated. As leachate migrates away from a landfill, it may cause serious pollution to the groundwater aquifer as well as adjacent surface waters (Quasim & Chiang, 1994).

MSW composition varies substantially with socio-economic conditions, location, season, waste collection and disposal methods, sampling and sorting procedures and many other factors. MSWs are made of different organic and inorganic fractions such as food, vegetables, paper, wood, plastics, glass, metals and other inert materials (Manna et al., 1999). After depletion of the limited volume of air available in void spaces of a waste bed, decomposition in a landfill takes place under anaerobic conditions. Anaerobic digestion requires moisture and a lack of water is generally responsible for retarding degradation of MSW in conventional landfills. Furthermore, the moisture that may be present is seldom uniformly distributed (Chugh et al., 1998). High moisture content of landfill body has positive effect on development of anaerobic environment, heat transfer and substrate diffusion (Lay et al., 1997).

The following biological, physical, and chemical events occur when solid wastes are placed in a sanitary landfill: (1) biological decay of organic materials, either aerobically or anaerobically, with the evaluation of gases and liquids; (2) chemical oxidation of waste materials; (3) escape of gases from the fill; (4) movement of liquids caused by differential heads; (5) dissolving and leaching of organic and inorganic materials by water and leachate moving through the fill; (6) movement of dissolved material by concentration gradients and osmosis; and (7) uneven settlement caused by consolidation of material into voids. Bacterial decomposition initially occurs under aerobic conditions because a certain amount of air is trapped within the landfill. However, the oxygen in the trapped air is soon exhausted (within days), and the long-term decomposition occurs under anaerobic conditions (Peavy et al., 1985). The decomposition process in a sanitary landfill has been discussed by numerous researchers (Quasim, 1965; Brunner & Keller, 1972; Pfeffer, 1992; Tchobanoglous et al., 1993; Reinhart & Al-Yousfi, 1996). Stanforth et al. (1979) developed generalized degradation curves expressing pH, oxygen, CO_2, CH_4, acetic acid, solubilized salts and redox potential. These generalized curves are illustrated in Figure 1.1.

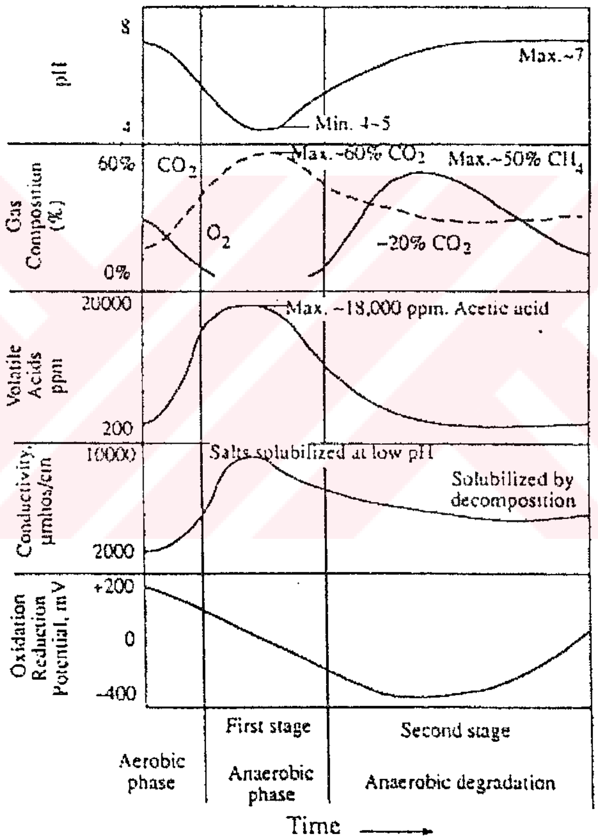

Figure 1.1 Generalized degradation curve of a theoretical landfill during decomposition process

Leckie et al. (1979) are reported that a landfill is considered stabilized when the following criteria are met: (1) Maximum settlement has occurred; (2) negligible gas production is occurring; and (3) leachate does not constitute a pollution hazard. Landfill gas generation is one of the characteristics of the solid waste landfilling.

Landfill gas is a mixture of CH_4 and CO_2, and small quantities of other gases (Price et al., 1998). The CH_4 yield is commonly expressed as a function of the reduction of either volatile solids (VS) or chemical oxygen demand (COD) (Lin et al., 1999).

1.1.2 Anaerobic treatment of municipal solid wastes and anaerobic treatment in simulated bioreactors

Anaerobic digestion has been up to now essentially applied to wastewater. However, anaerobic treatment of organic solid waste fits in well with the new requirements for waste management are: gases and odors emissions, energy saving and recycling (Laclos et al., 1997). There is increasing interest in using anaerobic digestion as a means of generating biogas from, and reducing the volume of, the organic fraction of municipal solid waste (OFMSW) (Wang & Banks, 2000). The organic fraction which forms the largest part is responsible for the negative aspects of landfilling (Cecchi et al., 1992). Anaerobic digestion is a net energy producing process (100-15- kWh_c per tonne of input waste) but its commercialization is not yet fully demonstrated. Yard waste contains much lignocelluloses material, which does not readily degrade under anaerobic conditions. In general if the material collected is predominantly kitchen waste anaerobic digestion is the most appropriate treatment method (Braber, 1995).

Low-solids anaerobic digestion is a biological process in which organic wastes are fermented at solids concentrations equal to or less than 4 to 8 percent. There are three basic steps involved whenever the low solids anaerobic digestion process is used to produce methane from the organic fraction of MSW. The second step involves the addition of moisture and nutrients, blending, pH adjustment to about 6.8, and heating of the slurry. The third step in the process involves the capture, storage and if necessary, separation of the gas component. High-solids anaerobic digestion is a biological process in which the fermentation occurs at a total solid content of about 22 percent or higher. The high-solids anaerobic digestion is a relatively new technology and its application for energy recovery from the organic fraction of MSW has not been developed fully. Two important advantages of the high-solids anaerobic digestion process are lower water requirements and higher gas production per unit volume of the reactor size. The major disadvantage of this process is limited full-scale operating experience is available (Tchobanoglous, 1993).

The process of anaerobic degradation of MSW in the landfill reaches the methanogenic phases as soon as possible after the refuse has been deposited, more organic material is transferred into the gaseous phase and less into the liquid phase (leachate). As a result biogas production increases, more profitable energy is available and less energy and cost are required for treatment of leachate (Iglesias et al., 2000).

The use of leachate containment, collection and recirculation on a landfill has provided opportunity transfer it into a controlled bioreactor system (Lay et al., 1998). The bioreactor landfill provides a similar approach and treatment as is utilized in organic solid waste digestion. The bioreactor landfill provides control and optimization, primarily through the addition of leachate or other liquid amendments, if necessary. Beyond that, bioreactor landfill operation may involve the addition of biosolids and other amendments, temperature control, and nutrient supplementation. However, technical challenges and research needs remain related to sustainability, liquid addition, leachate hydrodynamics, leachate quality, the addition of air, and cost analysis. The bioreactor landfill attempts to control, monitor, and optimize the waste stabilization process rather than contain the wastes as prescribed by most regulations (Reinhart et al., 2002). It was discussed the current status of the bioreactor landfill as it relates to design and operating concepts. Engineered bioreactor landfills are usually designed to maximize the infiltration of rainwater and snowmelt into the waste under controlled conditions. The design objectives of these landfills are to minimize leachate the migration into the subsurface environment and maximize landfill gas (LFG) generation rates under controlled conditions (Warith, 2002).

The three basic concepts for a landfill design operation were specified: dry landfill, bioreactor landfill and final storage quality landfill. In the bioreactor landfill decomposition rates and methane production are enhanced. In this type of reactor the acceleration of landfill stabilization is even more important than the enhancement of methane yield (Stegmann, 1999). Under this model, landfills become a bioreactor processing or digesting the waste rather than the more traditional dry tombs where the waste decomposes slowly or not at all. Using this approach the life of landfills can be greatly extended, perhaps indefinitely. Under this model: (1) landfills become processing facilities- rather than being kept dry, injecting leachate into the waste to accelerate the decomposition actively moistens the waste; additionally air can be actively introduced to the waste, which further hastens the decomposition process through the establishment of aerobic conditions, (2) landfills construction and engineering are substantially modified with regards to leachate collection, recirculation and gas collection and management, (3) the stabilized material resulting from the enhanced decomposition process will be used as daily, intermediate and final cover and could be potentially used for land reclamation and other applications (Read et al., 2001).

1.1.3 Production of leachate and its treatment

It is difficult to define the characteristics of leachate because compositions and concentrations of leachate from a landfill depend on various environmental conditions such as composition of wastes, age of the landfill, geology, temperature, moisture content and so on (Im et al., 2001). Landfill leachate initially is a high-strength wastewater, characterized by low pH, high BOD, COD, and by the presence of toxic chemicals (Quasim & Chiang, 1994). The initial phase of landfilled waste degradation generates leachate with high organics, ammonium, sulphate and chloride concentrations. Leachates may also have a high concentration of metals and contain some hazardous organic chemicals. The removal of organic material and ammonium from leachate is the usual prerequisite before discharging the leachate into natural waters (Kettunen et al., 1996). Representative data on the chemical characteristics of leachate are reported in Table 1.1.

Table 1.1 Composition of leachate produced from landfills (Peavy et al., 1985)

Constituent	Concentration (mg/L)	
	Range	Typical
BOD_5	2000 - 30.000	10.000
TOC	1500 - 20.000	6000
COD	3000 - 45.000	18.000
Total Suspended Solid	200 - 1000	500
Organic Nitrogen	10 - 600	200
Ammonia Nitrogen	10 - 800	200
Nitrate	5 - 40	25
Total Phosphorus	1 - 70	30
Ortophosphorus	1 - 50	20
Alkalinity as $CaCO_3$	1000 - 10.000	3000
pH	5.3 – 8.5 (unitless)	6 (unitless)
Total Hardness as $CaCO_3$	300 - 10.000	3500
Calcium	200 - 3000	1000
Magnesium	50 - 1500	250
Potassium	200 - 2000	300
Sodium	200 - 2000	500
Chloride	100 - 3000	500
Sulfate	100 - 1500	300
Total Iron	50 - 600	60

Disposal of domestic and commercial solid wastes in landfills leads to generation of leachate due to the inherent moisture of the wastes and to the external infiltrating liquids. Leachate characteristics change over time, because, as a landfill becomes older, there is a shift from a relatively short aerobic period which has two distinct sub-phases: an acidic phase followed by a methanogenic phase. Leachate from the acidic phase, "young" leachate, is characterized by high values of the organic pollutants. A large portion of the organic matter consists of volatile fatty acids (VFAs). The high concentration of VFA's also results in pH values as low as 4. In the methanogenic phase of the anaerobic decomposition period, methane gas-forming bacteria degrade the VFAs and reduce the organic strength of the leachate. The organic carbon that remains after this degradation is mainly due to substances with high molecular weight. These substances are less amenable to microbial degradation and, therefore, tend to remain in "older" leachates (Diamadopoulos, 1994).

Selection and design of a leachate treatment process is not simple. Important factors that govern the selection and design of treatment facilities include leachate characteristics, effluent discharge alternatives, technological alternatives, and cost and permit requirements (Quasim & Chiang, 1994). Anaerobic treatment methods are more suitable for the treatment of concentrated leachate streams, offer lower operating costs, the production of usable biogas product, and production of a pathogen free solids residue which can be used as cover material (Kettunen et al., 1996; Malina & Pohland, 1992; Im et al., 2001).

For treatment of landfill leachate, the suggested general approach is to utilize physical treatment processes in conjunction with (a) biological treatment and (b) chemical treatment, in particular, coagulation-flocculation, precipitation, chemical oxidation, carbon adsorption and membrane separation processes (Quasim & Chiang, 1994).

If a leachate meets the characteristics of a "young" leachate, both aerobic and anaerobic biological treatment can reduce the high, but easily degradable organic content. Physico-chemical treatment of this type of leachate is generally not appropriate, because of the predominant low molecular weight nature of the organic material. If the leachate meets the characteristics of an "old" leachate, or even after the leachate has undergone biological treatment, a significant biodegradable organic fraction has already been consumed. Therefore, physico-chemical treatment must be employed, before the effluent can be discharged (Diamadopoulos, 1994).

One of the most innovative and acclaimed methods of leachate treatment is the circulation of high strength leachate back to the landfill. By recirculating the leachate, the organic component of the leachate can be reduced by the active biological communities within the refuse mass (Quasim & Chiang, 1994). The Solid Waste Association of North America (SWANA) conducted a US survey in 1997 that identified over 130 leachate recirculating landfills (Gou & Guzzone, 1997). Similarly, Leckie et al., (1979); Stegmann, (1983); Pohland and Harper, (1986); Bae et al., (1998) reported that the leachate recycle is the most widely investigated landfill management procedure and has been shown to be successful in both pilot and full scales. Leachate introduction techniques include surface application and injection through vertical wells or horizontal trenches (Reinhart et al., 2002).

Leachate recirculation appears to be the most effective method of increasing the moisture content in a controlled reactor system, since the advantages of leachate recirculation include distribution of nutrients and enzymes, pH buffering, dilution of inhibitory compounds, recycling and distribution of methanogens, liquid storage and evaporation opportunities (Reinhart, 1996). Furthermore, Reinhart and Al-Yousfi, (1996) reported that the leachate recycle not only improves the leachate quality, but also shortens the time required for stabilization. In practice, leachate recirculation could reduce the time required for landfill stabilization from several decades to 2-3 years, thus minimizing the opportunity for long-term adverse environmental impact. In addition, leachate recirculation showed a 12-fold increase of gas production in the recirculating cell relative to the conventional cell.

If the volume of leachate recirculated is very high, problems such as saturation, ponding, and acidic conditions may occur. Ensiling problem may occur in a landfill cell, particularly at a high level of recirculation volumes. Ensiling is a result of inhibited anaerobic microbial activity leading to inhibitory fermentation products consisting primarily of volatile organic acids and alcohol. The primary causes of the ensiling problem are imbalance between acidogenesis and methanogenesis and low alkalinity in the landfill leachate. As a result of this process, several years are required for landfill stabilization. Therefore the leachate recirculation must be properly adjusted in order to have the minimal quantity and low-strength output (O'Keefe & Chynoweth, 2000). Ledakowicz and Kaczorek (2002) reported that the leachate recirculation can lead to the inhibition of methanogenesis as it may cause high concentrations of organic acids (low pH) which are toxic for the methanogens.

1.2 Literature review

In a study carried out by Laclos et al. (1997), anaerobic digestion of municipal solid organic waste was investigated in Valorga full-scale plant in Netherlands. The waste to be treated consists of food and garden waste. The result of the study demonstrates that anaerobic digestion can be considered as a reliable industrial process for the treatment of organic solid waste. Another study performed by Chugh et al. (1999), was to achieve accelerated degradation of unsorted MSW by applying techniques that may be viable in a full-scale landfill. The result of the study shows that 75 % of the rapidly biodegradable fraction mixed and unsorted MSW is degraded in about 2 months.

Plaza et al. (1996) investigated the treatability of MSW in Salta, Argentina. pH, biogas production, alkalinity, and VFA production were determined. They found that the organic fraction of MSW of Salta can be treated in an anaerobic digester. The study realized by Iglesias et al., (1998) an anaerobic digestion of MSW was carried out in a pilot-scale reactor to study the anaerobic fermentation as it happens in a sanitary landfill. The MSW used was taken from the Cogerse landfill site in Asturias, Spain. The experiments were performed in an opaque PVC reactor at 36 ^{0}C. At the end of the 400 days, the COD removal efficiency of the leachate was approximately 97 %.

İnanç et al., (2000) used three different reactors, (an UASB reactor, an anaerobic upflow filter and a hybrid bed reactor) for the anaerobic treatment of the leachate taken from the Kömürcüoda Sanitary Landfill located in İstanbul. Organic loading was increased gradually from 1.3 kg COD/m^3.day to 8.2 kg COD/m^3.day at a hydraulic retention time varied between 2.4 and 2 days. All the reactors showed similar performances against organic loadings with COD removal efficiencies of 80 % and 90 %.

Kettunen and Rintala (1998) showed that leachate can be treated on-site UASB reactor at low temperature. A pilot-scale UASB reactor was used to study the treatment of a municipal landfill leachate (COD 1.5-3.2 g/l) at a temperature of 13-23 ^{0}C. 65-75 % COD and up to 95 % BOD_7 removals were achieved at organic loading rates (OLR) of 2-4 kg COD $m^{-3}d^{-1}$. Similarly, in a study carried out by Kettunen et al., (1996) it was observed that anaerobic and sequential anaerobic-aerobic treatment of leachate is possible at low temperatures. The sequential process produced effluent quality (COD<380 mg/l, BOD<22 mg/l) close to the requirements for municipal wastewater treatment plants.

Different process configurations and operation models have been reported for the removal of organic substances and nitrogen removal from landfill leachates. Kuroda (1988) and Akunna et al., (1993) recommended that the biological treatment process using anaerobic-aerobic system as a feasible technology for simultaneous removal of organics and nitrogen. Ilies and Mavinic (2001) used four-Stage Bardenpho process for the biological nitrification and denitrification of a high ammonia landfill leachate. The study realized by Jokela et al., (2002) showed that nitrogen can be removed effectively from landfill leachate by using a nitrifying upflow biofilter with waste material as a filter medium combined with subsequent denitrification of the nitrified leachate in the landfill body.

Numerous researchers investigated the treatment of leachate using anaerobic or anaerobic/aerobic and physical and chemical processes (Shin et al., 2001; Lin et al., 2000; Hoilijoki et al., 2000; Kennedy & Lentz, 2000; Çalli et al., 2002; Diamadopoulos, 1994). Im et al., (2001) set up an anaerobic-aerobic system including simultaneous methanogenesis and denitrification to treat organic and nitrogen compounds in immature leachate from a landfill site. Denitrification and methanogenesis were successfully carried out in the anaerobic reactor while the organic removal and nitrification of NH_4-N were carried out in the aerobic reactor when rich organic substrate was supplied with appropriate hydraulic retention time. The maximum organic removal rate was 15.2 kg COD/m^3d in the anaerobic reactor while the maximum NH_4-N removal rate and maximum nitrification rate were 0.84

kg NH_4-N/m^3/d and 0.50 kg NO_3-N/m^3/d, respectively, in the aerobic reactor. The pH range for proper nitrification was 6-8.8 in the aerobic reactor. The study realized by Diamadopoulos (1994) investigated the characterization and treatment of recirculation-stabilized sanitary landfill leachate. The stabilized effluent forms a pond at the lowest point of the landfill. This stabilized leachate was characterized by an average COD value of 1141 mg/l, an average BOD value of 85 mg/l. Physico-chemical methods of treatment employed were coagulation, powdered activated carbon adsorption and air stripping of ammonia. The results showed that even after the combined treatment the COD remaining in water hardly dropped below 300 mg/l.

There are many references in the literature to successful operations in two-phase anaerobic fermentation of organic fraction of MSW and landfill leachate (O'Keefe & Chynoweth, 2000; Cho & Park, 1995; Mata-Alvarez & Llabres, 2000; Samani et al., 2002; Goel et al., 2001; Shin et al., 2001; Vieitez & Ghosh, 1999;). Libanio et al., (2003) investigated the integrated municipal solid waste and leachate treatment systems. The experiment consisted of a comparative analysis among three different lines of operation, each one consisting of three anaerobic MSW reactors: conventional landfill (line 1), raw leachate recycling (line 2), and integrated treatment, with seeded leachate recycling (line 3). For this purpose, an UASB reactor was installed in the integrated treatment line with the purpose of removing the organic load of the leachate of the MSW reactors and utilizing the biological sludge produced for inoculation of the waste digestion. At the end of the study; the lowest VFA and COD concentration were arised the leachate produced from line 3. VFA values of the leachate were 15, 5 and 2 g/l in line 1, 2 and 3, respectively. Similarly, COD values of the leachate were found 60, 12 and 7 g/l, respectively, at the end of the study.

Chan et al., (2002) investigated the impact of leachate recirculation on the co-disposal of three major wastes (municipal solid waste, sewage sludge and sediment dredging) using a laboratory column. Chemical parameters (pH, COD, NH_4-N, total-P) and gas production (total gas volume, production rates and concentrations of CH_4 and CO_2) were monitored for 11 weeks. Leachate recirculation reduced the waste stabilization time and was effective in enhancing gas production and improving the leachate quality, especially in terms of COD. The results of this study also indicated that leachate recirculation could maximize the efficiency and waste volume reduction rate of landfill sites.

In a study realized by Iglesias et al., (2000), the behavior of a sanitary landfill was reproduced in a pilot plant under controlled conditions. The experiment was carried out in an opaque PVC reactor at 36 ^{0}C with recirculation of the leachates. The MSW employed came from the regional landfill site of Asturias and the study was carried out in three stages. Firstly, 48.5 kg of MSW were introduced into the pilot plant (first cell) and several phases of the waste degradation were monitored: The methanogenic phase being reached after 264 days. In the second stage, 66 kg of new MSW was added on the top of the degraded waste of the first stage (second cell). In the third stage, 59 kg of new MSW were added on top of the waste digested in the two previous steps (third cell). The waste was digested faster in the second and third steps and the methanogenic phase was reached earlier (second step: 55 % CH_4 on day 20; third step: 50 % CH_4 on day 30).

The study realized by Özkaya et al., (2002) presents the investigation of leachate recirculation effects in İstanbul Odayeri Sanitary Landfill. In this study in perpendicular injection wells, 3000 m^3 of leachate periodically recirculated into these wells. It was determined that the methane component of landfill gas increased at wells in recirculation test area. Since recirculation increase the methanogenic activity CH_4 fraction of landfill gas increased about 10%, where it was about 45% before and 55% after recirculation. After the leachate recirculation, it was determined that BOD_5/COD ratio, which is a sign of the biological treatability, decreased from the 0.75 to 0.60. The results showed that, settlement of the recycle well was higher than that non-recycle well.

In the study performed by Chugh et al., (1998), experiments were carried out to understand how the recirculated leachate amount affects the waste degradation in 200-litre anaerobic reactors manufactured with stainless steel. Volume of leachate recirculated was tested under three different conditions: 2 percent, 10 percent and 30 percent of the initial volume of waste bed in the reactor. In the best case, the organic fraction of the waste was essentially entirely degraded within 2 months. Trends in pH, in gas production, in VFA and trends in COD were investigated. According to result of the study, flushing at a rate of 10 percent is suitable for waste stabilization.

In another study carried out by San and Onay, (2001) it was investigated the impact of various leachate recirculation regimes on municipal solid waste degradation. Leachate recirculation volume and frequency were changed periodically. This research showed that increased frequency of leachate recirculation accelerates the stabilization rate of waste matrix. About 2 L of recirculated leachate and four times per week recirculation strategy were found to provide the highest degree of waste stabilization.

Techniques used to enhance the biological degradation of the waste are leachate recirculation, recirculation volume, waste shredding, waste compaction, pH adjustment, aeration, and nutrient and sludge additions. Limited studies were performed about the effect of compaction of MSW in landfill bioreactor. Deeper fills, require more water to reach saturation, require longer time for decomposition, and distribute the bulk of extracted material over a long period of time. Deep fills offer greater contact time and longer travel distance, thus higher pollution concentrations will result (Quasim & Chiang, 1994). Since hydraulic conductivity is inversely related to specific weight, highly efficient use of airspace effectively reduces the ability to move the moisture through the waste. Since field capacity is also inversely related to waste density, increased compaction actually achieves the saturation level of MSWs with less addition (Reinhart et al., 2002).

Waste shredding affects the rate of waste degradation. In a study realized by Warith, (2002) it was determined that solid waste size, leachate recirculation and nutrient balance affect the rate of MSW biodegradation. In this study, shredding the MSW is an effective method of improving waste biodegradation compared to the trends established with un-shredded solid waste. The average pH levels of the shredded waste leachate samples were more neutral than the un-shredded MSW leachate samples.

Quasim and Chiang, (1994) are reported that, leachate from shredded fills has significantly higher concentrations of pollutants than those from un-shredded refuse. The rate of pollutant removal, solid waste decomposition rate, and the cumulative mass of pollutants released per unit volume of leachate is significantly increased in un-shredded fills compared to shredded ones.

The rate-limiting step in anaerobic digestion of organic solid waste is generally their hydrolysis. A size reduction of the particles and the resulting enlargement of the available specific surface can support the biological processes in two ways. Firstly, in case of substrate with a high content of fibres and a low degradability, yields with an improved digester gas production. This leads to a decreased amount of residues to be disposed of and to an increased quantity of useful digester gas. The second effect of the particle size reduction observed with all the substrates with those of low degradability as a reduction of the technical digestion time (Palmowski & Müller, 2000). In the study realized by Kim et al., (2000) serial basic tests were conducted for the determination of fundamental kinetics and for the actual application of kinetic parameters of food waste digestion with the measurements of methane production. The effects of food particle size and sodium ion concentration on the anaerobic thermophilic food waste digestion were investigated.

Alkalinity addition is one of the affecting parameter the waste degradation. Landfill leachate is generally acidic because of the accumulation of organic acids during the early life of the fill. Some neutralization may occur due to the dissolution of calcium carbonate and other minerals in the soil column. Alkalinity in leachate is due to carbonates, bicarbonates, silicates, borates, ammonia, organic bases, sulfides and phosphates (Quasim & Chiang, 1994). The alkalinity of water is a measure of its capacity to neutralize acids and is due primarily to the salts of weak acids. Alkalinity is one of the most central concepts in aquatic chemistry because it controls the pH and is thus a measure of the capacity of an aquatic system to buffer the pH in the presence of additional acids. If the acid concentrations (H_2CO_3 and VFA) exceed the available alkalinity, the reactor will "sour" (a drop in pH), severely inhibiting microbial activity, especially the methanogens (Speece, 1996). When methane production becomes "stuck" (ceases) the VFA may continue to accumulate, exacerbating the situation further. Methanogens prefer nearly neutral pH conditions with a generally accepted optimum range of approximately 6.5 to 8.2 (Anderson & Yang, 1992).

A balance between acid production and acid consumption is essential for a stable anaerobic process running at the highest possible rate. It is well known that the process stability strongly depends on the start-up of the reactor, which is a period when the VFA concentration must not become too high. Therefore, equilibrium between the acid phase and the methane generation is achieved. Plaza et al., (1996) investigated the anaerobic treatment of municipal solid waste disposed in Argentina. In their study, pH was controlled by the addition of sodium bicarbonate as a buffer at a minimum buffer/substrate ratio of 0.06 kg/kg TS. Adequate alkalinity, or buffer capacity, is necessary to maintain a stable pH in the digester for optimal biological activity. Alkalinity 5.75 provides a more accurate estimation of theoretical true bicarbonate alkalinity (Cobb & Hill, 1990). An alkalinity level ranged from 1000 to 5000 mg Ca CO_3/l was recommended by Tchobanoglous and Burton (1979).

The study realized by Gönüllü, (1987) explained the effect of organic matter content of solid wastes upon pollutant characteristics of leachate. High pH was observed in solid waste that has high ash content. After that, pH decreased through anaerobic conditions. Low pH observed in solid waste in summer because of high organic content. The study showed that pH and alkalinity is very important parameters for solid waste landfill operations.

The enhancement of solubilization of particulate organics is significant engineering consequence. The effect of alkaline, thermal and thermochemical pretreatments in the anaerobic digestion of co-mingled municipal solid waste and sewage sludge were investigated by Hamzawi et al., (1998). NaOH was added to the reactor in alkaline pretreatment study. The results of the study showed that alkaline pretreatment significantly increases the biodegradability of the waste mixture.

In the study realized by Warith, (2002) related to bioreactor landfills, three sets of bioreactor cells were used. The first was a control reactor cell, where only leachate was recirculated. In the second bioreactor cell, the pH buffered and nutrient added to the leachate prior to its recirculation and in the third cell wastewater treatment sludge was added to the leachate. NaOH was used for the adjustment of pH of the leachate. At the end of the study (after 18 weeks), the highest pH was observed in the sludge added reactor and the high reduced COD was observed in the pH buffered and nutrient added reactor.

In another study carried out by San and Onay, (2001) pH control was carried out by KOH, in order to the impact of various leachate recirculation regimes on municipal solid waste degradation. pH was measured as 7.3 on day 257, while it was 5.92 on day 250. The results of this study showed that four times per week recirculation strategy with a pH control provided the highest degree of stabilization as reflected by the leachate and gas parameters monitored.

Dinamarca et al., (2003) studied the influence of the pH in the first stage and hydrolytic stage, of the anaerobic digestion of the organic fraction of the urban solid waste in a two phase anaerobic reactor. The reactor was fed with a solution of the organic fraction of urban solid waste residues containing 5 to 7 % solids. Four reactors were used, the experiments were done at three controlled pHs; 6, 7, and 8, and one with free pH. The higher degradation of TSS and VSS was obtained in the reactors operated at pH 7 and 8.

The traditional method of landfill bioreactor operation involves enhancing the waste stabilization by anaerobic microorganisms (Reinhart et al., 2002). Under anaerobic conditions within a landfill site slow stabilization of the waste mass results in the production of methane, an explosive "green house" gas under US legislation (Clean Air Act) and a leachate which can pollute the groundwater over long periods of time (Read et al., 2001). Recently, increased interest has been focused on the introduction of oxygen to the landfill to create an aerobic bioreactor. Air is typically injected into the landfill with the same devices as used to extract the gas or inject the leachate to vertical and horizontal wells. Aerobic bioreactors have been promoted as a method to accelerate waste stabilization and to reduce the methane content in landfill gas (Reinhart et al., 2002). One of the current goals of biogasification research is to increase the methane content of biogas. A methane enrichment process (MEP) was evaluated involving the air purging of recycled digester contents to strip CO_2 and increase the methane content of biogas. The methane enrichment process involved the recycle of digester contents from the lower depth where solution of CO_2 is encouraged because of higher pressure. O'Keefe et al., (2000) investigated whether the aeration resulted in oxygen inhibition of microbial activities in anaerobic digestion of municipal solid wastes. No inhibitory effects were observed in measurements of microbial activities in digester samples.

A lysimeter study carried out by Stessel and Murphy, (1992) was undertaken to determine the quantities of moisture and air that would optimize the degradation. In this study, eight lysimeter were set up and they were operated at different air flow rates. Degradation was enhanced by the application of water, the recycling of leachate and the addition of air. Aerobic operation provided significantly faster rates of degradation and a well settlement of solid wastes.

Read et al., (2001) summarized the successful results of two separate aerobic landfill projects located in Georgia (USA) and discuss the potential economic and environmental impacts to worldwide solid waste management practices. The same landfill site was investigated by Hudgings and Harper, (1999) under aerobic conditions. The results of these studies showed that aerobic landfill system demonstrated: (1) a significant increase in the biodegradation rate of the MSW over anaerobic processes; (2) a reduction in the volume of the leachate as well as organic concentrations within the leachate and (3) significantly reduced the methane generation.

Murphy et al., (1995) investigated and compared the relationship of microbial mass and activity in biodegradation of solid waste under anaerobic and aerobic conditions. The results indicated that the aeration, even at a relatively low volume, with leachate recirculation, significantly accelerated the degradation of MSW. Purcell, (2000) explained the aerobic landfilling technology and the operational implications of aerobic landfilling. Operating landfills under aerobic conditions ("aerox" landfill) rather than conventional anaerobic conditions will potentially provide substantial environmental and financial benefits to landfill operators and society in general. Such conditions will enhance the rates of waste biostabilization and encouraged coupled nitrification and denitrification of ammoniacal nitrogen to virtually eliminate the need for water flushing. Ultimately, an aerox landfill could substantially reduce the timescales to final stabilization, maximize the void space utilization and achieve intergenerational equity by providing a sustainable approach to landfilling and waste management. The aerox landfill concept has also the potential to provide a cost-effective sustainable approach for managing wastes using leading edge landfill technology.

An interesting option for improving yields of anaerobic digestion of solid wastes is co-digestion (Mata-Alvarez & Llabres, 2000). The benefits of the co-digestion include: dilution of potential toxic compounds, improved balance of nutrients, synergistic effect of microorganisms, increased load of biodegradable organic matter and better biogas yield. Additional advantages include hygienic stabilization and increased digestion rate (Sosnowski et al., 2003). Co-disposal of MSW and sludge from municipal wastewater treatment plants has a significant effect upon the generation and quality of leachate (Quasim & Chiang, 1994). Anaerobic digestion of the organic food fraction of municipal solid waste, on its own or co-digested with primary sewage sludge, produces high quality biogas, suitable as renewable energy (Kiely et al, 1997).

Schmidell et al., (1986) presented the anaerobic digestion of MSW mixed with primary sewage sludge. The study was conducted using agitated reactors of 2 or 8 liters capacity, continuously operated at 35 ^{0}C and in the pH range 6.8 to7.2. The results of the study indicated that the great interest in achieving anaerobic digestion of MSW in the presence of sewage sludge, utilizing reactors with high solid content. The authors noticed that the digestion of MSW alone is possible, but the process presents a higher residual VFA concentration and a consequently lower conversion factor to gas.

Sosnowski et al., (2003) presented the results of investigation of methane fermentation of sewage sludge and OFMSW as well as the co-fermentation of both substrates. In the first experiment the primary sludge and thickened excess activated sludge were fed into bioreactor. The second co-fermentation experiment was conducted with the mixture of sewage sludge (75%) and OFMSW (25%) in the same bioreactor arrangement. The weight ratio of OFMSW to sewage sludge was 2:1 (dry solid basis). Generally, in the second experiment more biogas was produced due to larger loading of biodegradable organic matter in the feed-stock. The results of the study showed that the anaerobic co-digestion of sewage sludge and OFMSW seems to be an attractive method for environmental protection and energy savings.

Similarly, in a study realized by Warith, (2002) was shown that the highest degree of settlement was achieved through addition of sludge, where settlements were about 50 % within other reactors.

In the study carried out by Bae et al., (1998), performances of lab-scale lysimeters were evaluated to develop a new landfill system for the recovery of CH_4 from solid wastes. Lysimeters were operated at three different conditions: control (L-control), leachate recycle (L-recycle), and sludge recycle (L-sludge). After 430 days of operation, the amounts of COD recovered by CH_4 were 0.13, 0.29, and 22.5 kg for L-control, L-recycle, and L-sludge reactors, respectively. For L-sludge, 77 % of total COD outflow was recovered as CH_4 from L-control and L-recycle reactors. Stabilization of organics in L-sludge approached completion within 430 days, while other lysimeters still produced leachate with high COD. Results indicated that the continuous addition of active methanogenic population from the anaerobic digester rather than simple leachate recycle was effective for the rapid and significant CH_4 recovery from solid waste.

Landfills are employed for solid and hazardous waste disposal throughout the world. Unfortunately, many of these have not been properly designed, operated or maintained and have imposed adverse environmental impacts. Pohland and Gould, (1986) studied the effects of co-disposal of municipal refuse and industrial waste sludge in landfills. Four simulated landfill columns were constructed to investigate and detail the consequences of co-disposal of municipal refuse with industrial waste sludge. One column served as the control landfill and received 400 kg of municipal refuse of residential origin. The test columns (Columns 2, 3 and 4) received 400 kg of refuse plus 33.6 kg, 65.8 kg and 135.2 kg of metal plating sludge, respectively. In terms of conversion of COD and VFA, leachate from the control column was rapidly depleted in concentration, suggesting a normal sequence of refuse stabilization with some evidence of conversion of less readily available substrates during the terminal phase. A similar but somewhat delayed pattern of conversion was indicated for Column 2, suggesting that the lowest metal sludge loading tended to impede but not inhibit the conversion of readily available organic compounds. In contrast, both COD and VFA analysis for the leachates from Columns 3 and 4 indicated a definite inhibition of the normal progress of refuse stabilization. Unlike Column 2, relatively constant levels of leachate COD and VFA were maintained for these columns.

1.3 Objectives and scope of the study

Sanitary landfills represent a common, economical and environmentally acceptable method for the disposal of solid wastes. But, there are several concerns with the current landfilling process relating to its potential for air and water pollution. So, bioreactor landfill has been used for the treatment of MSW recently. The bioreactor landfill significantly improves the conversion and stabilization of the organic waste constituents. The bioreactor landfill requires certain management activities. Liquid addition and its management is the single most important and cost-effective operational modification available for enhancement of microbial decomposition processes. Other strategies, such as waste shredding, pH adjustment, compaction, aeration and mixed with industrial and sewage sludge may also serve to optimize the bioreactor process.

The first objective of this study was to evaluate the effects of leachate recycling and the effect of different recycling volumes on the chemical oxygen demand (COD) removal, VFA accumulation, alkalinity and pH variations in leachate samples and methane gas productions in laboratory scale simulated anaerobic reactors through the degradation of organic fraction of solid wastes collected from the kitchen of the Engineering Faculty in Dokuz Eylul University Campus. Furthermore, organic matter removal, water content, waste volume and quantity reduction were also investigated in laboratory scale simulated anaerobic reactors.

By the side of the leachate recirculation and recirculation volume, the other factors including waste shredding, compaction, aeration, alkalinity and sludge addition were investigated as the second objective of this study. Limited studies were performed to investigate the effect of waste compaction on the anaerobic treatment of MSW in simulated landfill bioreactor. Therefore, the effect of waste compaction on the reactor performance including organic fraction of solid wastes collected from the kitchen of the Engineering Faculty in Dokuz Eylul University Campus was determined.

Size reduction of solid waste affected the waste degradation and the leachate quality. At the third objective of this study, waste shredding was investigated from the point of view of solid waste degradation, leachate quality in terms of COD, NH_4-N, pH and VFA and methane gas productions in recycled laboratory scale simulated anaerobic reactors through the degradation of organic fraction of solid wastes.

Methane gas production and methane percentage have significant role in anaerobic treatment of solid waste. Methanogenic bacteria prefer optimum pH range of approximately 6.5 to 8.2. Therefore, alkalinity is very important parameter for methane gas production. Limited studies were performed to investigate the effect of alkalinity on the anaerobic treatment of the MSW in bioreactor. This study also reports the results of an examination of a landfill simulated anaerobic reactor treating MSW at varying $NaHCO_3$ alkalinity as the fourth scope of the study. The influences of bicarbonate alkalinity on leachate characteristics and on the degradation of MSW were investigated.

Recently, aerobic landfilling has become attractive method for disposal of solid waste due to rapid stabilization of the waste. But, there is no available data in the literature related to effect of aeration on the degradation of municipal solid waste, leachate quality and methane gas production in the anaerobic simulated bioreactor. The effects of aeration on the municipal solid waste degradation were determined as the fifth objective of this study. It was aimed to determine the COD removals, VFA accumulation, alkalinity and pH variations in the leachate samples and the methane gas productions and organic matter reduction of solid waste in recycled laboratory scale simulated anaerobic reactors through the degradation of organic fraction of solid wastes through different aeration regimes.

Sludge originated from wastewater treatment plants cause large scale pollution of land. Industrial and sewage sludge was mixed with MSW in anaerobic bioreactor in order to determine the co-digestion of sludge with MSW. The effect of sludge supplementation was investigated to the leachate quality and anaerobic reactor performance.

The other objective of this PhD dissertation is to investigate the inert COD, anaerobic toxicity (ATA), *Lumistox* toxicity and biochemical methane potential (BMP) levels of leachate samples originated from the organic fraction of MSW. Furthermore, a mass balance was performed for nitrogen (TN), total phosphorus (TP) and carbon contents of MSW and leachate samples in simulated anaerobic reactor.

As a conclusion, factors affecting the treatment efficiency of municipal solid wastes in simulated landfill bioreactors were investigated in the scope of this study. The characterization of leachate samples originated from the solid waste in simulated anaerobic landfilling bioreactor was performed. In other words, pH, COD, VFA, NH_4-N in leachate samples and water content, organic matter, carbon percent, quantity, TN, TP, ammonium of solid waste were monitored before and after stabilization period in simulated anaerobic reactor through stabilization of MSW taken from the kitchen of the Engineering Faculty in Dokuz Eylul University Campus.

CHAPTER TWO
MATERIALS AND METHODS

2.1 Used solid wastes

The reactors were loaded with a mixture of domestic waste collected from the solid waste produced in the kitchen of Engineering Faculty, Dokuz Eylül University during the PhD study. The characterization of the solid waste used in this study such as organic matter, water content and carbon percentage were given at the subsection "operating conditions" (See Tables 2.1., 2.2., 2.3., 2.4., 2.5., 2.7. and 2.9.).

2.2 Used lab-scale anaerobic simulated landfilling bioreactors

Initially, plexiglas bioreactors were constructed for treating the solid wastes. Methane measurements were carried out during the first 50 days and then the measurements were not carried out due to gas leaking from these reactors. Furthermore, these plexiglas bioreactors were not heated and operated under ambient conditions. After that, stainless-steel bioreactors were constructed and operations were carried out in these bioreactors.

2.2.1 Plexiglas anaerobic simulated landfilling bioreactors

To treat the municipal solid wastes, three plexiglas bioreactors were constructed. These bioreactors were designed in order to simulate the municipal solid waste landfill under controlled anaerobic conditions and were operated in batch mode. The schematic configuration of the reactor is shown in Figure 2.1. The reactors used in this work were cylindrical, 30cm in diameter and 100cm in height. The reactor has a removable and was hermetically sealed with a gasket and silicone sealant to maintain the anaerobic conditions. Several ports were provided on the top flange and on the sidewalls for withdrawing gaseous and liquid samples. There are two perforated plate, located on the top and on the bottom of the reactor. The leachate was collected in the bottom section of the solid waste reactor and was pumped to the top of the reactor with a peristaltic pump. There are four ports on the top of the reactor for addition of simulated rain water, measurements of the methane, total gas productions and methane percentage. No heating was realized in these bioreactors and operated under ambient conditions. The effects of leachate recirculation and recirculation volume on the degradation of MSWs were only investigated in these reactors.

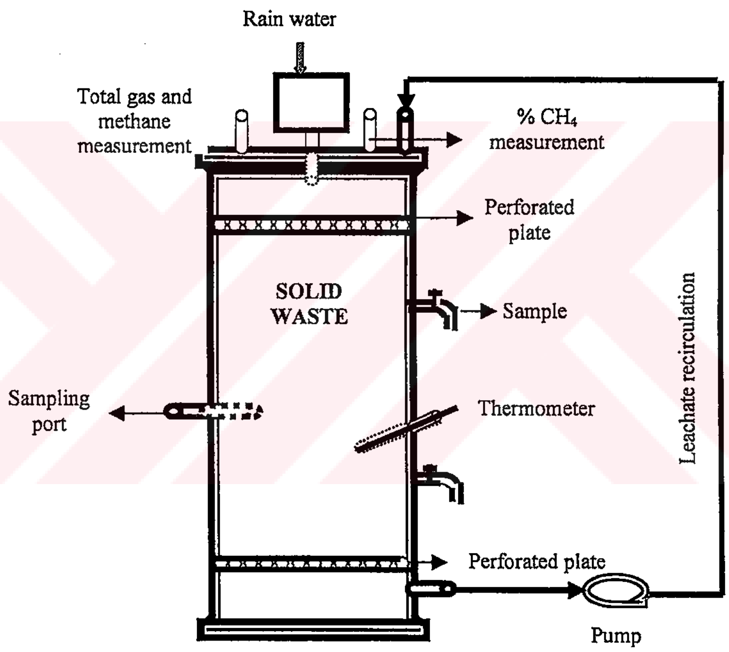

Figure 2.1 Schematic configuration of lab-scale simulated bioreactor (plexiglas)

2.2.2 Stainless-steel anaerobic simulated landfilling bioreactors

To treat the municipal solid wastes and to collect the methane gas, stainless-steel cylindrical bioreactors 10 cm diameter, and 30 cm high were constructed. The schematic configuration of these reactors is shown in Figure 2.2. These bioreactors were operated in batch mode at a temperature of 35-40 ^{0}C with an electronic digital heater under anaerobic conditions. The leachate was collected at the bottom section of the solid waste reactor and the effluent was recycled to the top of the reactor with a peristaltic pump. There are three separate ports on the top of the reactor for the addition of simulated rain water, measurement of the methane, total gas productions, percentage of methane and for recirculation of the leachate. A perforated aeration vessel was placed on the middle of the reactor for aeration the MSW.

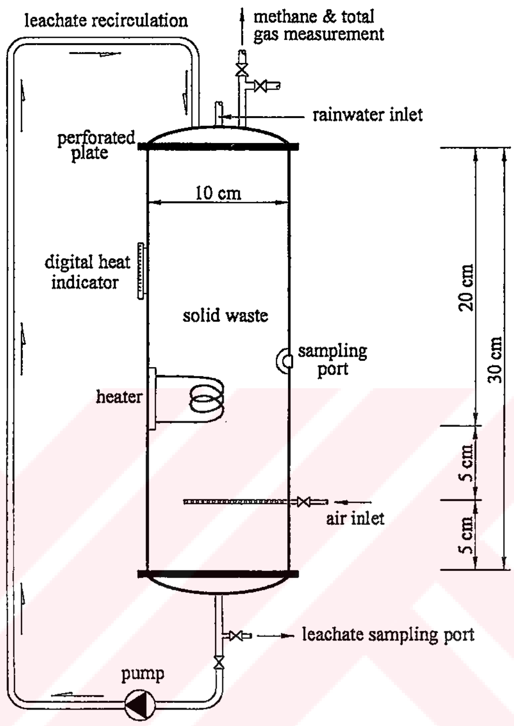

Figure 2.2 Schematic Configuration of Lab-Scale Simulated Bioreactor (stainless-steel)

2.3 Operating protocol for simulated anaerobic landfill bioreactors

2.3.1 Operating protocol to investigate the effects of leachate recirculation and recirculation volume

Table 2.1 shows the operating protocol and loading properties of the simulated anaerobic reactors. The reactors were loaded with a mixture of domestic waste collected from the solid waste produced in the kitchen of Engineering Faculty, Dokuz Eylül University, together with one liter of anaerobic sludge as seed. This solid waste contained approximately 75-95 % of organic waste, 2-6 % of paper and

1-2 % of plastics, glass and textiles. The water was added to the reactors by taking into consideration the seasonal meteorological conditions in order to simulate the rainfall. The first reactor was operated without recirculation (single pass reactor). The second reactor was operated with recirculation and the recirculation volume was 9l/day (Reactor9) which is 13 percent of the reactor volume. The third reactor was operated with recirculation and the recirculation volume was 21 l/day which is 30 percent of the reactor volume ($Reactor_{21}$). Organic matter and carbon percent were measured in dry solid (DS) for all steps of the study. Only this operation was carried out in plexiglas reactor.

Table 2.1 Reactor loading and operating protocol for simulated anaerobic landfilling bioreactors

	Single pass reactor	$Reactor_9$	$Reactor_{21}$
Loading date	April 25, 2002	April 30, 2002	May 7, 2002
Quantity of waste (kg)	26,5	29	24
Recirculation	without	with	with
Recir. volume (l/d)	-	9	21
Water content (%)	75	77	86
Organic matter	76	85	96
C (%)	42	47	53
Waste volume (l)	46	56	52
Operation time (day)	222	225	215

2.3.2 Operating protocol to investigate the effects of waste shredding and compaction

All the reactors were loaded with solid waste having different operational mode (see Table 2.2.). One reactor was operated with recirculation and was loaded with raw MSW (control), the second reactor was operated with recirculation and loaded with shredded waste and the third one was operated with recirculation and loaded with compacted wastes. Larger particles of the collected waste were broken down in size and the material was thoroughly mixed prior to loading the shredded reactor.

The MSW utilized in this reactor was shredded to a maximum of 1 cm in size. Since the previous study demonstrated that the leachate recirculation increased the leachate quality, 300 ml of leachate was recirculated daily with a peristaltic pump. The MSWs in the second reactor were compacted to a density of 583.3 kg/m^3 with a compression machine (ELE) in the Civil Engineering Laboratory held in Engineering Faculty campus. 100 ml of anaerobic sludge was added to the all reactors to straighten the growth of methanogen bacteria. The municipal solid wastes were collected from the kitchen of the Engineering Faculty in Dokuz Eylul University Campus. The solid waste contained approximately 95 % of organic waste, 6 % of paper and 2 % of plastics and textiles.

Table 2.2 Reactor loading and operating protocol for simulated anaerobic landfilling bioreactors

	Control reactor	Compacted reactor	Shredded reactor
Loading date	April 7, 2003	April 7, 2003	April 7, 2003
Quantity of waste (g)	1000	1400	1000
Used MSW	raw	compacted	shredded (0.5-1cm)
Recirculation	yes	yes	yes
Water content (%)	85	85	85
Organic matter (%)	91	91	91
Carbon (%)	50.5	50.5	50.5
Recirculation volume (ml/day)	300	300	300
Waste density (kg/m^3)	416.7	583.3	416.7
Operation time (day)	57	57	57

2.3.3 Operating protocol to investigate the effects of alkalinity

All the reactors were loaded with solid waste having different operational mode. The first reactor was operated with leachate recirculation (control-no alkalinity addition), the second reactor was operated with recirculation 3g/l $NaHCO_3$ alkalinity was added and the third was operated with leachate recirculation and 6g/l $NaHCO_3$ alkalinity was added. 50 ml of anaerobic sludge was added to the all reactors and mixed in order to provide the methanogenic conditions. Approximately 20 ml of $NaHCO_3$ was added on the top of the reactors, daily. Table 2.3. shows the operating protocol for the all reactors. The municipal solid wastes collected from the kitchen of the Engineering Faculty in Dokuz Eylul University Campus and contained approximately 96 % of organic waste, 3 % of paper and 1 % of textiles.

Table 2.3 Reactor loading and operating protocol for simulated anaerobic landfilling bioreactors

	Control reactor	3 g/l alkalinity added reactor	6 g/l alkalinity added reactor
Loading date	June 2, 2003	June 2, 2003	June 2, 2003
Quantity of waste (g)	1000	1000	1000
Recirculation	yes	yes	yes
Recirculation volume(ml/day)	300	300	300
Water content (%)	90	90	90
Org. Matter (%)	97	97	97
% C	54	54	54
Alkalinity addition ($NaHCO_3$)	no	3 g/l	6 g/l
Operation time (day)	65	65	65

2.3.4 Operating protocol to investigate the effects of aeration

All the reactors were loaded with solid waste having different operational mode. The first reactor was operated with recirculation (control-no aeration). The second reactor was aerated three days in a week during one hour (Run 1) and the last reactor was aerated one day in a week during one hour (Run 2). Table 2.4 shows the operating protocol for the all reactors. The municipal solid wastes collected from the kitchen of the Engineering Faculty in Dokuz Eylul University Campus. Composition of the waste consisted of approximately 92 % of organic waste, 5 % of paper and 3 % of plastics and textiles.

Table 2.4 Reactor loading and operating protocol for simulated anaerobic landfilling bioreactors

	Control reactor	Run 1	Run 2
Loading date	August 12, 2003	August 12, 2003	August 12, 2003
Quantity of waste (g)	1000	1000	1000
Recirculation	yes	yes	yes
Recirculation volume (ml/day)	300	300	300
Water content (%)	90	90	90
Org. Matter (%)	93	93	93
% C	51.66	51.66	51.66
Aeration frequency	No aeration	3 days in a week	1 day in a week
Aeration flowrate (m^3/min)	-	0.02	0.02
Operation time (day)	79	79	79

2.3.5 Operating protocol to investigate the effects of co-digestion of OFMSW and industrial sludge 1

All the reactors were loaded with solid waste having different operational mode. The first reactor (Control reactor) was operated with leachate recirculation (control-no industrial sludge addition); the second reactor (Run 1) was operated with recirculation and was conducted as a co-fermentation of the mixture of industrial sludge and organic fraction of municipal solid waste (OFMSW). The weight ratio of the OFMSW to industrial sludge was 1:1 (dry solid basis). The third reactor (Run 2) was operated with recirculation and was conducted as a co-fermentation of the mixture of industrial sludge and organic fraction of municipal solid waste (OFMSW). The weight ratio of the OFMSW to industrial sludge was 1:2 (dry solid basis). 50 ml of anaerobic sludge was added to the all reactors and mixed in order to provide the methanogenic conditions. Table 2.5 shows the operating protocol for the all reactors. In addition, characteristics of the industrial sludge were shown in Table 2.6 before co-disposal of solid waste. Heavy metals and AOX values are in acceptable levels according to Turkish Hazardous Waste Control Regulations given in Appendix 11A (Official gazette, 1995). The municipal solid wastes collected from the kitchen of the Engineering Faculty in Dokuz Eylul University Campus. The industrial sludge was taken from the belt filtering system of the DYO dye industry.

Table 2.5 Reactor loading and operating protocol for simulated anaerobic landfilling bioreactors

	Control reactor	Run 1	Run 2
Loading date	November 17, 2003	November 17, 2003	November 17, 2003
Quantity of waste (g)	1200	1200	1200
Weight ratio (OFMSW to industrial sludge)	No industrial sludge addition	1:1	1:2
Recirculation	with	with	with
Recirculation volume (ml/day)	300	300	300
Water content (%)	87	67	56
Organic matter	97	88	80
C (%)	54	49	44
Operation time (day)	98	98	98

Table 2.6 Characteristics of industrial sludge

Characteristics	Measured value	Characteristics	Measured value
Water content (%)	43	Cr (mg/l)	0.16
Organic matter (%)	73	Zn (mg/l)	0.58
C (%)	41	Cu (mg/l)	0.02
Total nitrogen (mg/l)	1000	Pb (mg/l)	0.01
Total phosphorus (mg/l)	400	Fe (mg/l)	0.8
Ammonium nitrogen(mg/l)	80	Mn (mg/l)	0.2
AOX (µg/l)	972	Ni (mg/l)	-
Sulfate (mg/kg wet waste)	450	Cd (mg/l)	-

2.3.6 Operating protocol to investigate the effects of co-digestion of OFMSW and industrial sludge 2

All the reactors were loaded with solid waste having different operational mode. The first reactor (Control reactor) was operated with leachate recirculation (control-no industrial sludge addition); the second reactor (Run 1) was operated with recirculation and was conducted as a co-fermentation of the mixture of industrial sludge and organic fraction of municipal solid waste (OFMSW). The weight ratio of the OFMSW to industrial sludge was 1:1 (dry solid basis). The third reactor (Run 2) was operated with recirculation and was conducted as a co-fermentation of the mixture of industrial sludge and organic fraction of municipal solid waste (OFMSW). The weight ratio of the OFMSW to industrial sludge was 1:2 (dry solid basis). 50 ml of anaerobic sludge was added to the all reactors and mixed in order to provide the methanogenic conditions. Table 2.7 shows the operating protocol for the all reactors. In addition, characteristics of the industrial sludge were shown in Table 2.8 before co-disposal of solid waste. Heavy metals and AOX values are in acceptable levels according to Turkish Hazardous Waste Control Regulations given in Appendix 11A (Official gazette, 1995). The municipal solid wastes collected from the kitchen of the Engineering Faculty in Dokuz Eylul University Campus. The industrial sludge was taken from the belt filtering system of the mixed sludge originated from textile, metal plating, electronic, chemistry and plastic industry at the Manisa Industrial Organized District.

Table 2.7 Reactor loading and operating protocol for simulated anaerobic landfilling bioreactors

	Control reactor	Run 1	Run 2
Loading date	May 3, 2004	May 3, 2004	May 3, 2004
Quantity of waste (g)	1200	1200	1200
Weight ratio (OFMSW to industrial sludge)	No mixed industrial sludge addition	1:1	1:2
Recirculation	with	with	with
Recirculation volume (ml/day)	300	300	300
Water content (%)	90	82	68
Organic matter	95	87	79
C (%)	52.8	48.3	43.9
Operation time (day)	30	30	30

Table 2.8 Characteristics of mixed industrial sludge

Characteristics	Measured value	Characteristics	Measured value
Water content (%)	67	Cr (mg/l)	0.05
Organic matter (%)	70	Zn (mg/l)	0.44
C (%)	38.8	Cu (mg/l)	0.14
Total nitrogen (mg/l)	1085	Pb (mg/l)	0.062
Total phosphorus (mg/l)	490	Fe (mg/l)	10.36
Ammonium nitrogen(mg/l)	69	Mn (mg/l)	0.3
AOX (µg/l)	1265	Ni (mg/l)	0.03
Sulfate (mg/kg wet waste)	885	Cd (mg/l)	0.02

2.3.7 Operating protocol to investigate the effects of co-digestion of OFMSW and sewage sludge

All the reactors were loaded with solid waste having different operational mode. The first reactor (Control reactor) was operated with leachate recirculation (control-no sewage sludge addition); the second reactor (Run 1) was operated with recirculation and was conducted as a co-fermentation of the mixture of sewage sludge and organic fraction of municipal solid waste (OFMSW). The weight ratio of the OFMSW to sewage sludge was 3:1 (dry solid basis). The third reactor (Run 2) was operated with recirculation and was conducted as a co-fermentation of the mixture of sewage sludge and OFMSW. The weight ratio of the OFMSW to sewage sludge was 1:3 (dry solid basis). 50 ml of anaerobic sludge was added to the all reactors and mixed in order to provide the methanogenic conditions. Table 2.7 shows the operating protocol for the all reactors. The municipal solid wastes collected from the kitchen of the Engineering Faculty in Dokuz Eylul University Campus. The sewage sludge was taken from the belt filtering system of the Çiğli Municipal Wastewater Treatment Facility.

Table 2.9 Reactor loading and operating protocol for simulated anaerobic landfilling bioreactors

	Control reactor	Run 1	Run 2
Loading date	March 2, 2004	March 2, 2004	March 2, 2004
Quantity of waste (g)	1000	1000	1000
Weight ratio (OFMSW to industrial sludge)	No sewage sludge addition	3:1	1:3
Recirculation	with	with	with
Recirculation volume (ml/day)	300	300	300
Water content (%)	90	88	87
Organic matter	93	92	80
C (%)	52	51	44
Operation time (day)	61	61	61

2.4 Analytical Procedures

2.4.1 Gas measurements

Gas productions were measured with liquid displacement method. Total gas was measured by passing it through a liquid containing 2% (v/v) H_2SO_4 and 10% (w/v) NaCl (Beydilli et al., 1998). Methane gas was detected by using a liquid containing 3% NaOH to scrub out the carbon dioxide from the biogas (Razo-Flores et al., 1997). The methane percentage in biogas was also determined by Dräger Pac®Ex methane gas analyzer.

2.4.2 Chemical oxygen demand (COD)

The soluble COD was measured colorimetrically by using closed reflux methods (APHA AWWA. 1992). First the samples were centrifuged for 10 min at 7000 rpm. Secondly, 2.5 ml volume samples were treated with 1.5 ml 10216 mg/l $K_2Cr_2O_7$, 33.3 g/l $HgSO_4$ and 3.5 ml 18 M H_2SO_4 which contains 0.55% (w/w) Ag_2SO_4. Thirdly the closed sample tubes were stored in a 148°C heater for two hours. Finally, after cooling the samples were measured at 600 nm with the Pharmacia LKB-NovaPec II spectrophotometer.

2.4.3 Inert COD

The effluent soluble COD (S_T) of a biological rector includes apart from the remaining portion of the readily biodegradable influent COD (S_S), initially inert COD, (S_I), that by passes the treatment system without any change, and COD associated with inert soluble microbial products (S_P) as illustrated below;

$$S_T = S_S + S_I + S_P \qquad (2.1.)$$

Inert COD content of the leachate was determined with glucose comparison method developed previously by Germirli et al. (1990) in all soluble form COD. In this method, two batch reactor were operated in parallel and started with the same initial COD, one being fed with the soluble part of the wastewater to be tested, and the other with glucose. The soluble COD in each reactor was measured periodically until a plateau value was reached, at which point the biodegradable substrate was almost entirely depleted (variations in COD within ± 5% were taken as an indication that the minimum COD was attained). This final residual COD, S_R, was assumed to be equal to sum of S_I and S_P. The COD of the reactor fed on the glucose reached a lower value, which was taken to represent S_P alone, as glucose itself would have contained no inert organic material. The S_I content of the wastewater was calculated from the equation 2.8 with assumption that $(S_P)_{wastewater} \cong (S_P)_{glucose}$;

$$S_I = (S_R)_{wastewater} - (S_P)_{glucose} \tag{2.2}$$

2.4.4 Biochemical oxygen demand (BOD $_5$), total organic carbon (TOC), adsorbable organic halogens (AOX), ammonium nitogen (NH_4-N), nitrate nitrogen (NO_3-N), total nitrogen (TN) and total phosphoru (TP)

BOD_5 was measured using the WTW Oxi Top IS 12 system. TOC was determined with DOHRMANN DC-190 Model High-Temperature TOC analyzer. AOX was measured using Heraous AOX-MT200 analyzer. Ammonium and nitrate nitrogen were quantified using specific chemical analysis kits (Merck-Spectroquant), and spectrometric methods were used for analysis.

Total Phosphate was measured using Cell Tests numbered 14543 and Total Nitrate was measured Cell Test numbered 14537 in a photometer SQ 300 Merck. Ammonia-nitrogen was measured using spectroquant kits numbered 14752. Nitrate nitrogen was measured using Cell Test numbered 14773 in a photometer SQ 300 Merck.

2.4.5 Total alkalinity (T.Alk), bicarbonate alkalinity (B.Alk.), and volatile fatty acid (VFA)

Total alkalinity of samples was determined by titration a sample with 0.1 N of standard sulphuric acid solution to a pH of 4.3. Bicarbonate alkalinity (B.Alk.) and total volatile fatty acid (VFA) concentrations were measured simultaneously according to titrimetric method proposed by Anderson &Yang, (1992). The test was carried out as follows: the pH of the sample was measured, the sample was titrated with standard sulphuric acid (0.1 N) through two stages (first to pH 5.1, then from 5.1 to 3.5), and the VFA and B.Alk concentrations were calculated with a computer program solving the equations 2.9 and 2.10.

$$A1 = \frac{[HCO_3^-] * ([H]_2 - [H]_1)}{[H]_1 + K_C} + \frac{[VA] * ([H]_2 - [H]_1)}{[H]_2 + K_{VA}} \tag{2.3}$$

$$A2 = \frac{[HCO_3^-] * ([H]_3 - [H]_1)}{[H]_3 + K_C} + \frac{[VA] * ([H]_3 - [H]_1)}{[H]_3 + K_{VA}} \tag{2.4}$$

where; A1 and A2 are the molar equivalent of the standard acid consumed to the firs and second endpoints; $[HCO_3^-]$ is the bicarbonate concentration; [VA] is the volatile fatty acid ion concentration; $[H]_{1,2,3}$ are the hydrogen ion concentrations of the original sample and at the first and the second endpoints; K_C is a conditional dissociation constant of carbonic acid; and K_{VA} is a combined dissociation constant of the volatile fatty acids (C_2 to C_6), it was assumed that this pair of constants, being 6.6×10^{-7} for bicarbonate and 2.4×10^{-5} for volatile acids.

2.4.6 pH

The pH was determined immediately after sampling to avoid any change due to CO_2 evolution, using a pH meter, type NEL pH 890.

2.4.7 Anaerobic toxicity assay (ATA)

ATA test was performed at 37°C using serum bottles with a capacity of 115 ml as described by Owen et al. (1979) and Donlon et al. (1995). Serum bottles were filled with stock solutions to give suitable Vanderbilt mineral medium, 3000 mg /l of glucose-COD, 667 mg /l of sodiumthioglycollate to provide the reductive conditions. Furthermore, 5000 mg /l of $NaHCO_3$ was used for maintaining the neutral pH. 4000 mg MLSS /l was used to provide the anaerobic microorganisms enriched in an anaerobic treatment plant of yeast industry. The glucose COD in the serum bottles was stoichiometrically replenished to 3000 mg /l with a stock solution after 3 days of exposure to leachate containing synthetic wastewater. The glucose COD level of 3000 mg /l ensured the presence of non-limiting substrate conditions in the serum bottles. Duplicate controls were performed on the assay containing no leachate. Methane production of each assay bottle was determined during subsequent 6 h of incubation period.

2.4.8 Biochemical Methane Potential (BMP)

BMP is a measure of sample biodegradability (Owen et al., 1979). The procedure for implementing the BMP assays involves placing an aliquot of the effluent sample, normally 50 ml, in a 125 ml serum bottle with an anaerobic inoculum. BMP test was performed at 37°C using serum bottles with a capacity of 115 ml as described by Owen et al. (1979) and Donlon et al. (1995). Serum bottles were filled with stock solutions to give suitable Vanderbilt mineral medium, 667 mg /l of sodiumthioglycollate to provide the reductive conditions. Furthermore, 5000 mg /l of $NaHCO_3$ was used for maintaining the neutral pH. 4000 mg MLSS /l was used to provide the anaerobic microorganisms enriched in an anaerobic treatment plant of yeast industry. Leachate samples were anaerobically added to the 115 ml serum bottles before the transfer of inoculated defined media duplicates were prepared for all samples. Duplicate controls were performed on the assay containing no leachate (only inoculum). BMP test were performed during 30-60 days. Methane production of each assay bottle was measured during of incubation period. BMP was obtained by subtracting the quantity of methane of the leachate sample from the quantity of methane of the control.

2.4.9 LUMIStox toxicity assay

Toxicity to the bioluminescent organism *Vibrio fischeri* was assayed using the LUMIStox measuring system according to DIN 38412 L34, L341, (1993). LUMISmini type photometer (Dr. LANGE Campany) was used for the lumistox assay. All samples were serially diluted in 2% NaCl (w/v), and each assay was performed at pH 7.0 and a temperature of 15°C. Sodium chloride (2%) was used as the control. Inhibition percentage (H %) values refer to decreasing activity in samples causing inhibitory effect of a test substances and/or a toxic wastewater during the light emission. The evaluation of inhibition is as follows:

Inhibition percent (H)	Result
$0<H<5$	non toxic
$5<H<20$	possibly toxic
$20<H<90$	toxic

2.4.10 Water content, organic matter and carbon percent

Organic matter and water content in municipal waste samples was measured using the Standard Methods. Carbon percent was calculated with equation 2.5 (Sorgun, 1987).

$$\% C = (100 - \% \text{ ash})/1.8 \qquad (2.5)$$

2.4.11 Sulfate and heavy metal concentrations

Initially, sludge sample was dried and grinded for preparation of eluate. 500 ml of distilled water was added on the 50 g of dried sludge. This mixture was stirring during 24 hours at room temperature. Prepared sludge sample was filtered with filter paper (ref. no 300211) twice. Filtered sample (eluate) was enrolled (APPA AWWA, 1992).

50 ml of eluate was adjusted at pH 2 with HCl for sulfate calculation. It was heated until boiling point and 5 ml of $BaCl_2$ was added. Sample was filtered with filter paper (ref. no 300211) after 30 minutes. Filter was treated with $AgNO_3$ until colorless. And then it was burned at 800 ^0C during one hour and sulfate concentration was calculated according to Standar Methods (APPA AWWA, 1992).

One ml of concentrated HNO_3 was added to 100 ml of sample for determination of heavy metal concentrations. It was filtered with filter paper (ref no 300211) after 2 hours. Heavy metal concentrations were determined using ATI UNICAM 929 Atomic Adsorption Spectrophotometer. Heavy metals were determined after they converted to ion condition and adsorbed with cathode lamb (APPA AWWA, 1992).

2.4.12 Statistical Analysis

The statistical analysis between x and y variables was carried out using Microsoft Excel program

CHAPTER THREE

RESULTS AND DISCUSSION

3.1 Effects of Leachate Recirculation and Recirculation Volume on the Degradation of MSWs

3.1.1 COD variations in leachate produced from the simulated anaerobic solid waste bioreactors

The variations in COD concentrations of the leachates collected at the bottom of the simulated anaerobic reactors are given in Figure 3.1. Due to rapid release and hydrolysis of organics from the municipal solid wastes into the leachate, the COD concentrations in the Reactor9 (recirculation rate = 9 l/day) and Reactor21 (recirculation rate = 21 l/day) increased to 80000 and 85000 mg/l from 45000 and 38000 mg/l, respectively, through first 50 days. The initial COD concentration in the leachate samples from the single pass reactor was very high and subsequently increased progressively within 125 days to about 90000 mg/l. The highest COD in this reactor was about 104000 mg/l on day 126. Onwards, the COD concentrations of single pass reactor started to decrease by day 222, and reached 48 000 mg/l. The decomposition process in Reactor9 and Reactor21 continued through days 56 and 90 as a result of different leachate recirculation rates applied. The increase in leachate recirculation rate in Reactor21 affected negatively the COD concentrations. Suitable recirculation rate like 9 liter per day resulted in faster decomposition of the solid waste Reactor9. This result is in accordance with the progression of microbial-mediated stabilization process with the study performed by Chugh et al. (1998). Since no water was added during the dry season (in summer), the COD concentrations in the Reactor$_9$ increased to about 72000 mg/l similar to the data reported by Iglesias et al. (2000). The COD value in Reactor $_{21}$ reached approximately 90000 mg/l during the dry season after 125 days of operation period, then it started to decrease and it was measured to be 52000 mg/l on day 215. Since this reactor was operated at a high leachate recirculation rate, this caused increases in COD concentrations of leachate.

The COD concentrations were 47000, 39000 and 52000 mg/l, respectively; in single pass reactor and Reactors$_9$ and $_{21}$ at the end of 220 days of anaerobic incubation period. The reason for high COD value in Reactor$_{21}$ may be the ensiling problem because of VFA accumulation at high leachate recirculation rate. These results showed that, high leachate recirculation rates have a negative effect on COD removal from the leachate. However, it is important to note that the leachate recirculation rates affected, significantly, the degradation of solid wastes.

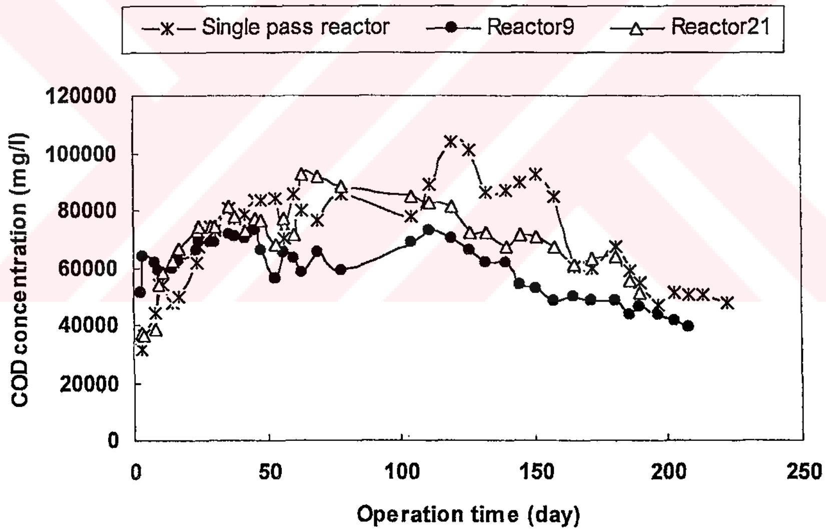

Figure 3.1 COD Variations in single pass reactor, Reactor$_9$ and Reactor$_{21}$

The COD concentrations measured in this study exhibit similar data to the findings of Reinhart & Al-Yousfi (1996). They reported that COD values in single pass landfilling is high (71000 mg/l) compared to recycled reactors (34000 and 54000 mg/l) after 300 days of operation. In another study carried out by Bae et al. (1998) it was shown that, the COD values increased progressively and a long time was needed for the COD concentrations to decrease in a lysimeter operated with no-leachate recirculation. San & Onay (2001) showed that the COD level increased to about 65000 mg/l until day 90, and than started to decrease to about 300000 mg/l in a reactor operated without leachate recirculation. The study realized by Iglesias et al. (2000) showed that the COD concentrations started to decrease after day 150, in a reactor without recycling.

According to some recent studies, different suggestions were reported about the COD decrease in leachates. Chugh et al. (1998) demonstrated that decreases in COD starts within 15 days in a recirculated solid waste reactor, However, Bae et al. (1998) showed that COD decreases start after about 100 days through anaerobic incubation. Similarly, Iglesias et al. (2000) reported that the COD values decreased after about 215 days. In the study carried out by San & Onay (2001), COD value started to decrease by day 125 in a recirculated reactor and is lower than the single-pass reactor operated with similar reactor configurations to our study.

3.1.2 VFA variations in leachate produced from the simulated anaerobic solid waste bioreactors

The concentration of volatile fatty acids in the leachates of all reactors have similar properties with the COD concentrations since the organic fraction of the municipal solid wastes hydrolyzed to intermediate organics and volatile fatty acids. A high linear correlation between COD removal efficiency and VFA removal efficiency was observed (R^2= 0.83). As seen in Figure 3.2, the initial VFA concentration in single pass reactor was approximately 10000 mg/l. However, it subsequently increased to about 30000 mg/l until day 52. High VFA concentrations in leachate showed that this reactor remained predominantly in the acidic phase. Already, there was high linear correlation between maximum VFA and minimum pH values (R^2= 0.93). However, this result does not show that the methanogens were completely absent in the solid wastes and in the leachate since the methane percentages of produced gas were monitored as 10 and 25% (See figures 3.5 and 3.6). The methanogen bacteria produced methane from the easily and slowly degradable organics while the acidogens formed volatile fatty acids from the organic matters in the solid wastes. On the other hand, the other source of methane could be attributed to methane production by hydrogen consuming bacteria which is produced from the complex organics and amino acids when volatile fatty acid is accumulated in the anaerobic reactor (McCarty, 1964). After day 52, the VFA concentrations in single pass reactor started to decrease and reached about 15000 mg/l by day 222. These data exhibit similar results to those obtained by Iglesias et al. (2000) and Reinhart & Al-Yousfi (1996), in which the COD concentration measured in the leachate exhibit similar data indicating the competition between acid and methane formation phases.

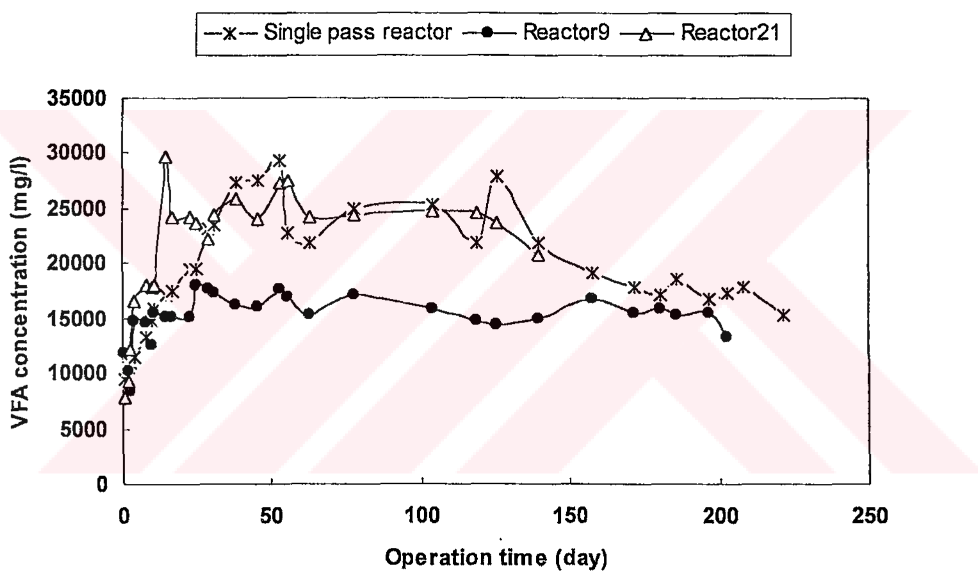

Figure 3.2 The VFA variations in single pass, $Reactor_9$ and $Reactor_{21}$

As shown in Figure 3.2, the initial VFA concentration in $Reactor_9$ was approximately 12000 mg/l. Afterwards, it decreased to 8400 mg/l, and then slowly increased to18000 mg/l. Despite low VFA concentrations at the beginning of the anaerobic operation in $Reactor_9$, it was observed that the VFA values in the leachate samples of the single pass reactor (VFA=15 000 mg/l) were higher than that of $Reactor_9$ (VFA=13000 mg/l) at the end of 220 days of anaerobic incubation period.

As can be seen in Figure 3.2, after 30 days of operation period the VFA concentrations in Reactor $_{21}$ increased rapidly and reached 30000 mg/l and varied between 24000 and 31000 mg/l indicating the ensiling problem. This originated from the imbalance between acidogenesis and methanogenesis in the landfill leachate as reported by O'Keefe & Chynoweth (2000). The last VFA value measured at the end of incubation period in Reactor $_{21}$ was 20000 mg/l. This value was higher than the leachate samples obtained from the single pass reactor and Reactor$_9$. These data showed the high recirculation rate results with VFA accumulation, resulting in low pH and alkalinity values. If the VFA/B.Alk. ratio is lower than 0.4 the anaerobic reactor is stable (Behling et al., 1997). But, Griffin et al. (1998) reported that if the VFA/B.Alk. ratio is approximately 1, the solid waste reactor is stable.

3.1.3 pH variations in leachate produced from the simulated anaerobic solid waste bio reactors

The pH values measured in the leachate samples are in accordance with the concentration of VFA monitored in all three reactors. Figure 3.3 shows the trends of pH in leachate samples for all reactors. The initial pH in the leachate from the single pass reactor was 5.75. However, the pH values decreased sharply to about 5.35 until day 40. After this day, the pH value increased slowly. The pH measured on day 222 was about 5.9 in the single pass reactor. This value of pH is not suitable for the growth of methanogenic bacteria and methanogenesis. The methane monitored in this reactor probably originated from the balance between VFA produced and consumed since the VFA released through the degradation of complex or simple organic solids converted to acetate and hydrogen, which they ultimately converted to methane through this process (Speece, 1996). Low pH values observed in this reactor could be attributed to the production of low alkalinity, which is not enough for maintaining the neutral pH and buffering the VFA produced (Speece, 1996). Recent studies have shown that methanogenesis is favored at a pH between 6.4 and 7.2 (Chugh et al. 1998). Similar to our results, Warith (2002) and San & Onay (2001) reported that the pH value of single-pass reactors is lower than the recirculated reactors. The measured pH was 5.5 on 250 days, which is not very suitable for methanogenic conditions.

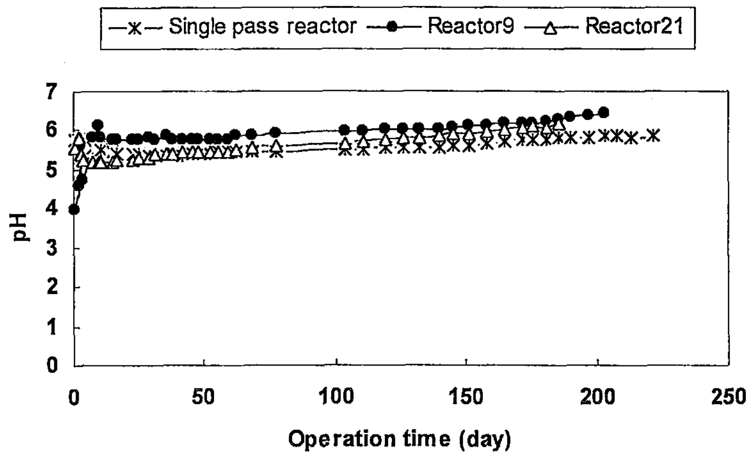

Figure 3.3 pH variations in single pass and recycled Reactors $_9$ and Reactor$_{21}$

The initial pH in the leachate samples from Reactor$_9$ is approximately 3.9. Although the initial pH value in Reactor$_9$ was significantly lower than that of single pass reactor, the pH in Reactor$_9$ increased to approximately 6.5 respectively at the end of the study. The study done by San & Onay (2001) exhibited similar results to our study, in which the pH value of recycled reactor was higher than single pass reactor by day 225. The initial pH in the leachate samples from Reactor$_{21}$ was approximately 5.56. It was observed that the rate of increase of pH in this reactor was faster than single pass reactor. Although an ensiling problem was observed in Reactor$_{21}$, the pH started to increase by day 65 and the last pH measured in this reactor was 6.16. The results showed that the pH levels in recirculated reactor were higher than the single pass reactor while the rate of increase of pH in Reactor$_{21}$ was found to be slower than Reactor$_9$.

The rapid increase in pH, even with high COD and VFA concentrations during the anaerobic incubation may be attributed to the production of NH_4-N (800-1000 mg/l) from the degradation of nitrogenous organic compounds from the food wastes (San & Onay, 2001). In this study the pH values suddenly increased above 6.0 on day 78, although no changes were found in single pass reactor. This sudden increase of pH in recycled reactors might result from the rapid utilization of VFA as mentioned in previous section.

One interesting point associated with pH is that methane production rate in recycled reactors reached its maximum level when the leachate pH was lower than 6. This might indicate that the number of methanogens in partially granulated sludge seeding rather than pH could be a limiting factor for methane production from solid wastes, although the number of methanogens was not enumerated (Bae et al. 1998).

3.1.4 Ammonium-nitrogen variations in leachate produced from the simulated anaerobic solid waste bioreactors

The initial concentrations of ammonium-nitrogen in both reactors were found to be different, indicating the heterogeneity in ammonium-nitrogen content in all reactors, although the anaerobic reactors were loaded with the same mixture of municipal solid wastes. Figure 3.4 shows the trends in ammonium concentration in leachate produced from the single pass Reactor, $Reactors_9$ and $Reactor_{21}$.

The ammonium-nitrogen was found at high concentrations in the municipal solid waste as a result of decomposition of organic matter containing nitrogen such as protein and amino acids. As a result of degradation of these nitrogenous organics the ammonium-nitrogen concentrations increased from 330, 890 and 1080 mg /l to a maximum of 1920, 1924 and 1850 mg/l, respectively, in the recycled reactors ($Reactor_9$ and $Reactor_{21}$.) and single pass reactor by day 120. The recirculation practice in the recycled reactors reintroduced ammonia to the system keeping its value as high as 1900 mg/l through days 124 and 136. Therefore, ammonia nitrogen concentration behavior was attributed directly to the leachate recirculation management strategy recirculated within the reactor providing an increased opportunity for accumulation and/or removal through biological nitrogen assimilation as reported by San & Onay (2001) and McCarthy (1964). After day 120, the ammonium concentration started to decrease, since the ammonia was consumed by the anaerobic bacteria to develop their cellular components (Öztürk, 1991).

Ammonia concentrations in the single pass reactors displayed evidence of washout, although the concentrations were maintained above 500 mg/l during the experimental period, indicating its availability for establishing a viable microbial population. These results agree with the findings of Chan et al. (2002), in which the ammonium concentration varied between 1000-1200 mg/l after 250 days of operation in landfill reactor operated without recycle.

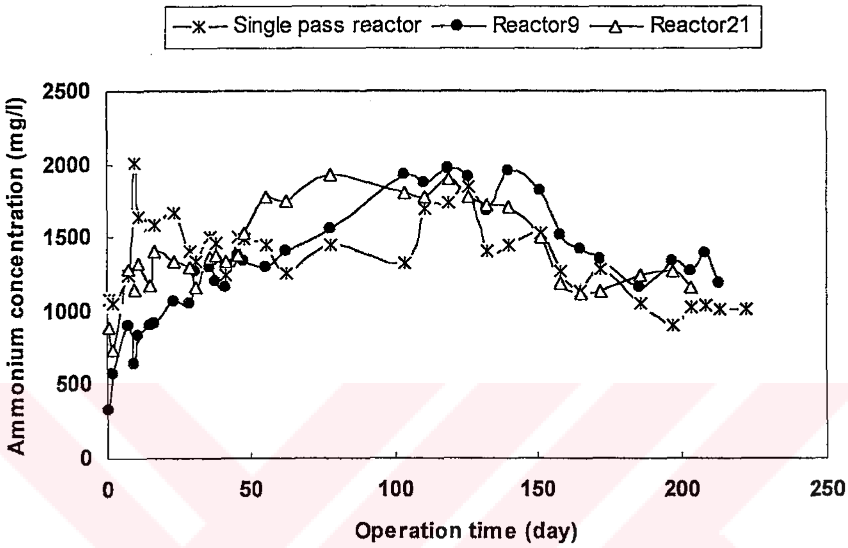

Figure 3.4 The ammonium variation in single pass, $Reactor_9$ and $Reactor_{21}$

In landfills, the release of soluble nitrogen from MSW into landfill leachate continues over a long period compared to that of soluble carbon compounds. Jokela et al. (2002) reported that this was the main source of nitrogenic proteins, which accounts for approximately 0.5 % of dry weight of MSW. Landfill leachate treatment is normally focused on the removal of organic matter and ammonia-nitrogen levels, which are quite important for possible inhibition of methane production under anaerobic conditions and the leachate toxicity is significantly correlated with COD and ammonia in untreated and treated leachate, as reported by Marttinen et al. (2002). In this study, high ammonium concentration may cause partial inhibition in anaerobic methanogenic bacteria in all three reactors since high COD and VFA concentrations were accompanied by accumulation of high concentrations of ammonia-nitrogen as reported by İnanç (2000) and Speece (1996).

3.1.5 Methane gas productions and methane percentages in simulated anaerobic solid waste bioreactors

The cumulative methane gas productions for single pass reactor and recycled reactors are given in Figures 3.5, 3.6, and 3.7, respectively. Methane measurements were carried out during the first 50 days since the measurements were not carried out due to gas leaking from the single-pass and recycled reactors. The overall volume of methane gas produced was much larger in the recycled reactors than the single pass reactor.

The increase in leachate recirculation rate from 9 to 21 l affected the methane gas production. An increase to three times of the recirculation volume caused decreases in cumulative methane gas productions. Based on these data, it was assumed that acidic conditions occurred in recycled $Reactor_{21}$ slowing down the activity of methanogens by decreasing the methane productions from 10.4-63.82 to 9.24-37.36 l on days 5 and 50, respectively, compared to $Reactor_9$. On day 34, the cumulative methane gas productions in recycled Reactors $_9$ and $_{21}$ was one and a half time greater than that from the single pass reactor (See Figures 3.5-3.7). Increases in leachate recirculation rate in reactor $_9$ had proven to impact directly on the gas generation potential since an optimum increase in leachate recirculation rate had a positive effect on the methanogenic population, enhancing their growth and compared to single pass reactor. Increased gas production was directly related to the higher degree of stabilization in the recycled reactors and may be attributed to the leachate recirculation strategy employed.

The methane percentage was approximately 10-25 % in the single pass reactor while the percentage of methane measured in $Reactor_9$ was between 40 and 60%, on days 28 (See Figures 5 and 6). From these results it can be concluded that the leachate recycle appeared to be somewhat beneficial in maintaining high methane composition. The propagation of methane producing bacteria was promoted with the leachate recycle and this promotion was further enhanced by adjusting the leachate recirculation rate.

Gas production rate of single pass and recycled reactors showed a relatively small peak around days 11 and 13, respectively. These small peaks may be related to the fermentation of easily biodegradable organics in solid wastes.

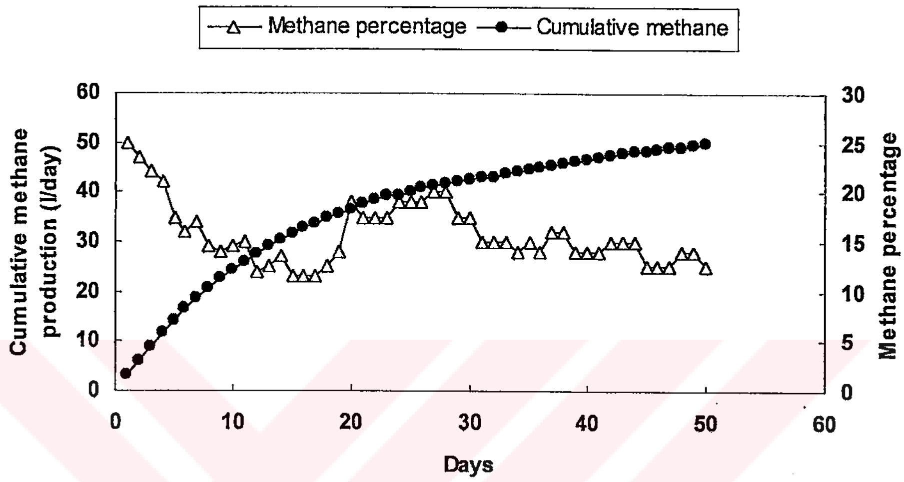

Figure 3.5 Quantity of methane and methane percentage in single pass reactor

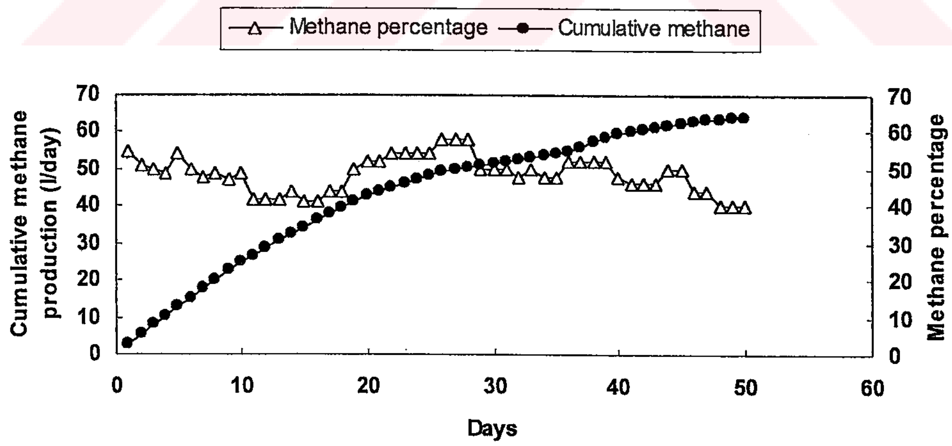

Figure 3.6 Quantity of methane and methane percentage in for Reactor$_9$

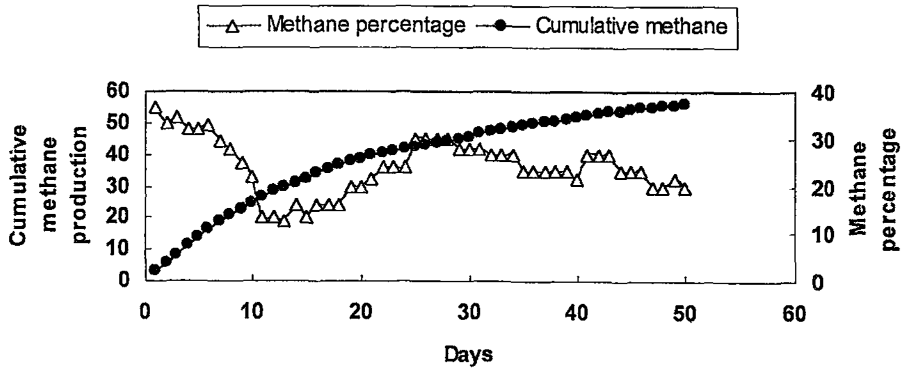

Figure 3.7 Quantity of methane and methane percentage in Reactor$_{21}$

The low methane production in Reactor$_{21}$ compared to Reactor$_9$ was considered to be another proof of washout, indicating the mobility of the system to develop an active methanogenic population and enhance the waste stabilization. Similarly, Reinhart & Al-Yousfi (1996) reported that leachate recirculation showed a 12-fold increase of gas production in the recirculating cell compared to conventional cell reactor. A high leachate recirculation rate has a positive effect when compared with non-recirculating reactors.

3.1.6 Variation of waste volume, carbon and organic matter in anaerobic solid waste bioreactors

Table 3.1 shows the treatment efficiencies of the reactors used in this study for treating solid food wastes. As can be seen, recycled Reactor$_9$ is the best reactor in terms of decreasing organic matter, carbon, volume removal efficiencies and quantity of waste removed. The removal efficiencies in quantity of the waste were 45%, 57 % and 49 %, in single pass, Reactor$_9$ and Reactor$_{21}$, respectively, at the end of 220 days of anaerobic incubation. As is shown, settlement in Reactor$_9$ was the greatest of all. As is known for decreases in solid waste volumes in landfills, the time factor is a very important parameter in terms of economical utilization of landfills in situ. The reductions in organic matter and percent C were at highest level in Reactor$_9$. High linear correlation between carbon removal efficiency and waste quantity reduction was observed (R^2= 0.89). These results showed that Reactor$_9$ exhibited high biodegradation rates compared to single pass and $Reactor_{21}$. The TN and TP values measured in the solid wastes showed that the single pass reactor exhibited lower TN and TP at the end of 220 days of anaerobic incubation than the initial values compared to the other two reactors. This could be explained by the washout of nitrogen and phosphorus in the reactor with no leachate recirculation and sufficient utilization of these nutrients by the anaerobic microorganisms.

Table 3.1 Comparison of the characteristics of anaerobic simulated bioreactors

	Initial (t=0 day)			**Final (t=220 day)**		
	Single pass	**$Reactor_9$**	**$Reactor_{21}$**	**Single pass**	**$Reactor_9$**	**$Reactor_{21}$**
Water content (%)	75	77	86	71	83	84
Org. Matter (%)	76	85	96	64	62	71
% C	42	47	53	35.5	34	39
TN (mg/kg) (in waste)	3300	3300	3300	2100	4200	3400
TP (mg/kg) (in waste)	690	690	690	340	1710	780

3.1.7 COD mass balance and degree of stabilization of solid wastes in simulated anaerobic solid waste bioreactors

As waste stabilization is directly related to the amount of methane produced, the amount of methane generated per kg of organic matter stabilized is taken to be an indicator of waste stabilization degree. Methane concentrations and the total volume of gas produced in all reactors were used to determine the total volume of methane produced during the experimental study. COD mass balance was calculated to evaluate the potential of methane recovery from the reactor. About 24.85, 64.61 and 37.36 l of methane was regenerated from the single pass and the recycled $Reactor_9$ and $Reactor_{21}$, respectively, on day 50. As the recycled leachate has a different capacity for extracting organics due to its high COD, differences in the amount of COD washed out was found between recycled and single pass reactors.

In order to determine the stabilization degree, the maximum mass of COD released was calculated by multiplying the maximum released COD and the available moisture in all the reactors for day 50. It was found that the maximum mass of COD release were equal to 1404, 948 and 1444 g in single pass, $Reactor_9$ and $Reactor_{21}$, respectively. Using these values, and taking into consideration the methane gas produced, it can be concluded that 4.4 % of COD was removed from the single pass reactor was converted to methane and 16 % and 6.44 % of COD removed were converted to methane in the $Reactor_9$ and $Reactor_{21}$, respectively.

The recycling $Reactor_9$ produced about 4 and 2.5 times more methane than single pass reactor and $Reactor_{21}$, respectively, indicating that leachate recycle has a positive effect on methane recoveries. These results agree with previous reports that the leachate recycle enhanced the gas production (Bae et al.1998; Christensen et al. 1992). Methane production in recycled $Reactor_9$ was 2.5 times greater than that in recycling $Reactor_{21}$ yielding 0.069 m^3/kg net waste or 0.21 m^3 methane/kg TS.

3.1.8 Mass balance for C in leachate and solid waste

Carbon removal is important parameter for solid waste treatment. Carbon quantity of leachate and solid waste was calculated before and after of operation periods. High carbon removal means high waste quantity and organic matter reductions. In addition, high carbon removal efficiency supplies economic advantage due to acquire disposal area.

26.5 kg of solid waste was introduced to the single pass bioreactor containing 75 % of water and 42 % of carbon. The dry solid and the water content of the solid waste were 6.6 kg and 19.9 kg (19.9 L), respectively. The initial COD value of the leachate was measured as 35867 mg/l.

The initial carbon content of solid waste is calculated as follows:

$$6.6 * 0.42 = 2.78 \text{ kg C} \tag{3.1}$$

By using the equation 3.2, the carbon (C) quantity of the leachate was calculated as follows:

$$C + O_2 \longrightarrow CO_2 \tag{3.2}$$

Assume that, the theoretical oxygen demand is equal to the initial COD value.

By taking into consideration the equation 3.2, the carbon (C) quantity in the leachate was calculated as 13.46 kg.

The addition of 5 L tap water to the control bioreactor was increased the water content of solid wastes in the single pass bioreactor 24.9 L.

The initial carbon (C) quantity was calculated as 335 kg by multiplying the leachate quantity (24.9 L) with the theoretical carbon quantity (13.46 kg C).

As a result, the total carbon (C) quantity in the solid waste and in the leachate sample was calculated as 335 + 2.78 = 337.78 kg.

After 222 days of operation period, the quantity of solid waste containing 71 % of water and 35.5 % of carbon decreased to 14.5 kg from 26.5 kg. As a result, 4.2 g of solid waste and 10.3 kg (10.3 L) of water remained in the single pass bioreactor.

The final carbon quantity in solid waste was calculated as follows:

$$4.2 * 0.36 = 1.5 \text{ kg C} \tag{3.3}$$

The final COD of the leachate was measured as 47941 mg/l, and the final theoretical carbon quantity in the leachate was calculated as 18 kg C using the equation 3.2.

The final leachate quantity was 4 L. The final water quantity of the system was calculated as follows:

$$10.3 \text{ L} + 4 \text{ L} = 14.3 \text{ L} \tag{3.4}$$

The final carbon quantity was calculated as 257.4 kg C by multiplying the leachate quantity (14.3 L) with theoretical carbon quantity (18 kg C).

As a result, the total carbon (C) quantity in solid waste and in the leachate samples of the system was calculated as 257.4 + 1.5 = 258.9 C.

Finally, the carbon removal efficiency of the total system was obtained as 23 % in single pass reactor.

The total carbon (C) quantities in the solid waste and in the leachate sample were 509.53 kg and 212.4 kg in $Reactor_9$ before and after operation period. The carbon removal efficiency of the total system was obtained as 58 % in $Reactor_9$. Similarly, the carbon removal efficiency of the total system was obtained as 23 % in $Reactor_{21}$.

These calculations are showed that $Reactor_9$ has an advantage related to carbon removal. Reactors operated with no leachate recirculation and high leachate recirculations are not suitable for carbon removal from the solid waste and leachate.

3.2 Effects of Shredding and Compaction on the Degradation of MSWs

3.2.1 COD variations in leachates produced from the control, compaction and shredded reactors

Figure 3.8 shows the daily variation of COD concentrations in leachate for the control, compaction and shredded reactors. As can be seen in this figure, the initial COD concentration in leachate samples collected from the control, compaction and shredded reactors were 14000, 25500 and 23500 mg/l, respectively. The COD value of the leachate in the control reactors increased to 21500 mg/l by days 8-9, and then started to decrease. Similarly, the COD values of the leachate taken from the compaction and shredded reactor increased to 33500 and 29200 mg/l, respectively. After days 8-10, the COD concentrations in these reactors started to decrease. The reason for this decrease in COD level may be the quick degradation of solid wastes in the lab-scale anaerobic MSW reactor. The results of this study showed that the COD value of the compaction reactor is continually higher than the control and shredded reactor. The COD values for the leachate from the control, compaction and shredded reactors were 7200, 6500 and 6000 mg/l; 6400, 7750 and 2300 mg/l respectively, on days 38 and 57. This indicates that the compaction increase the COD levels of the leachate and retards the degradation of solid wastes since the weights of the wastes were 1000 and 1400 g in control and compacted reactors, respectively, at the beginning of the anaerobic incubation. Lu et al. (1985) also reported that as the compaction rate was increased, the COD value of the leachate increased. Reinhart et al. (2002) claimed that when the compaction increased in the solid waste bioreactor, the moisture generating is significantly lower for microbial growth. Therefore the degradation process via microorganisms occurred slowly with a lag phase. Similarly, Quasim & Chinang (1994) reported that, baling shows opposite results relevant to leachate generation and the quality. Baling results showed that longer period required for stabilization of a large volume of dilute leachate compared to an un-baled refuse.

The COD concentrations measured for shredding reactor showed similar data with the findings of Warith (2002) which is reported that the COD value of no-shredding solid waste containing bioreactors is higher than the shredded reactor. Furthermore it was noted that MSWs having small size exhibited fast biodegradation. In our study, the data relevant to COD decreases in the shredded reactor also exhibited similar data with the study performed by Kim et al. (2000). Although the COD concentration in shredded reactor was higher than the control reactor, the biodegradation rate of the shredded reactor was faster than the control reactor.

According to the data obtained in this run it can be concluded that compaction is not a very suitable method for waste degradation in the simulated bioreactor, since long stabilization time required while waste shredding has an advantage in terms of waste biodegradation rate.

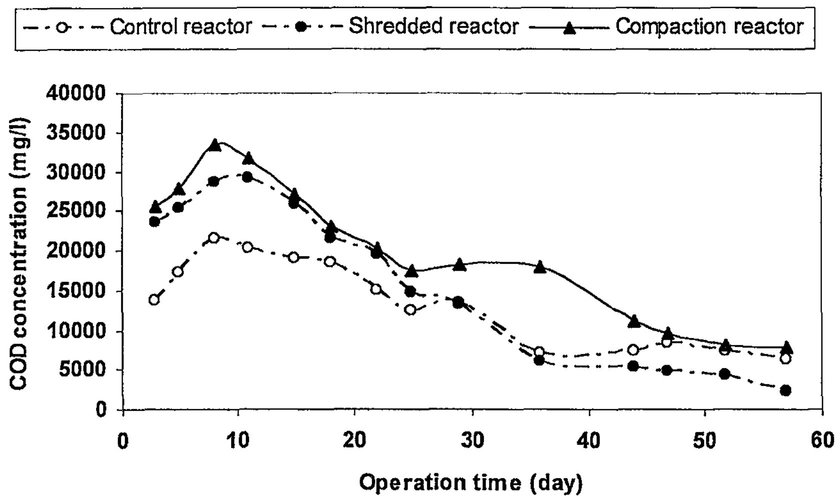

Figure 3.8 Variation of COD concentrations in the leachate samples from the control, shredded and compacted reactors through 57 days of anaerobic incubation

3.2.2 VFA variations in leachate produced from the control, compacted and shredded reactors

The concentration of VFA is an important parameter because of the stage and the degree of the stability of the anaerobic degradation process. As shown in Figure 3.9 the initial VFA concentrations in leachate samples were 5500, 12600 and 8500 mg/l in control, compaction and shredded reactors, respectively. The concentration of VFAs in leachate produced from the all reactors exhibit similar data with COD. A high linear correlation between COD removal efficiency and VFA removal efficiency was observed (R^2= 1). On days 15-16, the VFA concentrations of the control reactors increased to 11000-12300 mg/l while it started to decrease to 2755 and 2800 mg/l by day 57-58. The VFA values of the compaction and shredded reactors increased to 17 000 mg/l and 14250 mg/l on days 18-19. However, they down to about to 3000 mg/l and 50 mg/l by day 57. This may partially be explained by the fact that more resistant substances normally present in the leachate they attacked after the stabilization of the readily available organics since the BOD_5 levels decreased to 5330 and 2145 mg/l from 27452 and 24804 mg/l in compacted and shredded reactors, respectively (see Table 3.2). The VFA measurements showed that compacted solid wastes degraded slowly since methanogenesis lowered. This could be due to the low level of airspace between compacted wastes increase to move the moisture through the waste resulting in high VFA accumulation since the moisture could not be moved through the compacted wastes uniformly (Reinhart et al., 2002). In other words since hydraulic conductivity is inversely related to specific weight, compaction reduces the field capacity and resulting in lower degradation of VFAs. On the other hand high specific weight reduces the ability for the moisture to move through the waste in compacted reactor.

The changes from high levels of TVFA to considerably lower concentrations are indicative of the readily removal pattern of the organic pollutants from the shredded wastes since the specific surface area was increased with shredding. The results of this run showed that although the VFA concentrations in shredded reactor were higher than the control and compaction reactors, at the beginning of the incubation period, (between days 1 and 30) the VFA concentrations decreased to 50 mg/l, at the end of incubation period, indicating that waste shredding has an advantage on the stabilization of the solid wastes. If the VFA/B.Alk. ratio is lower than 0.4 the anaerobic reactor is stable (Behling et al., 1997). But, Griffin et al. (1998) reported that if the VFA/B.Alk. ratio is approximately 1, the solid waste reactor is stable.

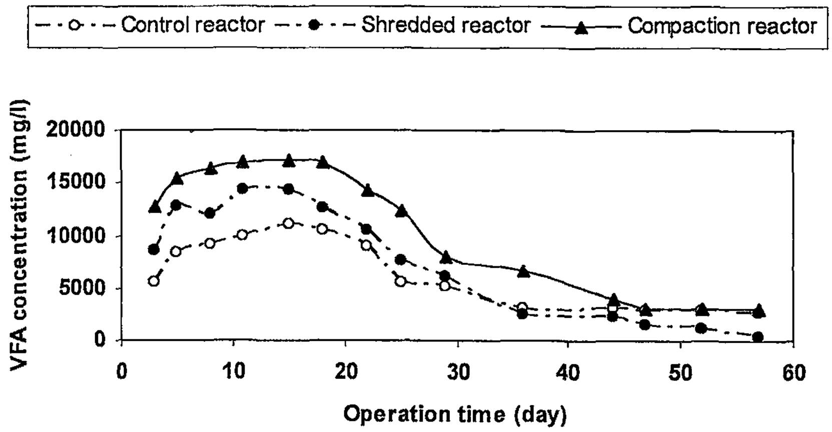

Figure 3.9 Variation of VFA concentrations in the leachate samples from the control, shredded and compaction reactors through 57 days of anaerobic incubation

3.2.3 pH variations in leachate produced from the control, compacted and shredded reactors

The pH of the leachate samples are in accordance with the concentration of VFA measured in all reactors. The variation of pH profiles over time is provided in Figure 3.10. As can be seen in this figure, during the first two weeks, the pH of the leachates from the control, compaction and shredded reactors were 6.04, 5.42 and 5.91, respectively, on the acidic side of the pH scale. In the control reactors, the pH values decreased to 5.29-5.30 within 15 days. This caused to the extension of the time required for the organic fraction of the waste to stabilize since methane forming anaerobes are known to be very sensitive to low pH (Bolzonella et al., 2003). In other words, as the decomposition slowly progresses, decreases in pH may inhibit the metabolism or the reproduction of methanogens. The pH levels started to increase by day 16 in compacting reactor. The conversion of fatty acids caused an increase in the pH levels within the shredded reactor. The methane fermentation phase started between weeks three and four in all reactors. Through the first 36 days, the pH values of the shredded reactor were lower than the control reactor. However, the pH values increased in this reactor within last 21 days. The last pH value measured in the shredded reactor was 7.25, indicating the suitable pH for growth of methanogenic bacteria. Comparing the pH levels released from the leachate of the shredded and un-shredded (control) MSW indicates that the time required for the biodegradation stage was reduced with shredded waste.

On day 57, the pH values measured in the control and compaction reactors were 6.89 and 6.78, respectively because of sludge buffering capability. During the hydrolysis and intermediate anaerobic degradation stage methanogenic bacteria slowly start to appear as mentioned by Warith (2002). As the methanogenesis and methane gas production increased the carbon dioxide and VFA concentrations decreased (Warith, 2002).

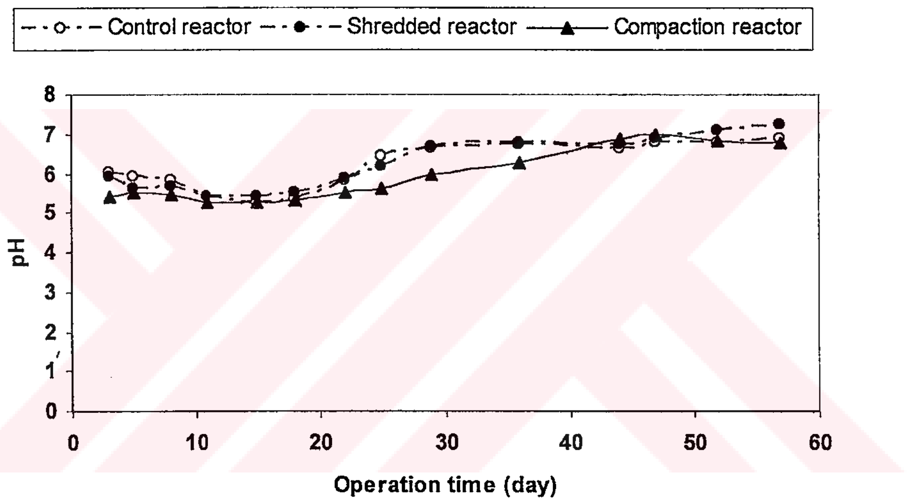

Figure 3.10 Variation of pH levels in the leachate samples from the control, shredded and compaction reactors through 57 days of anaerobic incubation

3.2.4 NH_4-N variations in leachate produced from the control, compacted and shredded reactors

The results of the NH_4-N concentrations measured in leachate samples over time from the control and compaction reactors were shown in Figure 3.11. The highest NH_4-N concentrations were measured to be 600, 520 and 558 mg/l by day 8 in compacted, control and shredded reactors through mineralization of organic nitrogenous compounds. It was observed that the NH_4-N concentrations in compacted reactor is higher than that control and shredded reactors since the compaction process press and degrade the solid waste resulting in high decomposition of proteins. Compaction increased the saturation of the waste by moisture and resulting in more favorable conditions for biological degradation of protein and amino acids. The NH_4-N concentrations down to about 300 and 400 mg/l on day 40 indicating the partial degradation of the nitrogenous compounds, in all aforementioned reactors. On day 57 the NH_4-N concentrations remained at between 400-450 mg/l in the compacted, shredded and control reactors indicating that the partial degradation of proteins could cause 50% reduction in the NH_4-N concentrations due to the non-acclimatization of high ammonia concentrations by methanogenic bacteria. Therefore the accumulation of ammonia could have an inhibitory effect. A lag phase time was dependent on NH_3-N level and is more sensitive factor than the NH_4-N level for unacclimated bacterial system (Mata-Alvarez et al., 2000). In this study, it was observed that, there is no significant difference between control and compaction reactor. The highest NH_4-N concentrations were 650 mg/l in shredded reactor indicating that size reduction in MSW improved the degradation of nitrogenous organic substances.

As reported by Marttinen et al. (2002), the landfill leachate treatment is normally focused on the removal of organic nitrogenous and carbonaceous matters and ammonia nitrogen levels since both three parameters are quite important for possible inhibition of methane production under anaerobic conditions. It is important to note that most of the nitrogen in the solid waste bioreactors is in the ammonia forms following the degradations of proteins and amino acids (İnanç et al., 2000). Leachate toxicity significantly correlated with the COD and ammonia in untreated and treated leachate (Marttinen et al., 2002). Ammonium concentrations as high as 400 mg/l may be inhibit the growth of anaerobic methanogenic bacteria in all reactors (Speece, 1996).

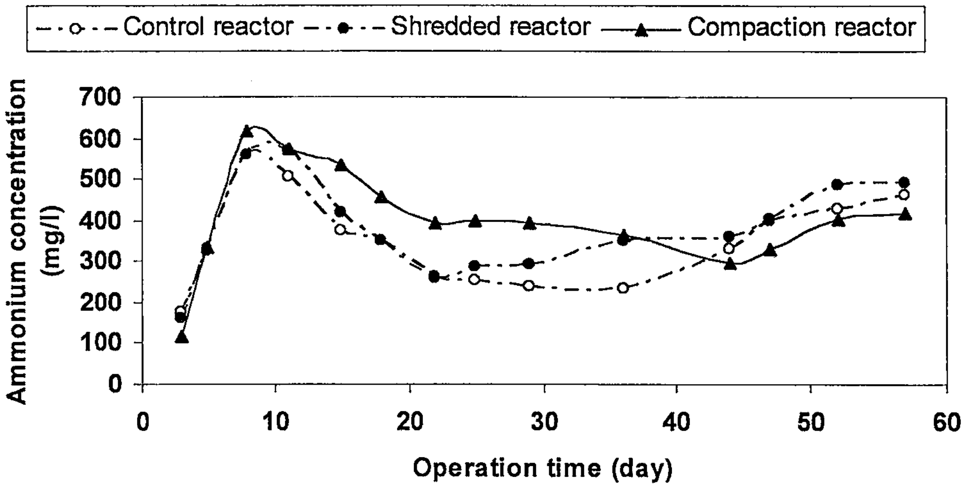

Figure 3.11 Variation of NH_4-N concentrations in the leachate samples from the control, shredded and compaction reactors through 57 days of anaerobic incubation

3.2.5 Methane gas productions and methane percentages in simulated anaerobic solid waste bioreactors

The quantity of methane in control, compacted and shredded reactors were shown in Figure 3.12. As can be seen in this figure, the maximum cumulative methane gas production was recorded as 13.8 L, 21.6 L and 15.5 L in control, compaction and shredded reactors, respectively at the end of 57 days. High linear correlation between COD removal efficiency- VFA removal efficiency and methane quantity was observed (R^2=1). The reason for the high cumulative methane in compaction reactor is the high quantity of municipal organic solid wastes in this reactor. Approximately methane percentages were 55 %, 56 % and 61 % in control, compaction and shredded reactors, respectively on day 50 (See Figure 3.13). Initial methane percentage of shredded reactor was the highest. In other words, biodegradation rate was the highest in shredded reactor. Methane percentage of the control, compaction and shredded reactors were 36 %, 46 % and 60 %, respectively, at the end of the 57 day of operation period. Despite the compaction reactor has a high quantity of waste, methane percentage of the compaction reactor was found to be lower than the shredded reactor. Similar results were found by Angelidaki & Ahring (1999). In this study the effect of particle size on the methane productions was quantified resulting in an increase of 17 in the percentage of biogas through mechanical maceration of bio-fibers contained manure. They reported that smaller the fibres, the higher the biogas potential.

The results of this study showed that size reduction of particles in MSWs and the resulting increase in the specific surface available to the medium improves the anaerobic biological process. If the waste has a high size and low degradability, shredding leads to improved gas productions. Size reduction can lead to more rapid digestion as reported by Palmowski & Muller (2000) and Angelidaki & Ahring (1999).

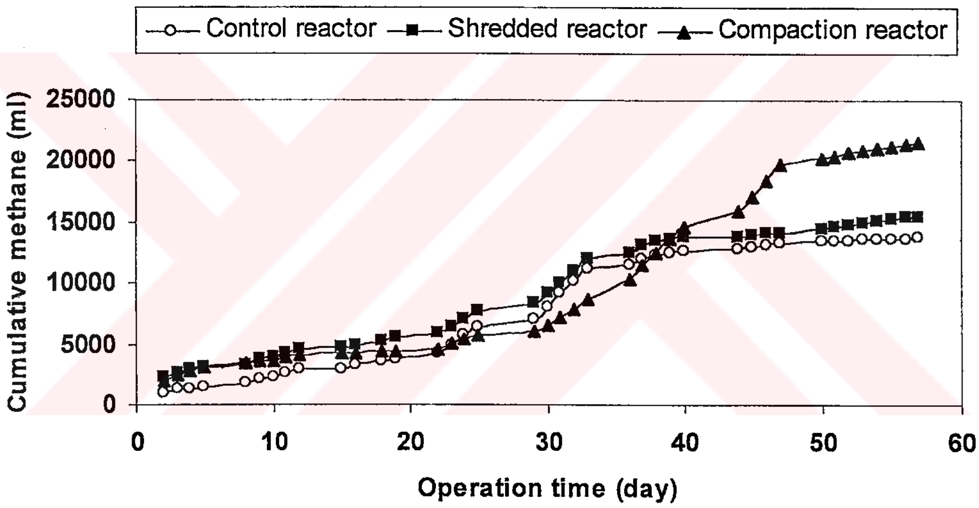

Figure 3.12 Variation in cumulative methane gas productions in the control, shredded and compaction reactors through 57 days of anaerobic incubation

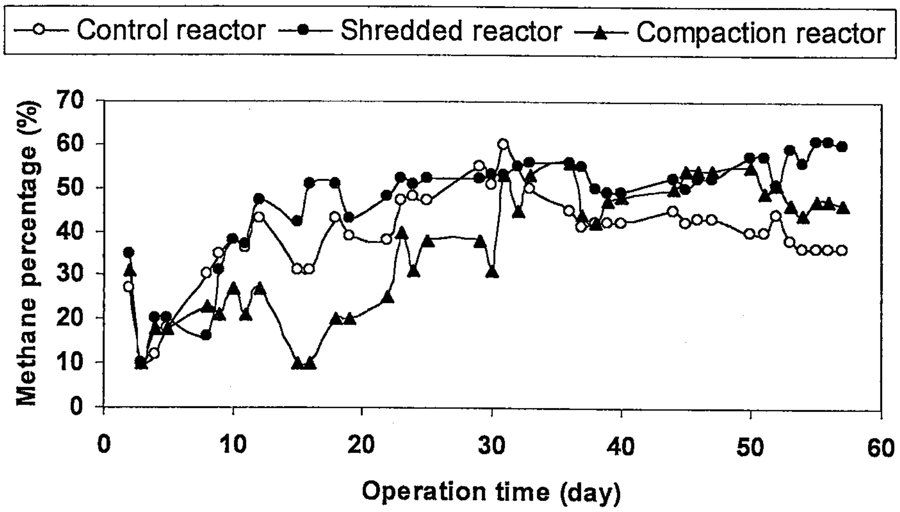

Figure 3.13 Variation in methane percentages in the control, shredded and compacted reactor through 57 days of anaerobic incubation

3.2.6 BOD_5 and TOC concentrations in simulated anaerobic solid waste bioreactors

In order to study in greater detail the proportion of biodegradable organic carbon in the leachate it was considered to determine the BOD_5/COD ratios. Table 3.2 shows the computed values of these ratios, BOD_5, COD, and TOC concentrations in the leachate samples of the all reactors studied for days 5 and 47. The BOD_5 values were ranging initially from 16661, 27152, 24804 mg/l to 4251, 5330, 2145 mg/l at the end of anaerobic incubation in control, compacted and shredded reactors, respectively. The BOD_5 values decreased substantially by 74, 80 and 91 % in the aforementioned reactors, respectively. It was observed that the high COD concentrations in the leachate only lasted for 50 days followed by a quick COD declining through 2 weeks (data not shown). The experimental results indicate that better MSW stabilization was achieved in the shredded reactor at a high rate than that of compacted and control reactors. The BOD_5/COD ratio indicates the changes in the amount of biodegradable compounds in the leachate. Initially, all the reactors have high BOD_5/COD ratios such as 0.97 indicating the high degradability of leachate (Quasim & Chiang, 1994). On day 47, BOD_5/COD ratio decreased approximately to 0.5 from 0.97. This ratio implies a highly biodegradable leachate. In other words, this level shows the increasing biodegradability of organics due to solubilization through methanogenesis. As the organic content biodegradation of MSW occurs, the BOI_5/COD ratio decreased. This decreases indicated that the organic wastes was degraded through fermentation phase which is showing a decreasing biodegradability due to methane formation. The BOD_5/COD ratio of the shredded reactor was the lowest. This result indicated that, the organic waste in shredded reactor is converted rapidly to methane via methanogenesis.

If the BOD_5/COD ratio were between 0.02 and 0.13, this implies that the leachate has a low biodegradability through anaerobic phase. When this ratio is between 0.4 and 0.8, this implies the high biodegradability of the leachate (Otieno, 1994). The BOD_5/COD ratio measured in the study shows similar data with the findings of Ledakowicz & Kaczorek (2002). In their study, BOD_5/COD ratio dropped from 0.55 to 0.2 on the 80^{th} day.

TOC give an indication of the amount of organic substrate in the leachate. TOC value of the shredded reactor was determined as 10500 mg/l on day 5. However, it decreased to 729 mg/l, resulted a TOC removal efficiency of 93 % on day 47. This result indicated that, initially, the shredding waste was released organic carbon at high concentrations since the shredded wastes biodegraded very rapidly. This hypothesis is supported by the significant deduction in BOD_5/COD ratio as aforementioned.

The accumulation of carbon dioxide in the reactors causes increases in TOC concentrations through anaerobic degradation (Otieno, 1994). In our study, although the initial TOC values were found to be higher, the TOC values determined in the end of incubation day were at lower level. This result indicated that the organic waste converted to methane under anaerobic conditions at the end of 57 days. TOC values measured in all anaerobic reactors exhibit similar data with the results obtained by Quasim & Chiang (1994).

Table 3.2 BOD_5, TOC values andBOD_5/COD ratios of the bioreactors

	Control reactor		Compacted reactor		Shredded reactor	
	Day 5	Day 47	Day 5	Day 47	Day 5	Day 47
BOD_5 (mg/l)	16760	4256	27152	5330	24804	2145
BOD_5/COD ratio	0.97	0.5	0.97	0.55	0.97	0.44
TOC (mg/l)	6315	2734	9751	3513	10500	729

3.2.7 Anaerobic toxicity (ATA) and inert COD assays

Table 3.3 illustrates the results of the ATA tests indicating the quantities of methane produced from the control (glucose) and leachate containing serum bottles through three days of anaerobic incubation. At the end of the ATA test, it was found that there is no significant toxicity under anaerobic conditions since no decreases in methane gas productions was observed in all reactors. This result can be explained by the no toxic and inhibitor organic and inorganic chemicals in the reactors since the organic solid wastes taking from the kitchen of the Engineering Faculty Campus does not include any toxic substance. When the leachate percentage was increased in the serum bottles, the quantity of methane produced increased, indicating the utilization of leachate as suitable carbon source by the methanogenic microorganisms through anaerobic degradation. Based on these results it can be concluded that that non of leachate samples has a toxic effects to the anaerobic microorganisms.

The results of inert COD assays showed that inert COD level was found to be approximately 10 % of the initial COD levels (approximately 250 mg/l) in all reactors. Figure 3.14 shows the COD variations in raw leachate samples taken from the shredded reactor together with the glucose COD. This indicates that the COD of leachate samples could be treated up to 90% which is the maximum COD removal efficiency reached under favorable anaerobic conditions. At the end of the biochemical methane potential (BMP) tests it was found that 225 g/l and 208 g/l COD were converted to methane in leachate samples from the shredded and compacted reactors under anaerobic conditions (data not shown) indicating the anaerobic effluent in compacted reactor has a lower methanogenic activity compared to shredded reactor. However it is important to note that both leachate samples did not exhibit toxicity.

Table 3.3 Methane quantities of glucose and leachate samples

	Quantity of Methane (ml/day)	
	Compacted reactor (After 3 days)	Shredded reactor (After 3 days)
Glucose 0 % leachate (control)	28	33
25 % leachate	34	39
50 % leachate	44	47
75 % leachate	48	50
100 % leachate	54	54

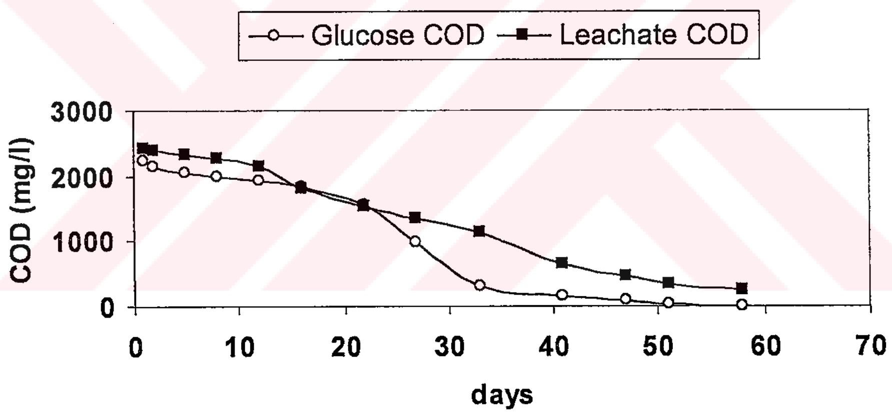

Figure 3.14 Variation in inert COD levels in the leachate and glucose containing samples

3.2.8 Comparison of the characteristics of the MSW in the reactors

As can be seen in Table 3.4 the organic matter reduction of MSW in shredded reactor is the highest level. The percentage of organic matter reduction of MSW in controls, compaction and shredded reactors are 27 %, 23 % and 31 %, respectively through 57 days of incubation period. The TN, TP and NH_4-N concentrations in

MSW reduced to 300, 400 and 100 from 8000, 6500 and 560 mg/g in shredded reactor by day 57. This shows that the methanogenic microorganisms consumed nitrogen and phosphorus through the degradation of carbonaceous compounds. The reductions in C percentage and waste quantity in shredded reactor was found to be at higher level. A high waste volume reduction was achieved in the shredded reactor than the compacted reactor. This parameter is very important for the volume reduction used and for the economical utilization of the lands. These results exhibit similar data with the data obtained by Engelhart et al. (1999) including the effects of mechanical disintegration on the anaerobic biodegradability of sewage sludge. The results obtained in this study showed that the shredded reactor exhibits high biodegradation rates compared to the control and the compaction reactors.

Table 3.4 Comparison of characteristics of the simulated anaerobic landfilling MSW reactors

	Initial			Final		
	Control	Compacted	Shredded	Control	Compacted	Shredded
Water content (%)	85	85	85	86	89	88
Org. Matter (%) (in DS)	91	91	91	67	70	63
% C (in DS)	51	50.5	50.5	38	39	35
TN (mg/kg) (in waste)	8000	8000	8000	500	300	300
TP (mg/kg) (in waste)	6500	6500	6500	900	300	400
NH_4-N(mg/kg) (in waste)	560	560	560	140	300	100
Waste Quantity (g)	1000	1400	1000	299	589	285

3.2.9 Mass balance for C in leachate and solid waste

Carbon removal is important parameter for solid waste treatment. Carbon quantity of leachate and solid waste was calculated before and after of operation periods. High carbon removal means high waste quantity and organic matter reductions. In addition, high carbon removal efficiency supplies economic advantage due to acquire disposal area.

1000 g of solid waste was introduced to the control bioreactor containing 85 % of water and 50.5 % of carbon. The dry solid and the water content of the solid waste were 150 g and 850 g (0.85 L), respectively. The initial COD value of the leachate was measured as 13716 mg/l.

The initial carbon content of solid waste is calculated as follows:

$$150 * 0.505 = 75.75 \text{ g C} \qquad (3.5)$$

By using the equation 3.2, the carbon (C) quantity of the leachate was calculated as follows:

Assume that, the theoretical oxygen demand is equal to the initial COD value.

By taking into consideration the equation 3.2, the carbon (C) quantity in the leachate was calculated as 5.13 g.

The addition of 0.5 L tap water to the control bioreactor was increased the water content of solid wastes in the control bioreactor 1.35 L.

The initial carbon (C) quantity was calculated as 6.9 g by multiplying the leachate quantity (1.35 L) with the theoretical carbon quantity (5.13 g C).

As a result, the total carbon (C) quantity in the solid waste and in the leachate sample was calculated as 75.75 + 6.9 = 82.65 g.

After 57 days of operation period, the quantity of solid waste containing 86 % of water and 37 % of carbon decreased to 298 g from 1000 g. As a result, 41.72 g of solid waste and 256.28 g (0.26 L) of water remained in the control bioreactor.

The final carbon quantity in solid waste was calculated as follows:

$$41.72 * 0.37 = 15.4 \text{ g C} \tag{3.6}$$

The final COD of the leachate was measured as 6405 mg/l, and the final theoretical carbon quantity in the leachate was calculated as 2.4 g C using the equation 3.2.

The final leachate quantity was 0.4 L. The final water quantity of the system was calculated as follows:

$$0.26 \text{ L} + 0.4 \text{ L} = 0.66 \text{ L} \tag{3.7}$$

The final carbon quantity was calculated as 1.58 g C by multiplying the leachate quantity (0.66 L) with theoretical carbon quantity (2.4 g C).

As a result, the total carbon (C) quantity in solid waste and in the leachate samples of the system was calculated as 15.4 + 1.58 = 16.98 g.

Finally, the carbon removal efficiency of the total system was obtained as 79 % in control reactor.

The total carbon (C) quantities in the solid waste and in the leachate sample were 122.2 g and 28.3 g in compacted reactor before and after operation period. The carbon removal efficiency of the total system was obtained as 76 % in compacted reactor. Similarly, the carbon removal efficiency of the total system was obtained as 86 % in shredded reactor.

These calculations are showed that carbon removal efficiency in shredded reactor is significantly higher than the control and the compacted reactors. According to the control reactor, carbon removal efficiency in compacted reactor is lower because of high solid waste content.

3.3 Effects of Alkalinity on Degradation of MSWs

3.3.1 COD variations in leachate samples produced from the control and alkalinity supplemented simulated landfill bioreactors

Figure 3.15 shows the daily variation of COD concentrations in leachate for the control (no alkalinity addition), 3 g/l and 6g/l $NaHCO_3$ supplemented reactors. As seen in this figure, the initial COD concentration in leachate samples collected from the control, 3g/l and 6g/l $NaHCO_3$ containing reactors were 16004, 16121 and 16200 mg/l, respectively. The initial COD values of these reactors were found to be similar due to all the reactors contain the same solid waste. The COD value of the leachate in the control reactors increased to 40658 mg/l until day 21, and then started to decrease. Similarly, the COD values of the leachate taken from the 3g/l and 6g/l $NaHCO_3$ containing reactors increased to 30353 and 22850 mg/l until day 7. After day 7, the COD concentrations in these reactors started to decrease. The reason of this decrease in COD level may be the quick degradation of solid wastes in the lab-scale anaerobic MSW reactor and the positive effect of alkalinity on anaerobic degradation. The results of this study showed that the COD value of the control reactor is continually higher than the 3g/l and 6g/l $NaHCO_3$ containing reactors. The COD values of the leachate from the control, 3g/l and 6g/l $NaHCO_3$ containing reactors were 18964, 3865 and 2908 mg/l respectively, on the last operation day. This indicates that the addition of alkalinity to the solid waste bioreactors has a positive effect on the anaerobic degradation of solid wastes. Addition of alkalinity provides suitable pH for the growth of methanogenic bacteria. The organic matter easily converts to methane through the methanogenesis. However, the degradation process occurred slowly in control reactor, because of unsuitable alkalinity for methanogen bacteria. The time required for stabilization of COD was shortened by the addition of alkalinity.

One of the major problems is inadequate alkalinity/leachate COD ratio in the operation of landfilling simulated anaerobic bioreactor due to high COD concentrations of leachate. This may cause to minimum pH in the anaerobic reactor to fall below 6.2 which can lead to failure of the system. Therefore, sufficient bicarbonate alkalinity must be present to neutralize the volatile fatty acids originated from the degradation of COD.

Speece (1996) and Anderson & Yang (1992) were reported that if the acid concentrations (H_2CO_3 and VFA) exceed the available alkalinity, the reactor will "sour" (a drop in pH), severely inhibiting microbial activity, especially the methanogens. When methane production becomes "stuck" (ceases) the VFA may continue to accumulate, exacerbating the situation further. Methanogens prefer nearly neutral pH conditions with a generally accepted optimum range of approximately 6.5 to 8.2 (Speece, 1996). Alkalinity addition was used in numerous studies to neutralize the pH through the anaerobic treatment of MSW. $CaCO_3$, $NaHCO_3$, KOH and NaOH were used for alkalinity supply (Plaza et al., 1996; Hamzawi et al., 1998; Warith, 2002; San & Onay, 2001; Laclos et al., 1997). In these study, alkalinity supplemented reactors have advantages related to methane generation and COD reduction.

Souza et al. (1992) and Moosbruger et al. (1993) found that an alkalinity/COD ratio 0.5 in the influent decreased the pH to 6.6 which is considered as the lower limit value recommended for the anaerobic digestion processes. In our study, these ratios were 0.22, 0.98 and 1.3 in control, 3g/l and 6g/l $NaHCO_3$ supplemented reactor, respectively. With carbohydrate wastes the alkalinity requirement is 1.2-1.6g alkalinity as $CaCO_3$/g influent COD which is sufficient to maintain the pH above 6.6

(Speece, 1996). In this study the suitable alkalinity for maximum COD removal was 4000 alkalinity as $NaHCO_3$/g influence COD in 6 g/l $NaHCO_3$ supplemented reactor.

Since 6 g/l of $NaHCO_3$ concentration provided to optimum buffering capacity to convert effectively the leachate COD to methane and VFA, it could be suggested as optimum bicarbonate alkalinity concentration in influent to maintain the pH above 6.6. This value corresponds to an Alk/COD ratio of 1.3 for optimum operation which is higher than the ratio proposed by Gonzales et al. (1998) (0.4), Souza et al (1992) and Moosbruger et al. (1993) (0.5) and Speece (1996) (1.2).

The COD concentrations in alkalinity supplemented reactors showed similar data with the findings of Warith (2002) which is reported that the COD value of control reactor is higher than the alkalinity added reactors. According to the data obtained in this study it can be concluded that alkalinity addition is a very suitable for waste degradation in simulated landfill anaerobic bioreactor, since short stabilization time required for the COD concentrations in leachate samples.

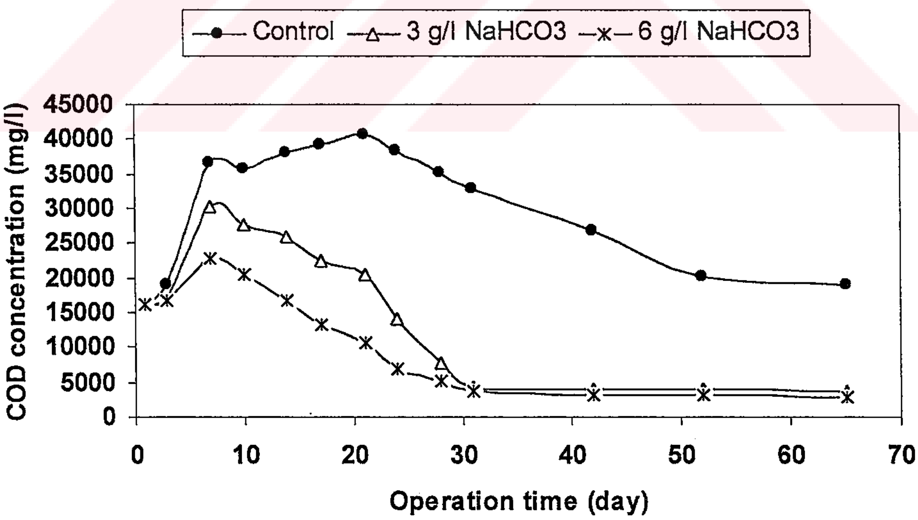

Figure 3.15 Trends in COD concentrations in leachate from the control, 3g/l and 6g/l $NaHCO_3$ containing reactors

3.3.2 VFA variations in leachate samples produced from the control, 3g/l and 6g/l $NaHCO_3$ alkalinity supplemented reactors

The concentration of VFA is an important parameter because of the degree of the stability of the anaerobic process. As shown in Figure 3.16 the initial VFA concentrations in leachate samples were 10052, 10169 and 10103 mg/l in control, 3g/l and 6g/l $NaHCO_3$ containing reactors, respectively. The concentration of VFAs in leachate produced from the all reactors exhibit similar data with COD. A high linear correlation between COD removal efficiency and VFA removal efficiency was observed (R^2=1). On days 17, the VFA concentration of the control reactor increased to 21080 mg/l, and then started to decrease. The VFA values of the 3g/l and 6g/l $NaHCO_3$ containing reactors increased to 30353 and 22850 mg/l on day 7. However, they down to about to 3865 and 1285 mg/l by day 65. The VFA concentration of control reactor was measured as 6913 mg/l on the last operation day (day 65). The VFA measurements showed that solid wastes in control reactor (no alkalinity addition) degraded slowly. As clearly seen in Figure 3.16, the addition of alkalinity has an advantage in terms of low VFA production.

Adequate alkalinity, or buffer capacity, is necessary to maintain a stable pH in the digester for optimal biological activity. A pH of 5.75 provides a more accurate estimation of theoretical true bicarbonate alkalinity (Cobb & Hill, 1990). An alkalinity varied between 1000 and 5000 mg Ca CO_3/l, was recommended for anaerobic treatment depending to COD and produced VFA (Tchobanoglous & Burton, 1979). Traditionally, the total alkalinity in an anaerobic digester includes all the bicarbonate alkalinity and approximately 80% of the volatile fatty acids. Because only bicarbonate alkalinity is usable for neutralizing the volatile acids, total alkalinity does not always represent the available buffering capacity in a digester (Anderson & Yang, 1992). A stable anaerobic treatment system requires a balance among all organisms. The maintenance of this balance is normally indicated by a low VFA concentration and a stable pH. Large molecular weight organic materials such as cellulose first have to be hydrolyzed to small molecular materials via breakdown of hydrolytic enzymes, production of intermediates (glucose) and further have to convert to VFA, methane and degraded inorganic, organic metabolite products. When the system is in balance, the methanogens could be inactivated by unfavorable environmental conditions, e.g., pH drop, accumulation of VFA, intermetabolites and toxicity of aromatic amines due to their toxic properties (Kuai et al., 1998).

Behling et al. (1997) reported that, if an UASB reactor is stable, the TVFA/ B.Alk. ratio of reactor is lower than 0.4. In our study, TVFA/ B.Alk. ratio is higher than 0.4 in control reactor. This ratio is lower than 0.4 in 3g/l and 6g/l $NaHCO_3$ containing reactors on days 31 and 52, respectively (data not shown). In addition, Griffin et al. (1998) reported that if the VFA/B.Alk. ratio is approximately 1, the solid waste reactor is stable. High VFA concentration cause severely inhibition in the microbial activity, especially in methane gas production. High levels of VFA persistence will be reflected low COD removals under high COD concentrations resulting in VFA accumulation through insufficient alkalinity in the influent. In this study, measured VFA concentration showed that alkalinity addition has a positive effect on solid waste biodegradation in simulated bioreactor.

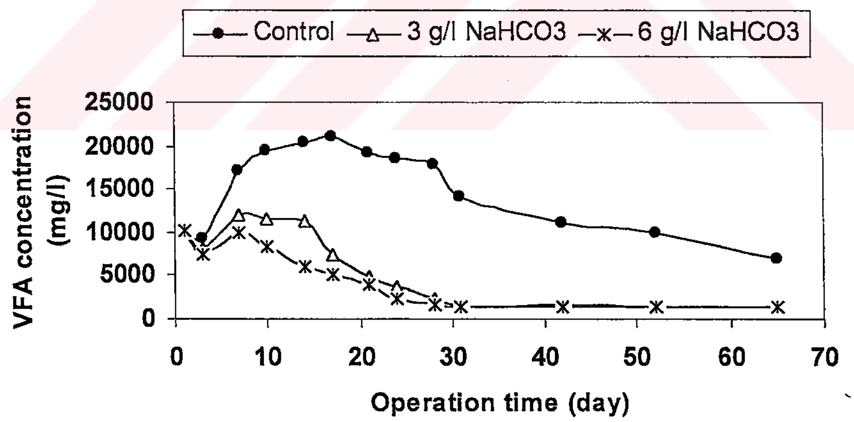

Figure 3.16 Trends in VFA concentrations in leachate from the control, 3g/l and 6g/l $NaHCO_3$ containing reactors

3.3.3 pH variations in leachate samples produced from the control, 3g/l and 6g/l $NaHCO_3$ alkalinity supplemented reactors

The pH levels measured in the leachate samples are in accordance with the concentration of VFA measured in all reactors. The variation of pH profiles over time is provided in Fig 3.17. As can be seen in this figure, during the first two weeks, the pH of the leachates from the control, 3g/l and 6g/l $NaHCO_3$ containing reactors were 5.32, 5.16 and 5.30, respectively, on the acidic side of the pH scale. In the control reactor, the pH values decreased to 5 within 7 days. This caused to the extension of the time required for the stabilization of organic fraction of the waste to stabilize since methane forming anaerobes are known to be very sensitive to low pH (Bolzenella et al., 2003). In other words, as the decomposition slowly progresses, decreases in pH may inhibit the metabolism or the reproduction of methanogens. The pH levels started to increase by day 28 in control reactor. The pH level of the control reactor was 6.54 on day 65. The conversion of fatty acids caused an increase in the pH levels within the alkalinity supplemented reactors. The pH values in the alkalinity containing reactors regularly increased. The last pH value measured in the 3g/l and 6g/l $NaHCO_3$ containing reactors were 7.19 and 7.31, respectively, indicating the suitable pH for growth of methanogenic bacteria. In this study the measured pH levels was found to be higher than the data obtained by Plaza et al. (1996) which was used $CaCO_3$ for alkalinity. In their study the pH varied between 6-6.3, while the pH levels were 6.4-7.3 in this study.

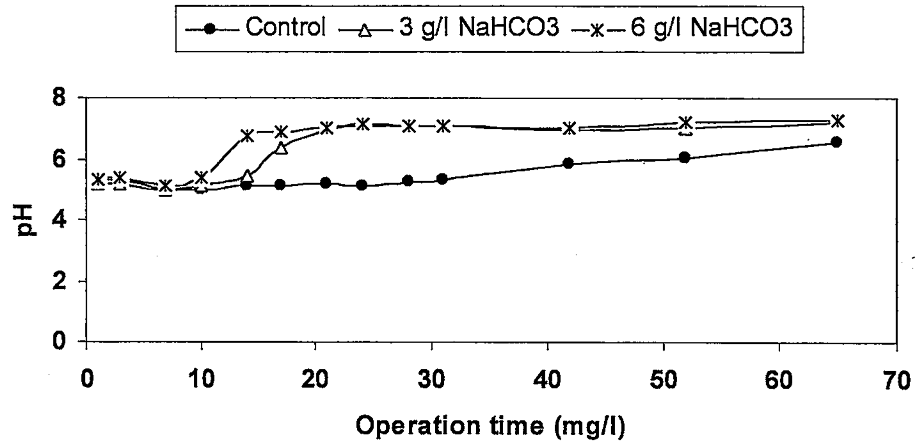

Figure 3.17 Trends in pH concentrations in leachate from the control, 3g/l and 6g/l $NaHCO_3$ containing reactors

3.3.4 NH_4-N variations in leachate produced from the control and alkalinity supplemented simulated landfill reactors

The variations in NH_4-N concentrations measured in leachate samples in the control, 3g/l and 6g/l $NaHCO_3$ containing reactors were shown in Figure 3.18. The highest NH_4-N concentrations were measured to be 764, 762 and 650 mg/l in control, 3g/l and 6g/l $NaHCO_3$ containing reactors through the mineralization of organic nitrogenous compounds. It was observed that the NH_4-N concentrations in 6g/l $NaHCO_3$ containing reactor are lower than the others. Furthermore, in this study, it was observed that, there are no significant differences in NH_4-N concentrations between control, 3g/l and 6g/l $NaHCO_3$ containing reactors.

As reported by Marttinen et al. (2002) the landfill leachate treatment is normally focused on the removal of organic nitrogenous and carbonaceous matters and ammonia nitrogen levels since both three parameters are quite important for possible inhibition of methane production under anaerobic conditions. It is important to note that most of the nitrogen in the solid waste bioreactors is in the ammonia forms following the degradations of proteins and amino acids (İnanç et al., 2000).

Since the NH_4-N concentration in the leachate samples is high, the generated ammonium bicarbonate alkalinity contributes to total alkalinity in effluent samples. Similar results were reported by Dinamarca et al. (2003) which they found that the presence of proteins and other nitrogenated compounds gives to the reactor adequate buffer capacity. On the other hand since the reserve alkalinity is the bicarbonate alkalinity maintaining the pH above 6.2-6.6 in the anaerobic simulated reactor; it can be assumed that this alkalinity was provided in our system since the lower pH was recorded as 6.4.

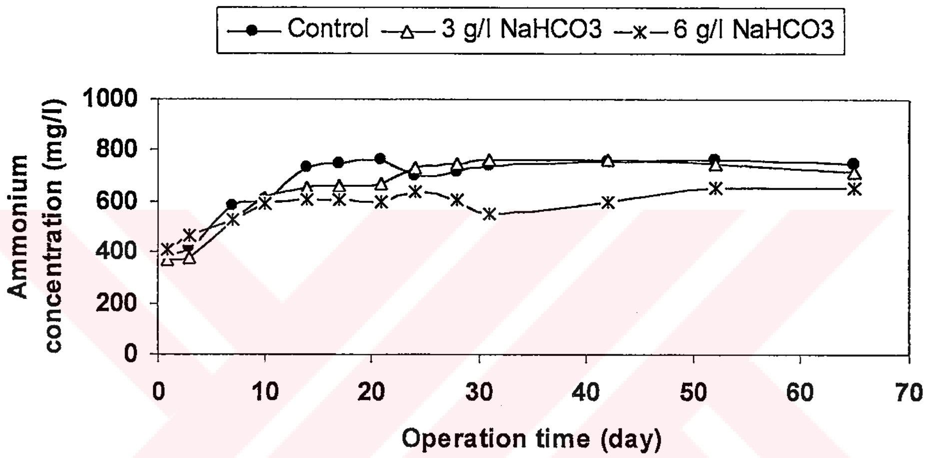

Figure 3.18 Trends in NH_4-N concentrations in leachate from the control, 3g/l and 6g/l $NaHCO_3$ containing reactors

3.3.5 Methane gas productions and methane percentages in simulated anaerobic solid waste bioreactors

The quantity of methane and methane percentages of control, 3g/l and 6g/l $NaHCO_3$ containing reactors were shown in Figures 3.19, 3.20 and 3.21, respectively. As can be seen in these figures, the maximum cumulative methane gas production was recorded as 12 L, 18.9 L and 22.6 L in control, 3g/l and 6g/l $NaHCO_3$ containing reactors, respectively at the end of 65 days. High linear correlation between COD removal efficiency- VFA removal efficiency and methane quantity was observed (R^2=0.88). The reason for the high cumulative methane in 6g/l reactor is the fast degradation of municipal organic solid wastes in this reactor through methanogenesis. Alkalinity addition was also increased the rate of conversion of methane. While the methane percentage of control reactor was approximately 37 %, the methane percentages in 3g/l and 6g/l $NaHCO_3$ containing reactors were 64 % and 65 %, respectively on day 24. During the operation period, total methane percentage of 6g/l $NaHCO_3$ containing reactor was the highest. In other words, the biodegradation rate was the highest in 6g/l $NaHCO_3$ containing reactor. In this study, the methane percentages measured in alkalinity added reactors are higher than the study realized by San & Onay (2001). They measured a methane percentage about 45 % in a recycled reactor. They reported that buffering of leachate resulted in establishing environmental conditions favored by methanogens. Speece (1996) and Anderson & Yang (1992) were reported that methanogens prefer nearly neutral pH conditions with a generally accepted optimum range of approximately 6.5 to 8.2.

Methane gas productions and methane percentages in simulated anaerobic solid waste bioreactors were shown that the alkalinity addition has a positive effect on biodegradation of municipal solid waste in simulated bioreactors due to high methane gas productions and high methane percentages.

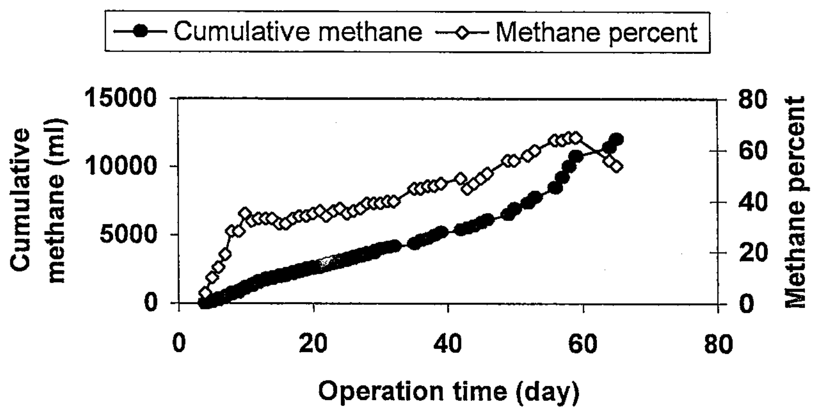

Figure 3.19 Cumulative methane gas productions and methane percentage of control reactor

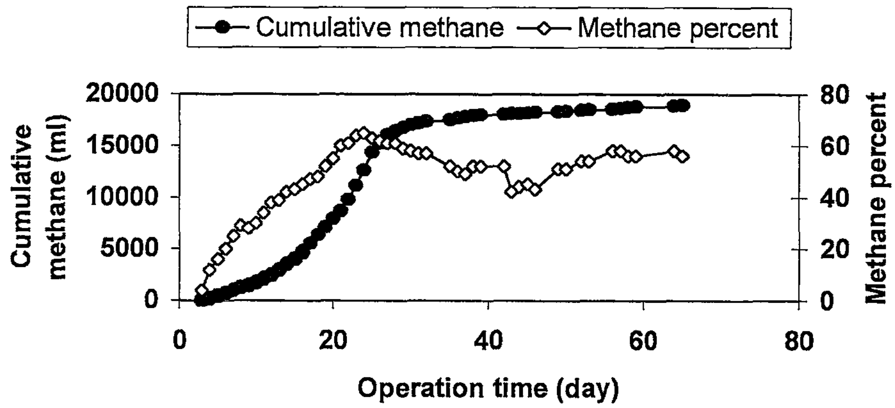

Figure 3.20 Cumulative methane gas productions and methane percentage of 3g/l $NaHCO_3$ containing reactor

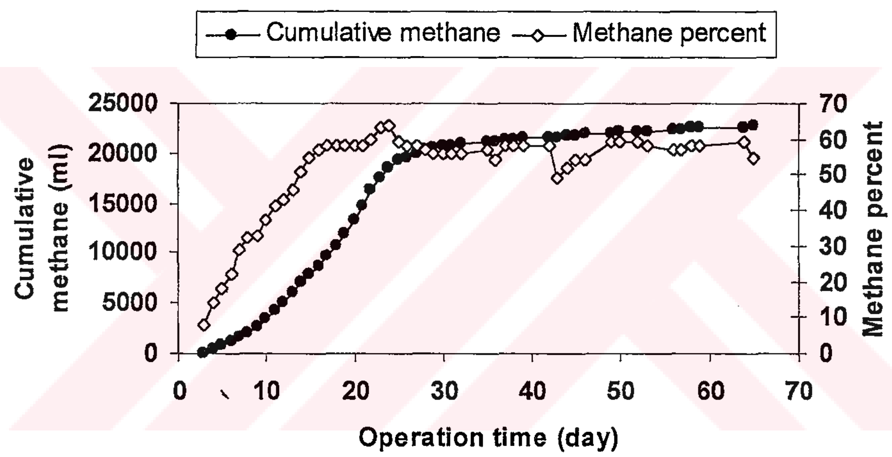

Figure 3.21 Cumulative methane gas productions and methane percentage of 6g/l $NaHCO_3$ containing reactor

3.3.6 BOD_5 concentrations and BOD_5/COD ratios in the leachate samples from the simulated anaerobic solid waste bioreactors

In order to study in greater detail the proportion of biodegradable organic carbon in the leachate it was considered to determine the BOD_5/COD ratios. Table 3.5 shows the BOD_5, COD concentrations and BOD_5/COD ratios in the leachate samples of the all reactors studied for on days 10, 28 and 52. The BOD_5 values decreased to 9965, 1053, 771 mg/l from initial 32091, 21964, 16019 mg/l at the end of anaerobic incubation in control, 3g/l and 6g/l $NaHCO_3$ containing reactors, respectively. The BOD_5 values decreased substantially by 69, 95 and 96 % in the aforementioned reactors, respectively. The experimental results indicate that higher MSW stabilization rate was achieved in the 6g/l $NaHCO_3$ containing reactor than that of control and 3g/l $NaHCO_3$ containing reactors. Initially, all the reactors have high BOD_5/COD ratios such as 0.9 indicating the high degradability of leachate (Quasim & Chiang, 1994). On day 52, BOD_5/COD ratio decreased approximately to 0.25 from 0.78 in 6g/l $NaHCO_3$ containing reactor. This ratio implies a highly biodegradable leachate. In other words, this result shows that the increasing biodegradability of organics due to solubilization of wastes through methanogenesis under buffered environments. As the biodegradation of organic content of MSW occurs, the BOD_5/COD ratio decreased. This decreases indicated that the organic wastes was degraded through fermentation phase which is showing a decreasing biodegradability due to methane formation. The BOD_5/COD ratio of the 6g/l $NaHCO_3$ containing reactor was the lowest. This result indicated that, the organic waste in alkalinity added reactor is converted rapidly to methane via methanogenesis.

If the BOD_5/COD ratio were between 0.02 and 0.13, this implies that the leachate has a low biodegradability through anaerobic phase. When this ratio is between 0.4 and 0.8, this implies the high biodegradability of the leachate (Otieno, 1994). The BOD_5/COD ratio measured in the study shows similar data with the findings of Ledakowicz & Kaczorek (2002). In their study, the BOD_5/COD ratio dropped from 0.55 to 0.2 on the 80^{th} day.

Table 3.5 BOD_5, COD concentration and BOD_5/COD ratios of the bioreactors

	Control			3g/l			6g/l		
	Day 10	Day 28	Day 52	Day 10	Day 28	Day 52	Day 10	Day 28	Day 52
BOD_5 (mg/l)	32091	24050	9965	21964	4104	1053	16019	2615	644
COD (mg/l)	35712	35200	20214	27549	7680	3920	20459	5250	2908
BOD_5/COD ratio	0.9	0.68	0.49	0.8	0.53	0.27	0.78	0.5	0.25

3.3.7 Comparison of characteristics of simulated anaerobic landfilling reactors

As can be seen in Table 3.6 the organic matter reduction of MSW in 6g/l $NaHCO_3$ containing reactor is the highest level. The reduction of organic matter percentage of MSW in control, 3g/l and 6g/l $NaHCO_3$ containing reactors are 33 %, 40 % and 47 %, respectively through 65 days of incubation period. Similarly, reduction in C percentage in 6g/l $NaHCO_3$ containing reactor is higher than the others. Reduction of waste quantity in 6g/l $NaHCO_3$ containing reactor is the best. A high linear correlation between carbon removal efficiency and waste quantity reduction was observed (R^2=0.99). This parameter is very important for the volume reduction and economy based on the location. These results showed that the 6g/l $NaHCO_3$ containing reactor exhibits high biodegradation rates compared to the control and 3g/l $NaHCO_3$ containing reactor. TN removal efficiencies were 86 %, 94.9 % and 95.1 % in control, 3g/l and 6g/l $NaHCO_3$ containing reactors while TP removal efficiencies were 94.9 %, 95.6 % and 95.9 % in the same reactors, respectively.

Table 3.7 summarizes leachate characteristics for the all reactors. As can be seen in Table 3.7, 6g/l reactor has the best result in terms of decreasing of COD and VFA accumulation and increasing of pH.

Table 3.6 Comparison of characteristics of the reactors

	Initial			Final		
	Control	3g/l	6g/l	Control	3g/l	6g/l
Water content (%)	90	90	90	91	92	92
Org. Matter (%) (in DS)	97	97	97	65	58	51
% C (in DS)	54	54	54	36	32	28
TN (mg/g) (in waste)	4350	4350	4350	610	220	213
TP (mg/g) (in waste)	1050	1050	1050	53	46	43
NH_4-N (mg/g) (in waste)	155	155	155	38	36	35
Waste Quantity (g)	1000	1000	1000	213	140	120

Table 3.7 Comparison of characteristics of leachate in the first and last operation days for all the reactors

	t=0 (day)			t= 65 (day)		
	Control	3 g/l	6 g/l	Control	3 g/l	6 g/l
COD (mg/l)	16004	16121	16200	18964	3865	2908
VFA (mg/l)	10052	10169	10103	6913	1413	1285
pH	5.32	5.16	5.30	6.54	7.19	7.31
Bicarbonate Alkalinity* (mg/l)		1220	1414		3800	4002
NH_4- N (mg/l)	388	370	406	750	713	650

* First bicarbonate alkalinity value was measured on day 14

3.3.8 COD mass balance and degree of stabilization of solid wastes

As the waste stabilization is directly related to the amount of methane produced and methane percentage of the total gas, the amount of methane generated per kg of organic matter stabilized is taken to be an indicator of waste stabilization degree. A COD mass balance was calculated to evaluate the potential of methane recovery from the reactors. About 12, 18.9 and 22.6 l of methane was regenerated from the control, 3 g/l $NaHCO_3$ and 6 g/l $NaHCO_3$ added reactors, respectively, on day 65. These results are comparable whit the study performed by San & Onay (2001) and Ledakowicz & Kaczorek (2002) which they found that 78 l CH_4 was produced after 250 days of incubation period and 35 l was produced after 140 days of incubation period in 75 and 15 l reactors, respectively, and 71% of COD removed was converted to methane.

In order to determine the stabilization degree, the maximum mass of COD released was calculated by multiplying the maximum released COD and the available moisture in all the reactors for day 57. It was found that the maximum mass of COD release was equal to 40.1, 30.3 and 22.9 g in control, 3 g/l $NaHCO_3$ and 6 g/l $NaHCO_3$ added reactors, respectively. Using these values, and taking into consideration the methane gas produced, it can be concluded that 28 % of COD was removed from the control reactor was converted to methane and 44 % and 65 % of COD removed were converted to methane in 3 g/l $NaHCO_3$ and 6 g/l $NaHCO_3$ added reactors, respectively. In the studies performed by San & Onay (2001) it was found that 70 % of COD removed was converted to methane degrading the MSWs after the operation period.

As the alkalinity supplemented reactors have higher capacity for extracting the COD from the MSW compared to control reactor, addition of alkalinity increased the specific methane yield to about 0.23 and 0.30 m^3/ kg TS $_{added\ waste}$ in 3 g/l $NaHCO_3$ and 6 g/l $NaHCO_3$ added reactors, respectively, whereas the methane yield in control reactor was 0.13m^3/ kg TS. These results are significantly higher than the studies performed by Chugh et al. (1998) and Mata-Alvarez et al. (2000) which they found that the specific methane yields were about 0.12 m^3/ kg TS $_{added\ waste}$ and 0.8 m^3/ kg TS $_{added\ waste.}$

3.3.9 Mass balance for C in leachate and solid waste

Carbon removal is important parameter for solid waste treatment. Carbon quantity of leachate and solid waste was calculated before and after of operation periods. High carbon removal means high waste quantity and organic matter reductions. In addition, high carbon removal efficiency supplies economic advantage due to acquire disposal area.

1000 g of solid waste was introduced to the control bioreactor containing 90 % of water and 54 % of carbon. The dry solid and the water content of the solid waste were 100 g and 900 g (0.9 L), respectively. The initial COD value of the leachate was measured as 16004 mg/l.

The initial carbon content of solid waste is calculated as follows:

$$100 * 0.54 = 54 \text{ g C} \tag{3.8}$$

By using the equation 3.2, the carbon (C) quantity of the leachate was calculated as follows:

Assume that, the theoretical oxygen demand is equal to the initial COD value.

By taking into consideration the equation 3.2, the carbon (C) quantity in the leachate was calculated as 6 g.

The addition of 0.5 L tap water to the control bioreactor was increased the water content of solid wastes in the control bioreactor 1.4 L.

The initial carbon (C) quantity was calculated as 8.4 g by multiplying the leachate quantity (1.4 L) with the theoretical carbon quantity (6 g C).

As a result, the total carbon (C) quantity in the solid waste and in the leachate sample was calculated as 54 + 8.4 = 62.4 g.

After 65 days of operation period, the quantity of solid waste containing 91 % of water and 36 % of carbon decreased to 213 g from 1000 g. As a result, 19.17 g of solid waste and 193.83 g (0.19 L) of water remained in the control bioreactor.

The final carbon quantity in solid waste was calculated as follows:

$$19.17 * 0.36 = 6.9 \text{ g C} \tag{3.9}$$

The final COD of the leachate was measured as 18964 mg/l, and the final theoretical carbon quantity in the leachate was calculated as 7.13 g C using the equation 3.2.

The final leachate quantity was 0.4 L. The final water quantity of the system was calculated as follows:

$$0.19 \text{ L} + 0.4 \text{ L} = 0.59 \text{ L} \tag{3.10}$$

The final carbon quantity was calculated as 4.2 g C by multiplying the leachate quantity (0.59 L) with theoretical carbon quantity (7.13 g C).

As a result, the total carbon (C) quantity in solid waste and in the leachate samples of the system was calculated as 6.9 + 4.2 = 11.11 g.

Finally, the carbon removal efficiency of the total system was obtained as 82 % in control reactor.

The total carbon (C) quantities in the solid waste and in the leachate sample were 62.47 g and 4.35 g in 3 g/l $NaHCO_3$ alkalinity added reactor before and after operation period. The carbon removal efficiency of the total system was obtained as 93 % in 3 g/l $NaHCO_3$ alkalinity added reactor. Similarly, the carbon removal efficiency of the total system was obtained as 95 % in 6 g/l $NaHCO_3$ alkalinity added reactor.

These calculations are showed that carbon removal efficiency in alkalinity added reactors are significantly higher than the control reactor. As a result, alkalinity addition to the solid waste bioreactors is very important parameter related to carbon removal from solid waste and leachate.

3.4 Effect of Aeration on Degradation of MSWs

3.4.1 COD variations in leachates produced from the control and aerated reactors (run1 and run2)

Figure 3.22 shows the daily variation of COD concentrations in leachate for the control (no aeration), R1 (aeration three days in a week during one hour) and R2 (aeration one day in a week during one hour) reactors. As can be seen in this figure, the initial COD concentration in leachate samples collected from the control, R1 and

R2 reactors were 19882, 20624 and 22026 mg/l, respectively. The COD values of the reactors were similar due to all of the reactors contain the same solid waste. The COD value of the leachate in the control reactors increased to 39092 mg/l until day 21, and then started to decrease from 39092 mg/l to 1504 mg/l by day 79. Similarly, the COD values of the leachate taken from the aerated reactors (R1 and R2) increased to 42967 and 33650 mg/l until day 21. After day 21, the COD concentrations in these reactors started to decrease to 6430 mg/l and 861 mg/l, respectively. Aeration was started on day 28. The highest COD value measured in R1 (aerated to three days in a week) among the three reactors during the operation period. The COD concentrations of control, R1 and R2 reactors were 8045, 35794 and 7468 mg/l, respectively, on day 58 while they were 1504, 6436 and 861 mg/l on day 80. In the study realized by Stessel & Murphy (1992), it was found that the COD value of the aerated lysimeter was lower than the non-aerated (strictly anaerobic) reactor. COD concentration was approximately 15000 mg/l in anaerobic lysimeter, while was only 2000 mg/l in aerobic lysimeter. Purcell (2000) indicated that leachate COD concentrations were reduced by 90 % in the aerobic cell compared to the anaerobic control cell. The final COD concentrations in leachate for control, R1 and R2 reactors were 1504, 6436 and 861 mg/l, respectively. In this study, it was found that aeration once in a week caused low COD value in R2. Some researchers have claimed that anaerobic conditions within a landfill caused slow stabilization and aerobic degradation can significantly increase the rate of waste decomposition (Read et al., 2001; Hudgings & Harper, 1999; Murphy et al., 1995; Purcell, 2000). They recommended perpetual aeration in a landfill. However, batch aeration was applied in this study to investigate the effect of aeration on degradation of MSW, leachate and gas quality in simulated bioreactors.

The results of this study showed that once in a week aeration in R2 has a positive effect related to leachate COD in simulated bioreactor while the methane production decreased due to oxygen. However, the COD values measured in leachate samples of the anaerobic control reactor was considerably lower compared to R1 and exhibits approximately similar results with R2.

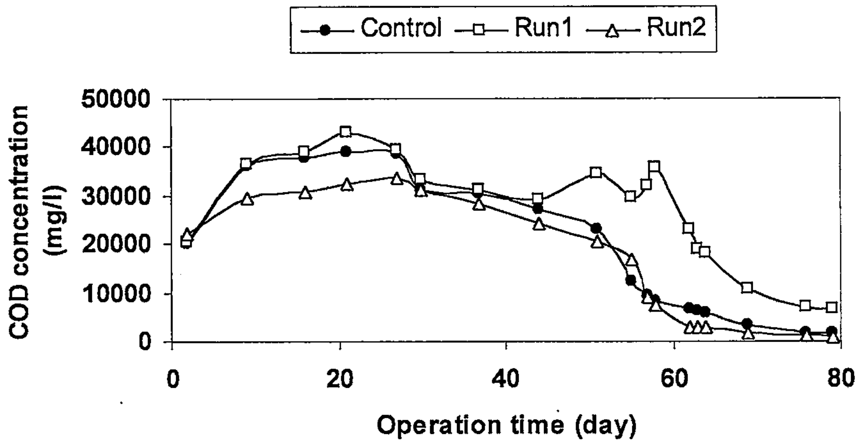

Figure 3.22 Trends in COD concentrations in leachate from the control, R1 and R2 reactors

3.4.2 VFA variations in leachates produced from the control and aerated reactors (run1 and run2)

The concentration of VFA is an important parameter because of the degree of the stability of the anaerobic process. As shown in Figure 3.23 the initial VFA concentrations in leachate samples were 9004, 9384 and 11304 mg/l in control, R1 and R2 reactors, respectively. The concentration of VFAs in leachate produced from the all reactors exhibit similar data with COD. A high linear correlation between COD removal efficiency and VFA removal efficiency was observed (R^2= 0.84). In addition, it was found that high linear correlation between maximum VFA and minimum pH values (R^2 = 0.96). On days 30, the VFA concentration of the control reactor increased to 11632 mg/l, and then started to decrease. The VFA values of the R1 and R2 reactors increased to 42967 and 33650 mg/l on day 21, respectively. The VFA concentrations in R2 were rapidly decreased after the aeration was started. O'Keefe & Chynoweth (2000) a sudden increase in production of VFAs was observed, immediately after aeration. It appears that during aeration the metabolic rate of facultative bacteria VFA produced were immediately metabolized. However, the VFA concentration in R1 was higher than that of the control reactor, despite aeration. At the end of the study, the final VFA concentrations in leachate samples were 1504, 3264 and 880 mg/l in control, R1 and R2 reactors, respectively. If the

VFA/B.Alk. ratio is lower than 0.4 the anaerobic reactor is stable (Behling et al., 1997). But, Griffin et al. (1998) reported that if the VFA/B.Alk. ratio is approximately 1, the solid waste reactor is stable.

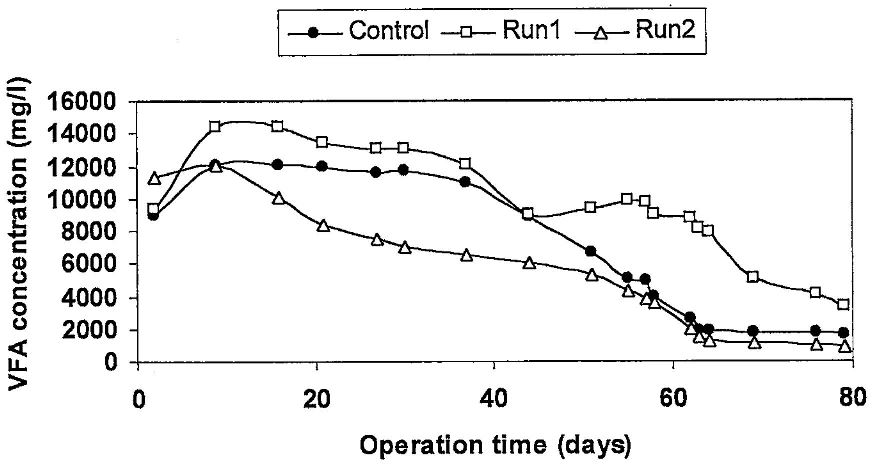

Figure 3.23 Trends in VFA concentrations in leachate from the control, R1 and R2 reactors

3.4.3 pH variations in leachates produced from the control and aerated reactors (run1 and run2)

The pH of the leachate samples are in accordance with the concentration of VFA measured in all reactors. The variation of pH profiles over time is provided in Figure 3.24. As can be seen in this figure, during the first two weeks, the pH of the leachates from the control, R1 and R2 reactors were 5.37, 5.36 and 5.17, respectively, on the acidic side of the pH scale. The pH values decreased to 5.17, 4.75 and 5.16 within 9 days in the control, R1 and R2 reactors, respectively. This caused to the extension of the time required for the organic fraction of the waste to stabilize since methane forming anaerobes are known to be very sensitive to low pH (Bolzonella et al., 2003). In other words, as the decomposition slowly progresses, decreases in pH may inhibit the metabolism or the reproduction of methanogens. The pH levels started to increase by day 27 in control reactor. The pH level of the control reactor was 6.98 on last operation day. The last pH value measured in the R1 and R2 reactors were 6.76 and 7.98, respectively. The highest pH value was monitored in R2 reactor. This value is in accordance with the data obtained by Stessel & Murphy (1992). In their study, the pH value of the aerated lysimeter was higher than non-aerated lysimeter. The pH value of the aerated lysimeter was about 8, while the pH value of the non-aerated lysimeter was 6.4. This study showed that R2 reactor has an advantage based on pH since the pH levels measured in control, R1 and R2 reactors were 6.98, 6.76 and 7.98, respectively, on day 79.

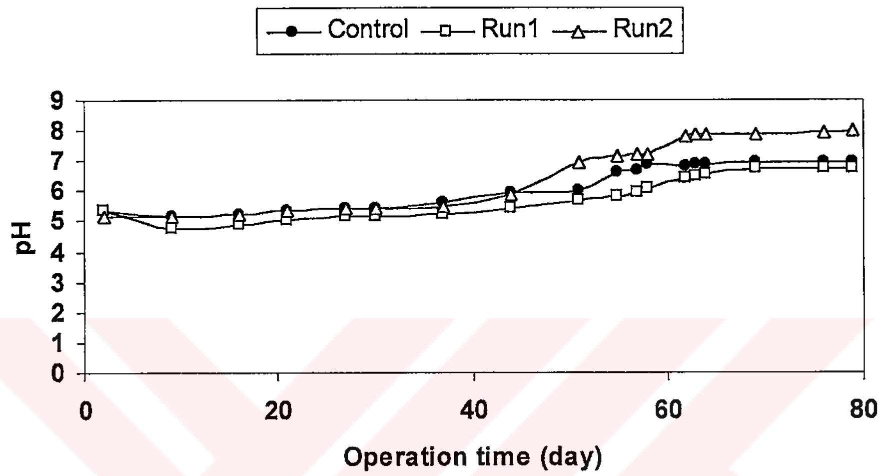

Figure 3.24 Trends in pH levels in leachate from the control, R1 and R2 reactors

3.4.4 NH_4-N variations in leachates produced from the control and aerated reactors (run1 and run2)

The results of the NH_4-N concentrations measured in leachate samples over time from the control, R1 and R2 reactors were shown in Figure 3.25. The highest NH_4-N concentrations were measured to be 780, 453 and 440 mg/l in control, R1 and R2 reactors through mineralization of organic nitrogenous compounds. It was observed that the NH_4-N concentrations in aerated bioreactors are lower than the control reactor. NH_4-N concentrations were 550, 110 and 139 mg/l in control, R1 and R2 reactors, respectively, on the last operation day. NH_4-N was converted to NO_3-N via nitrification in the presence of oxygen. The lowest NH_4-N value was observed in R1 reactor because of extended aeration. The results of this run showed that the aeration has an advantage related to NH_4-N removal since the NH_4-N oxidized to NO_3-N.

As reported by Marttinen et al. (2002), the landfill leachate treatment is normally focused on the removal of organic nitrogenous and carbonaceous matters and ammonia nitrogen levels since both three parameters are quite important for possible inhibition of methane production under anaerobic conditions. It is important to note that most of the nitrogen in the solid waste bioreactors is in the ammonia forms following the degradations of proteins and amino acids (İnanç et al., 2000). Leachate toxicity significantly correlated with the COD and ammonia in untreated and treated leachate (Marttinen et al., 2002). Ammonium concentrations as high as 400 mg/l may be inhibit the growth of anaerobic methanogenic bacteria in all reactors (Speece, 1996).

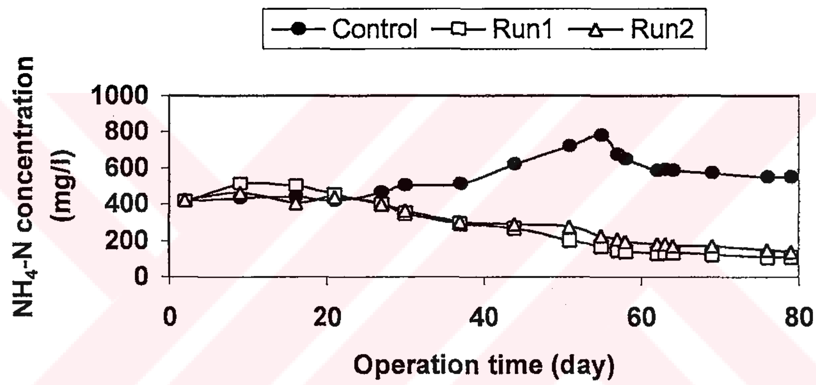

Figure 3.25 Trends in NH_4-N concentrations in leachate from the control, R1 and R2 reactors

3.4.5 NO_3-N variations in leachates produced from the control and aerated reactors (run1 and run2)

NO_3-N concentrations in control R1 and R2 reactors were shown in Figure 3.26. R1 and R2 reactors were aerated from day 28 to day 79. As can be seen in this figure, initial NO_3-N concentrations were 0.9, 9.6 and 3.1 mg/l in control, R1 and R2 reactors, respectively. NO_3-N concentrations of R1 were higher than the others due to extended aeration. NO_3-N concentrations of R1 and R2 reactors were gradually decreased on day 79 from 9.6 and 3.1 to 2.7 and 1.8 mg/l, respectively. This could be explained by the partial denitrification of NO_3-N in the non-aerated phase of aerated bioreactors. NO_3-N was converted to N_2 in aerated bioreactors (R1 and R2) at non-aerated phase through denitrification process. Purcell (2000) reported that organic nitrogen is converted to ammonia nitrogen through hydrolysis and deamination of amino acids. Under favorable aerobic conditions, the ammonia nitrogen is oxidized to nitrate by nitrifying bacteria such as *Nitrobacter* and *Nitrosomanas* via nitrification. Under anoxic conditions, denitrification processes will potentially reduce the transformation of nitrate to nitrogen gas. In landfill sites, air injection could be used to give rise the similar nitrification and denitrification processes.

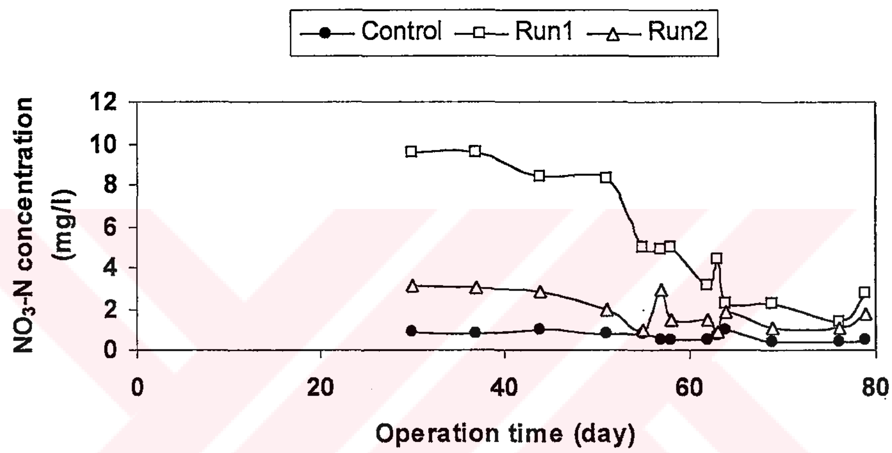

Figure 3.26 Trends in NO_3-N concentrations in leachate from the control, R1 and R2 reactors

3.4.6 Methane gas productions and methane percentages in simulated solid waste bioreactors

The quantity of methane and methane percentages of control, R1 and R2 reactors were shown in Figures 3.27 3.28 and 3.29, respectively. The maximum cumulative methane gas production was recorded as 11.2 L, 0.9 L and 3.6 L in control, R1 and R2 reactors, respectively at the end of 79 days. Both two aerated runs resulted in inhibition in methane gas productions. Productions of methane were determined only at non-aerated phase in R1 and R2. As can be seen in figures 3.28 and 3.29, no significant methane generation was occurred in aeration days. When the aeration was ceased the methane gas productions were 16.2, 9, 10.8 ml on days 38, 55 and 69 in

R1. The methane percentages were 9 %, 5 % and 6% in R1 on the aforementioned days (see Figure 3.28). For R2 reactor, when the aeration was ceased the methane gas productions were 412.8, 122.4, 100.8 and 52.8 ml on days 49, 63, 70 and 77 while the methane percentages were 24 %, 34 %, 28 % and 22 % (See Figure 3.29). It was observed that the methane gas content in R2 reactor was greater than R1 reactor in aerated runs. The higher methane enrichment in R2 reactor was probably from the high pH in R2 reactor resulted in decreased solubility of CO_2 in the leachate and therefore stripping of CO_2 from the leachate. Therefore it can be concluded that the level of aeration influences the methane enrichment by driving CO_2 from the pore space and headspace of anaerobic landfilling simulated reactors. Read et al. (2001) were reported that, methane concentrations decreased by at least 80 % in aerobic landfill compared to anaerobic landfill. In other related work, Leikam et al. (1997) indicated that methane concentrations in landfill gas could be reduced from 60 % to 10-15 % 7-10 days by air injection.

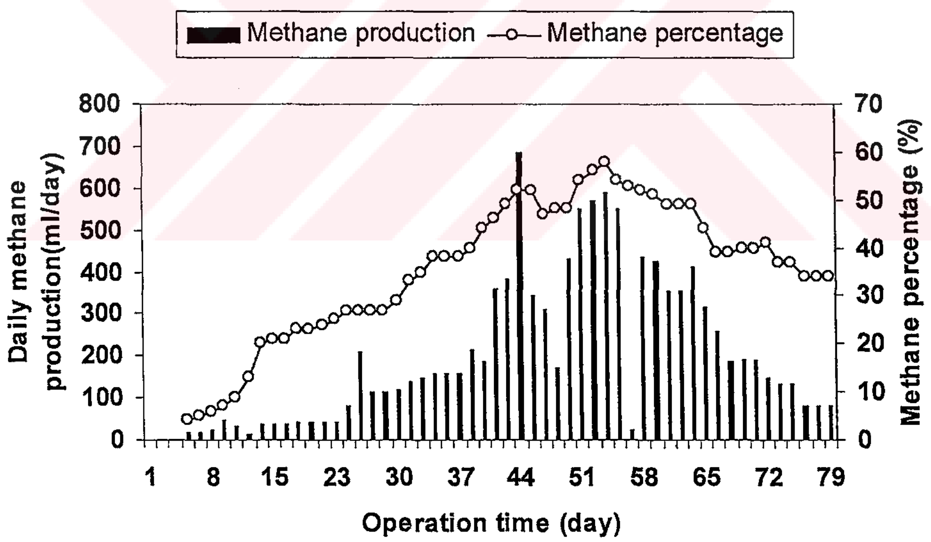

Figure 3.27 Methane production and methane percentage of control reactor

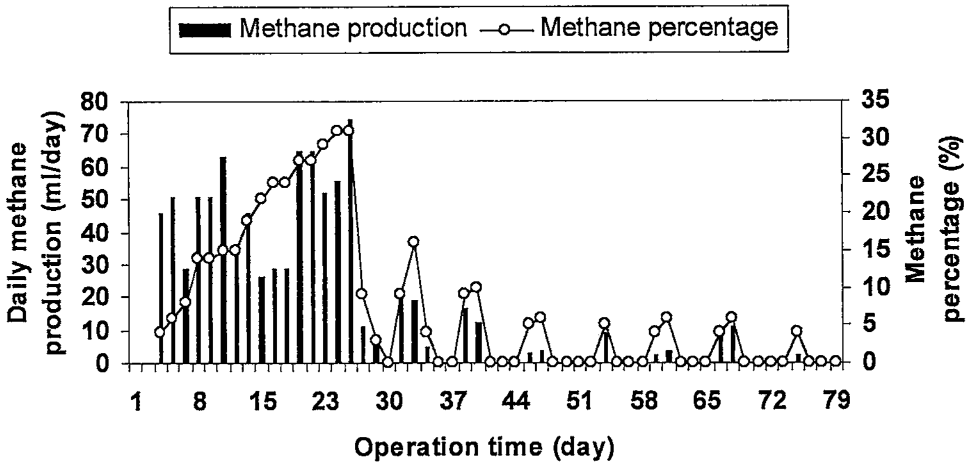

Figure 3.28 Methane production and methane percentage of R1 reactor

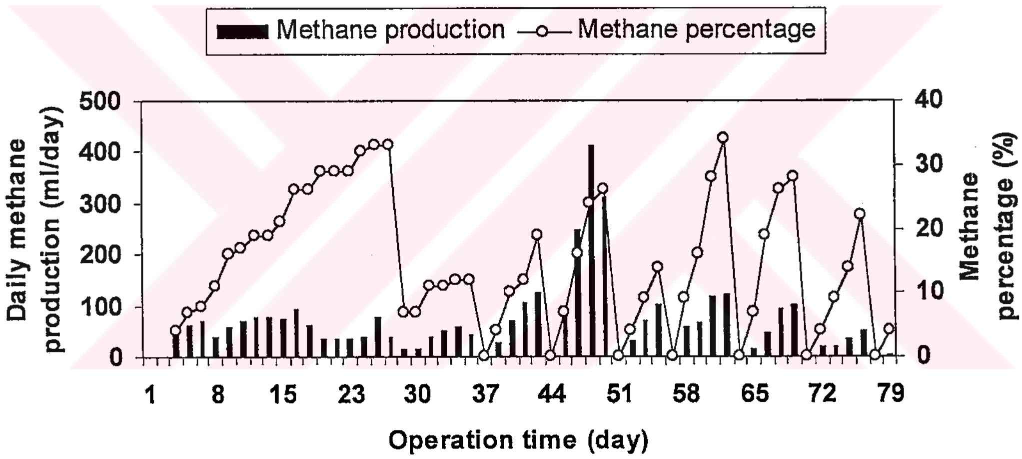

Figure 3.29 Methane production and methane percentage of R2 reactor

3.4.7 BOD_5, COD and BOD_5/COD ratios in leachate samples produced from the simulated solid waste bioreactors

Table 3.8 shows the COD, the BOD_5 concentrations and the BOD_5/COD ratios in the leachate samples of the all reactors studied for days 37, 51 and 62. The BOD_5 values initially were from 23865, 22968, 21864 mg/l in control, R1 and R2 reactors, respectively. These values reduced to 2152, 6100, 709 mg/l in control, R1 and R2 reactors, respectively. At the end of anaerobic/semi aerobic incubation the BOD_5

values decreased substantially by 91, 73 and 97 % in the aforementioned reactors, respectively. The experimental results indicate that better MSW stabilization was achieved in the R2 reactor at a high rate than that of control and R1 reactors. The BOD_5/COD ratio indicates the variations in the amount of biodegradable compounds of leachate. On day 62, the BOD_5/COD ratio decreased approximately to 0.23 from 0.77 in R2 reactor. This ratio implies a highly biodegradable leachate. As the biodegradation of organic content of MSW occurs, the BOD_5/COD ratio decreased. This decreases indicated that the organic wastes was degraded through fermentation phase which is showing a decreasing biodegradability. The BOD_5/COD ratio of the R2 reactor was the lowest. This result indicated that, the organic waste in R2 reactor is degraded rapidly.

If the BOD_5/COD ratio were between 0.02 and 0.13, this implies that the leachate has a low biodegradability through anaerobic phase (Otieno, 1994). When this ratio is between 0.4 and 0.8, this implies the high biodegradability of the leachate (Otieno, 1994). The BOD_5/COD ratio measured in the study shows similar data with the findings of Ledakowicz & Kaczorek (2002). In their study, the BOD_5/COD ratio dropped from 0.55 to 0.2 on the 80^{th} day. Read et al. (2001) indicated that BOD concentrations in the leachate were reduced by the aerobic process at least 70 %.

Table 3.8 BOD_5 concentration and BOD_5/COD ratios of the simulated bioreactors

	Control			R1			R2		
	Day 37	Day 51	Day 62	Day 37	Day 51	Day 62	Day 37	Day 51	Day 62
BOD_5 (mg/l)	23865	11500	2152	22968	15500	6100	21864	9050	709
COD (mg/l)	30253	22768	6520	31012	34310	23015	28285	20542	3057
BOD_5/COD	0.79	0.5	0.33	0.74	0.45	0.27	0.77	0.44	0.23

3.4.8 Determination of leachate toxicity in simulated bioreactors by using *lumistox* toxicity test

Tables 3.9, 3.10 and 3.11 show the percent inhibititory (H %) effects of leachate originated from the control, R1 and R2 reactors, respectively. Leachate samples originated from the bioreactors were found toxic according to Environmental protection serves for toxicity test using luminescent bacteria (EPS) (20<H< 90) (DIN, 1993). In other words, when the percent inhibitory effect (%H) varied between 20 % and 90 %, the effect is toxic (Dr. LÀNGE, 1994). 1/1, 1/5, 1/10 and 1/20 dilution rates were applied on leachate samples for examine the dilution factor (G_L) indicating the IC_{50} values (dilutions inhibited 50 % light intensity of vibrio fisheri) of leachate samples. Figure 3.30 shows the G_L values indicating IC_{50} values of leachate samples. As can be seen in Figure 3.30, the IC_{50} value of the R2 reactor is 16 while the IC_{50} value of the control and R1 reactors is approximately 20. It can be concluded that the leachate samples inhibited 50 % light intensity of luminescence bacteria "vibrio fisheri" even diluted 16 and 20 times in R2, R1 and control reactors. Tables 3.9, 3.10 and 3.11 and Figure 3.30 showed that intermittent aeration has not a significant effect on toxicity removal from the leachate originated from the anaerobic landfill bioreactors. Leachate toxicity may be originated from high NH_4-N and inert COD levels of leachate samples (data for inert COD was not shown). COD and IC_{50} values of the R2 reactor were the lowest between three reactors.

Table 3.9 The percent inhibitory effects of leachate samples from the control reactor

Inhibition H (%)	Time (Minute)	Dilution Factor (G_L)			
		1	5	10	20
H_5	5	93	76	65	45
H_{15}	15	96	77	69	49
H_{30}	30	98	78	71	51

Table 3.10 The percent inhibitory effects of leachate samples from the R1 reactor

Inhibition H (%)	Time (Minute)	Dilution Factor (G_L)			
		1	5	10	20
H_5	5	92	73	62	47
H_{15}	15	93	74	64	49
H_{30}	30	94	76	65	50

Table 3.11 The percent inhibitory effects of leachate samples from the R2 reactor

Inhibition H (%)	Time (Minute)	Dilution Factor (G_L)			
		1	5	10	20
H_5	5	92	68	54	39
H_{15}	15	92	70	56	40
H_{30}	30	93	73	59	43

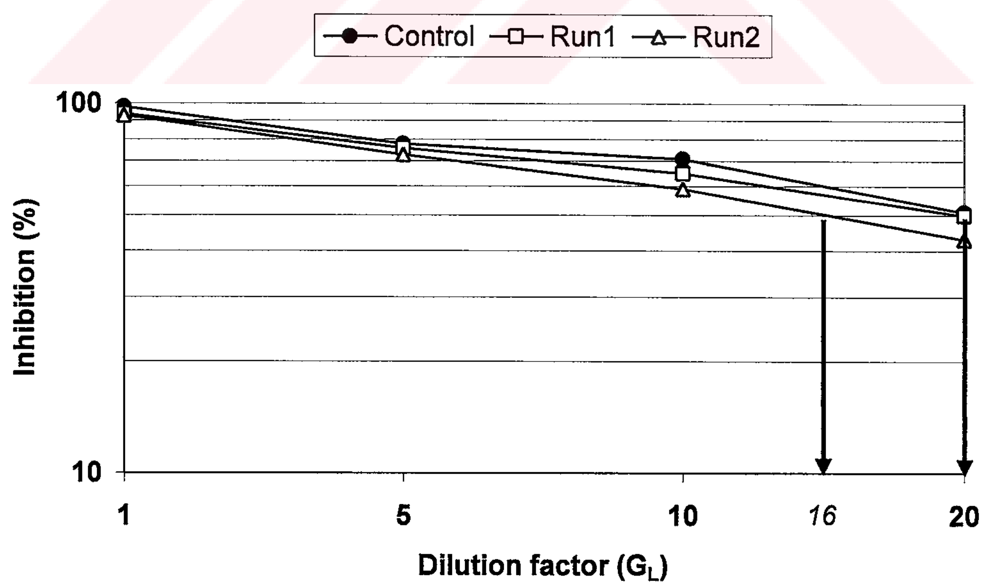

Figure 3.30 G_L values indicating IC_{50} values of leachate samples from the control, R1 and R2 reactors

3.4.9 Comparison of characteristics of the reactors

As can be seen in Table 3.12 the organic matter reduction of MSW in R1 reactor is the highest level. The organic matter reduction percent of MSW in control, R1 and R2 reactors are 37 %, 52 % and 45 %, respectively through 79 days of incubation period. Similarly, C % reduction and waste quantity reduction in R1 reactor is the best. This parameter is very important for the volume reduction and for the economy of lands. A high linear correlation between carbon removal efficiency and waste quantity reduction was observed (R^2= 0.99). O'Keefe & Chynoweth (2000) were reported that aeration of the simulated landfill cells resulted in acceptable volatile solids reduction. These results showed that the R1 reactor exhibits high biodegradation rates compared to the control and R2 reactors. TN, TP and NH_4-N removal efficiencies were 50 %, 67 % and 36 % in control reactor. However, TN, TP and NH_4-N removal efficiencies were 61 %, 55 % and 75 % in R1 while the same parameters were 57 %, 67 % and 59 % in R2. The final leachate quantities were 310, 100 and 260 ml in control, R1 and R2 reactors, respectively. Read et al. (2001) reported that, aerobic process was reduced the leachate quantity by over 85 %. Table 3.13 shows leachate characteristics for the all reactors. R2 reactor has the best result in terms of decreasing of COD and VFA accumulation and increasing of pH.

Table 3.12 Comparison of characteristics of the reactors

	Initial			Final		
	Control	R1	R2	Control	R1	R2
Water content (%)	90	90	90	91	88	89
Org. Matter (%) (in DS)	93	93	93	59	45	51
% C (in DS)	51.66	51.66	51.66	32.78	25	28.3
TN (mg/g) (in waste)	11100	11100	11100	5600	4300	4800
TP (mg/g) (in waste)	2450	2450	2450	800	1100	800
NH_4-N (mg/g) (in waste)	630	630	630	405	160	260
NO_3-N (mg/g) (in waste)				300	500	600
Waste Quantity (g)	1000	1000	1000	308.17	244.37	276.47
Final Leachate Quantity (ml)				310	100	260

Table 3.13 Comparison of characteristics of leachate in the first and last operation days for all the reactors

	t=0 (day)			t= 79 (day)		
	Control	R1	R2	Control	R1	R2
COD (mg/l)	19882	20624	22026	1504	6436	861
VFA (mg/l)	9004	9384	11304	1650	3264	880
pH	5.37	5.36	5.17	6.98	6.76	7.98
NH_4- N (mg/l)	420	416	422	550	110	139

3.4.10 Mass balance for C in leachate and solid waste

Carbon removal is important parameter for solid waste treatment. Carbon quantity of leachate and solid waste was calculated before and after of operation periods. High carbon removal means high waste quantity and organic matter reductions. In addition, high carbon removal efficiency supplies economic advantage due to acquire disposal area.

1000 g of solid waste was introduced to the control bioreactor containing 90 % of water and 51.66 % of carbon. The dry solid and the water content of the solid waste were 100 g and 900 g (0.9 L), respectively. The initial COD value of the leachate was measured as 19882 mg/l.

The initial carbon content of solid waste is calculated as follows:

$$100 * 0.52 = 52 \text{ g C} \qquad (3.11)$$

By using the equation 3.2, the carbon (C) quantity of the leachate was calculated as follows:

Assume that, the theoretical oxygen demand is equal to the initial COD value.

By taking into consideration the equation 3.2, the carbon (C) quantity in the leachate was calculated as 7.46 g.

The addition of 0.5 L tap water to the control bioreactor was increased the water content of solid wastes in the control bioreactor 1.4 L.

The initial carbon (C) quantity was calculated as 10.44 g by multiplying the leachate quantity (1.4 L) with the theoretical carbon quantity (7.46 g C).

As a result, the total carbon (C) quantity in the solid waste and in the leachate sample was calculated as 52 + 10.44 = 62.44 g.

After 79 days of operation period, the quantity of solid waste containing 91 % of water and 32.78 % of carbon decreased to 308.17 g from 1000 g. As a result, 27.7 g of solid waste and 280.5 g (0.28 L) of water remained in the control bioreactor.

The final carbon quantity in solid waste was calculated as follows:

$$27.7 * 0.33 = 9.14 \text{ g C} \tag{3.12}$$

The final COD of the leachate was measured as 1504 mg/l, and the final theoretical carbon quantity in the leachate was calculated as 0.56 g C using the equation 3.2.

The final leachate quantity was 0.4 L. The final water quantity of the system was calculated as follows:

$$0.28 \text{ L} + 0.4 \text{ L} = 0.68 \text{ L} \tag{3.13}$$

The final carbon quantity was calculated as 0.38 g C by multiplying the leachate quantity (0.68 L) with theoretical carbon quantity (0.56 g C).

As a result, the total carbon (C) quantity in solid waste and in the leachate samples of the system was calculated as 9.14 + 0.38 = 9.52 g.

Finally, the carbon removal efficiency of the total system was obtained as 85 % in control reactor.

The total carbon (C) quantities in the solid waste and in the leachate sample were 62.82 g and 8.1 g in R1 reactor before and after operation period. The carbon removal efficiency of the total system was obtained as 87 % in R1 reactor. Similarly, the carbon removal efficiency of the total system was obtained as 86 % in R2 reactor.

These calculations are showed that carbon removal efficiency in aerated reactors is a little bit higher than the control reactor.

3.5 Effect of Industrial Sludge Addition 1 on Degradation of MSWs

3.5.1 COD variations in leachate produced from the simulated anaerobic solid waste reactors

COD was monitored as an indicator parameter of the leachate organic strength. Figure 3.31 shows the daily variation of COD concentrations in leachate for the control (no sludge addition), run 1 (waste/sludge ratio 1:1) and run 2 (waste/sludge ratio 1:2) reactors. As can be seen in this figure, the initial COD concentration in leachate samples collected from the control, run 1 and run 2 reactors were 29050, 18695 and 17104 mg/l, respectively. The initial COD value of the control reactor was higher than the others because of containing high organic matter. The COD value of the leachate in the control reactors increased to 41900 mg/l until day 28, and then started to decrease from 41900 mg/l to 7128 mg/l by day 98. Although the control reactor has a high COD value of, decreasing of the COD was faster than the industrial sludge added reactors. The COD values in the leachate samples taken from the industrial sludge added reactors (run 1 and run 2) increased to 31214 and 26807 mg/l until day 17 and 9, respectively. The highest COD value was measured in control reactor among the three reactors during the operation period. The final COD concentrations of run 1 and run 2 reactors were 5714 and 4205 mg/l, respectively, on day 98. In the study realized by Pohland & Gould, (1986), it was found that the COD value of the metal plating sludge containing reactors were higher than the control reactor. COD concentration was approximately 7000 mg/l in industrial sludge containing reactor, while was only 500 mg/l in control reactor at the end of the study. The sludge was containing high concentrations of heavy metals such as 500 mg/l of zinc and 120 mg/l of iron. They reported that COD decreasing in high heavy metal containing reactors were slower than the control reactor. Çinar et al. (2004) found the COD value of the leachate originated from waste activated sludge containing reactor was lower than the control (containing no-waste activated sludge) reactor.

The lower level of COD and VFA concentrations in industrial sludge containing leachate samples could be attributed to a much higher level of aceticlastic methanogens compared to MSW sludge as reported by Stroot et al. (2001). Significant population of VFA and COD degrading microorganisms are able to consume the VFA rapidly without any accumulation. The result of this study showed that co-digestion of OFMSW with industrial sludge has a relatively positive effect in the decreasing of COD concentrations in simulated bioreactors. A high linear correlation between COD removal efficiency and methane quantity was observed (R^2= 0.8).

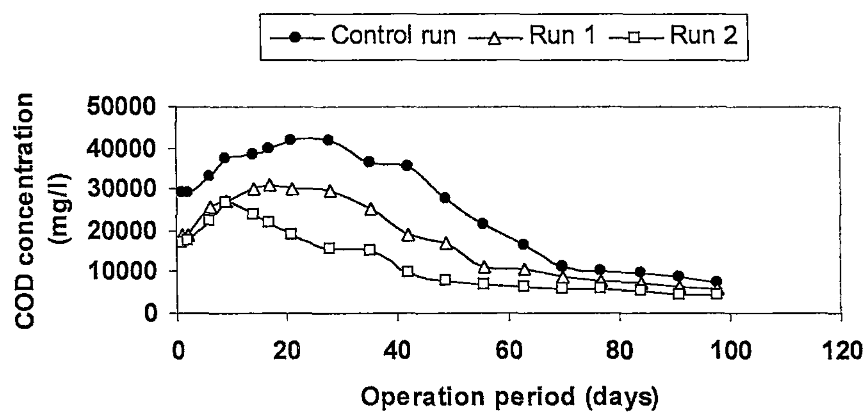

Figure 3.31 Daily variations of COD concentrations in leachate for the control, run1 and run2

3.5.2 VFA variations in leachate produced from the simulated anaerobic solid waste reactors

The concentration of VFA is an important parameter because of the degree of the stability of the anaerobic process. As shown in Figure 3.32 the initial VFA concentrations in leachate samples were 12600, 8994 and 9460 mg/l in control, run 1 and run 2 reactors, respectively. The concentration of VFAs in leachate produced from the all reactors exhibit similar data with COD. A high linear correlation between COD removal efficiency and VFA removal efficiency was observed (R^2= 0.92). On days 17, the VFA concentration of the control reactor increased to 22005 mg/l, and then started to decrease. The VFA values of the run 1 and run 2 reactors increased to 16783 and 14878 mg/l on day 9, respectively. The highest VFA value occurred in control reactor among three reactors since contains high organic matter. Organic matter degradation in initial phase of the fermentation caused high VFA concentration. At the end of the study, the final VFA concentrations in leachate samples were 1605, 1310 and 576 mg/l in control, run 1 and run 2 reactors, respectively. VFA reduction in control reactor was the highest within three reactors despite has a high final value of the VFA. The lower VFA concentration in industrial sludge containing reactors could be attributed to synergistic effects of microorganisms in MSW and industrial sludge through hydrolysis of organic compounds.

In the leachate samples taken from the industrial sludge containing MSW reactor will contain more balanced population where the growth of acidifying bacteria is moderated by the rate of these bacteria are able to hydrolyze insoluble substrates (Nopharatana et al., 1998). Therefore in the leachate samples from the industrial sludge containing run 1 and run 2 reactors exhibit low VFA concentrations compared to control reactors. If the VFA/B.Alk. ratio is lower than 0.4 the anaerobic reactor is stable (Behling et al., 1997). But, Griffin et al. (1998) reported that if the VFA/B.Alk. ratio is approximately 1, the solid waste reactor is stable.

Schmidell et al. (1986) reported that, high quantity of the sewage sludge within the solid waste reactor has a low VFA concentration. Contrarily, in the study carried out by Pohland & Gould (1986), VFA concentration of the industrial sludge added reactor was higher than the VFA concentration of the control reactor.

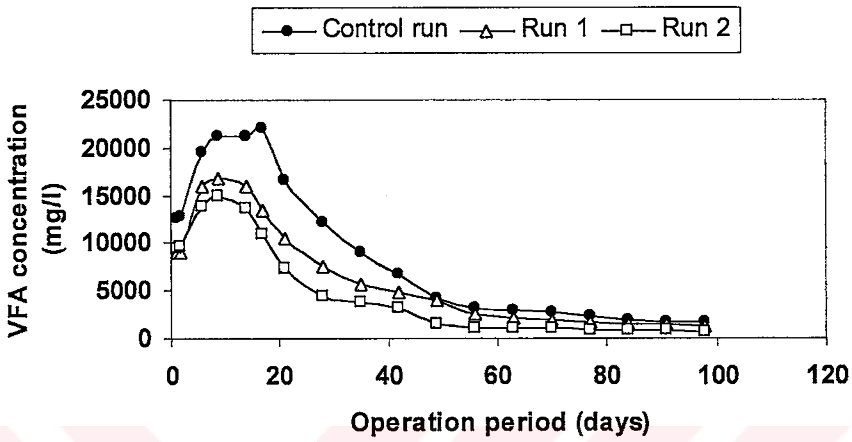

Figure 3.32 Daily variations of VFA concentrations in leachate for the control, run1 and run2

3.5.3 pH variations in leachate produced from the simulated anaerobic solid waste reactors

The pH of the leachate samples are in accordance with the concentration of VFA measured in all reactors. The variation of pH profiles over time is provided in Figure 3.33. As can be seen in this figure, the initial pH of the leachates from the control, run 1 and run 2 reactors were 5.38, 6.03 and 5.77, respectively. The pH value of the run 2 was higher than run 1 and control run on day 6. The highest pH value of control run was 6.31 on the last operation day, while the pH values were between 6.5 and 7 in industrial sludge added reactors during the study. This study showed that run 2 has an advantage in terms of pH since the pH levels measured in control, run 1 and run 2 reactors were 6.31, 7.16 and 7.25, respectively, on day 98.

Warith (2002) found that the highest pH value in sewage sludge addition reactor between pH value of the control and nutrient added reactors. Similarly with our study, the pH value of the sludge added reactors was found approximately 7.5 in the study performed by Warith (2002). In addition, the study realized by Pohland & Gould (1986) was shown that the pH value of the metal plating industrial sludge added reactor was higher than the pH value of the control reactor.

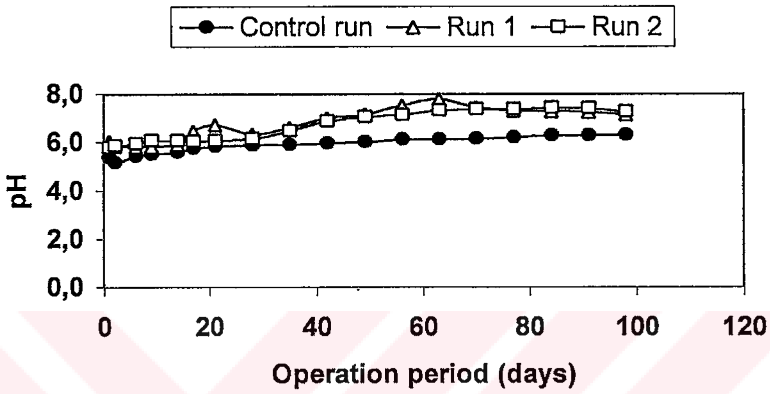

Figure 3.33 Daily variation of pH concentrations in leachate for the control, run 1 and run 2

3.5.4 NH_4-N variations in leachate produced from the simulated anaerobic solid waste reactors

The results of the NH_4-N concentrations measured in leachate samples over time from the control run 1 and run 2 reactors were shown in Figure 3.34. The highest NH_4-N concentrations were measured to be 701, 464 and 362 mg/l control, run 1 and run 2 reactors through mineralization of organic nitrogenous compounds. It was observed that the NH_4-N concentrations in control reactor is higher than that of run1 and run 2 reactors since the control reactor has a high organic matter. The initial NH_4-N concentrations measured in leachate were 194, 154 and 91 mg/l in control, run 1 and run 2 reactors. The NH_4-N concentrations of control reactor were always higher than industrial sludge added reactors during the operation period. In addition, the NH_4-N concentration in high industrial sludge added reactor was lower than low industrial sludge added reactor.

As reported by Marttinen et al. (2002), the landfill leachate treatment is normally focused on the removal of organic nitrogenous and carbonaceous matters and ammonia nitrogen levels since both three parameters are quite important for possible inhibition of methane production under anaerobic conditions. It is important to note that most of the nitrogen in the solid waste bioreactors is in the ammonia forms following the degradations of proteins and amino acids (İnanç et al., 2000).

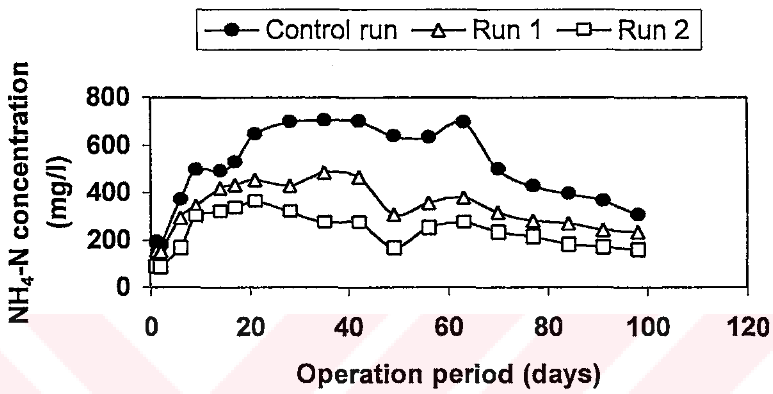

Figure 3.34 Daily variation of NH_4-N concentrations in leachate for the control, run 1 and run 2

3.5.5 Methane gas productions and methane percentages in simulated anaerobic solid waste bioreactors

The quantity of methane in control, run 1 and run 2 reactors were shown in Figure 3.35. As can be seen in this figure, the maximum cumulative methane gas production was recorded as 12.7 L, 6.7 L and 5.2 L in control, run 1 and run 2 reactors, respectively at the end of 98 days. The reason for the high cumulative methane in control reactor is the high quantity of organic wastes in this reactor. Cecchi et al. (1988) reported that cumulative biogas production of mixtures increased with increasing proportions of MSW. Similarly, Sosnowski et al. (2003) found that higher cumulative methane gas in high quantity of solid waste relative to sewage sludge containing reactor than low solid waste containing reactor. Methane percentage in control, run 1 and run 2 reactors were shown in Figure 3.36. Approximately methane percentages were 62 %, 44 % and 37 % in control, run 1 and run 2 reactors, respectively on day 50. Methane percentage of the control, run 1 and run 2 reactors were 31 %, 20 % and 12 %, respectively, at the end of the 98 days of operation period. These results showed that, degradation period was continuing in the control reactor while the degradation periods of industrial sludge added reactors ended. Çinar et al. (2004) investigated the cumulative gas production in sewage sludge containing and non containing solid waste reactors. They found that the gas quantity of sewage sludge contained reactor was higher than the only solid waste containing reactors due to its higher organic content.

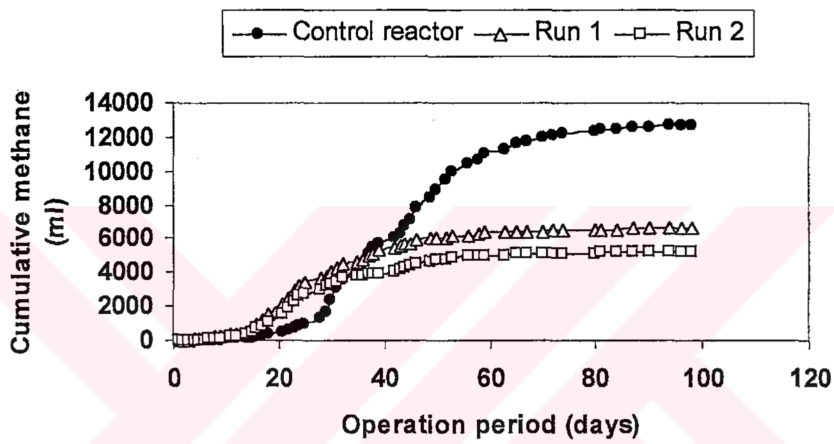

Figure 3.35 Variation in cumulative methane gas productions in the control, run 1 and run 2 reactors through 98 days of anaerobic incubation

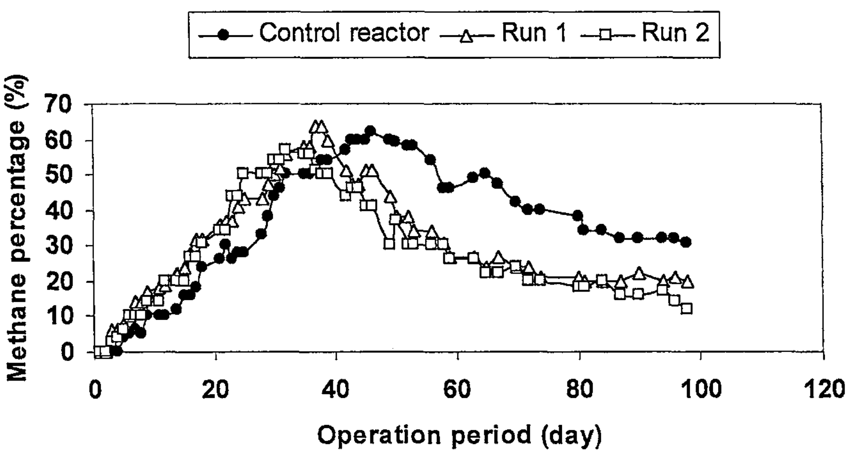

Figure 3.36 Variation in methane percentages in the control, run 1 and run 2 reactor through 98 days of anaerobic incubation

3.5.6 Bioefficiency of anaerobic process

The methane yield was found as 0.148 g CH_4-$COD_{removed}$/gVSS add in control reactor while the methane yields were 0.05 CH_4-$COD_{removed}$/gVSS add and 0.04 CH_4-$COD_{removed}$/gVSS add in run 1 and run 2 reactors. It was found that the maximum mass of removed COD were equal to 34.8, 25.5 and 22.6 g in control, run 1 and run 2 reactors on day 98. Using these values, and taking into consideration the methane gas produced, it can be concluded that 93 % of COD was removed from the control reactor was converted to methane and 67 % and 58 % of COD removed were converted to methane in run 1 and run 2 reactors, respectively on day 98.

As shown the calculated methane yield was higher in control reactor since MSW primarily consists of easily biodegradable organic matter. This contributed to better biological degradation.

3.5.7 BOD_5, inert COD concentrations, BOD_5/COD ratios and ATA test results in leachate samples produced from the simulated anaerobic solid waste bioreactors

In order to study the proportion of biodegradable organic carbon in the leachate it was considered to determine the BOD_5/COD ratios. Table 3.14 shows the computed values of these ratios, BOD_5, COD concentrations, and BOD_5/COD ratios in the leachate samples of the all reactors studied for days 14, 49 and 84. The BOD_5 values were ranging initially from 35631, 28000, 20000 mg/l to 2786, 2592, 2048 mg/l at the end of anaerobic incubation in control, run 1 and run 2 reactors, respectively. The BOD_5 values decreased substantially as 92, 90 and 89 % in the aforementioned reactors, respectively. Although the control reactor has high initial BOD_5 concentrations, the highest BOD_5 decreases were occurred in this reactor. The experimental results indicate that, the addition of industrial sludge not significantly retarded the decreasing of BOD_5 removals. In the study carried out by Warith (2002), the highest BOD_5 value was occurred in the sewage sludge added reactor. In our study, BOD_5 values in industrial sludge added reactors were higher than BOD_5 value of the control reactor since the industrial sludge contains surplus biodegradable organic matter in proportion 1:1 and 1:2. The BOD_5/COD ratio indicates the changes in the amount of biodegradable compounds in the leachate. Initially, all the reactors have high BOD_5/COD ratios approximately 0.92 indicating the high degradability of leachate as reported by Quasim & Chiang (1994). On day 49, BOD_5/COD ratio decreased approximately to 0.29 from 0.93 in control reactor on days 84. The BOD_5/COD ratios decreased to 0.36 from 0.92 and to 0.39 from 0.84 in run 1 and run 2 reactors, respectively by days 84. This ratio implies a highly biodegradable leachate. In other words, this level shows the increasing biodegradability of organics due to solubilization of organic substances through methanogenesis. As the organic content biodegradation of MSW occurs, the BOD_5/COD ratio decreased. This decreases indicated that the organic wastes was degraded through fermentation phase which is showing a decreasing biodegradability due to methane formation. The BOD_5/COD ratio of the control reactor was the lowest. This result indicated that, the organic waste in control reactor is converted rapidly to methane via methanogenesis.

Table 3.14 BOD_5, COD concentrations and BOD_5/COD ratios in the leachate samples of the bioreactors

	Control Reactor			Run 1			Run 2		
	Day 14	Day 49	Day 84	Day 14	Day 49	Day 84	Day 14	Day 49	Day 84
BOD_5(mg/l)	35631	12998	2786	28000	9100	2592	20000	4200	2048
COD(mg/l)	38313	27656	9604	30313	16804	7200	23922	7623	5250
BOD_5/COD	0.93	0.47	0.29	0.92	0.54	0.36	0.84	0.55	0.39

Table 3.15 illustrates the results of the ATA tests indicating the quantities of methane produced from the control (glucose) and leachate containing serum bottles through three days of anaerobic incubation. At the end of the ATA test, it was found that there is significant toxicity in industrial sludge added reactors (especially in run 2) under anaerobic conditions since decreases in methane gas productions was observed. This can be explained by the AOX and heavy metal content of industrial sludge added reactors. No toxicity was observed in control reactor. This result can be

explained by the no toxic and inhibitor organic and inorganic chemicals content of control reactor since the organic solid wastes were taking from the kitchen of the Engineering Faculty Campus. When the leachate percentage was increased in the serum bottles for control reactors, the quantity of methane produced increased, indicating the utilization of leachate as suitable carbon source by the methanogenic microorganisms through anaerobic degradation. Contrarily, the methane gas productions decreased in industrial sludge containing leachate samples indicating the toxicity of DYO dye industry sludge on methane bacteria through methanogenesis.

Table 3.15 Methane quantities of control and leachate samples at different conditions

	Quantity of Methane (ml/day) (n=3 mean value)	
	(After 3 days)	(After 6 hours)
Glucose 0 % leachate (control)	35	33
Glucose 0 % leachate (control)	34	33
25 % leachate (Control reactor)	37	36
50 % leachate (Control reactor)	43	42
75 % leachate (Control reactor)	50	51
100 % leachate (Control reactor)	54	53
25 % leachate (Run 1)	29	27
50 % leachate (Run 1)	26	25
75 % leachate (Run 1)	21	20
100 % leachate (Run 1)	17	16
25 % leachate (Run 2)	19	16
50 % leachate (Run 2)	15	12
75 % leachate (Run 2)	9	8
100 % leachate (Run 2)	4	5

The results of inert COD assays in leachate samples showed that inert COD level was found to be approximately 8 %, 10 % and 12 % of the initial COD levels in control, run 1 and run 2 reactors, respectively. High inert COD levels in industrial sludge containing reactors could be attributed to high AOX, heavy metal contains of aforementioned sludge. This indicates that the COD of leachate samples could be treated up to approximately 90% which is the maximum COD removal efficiency reached under favorable anaerobic conditions.

3.5.8 Comparison of the characteristics of the MSW in the reactors

As can be seen in Table 3.16 the organic matter reduction of MSW in control reactor is the highest level. The percentage of organic matter reduction of MSW in control, run 1 and run 2 reactors are 42 %, 16 % and 10 %, respectively through 98 days of incubation period. In addition, waste settlement in control reactor is the highest level. On the contrary in the study realized by Schmidell et al. (1986); the organic matter reduction decreased, when the sludge quantity was increased. This could be explained by the utilization of sewage sludge in their study. In our study dye industry sludge was used. On the contrary of the study realized by Warith (2002) in this study, the lowest settlement was achieved in industrial sludge added reactors. The settlement was about 33 % while the settlement level was about 57 % in control reactor. The reductions in C percentage and waste quantity in control reactor was found to be at higher level. A high linear correlation between carbon removal efficiency and waste quantity reduction was observed (R^2= 0.99). It is important to note that, settlement is very important parameter related to landfilling economy. The TN, TP and NH_4-N reduction in control reactor is the highest level. The TN, TP and NH_4-N concentrations in MSW reduced to 614, 314 and 121 from 10900, 2300 and 500 mg/kg in control reactor by day 98. This shows that the methanogenic microorganisms consumed nitrogen and phosphorus through the degradation of carbonaceous compounds. The heavy metal was measured at the end of the operation period for run 2 (See Table 3.16). Total crom, zinc and iron were decreased from 0.16, 0.58 and 0.8 mg/l to 0.07, 0.21 and 0.2 mg/l, respectively on day 98. Copper, lead and manganese were not detectable at the end of the operation period.

Table 3.16 Comparison of characteristics of the simulated anaerobic landfilling MSW reactors

	Initial			Final		
	Control	Run 1	Run 2	Control	Run 1	Run 2
Water content (%)	87	67	56	89	54	51
Org. Matter (%) (in DS)	97	88	80	56	74	72
% C (in DS)	54	49	44	31	41	40
TN (mg/kg) (in waste)	10900	6200	4300	614	937	643
TP (mg/kg) (in waste)	2300	700	500	314	142	102
NH_4-N (mg/kg) (in waste)	500	470	230	121	112	84
Waste Height (cm)	30	30	30	13	18	20
Waste Quantity (g)	1200	1200	1200	420	674	791
Cr (mg/l)						0.07
Zn						0.21
Cu						-
Pb						-
Fe						0.2
Mn						-
Ni						-
Cd						-

3.5.9 Mass balance for C in leachate and solid waste

Carbon removal is important parameter for solid waste treatment. Carbon quantity of leachate and solid waste was calculated before and after of operation periods. High carbon removal means high waste quantity and organic matter reductions. In addition, high carbon removal efficiency supplies economic advantage due to acquire disposal area.

1200 g of solid waste was introduced to the control bioreactor containing 87 % of water and 53.89 % of carbon. The dry solid and the water content of the solid waste were 156 g and 1044 g (1 L), respectively. The initial COD value of the leachate was measured as 29050 mg/l.

The initial carbon content of solid waste is calculated as follows:

$$156 * 0.54 = 84 \text{ g C} \tag{3.14}$$

By using the equation 3.2, the carbon (C) quantity of the leachate was calculated as follows:

Assume that, the theoretical oxygen demand is equal to the initial COD value.

By taking into consideration the equation 3.2, the carbon (C) quantity in the leachate was calculated as 10.88 g.

The addition of 0.5 L tap water to the control bioreactor was increased the water content of solid wastes in the control bioreactor 1.5 L.

The initial carbon (C) quantity was calculated as 16.32 g by multiplying the leachate quantity (1.5 L) with the theoretical carbon quantity (10.88 g C).

As a result, the total carbon (C) quantity in the solid waste and in the leachate sample was calculated as 84 + 16.32 = 100.32 g.

After 98 days of operation period, the quantity of solid waste containing 89 % of water and 31.11 % of carbon decreased to 420 g from 1200 g. As a result, 46.2 g of solid waste and 373.8 g (0.37 L) of water remained in the control bioreactor.

The final carbon quantity in solid waste was calculated as follows:

$$46.2 * 0.31 = 14.3 \text{ g C} \tag{3.15}$$

The final COD of the leachate was measured as 7128 mg/l, and the final theoretical carbon quantity in the leachate was calculated as 2.67 g C using the equation 3.2.

The final leachate quantity was 0.4 L. The final water quantity of the system was calculated as follows:

$$0.37\ L + 0.4\ L = 0.77\ L \qquad (3.16)$$

The final carbon quantity was calculated as 2.05 g C by multiplying the leachate quantity (0.77 L) with theoretical carbon quantity (2.67 g C).

As a result, the total carbon (C) quantity in solid waste and in the leachate samples of the system was calculated as 14.3 + 2.05 = 16.35 g.

Finally, the carbon removal efficiency of the total system was obtained as 84 % in control reactor.

The total carbon (C) quantities in the solid waste and in the leachate sample were 203.1 g and 73.73 g in R1 reactor before and after operation period. The carbon removal efficiency of the total system was obtained as 64 % in R1 reactor. Similarly, the carbon removal efficiency of the total system was obtained as 35 % in R2 reactor.

These calculations are showed that carbon removal efficiency in industrial sludge added reactors is significantly lower than the control reactor. Industrial sludge addition has a negative effect on carbon removal from solid waste and leachate.

3.6 Effect of Industrial Sludge Addition 2 on Degradation of MSWs

3.6.1 COD variations in leachate produced from the simulated anaerobic solid waste reactors

COD was monitored as an indicator parameter of the leachate organic strength. Figure 3.37 shows the daily variation of COD concentrations in leachate for the control (no sludge addition), run 1 (waste/sludge ratio 1:1) and run 2 (waste/sludge ratio 1:2) reactors. As can be seen in this figure, the initial COD concentrations in leachate samples collected from the control, run 1 and run 2 reactors were 27415, 19004 and 17109 mg/l, respectively. The initial COD value of the control reactor was higher than the others because contains high organic matter. The COD value of the leachate in the control reactors increased to 43719 mg/l until day 25, and then started to decrease from 43719 mg/l to 396564 mg/l by day 30. The COD values in the leachate samples taken from the mixed industrial sludge added reactors (run 1 and run 2) increased to 31104 and 28105 mg/l until day 15, respectively. The highest COD value was measured in control reactor among the three reactors during the operation period. pH values in the control reactor was not suitable for the growth of anaerobic bacteria. This could be explained by the slow COD decreases in the control reactor in the first 30 days of incubation period. The final COD concentrations of run 1 and run 2 reactors were 27160 and 15964 mg/l, respectively, on days 30. In the study realized by Pohland & Gould, (1986), it was found that the COD value of the metal plating sludge containing reactors were higher than the control reactor. COD concentration was approximately 7000 mg/l in industrial sludge containing reactor, while it was only 500 mg/l in control reactor at the end of the study. The sludge contains heavy metals at high concentrations such as 500 mg/l of zinc and 120 mg/l of iron. In the aforementioned study it was reported that COD decreases in reactors containing high heavy metal concentrations were slower than that the control reactor. However, in this study, the heavy metal concentrations of reactor no containing mixed sludge was low. Çinar et al. (2004) found the COD value of the leachate originated from the reactor containing waste activated sludge was lower than the control (containing no-waste activated sludge) reactor.

The lower level of COD and VFA concentrations in the leachate samples produced from the mixed industrial sludge containing reactors could be attributed to high activity of aceticlastic methanogens compared to MSW sludge as reported by Stroot et al. (2001). Significant population of VFA and COD degrading microorganisms are able to consume the VFA rapidly without any accumulation. A high linear correlation between COD removal efficiency and VFA removal efficiency was observed (R^2= 0.84).

The result of this study showed that co-digestion of OFMSW with mixed industrial sludge has a relatively positive effect in the decreasing of COD concentrations in simulated anaerobic bioreactors.

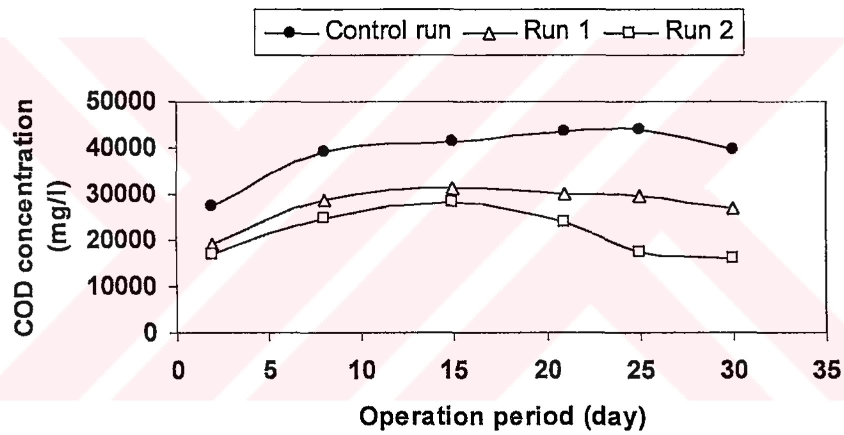

Figure 3.37 Daily variations of COD concentrations in leachate for the Control, Run1 and Run2 reactors

3.6.2 VFA variations in leachate produced from the simulated anaerobic solid waste reactors

The concentration of VFA is an important parameter because indicates the degree of the stability of the anaerobic process. As shown in Figure 3.38 the initial VFA concentrations in leachate samples were 27415, 9650 and 8669 mg/l in control, run 1 and run 2 reactors, respectively. The concentration of VFAs in leachate produced from the all reactors exhibit similar data with COD. A linear correlation between

VFA removal efficiency and methane gas production was observed (R^2= 0.77). On days 15, the VFA concentration of the control reactor increased to 23413 mg/l, and then started to decrease. The VFA values of the run 1 and run 2 reactors increased to 17105 and 15303 mg/l on days 15, respectively. The highest VFA value was measured in control reactor among three reactors since contains high amount of organic matter. The degradation of organic matter in initial phase of the fermentation caused high VFA concentration. At the end of the 30 days, the final VFA concentrations in leachate samples were 10354, 6120 and 4215 mg/l in control, run 1 and run 2 reactors, respectively. VFA reduction in control reactor was the highest within three reactors despite has a high final concentration of VFA at the end of anaerobic incubation. The lower VFA concentration in reactors containing mixed industrial sludge could be attributed to synergistic effects of microorganisms in MSW and industrial sludge through hydrolysis of organic compounds. High linear correlation between maximum VFA and minimum pH value was observed (R^2= 0.99).

In the leachate samples taken from the MSW reactor containing industrial sludge could contain more balanced population where the growth of acidifying bacteria is moderated by the rate of these bacteria and are able to hydrolyze insoluble substrates (Nopharatana et al., 1998). Therefore in the leachate samples from the run 1 and run 2 reactors containing industrial sludge exhibit low VFA concentrations compared to control reactor. If the VFA/B.Alk. ratio is lower than 0.4 the anaerobic reactor is stable (Behling et al., 1997). However, Griffin et al. (1998) reported that if the VFA/B.Alk. ratio is approximately 1, the solid waste reactor is stable. In this study the VFA/B.Alk. ratio was approximately 0.8 at the end of the 30 days indicating the steady-state conditions according to the value suggested by Griffin et al. (1998).

Schmidell et al. (1986) reported that, high quantity of the sewage sludge within the solid waste reactor produce low VFA concentration. Contrarily, in the study carried out by Pohland & Gould (1986), VFA concentration of the industrial sludge added reactor was higher than the VFA concentration of the control reactor. In this study similar result was obtained with the studies performed by Schmidell et al. (1986).

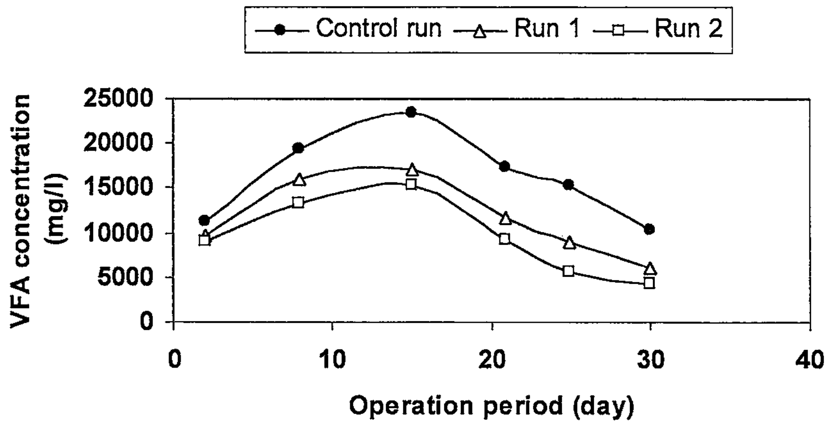

Figure 3.38 Daily variation of VFA concentrations in leachate for the Control, Run1 and Run2 reactors

3.6.3 pH variations in leachate produced from the simulated anaerobic solid waste reactors

The pH of the leachate samples are in accordance with the concentration of VFA measured in all reactors. The variation of pH profiles over time is provided in Figure 3.39. As can be seen in this figure, the initial pH of the leachates from the control, run 1 and run 2 reactors were 5.61, 6.02 and 6.1, respectively. The pH value of the run 2 was higher than run 1 and control reactors during the anaerobic operation period. The highest pH value of control run was 5.86 on the last operation day, while the pH values were between 6.7 and 7.2 in mixed industrial sludge added reactors through the study. This study showed that run 2 has an advantage in terms of pH since the pH levels measured in control, run 1 and run 2 reactors were 5.86, 7 and 7.2, respectively, on day 30.

Warith (2002) found that the highest pH value was in sewage sludge added reactor among the control and nutrient added reactors. Similarly in our study, the pH value of sludge added reactors was found approximately 7.5. In addition, the study realized by Pohland & Gould (1986) was shown that the pH value industrial sludge added reactor taking from the metal plating industry was higher than the pH value of the control reactor. In our study similar pH values were obtained with the experience performed by Schmidell et al. (1986).

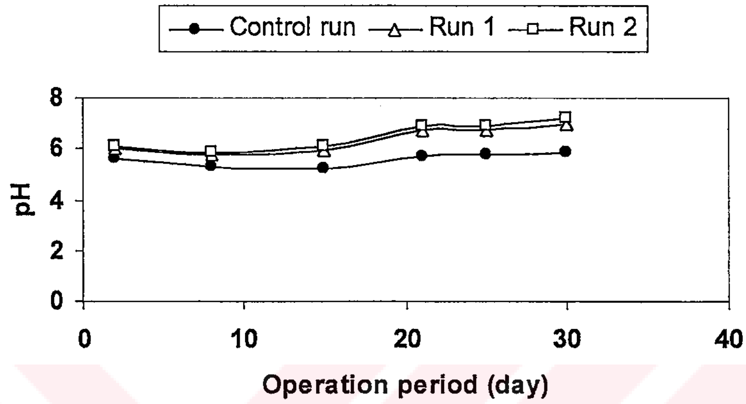

Figure 3.39 Daily variation of pH concentrations in leachate for the Control, Run 1 and Run 2 reactors

3.6.4 NH_4-N variations in leachate produced from the simulated anaerobic solid waste reactors

The results of the NH_4-N concentrations measured in leachate samples over time from the control, run 1 and run 2 reactors were shown in Figure 3.40. The highest NH_4-N concentrations were measured to be 618, 432 and 305 mg/l control, run 1 and run 2 reactors through mineralization of organic nitrogenous compounds. It was observed that the NH_4-N concentrations in control reactor is higher than that of run 1 and run 2 reactors since the control reactor has high amount of organic matter content. The initial NH_4-N concentrations measured in leachate were 344, 215 and 121 mg/l in control, run 1 and run 2 reactors. The NH_4-N concentrations of control reactor were always higher than the industrial sludge added reactors during 30 days of anaerobic operation period. In addition, the NH_4-N concentration in leachate samples produced from the high mixed industrial sludge added reactor was lower than the low mixed industrial sludge added reactor.

As reported by Marttinen et al. (2002), the landfill leachate treatment is normally focused on the removal of organic nitrogenous and carbonaceous matters and ammonia nitrogen levels since both three parameters are quite important for possible inhibition of methane production under anaerobic conditions. It is important to note that most of the nitrogen in the solid waste bioreactors is in the ammonia forms following the degradations of proteins and amino acids (İnanç et al., 2000).

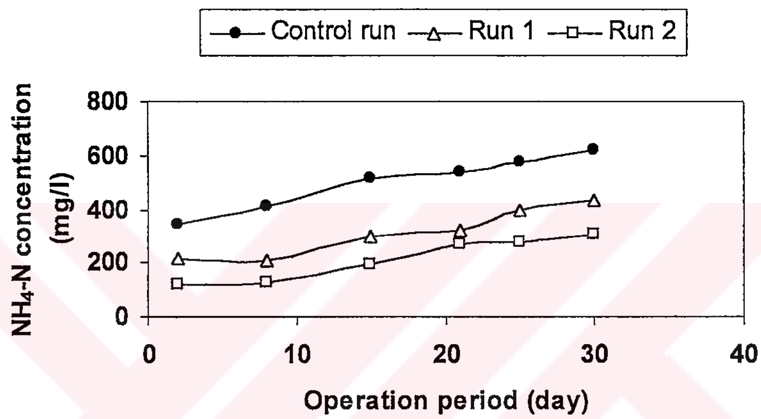

Figure 3.40 Daily variation of NH_4-N concentrations in leachate for the Control, Run 1 and Run 2 reactors

3.6.5 Methane gas productions and methane percentages in simulated anaerobic solid waste bioreactors

The quantity of methane in control, run 1 and run 2 reactors were shown in Figure 3.41. As can be seen in this figure, the maximum cumulative methane gas production was recorded as 13.5 L, 16.9 L and 17.1 L in control, run 1 and run 2 reactors, respectively at the end of 30 days. The reason for the high cumulative methane production in run 1 and run 2 reactors is the rapid degradation of organic wastes in these reactors. Cecchi et al. (1988) reported that cumulative biogas production of mixtures increased with increasing proportions of MSW. Similarly, Sosnowski et al. (2003) found that higher cumulative methane gas productions in high quantity solid waste containing reactor than that low solid waste containing reactor. Methane percentage in control, run 1 and run 2 reactors were shown in Figure 3.42. Methane percentage of the control, run 1 and run 2 reactors were 39 %, 46 % and 59 %, respectively, at the end of the 30 days of operation period. These results showed that, degradation period was continuing in the all reactors. It is important to note that, methanogenesis process in mixed sludge added reactors were faster than the control reactor accomplished with high methane gas productions and methane percentages.

Çinar et al. (2004) investigated the cumulative gas production in sewage sludge containing and non containing solid waste reactors. They found that the gas quantity of sewage sludge contained reactor was higher than the only solid waste containing reactors due to its higher organic content.

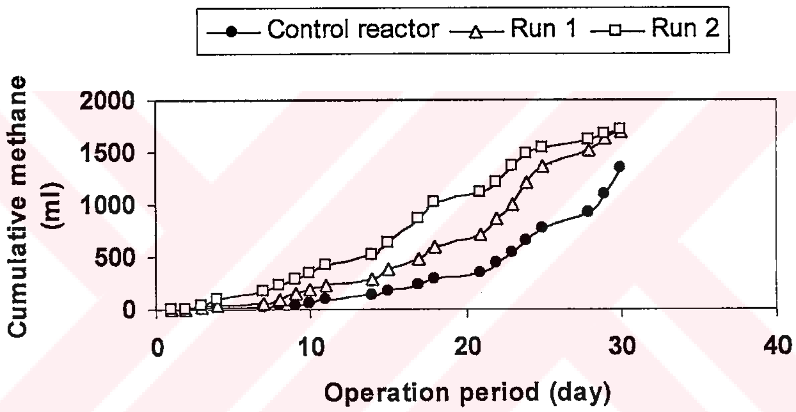

Figure 3.41 Variation in cumulative methane gas productions in the Control, Run 1 and Run 2 reactors through 30 days of anaerobic incubation

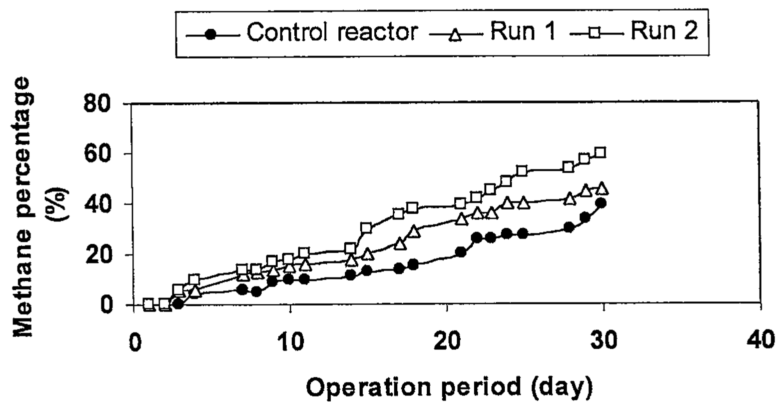

Figure 3.42 Variation in methane percentages in the Control, Run 1 and Run 2 reactors through 30 days of anaerobic incubation

3.6.6 Bioefficiency of anaerobic process

It was found that the maximum mass of removed COD were equal to 4.07, 3.9 and 12.1 g in control, run 1 and run 2 reactors on day 30. Using these values, and taking into consideration the methane gas produced, it can be concluded that 88 % of COD was removed from the control reactor was converted to methane and 91 % and 72 % of COD removed were converted to methane in run 1 and run 2 reactors, respectively on day 30.

As shown the calculated methane yield was higher in run 2 reactor since MSW primarily consists of easily biodegradable organic matter and positive effect of sludge addition at a MSW/mixed sludge ratio of 1:1. This contributed to better anaerobic biological degradation through methanogenesis.

3.6.7 BOD_5, inert COD concentrations, BOD_5/COD ratios, TOC results in leachate samples produced from the simulated anaerobic solid waste bioreactors

In order to study the proportion of biodegradable organic carbon in the leachate samples it was considered to determine the BOD_5/COD ratios. Table 3.17 shows the computed values of these ratios, BOD_5, COD concentrations and TOC values in the leachate samples of the all reactors studied for days 8, 21 and 30. The BOD_5 values were ranging initially from 37020, 26650, 21242 mg/l to 23795, 16750, 9740 mg/l at the end of anaerobic incubation in control, run 1 and run 2 reactors, respectively. The BOD_5 values decreased substantially, as 36, 38 and 54 % in the aforementioned reactors, respectively on days 30. The highest BOD_5 decreases occurred in run 2 reactor through first 30 day. The experimental results indicate that, the addition of mixed industrial sludge not retarded the BOD_5 removals. In the study carried out by Warith (2002), the highest BOD_5 value was occurred in the sewage sludge added reactor. The BOD_5/COD ratio indicates the changes in the amount of biodegradable compounds in the leachate samples. Initially, all the reactors have high BOD_5/COD ratios, approximately 0.9, indicating the high degradability of leachate as reported by Quasim & Chiang (1994). The BOD_5/COD ratio decreased approximately to 0.60

from 0.95 in control reactor on days 30. The BOD_5/COD ratios decreased to 0.61 from 0.93 and to 0.61 from 0.86 in run 1 and run 2 reactors, respectively by days 30 (See Table 3.17). This ratio implies a highly biodegradable leachate. In other words, this level shows the increases of biodegradability of organics in MSW,due to solubilization of organic substances through methanogenesis. As the biodegradation of organic content in MSW occurs, the BOD_5/COD ratio decreased. This decreases indicated that the organic wastes was degraded through fermentation phase which is showing a decreases in biodegradability due to methane formation. The BOD_5/COD ratio of the control reactor was the lowest. This result indicated that, the organic waste in control reactor is converted rapidly to methane via methanogenesis.

TOC give an indication of the amount of total organic carbon in the leachate. TOC value of the run 2 reactor was the lowest within 30 days of anaerobic incubation period. TOC value of the run 2 reactor decreased to 5510 mg/l from 8239 mg/l. The accumulation of carbon dioxide in the reactors causes increases in TOC concentrations through anaerobic degradation (Otieno, 1994). TOC values measured in all anaerobic reactors exhibit similar trend with the results obtained by Quasim and Chiang (1994).

Table 3.17 BOD_5, COD concentrations, BOD_5/COD ratios and TOC concentratios in the leachate samples of the bioreactors

	Control Reactor			Run 1			Run 2		
	Day 8	Day 21	Day 30	Day 8	Day 21	Day 30	Day 8	Day 21	Day 30
BOD_5 (mg/l)	37020	30535	23795	26620	19205	16570	21242	15120	9740
COD (mg/l)	38964	43618	39654	28619	30005	27160	24699	23995	15964
BOD_5/COD	0.95	0.7	0.6	0.93	0.64	0.61	0.86	0.63	0.61
TOC (mg/l)	12176	16155	14100	8950	10300	9000	8239	7750	5510

3.6.8 Determination of leachate toxicity in simulated bioreactors using ATA test

Table 3.18 illustrates the results of the ATA tests indicating the quantities of methane produced from the control (glucose) and leachate containing serum bottles through three days and 6 hours of anaerobic incubation. At the end of the ATA test, it was found that there is significant toxicity in mixed industrial sludge added reactors (especially in run 2) under anaerobic conditions since decreases in methane gas productions was observed. This can be explained by the AOX and heavy metal content of mixed industrial sludge added reactors (See Table 2.8). No toxicity was observed in control reactor. This result can be explained by the no toxic and inhibitor organic and inorganic chemicals content of the control reactor since the organic solid wastes were taking from the kitchen of the Engineering Faculty Campus. When the leachate percentage was increased in the serum bottles for control reactors, the quantity of methane produced increased, indicating the utilization of leachate as suitable carbon source by the methanogenic microorganisms through anaerobic degradation. Contrarily, the methane gas productions decreased in leachate samples produced from the reactors containing mixed industrial sludge indicating the toxicity of the mixed sludge originated from the textile, metal plating, electronic, chemistry and plastic industries in Manisa Industrial Organized District on methane bacteria through methanogenesis.

The results of inert COD assays in leachate samples showed that inert COD level was found to be approximately 8 %, 13 % and 15 % of the initial COD levels in control, run 1 and run 2 reactors, respectively. High inert COD levels in mixed industrial sludge containing reactors could be attributed to high AOX, heavy metal contains of aforementioned sludge. This indicates that the COD of leachate samples could be treated up to approximately 85-90 % which is the maximum COD removal efficiency reached under favorable anaerobic conditions.

Table 3.18 Methane quantities in ATA test for control and leachate samples at different dilutions

	Quantity of Methane (ml/day) (n=3 mean value)	
	(After 3 days)	(After 6 hours)
Glucose 0 % leachate (control)	35	32
Glucose 0 % leachate (control)	35	31
25 % leachate (Control reactor)	36	35
50 % leachate (Control reactor)	40	39
75 % leachate (Control reactor)	48	44
100 % leachate (Control reactor)	53	50
25 % leachate (Run 1)	27	26
50 % leachate (Run 1)	26	24
75 % leachate (Run 1)	20	20
100 % leachate (Run 1)	14	12
25 % leachate (Run 2)	18	15
50 % leachate (Run 2)	12	10
75 % leachate (Run 2)	8	8
100 % leachate (Run 2)	2	3

3.6.9 Determination of leachate toxicity in simulated bioreactors by using *lumistox* toxicity test

Tables 3.19, 3.20 and 3.21 show the percent inhibititory (H %) effects of leachate originated from the control, run 1 and run 2 reactors, respectively. Leachate samples originated from the bioreactors were found toxic according to Environmental protection serves for toxicity test using luminescent bacteria (EPS) ($20<H<90$) (DIN, 1993). In other words, when the percent inhibitory effect (%H) varied between 20 % and 90 %, the effect is toxic (Dr. LANGE, 1994). 1/1, 1/5, 1/10 and 1/20 dilution rates were applied on leachate samples for examine the dilution factor (G_L) indicating the IC_{50} values (dilutions inhibited 50 % light intensity of V*ibrio fisheri*) of leachate samples. Figure 3.43 shows the G_L values indicating IC_{50} values of leachate samples. As can be seen in Figure 3.43, the IC_{50} value of the control reactor is 20 while the IC_{50} value of the run 1 and run 2 reactors is higher than 20 (approximately 25). It can be concluded that the leachate samples inhibited 50 % light intensity of luminescence bacteria "*Vibrio fisheri*" even diluted 20 and 25 times in control and run 1, run 2 reactors. Toxicity in control reactor originated by high COD and ammonium concentrations. Tables 3.19, 3.20 and 3.21 and Figure 3.43 showed that addition of mixed industrial sludge to the MSW reactor contributed to toxicity on leachate originated from the anaerobic landfill bioreactors. Leachate toxicity may be originated from heavy metal contents of mixed industrial sludge.

Table 3.19 The percent inhibitory effects of leachate samples from the control reactor

Inhibition H (%)	Time (Minute)	Dilution Factor (G_L)			
		1	5	10	20
H_5	5	90	71	60	41
H_{15}	15	93	74	65	45
H_{30}	30	95	75	69	49

Table 3.20 The percent inhibitory effects of leachate samples from the run 1 reactor

Inhibition H (%)	Time (Minute)	Dilution Factor (G_L)			
		1	5	10	20
H_5	5	91	72	61	44
H_{15}	15	93	75	66	46
H_{30}	30	96	78	73	56

Table 3.21 The percent inhibitory effects of leachate samples from the run 2 reactor

Inhibition H (%)	Time (Minute)	Dilution Factor (G_L)			
		1	5	10	20
H_5	5	92	77	66	47
H_{15}	15	96	78	68	53
H_{30}	30	99	82	76	62

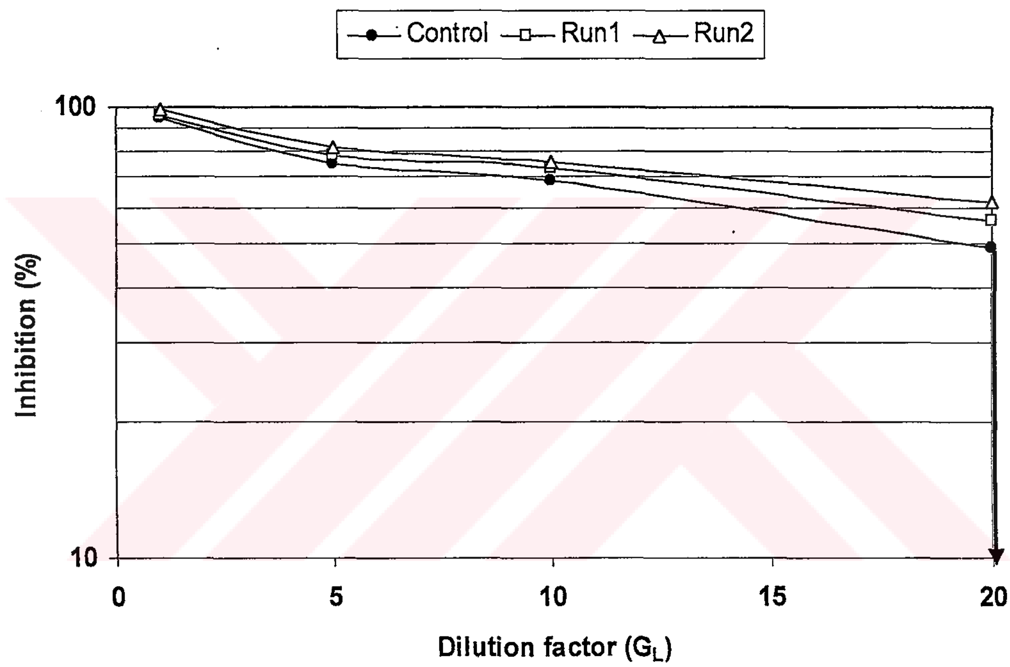

Figure 3.43 G_L values indicating IC_{50} values of leachate samples from the Control, Run 1 and Run 2 reactors

3.6.10 Comparison of the characteristics of the MSW in the anaerobic simulated bioreactors

As can be seen in Table 3.22 the organic matter reduction of MSW in control reactor is the highest level. The percentage of organic matter reduction of MSW in control, run 1 and run 2 reactors are 29 %, 10 % and 8 %, respectively through 30 days of incubation period. In addition, waste settlement in control reactor is the highest level. On the contrary in the study realized by Schmidell et al. (1986); the reduction of organic matter decreased, when the sludge quantity was increased. This was explained by the utilization of sewage sludge. In our study mixed industry sludge was used. On the contrary of the study realized by Warith (2002) in the study mentioned above, the lowest settlement was achieved in industrial sludge added reactors. The settlement was about 33 % while the settlement level was about 57 % in control reactor. The reductions in C percentage and waste quantity in control reactor was found to be at higher level. A linear correlation between carbon removal efficiency and waste quantity was observed (R^2= 0.78). Waste quantity reductions were 55 %, 30 % and 22 % in control, run 1 and run 2 reactors, respectively. It is important to note that, settlement is very important parameter related to landfilling economy. The TN, TP and NH_4-N reduction in run 2 reactor is the highest level on days 30. The TN, TP and NH_4-N concentrations in MSW reduced to 1888, 195 and 70 from 4195, 435 and 205 mg/kg in control reactor by days 30. This shows that the methanogenic microorganisms consumed nitrogen and phosphorus through the degradation of carbonaceous compounds. The measured heavy metal concentrations showed that Cr, Zn, Cu, Pb, Fe and Mn removal efficiencies were 50 %, 28 %, 80 %, 74 %, 21 %, 95 %, 100 % and 100 % in run 2 reactor after 30 days of incubation period (See Table 3.22).

Table 3.22 Comparison of characteristics of the simulated anaerobic landfilling MSW reactors

	Initial			Final		
	Control	Run 1	Run 2	Control	Run 1	Run 2
Water content (%)	90	82	68	91	75	65
Org. Matter (%) (in DS)	95	87	79	67	78	73
% C (in DS)	52.8	48.3	43.9	37	43.5	40.4
TN (mg/kg) (in waste)	10395	6000	4195	5717	2700	1888
TP (mg/kg) (in waste)	2165	695	435	1080	312	195
NH_4-N (mg/kg) (in waste)	450	400	205	180	160	70
Waste Height (cm)	30	30	30	16	18	20
Waste Quantity (g)	1200	1200	1200	540	840	936
Cr (mg/l)		0.02	0.04		0.01	0.02
Zn		0.24	0.36		0.18	0.26
Cu		0.09	0.10		-	0.02
Pb		0.01	0.039		-	0.01
Fe		7.41	9.13		4.95	7.18
Mn		0.1	0.2		-	0.01
Ni		-	0.01		-	-
Cd		-	0.01		-	-

3.6.11 Mass balance for C in leachate and solid waste

Carbon removal is important parameter for solid waste treatment. Carbon quantity of leachate and solid waste was calculated before and after of operation periods. High carbon removal means high waste quantity and organic matter reductions. In addition, high carbon removal efficiency supplies economic advantage due to acquire disposal area.

1200 g of solid waste was introduced to the control bioreactor containing 90 % of water and 52.8 % of carbon. The dry solid and the water content of the solid waste were 120 g and 1080 g (1.08 L), respectively. The initial COD value of the leachate was measured as 27415 mg/l.

The initial carbon content of solid waste is calculated as follows:

120 * 0.528 = 63.4 g C (3.17)

By using the equation 3.2, the carbon (C) quantity of the leachate was calculated as follows:

Assume that, the theoretical oxygen demand is equal to the initial COD value.

By taking into consideration the equation 3.2, the carbon (C) quantity in the leachate was calculated as 10.28 g.

The addition of 0.5 L tap water to the control bioreactor was increased the water content of solid wastes in the control bioreactor to 1.58 L.

The initial carbon (C) quantity was calculated as 16.24 g by multiplying the leachate quantity (1.58 L) with the theoretical carbon quantity (10.28 g C).

As a result, the total carbon (C) quantity in the solid waste and in the leachate sample was calculated as 63.4 + 16.24 = 79.64 g.

After 30 days of operation period, the quantity of solid waste containing 91 % of water and 37 % of carbon decreased to 540 g from 1200 g. As a result, 48.6 g of solid waste and 491.4 g (0.49 L) of water remained in the control bioreactor.

The final carbon quantity in solid waste was calculated as follows:

48.6 * 0.37 = 18 g C (3.18)

The final COD of the leachate was measured as 39654 mg/l, and the final theoretical carbon quantity in the leachate was calculated as 14.89 g C using the equation 3.2.

The final leachate quantity was 0.4 L. The final water quantity of the system was calculated as follows:

$$0.49\ L + 0.4\ L = 0.89\ L \qquad (3.19)$$

The final carbon quantity was calculated as 13.25 g C by multiplying the leachate quantity (0.89 L) with theoretical carbon quantity (14.89 g C).

As a result, the total carbon (C) quantity in solid waste and in the leachate samples of the system was calculated as 18 + 13.25 = 31.25 g.

Finally, the carbon removal efficiency of the total system was obtained as 61 % in control reactor.

The total carbon (C) quantities in the solid waste and in the leachate sample were 114.85 g and 102.85 g in run 1 reactor before and after operation period. The carbon removal efficiency of the total system was obtained as 10 % in run 1 reactor. Similarly, the carbon removal efficiency of the total system was obtained as 23 % in run 2 reactor.

These calculations showed that carbon removal efficiency in mixed industrial sludge added reactors is significantly lower than the control reactor. Mixed industrial sludge addition has a negative effect on carbon removal from solid waste and leachate. However co-digestion of industrial sludge with municipal waste will be provided a remediation process for the removal of toxic and inhibitory substances containing sludge.

3.7 Effect of Sewage Sludge Addition on Degradation of MSWs

3.7.1 COD variations in leachate produced from the simulated anaerobic solid waste reactors

COD was monitored as an indicator parameter of the leachate organic strength. Figure 3.44 shows the daily variation of COD concentrations in leachate for the control (no sludge addition), run 1 (waste/sludge ratio 3:1) and run 2 (waste/sludge ratio 1:3) reactors. As can be seen in this figure, the initial COD concentration in leachate samples collected from the control, run 1 (solid waste to sewage sludge ratio 3:1) and run 2 (solid waste to sewage sludge ratio 1:3) reactors were 26230, 25855 and 17986 mg/l, respectively. The initial COD value of the control reactor was higher than the others because contains high organic matter. The COD value of the leachate in the control reactors increased to 41067 mg/l by day 14, and then started to decrease to 3214 mg/l from 41067 mg/l by day 61. The COD values in the leachate samples taken from the sewage sludge added reactors (run 1 and run 2) increased to 40478 and 26390 mg/l until day 14 and 7, respectively. The highest COD value was measured in control reactor among the three reactors during the operation period. The final COD concentrations of run 1 and run 2 reactors were 2679 and 841 mg/l, respectively, on day 61. Çinar et al. (2004) found the COD value of the leachate originated from sludge containing reactor was lower than the control (containing no-sludge) reactor. In addition, Schmidell et al. (1986) showed that COD concentration in high sewage sludge containing reactor was lower than low sewage sludge containing reactor. On the contrary, in a study realized by Warith (2002) it was showed that COD value of the sludge containing reactor was higher than the control reactor. Besides, Bae et al. (1998) found that COD value of the sludge containing reactor was very lower than the control reactor.

The decrease in leachate COD concentration in sewage sludge added reactor can be explained by the rapid conversion of hydrolysis product to methane via methanogens. A high linear correlation between COD removal efficiency and VFA removal efficiency was observed (R^2= 0.84). In addition, there is a high linear correlation between COD removal efficiency and methane quantity (R^2= 0.96). The aforementioned reactors were richer in soluble substrate and microbial populations. Therefore although the hydrolysis of organic compounds was enhanced they can be readily converted to methane through methanogenesis resulting in low COD concentrations.

The result of this study showed that co-digestion of OFMSW with sewage sludge has a relatively positive effect in the decreasing of COD concentrations in simulated anaerobic landfilling bioreactors.

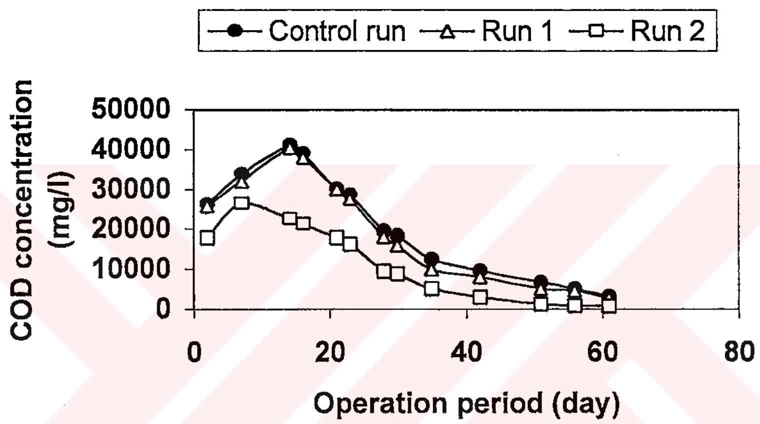

Figure 3.44 Daily variation of COD concentrations in leachate for the control, run1 and run2

3.7.2 VFA variations in leachate produced from the simulated anaerobic solid waste reactors

The concentration of VFA is an important parameter because of the degree of the stability of the anaerobic process. As shown in Figure 3.45 the initial VFA concentrations in leachate samples were 9173, 7729 and 7394 mg/l in control, run 1 and run 2 reactors, respectively. The concentration of VFAs in leachate produced from the all reactors exhibit similar data with COD levels. A hgh linear correlation between VFA removal efficiency and methane quantity was observed (R^2= 0.96). On days 23, the VFA concentration of the control reactor increased to 16754 mg/l, and then started to decrease. The VFA values of the run 1 and run 2 reactors increased to 15250 and 10954 mg/l on day 23 and 14, respectively. The highest VFA value occurred in control reactor among the three reactors since contains high organic matter. Organic matter degradation in initial phase of the fermentation caused high VFA concentration. A high linear correlation between maximum VFA and minimum pH value was observed (R^2= 0.96). At the end of the study, the final VFA concentrations in leachate samples were 1204, 995 and 705 mg/l in control, run 1 and run 2 reactors, respectively. The lower VFA concentration was shown in sewage sludge containing reactors. Schmidell et al. (1986) reported that, high quantity of the sewage sludge within the solid waste reactor has a low VFA concentration due to microbial activity of seed. Similarly, Bae et al. (1998) found that the VFA concentrations in sewage sludge containing reactor was lower than the control reactor.

In this study the VFA/B.Alk. ratio was found as 0.9 in control reactor indicating the stability of anaerobic landfilling reactor. If the VFA/B.Alk. ratio is lower than 0.4 the anaerobic reactor is stable (Behling et al., 1997). But, Griffin et al. (1998) reported that if the VFA/B.Alk. ratio is approximately 1; the solid waste reactor is stable. Compared the suggestions given above it can be concluded that the simulated reactor exhibits steady-state conditions.

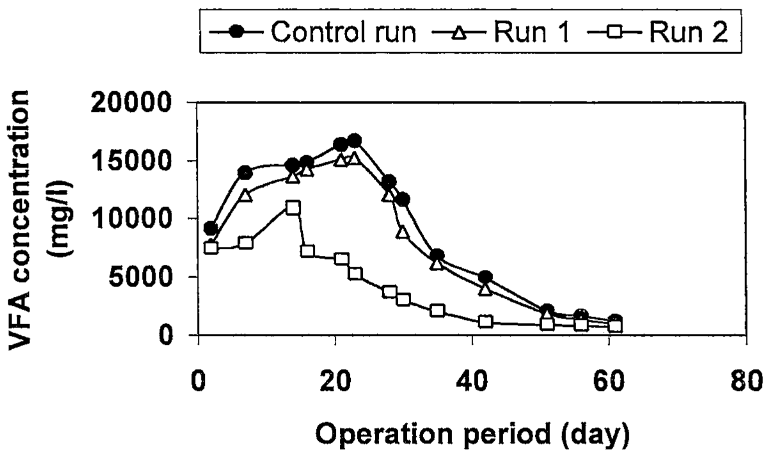

Figure 3.45 Daily variation of VFA concentrations in leachate for the control, run1 and run2

3.7.3 pH variations in leachate produced from the simulated anaerobic solid waste reactors

The pH of the leachate samples are in accordance with the concentration of VFA measured in all reactors. The variation of pH profiles over time is illustrated in Figure 3.46. As can be seen in this figure, the initial pH of the leachates from the control, run 1 and run 2 reactors were 5.72, 5.71 and 6.01, respectively. The pH value in run 2 was higher than that run 1 and control reactors during the anaerobic operation period. This study showed that run 2 has an advantage in terms of pH since the pH levels measured in control, run 1 and run 2 reactors were 7.2, 7.4 and 7.6, respectively, on day 61. Despite the pH values of the bioreactors were similar at the end of the study, the pH value of the run 1 and control reactors (particularly in control reactor) were measured approximately 5.5 during the operation period.

The low pH values were attributed to the generation and accumulation of volatile organic acids. Although this was supported by the high leachate COD and VFA concentrations (except run 1) seed additions significantly improve the leachate quality. The pH values remained almost constant at a range of 7.1-7.6 in MSW to sewage sludge ratio of 1:3 containing run 2 reactors. Probably in run 1 the seed was not enough to improve the buffer capacity of the system.

Warith (2002) found that the highest pH value measured in sewage sludge added reactor among the control and nutrient added reactors. Similarly in our study, the pH value of the sewage sludge added reactors was found approximately 7.5 similar to the study performed by Warith (2002). In addition, the study realized by Bae et al. (1998) showed that the pH value of the sewage sludge added reactor was measured approximately 8 while the pH value in the control reactor was measured approximately 6.

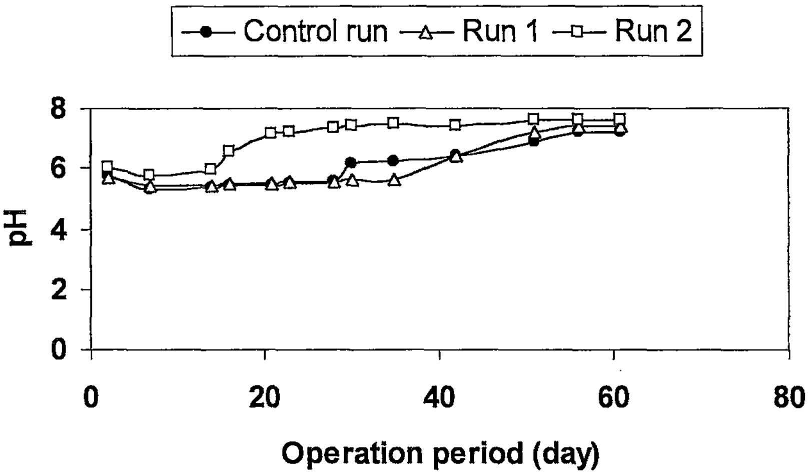

Figure 3.46 Daily variation of pH concentrations in leachate for the control, run 1 and run 2

3.7.4 NH_4-N variations in leachate produced from the simulated anaerobic solid waste reactors

The results of the NH_4-N concentrations measured in leachate samples over time from the control run 1 and run 2 reactors were shown in Figure 3.47. The highest NH_4-N concentrations were measured to be 540, 790 and 1517 mg/l control, run 1 and run 2 reactors through mineralization of organic nitrogenous compounds. It was observed that the NH_4-N concentrations in run 1 is higher than that of control and run 2 reactors since the rate of mineralization of organic nitrogenous compounds in sewage sludge added reactor was higher than the control reactor. The initial NH_4-N concentrations measured in leachate were 548, 693 and 895 mg/l in control, run 1 and run 2 reactors, respectively. The NH_4-N concentrations of sewage sludge added reactors were always higher than the control reactor during the operation period. In addition, the NH_4-N concentration in high sewage sludge added reactor was higher than the low sewage sludge added reactor. This could be attributed to high protein and amino acid content of sewage sludge. The final NH_4-N concentrations measured in leachate were 100, 160 and 220 mg/l in control, run 1 and run 2 reactors.

As reported by Marttinen et al. (2002), the landfill leachate treatment is normally focused on the removal of organic nitrogenous and carbonaceous matters and ammonia nitrogen levels since both three parameters are quite important for possible inhibition of methane production under anaerobic conditions. It is important to note that most of the nitrogen in the solid waste bioreactors is in the ammonia forms following the degradations of proteins and amino acids (İnanç et al., 2000).

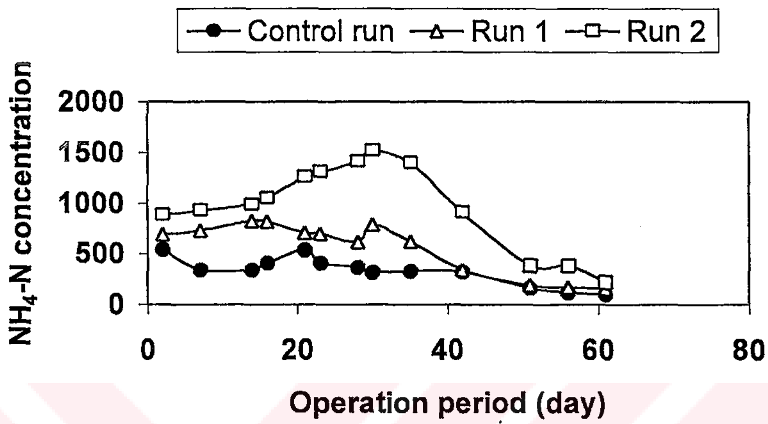

Figure 3.47 Daily variation of NH_4-N concentrations in leachate for the control, run 1 and run 2

3.7.5 Methane gas productions and methane percentages in simulated anaerobic solid waste bioreactors

Methane gas productions were monitored as an indication of the progression of waste decomposition in the reactors. The quantity of methane in control, run 1 and run 2 reactors were shown in Figure 3.48. As can be seen in this figure, the maximum cumulative methane gas production was recorded as 12.6 L, 14.9 L and 23.7 L in control, run 1 and run 2 reactors, respectively at the end of 61 days. The reason for the high cumulative methane level in sewage sludge added reactors is the high biodegradation rate of organic wastes by microorganisms in these reactors. However, Sosnowski et al. (2003) found that higher cumulative methane gas productions are in high quantity in solid waste containing reactor compared to sewage sludge containing reactor. In a study performed by Çinar et al. (2004) exhibited similar data with our results. In this study cumulative methane gas in sludge containing reactor was higher than the control reactor. In addition, Schmidell et al. (1986) reported that when the proportions of sewage sludge were increased, methane gas production increased. Methane percentage in control, run 1 and run 2 reactors were shown in Figure 3.49. The highest methane percentages were 58 %, 60 % and 70 % in control, run 1 and run 2 reactors, respectively during the operation period. Methane production was approximately 20 ml/day in run 2 while methane production was approximately 75 ml/day in control reactor on day 61. This result showed that, degradation of organic substances was continuing in the control reactor while the degradation of organic materials in sewage sludge added reactors was ended.

It was found that the cumulative gas production of the mixtures of sewage sludge and the OFMSW increased with increasing sewage sludge volume. A high value of specific biogas production per gram of total volatile suspended solid added was achieved resulting in 0.06 and 0.1 $dm^3/gVSS_{added}$. The higher methane percentages in run 1 and run 2 reactors can be attributed to the sewage sludge containing high amounts of various microbial species and soluble substrates together with MSW. Furthermore the times required to reach the maximum methane gas production were found to be approximately 43 and 28 days in control and run 2 reactors, respectively. The onset of methanogenesis was delayed due to accumulation of VFA and low pH values resulting in low methane percentages in control reactors.

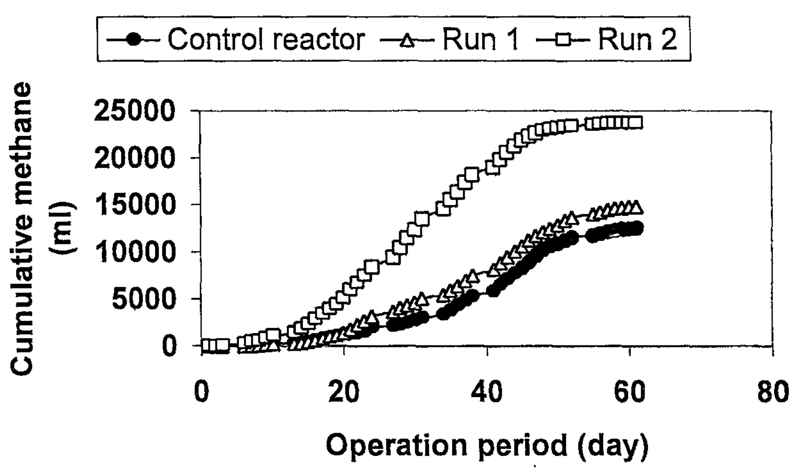

Figure 3.48 Variation in cumulative methane gas productions in the control, run 1 and run 2 reactors through 61 days of anaerobic incubation

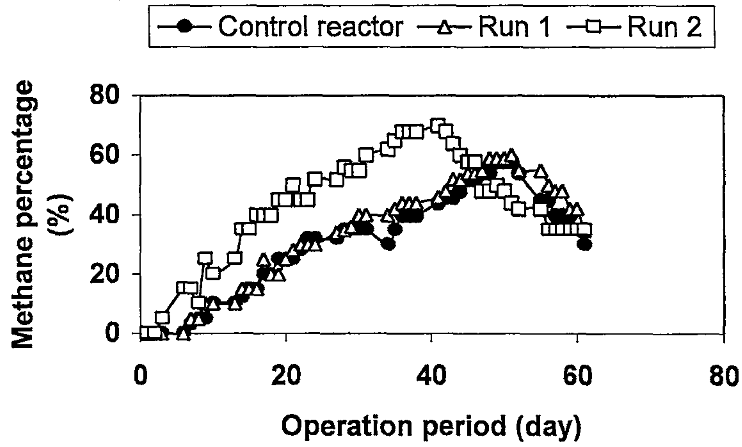

Figure 3.49 Variation in methane percentages in the control, run 1 and run 2 reactors through 61 days of anaerobic incubation

3.7.6 BOD_5, BOD_5/COD ratios and TOC in leachate samples taken from the simulated anaerobic solid waste bioreactors

In order to determine the proportion of biodegradable organic carbon in the leachate samples it was determined the BOD_5/COD ratios. Table 3.23 shows the computed for BOD_5, COD concentrations, BOD_5/COD ratios and TOC values in the leachate samples of the all reactors studied for days 14, 30 and 56. The BOD_5 values were ranging initially from 35005, 33596, 16874 mg/l to 1896, 1616, 237 mg/l at the end of anaerobic incubation in control, run 1 and run 2 reactors, respectively. The BOD_5 values decreased substantially as 94, 95 and 99 % in the aforementioned reactors, respectively. The highest BOD_5 decreases were occurred in reactor containing a MSW to sewage sludge ratio of 1:3 (run 2). The experimental results indicate that, the addition of sewage sludge significantly increased the BOD_5 removals. In the study carried out by Warith (2002), the highest BOD_5 value was occurred in the sewage sludge added reactor. The BOD_5/COD ratio indicates the changes in the amount of biodegradable compounds in the leachate. Initially, all the reactors have high BOD_5/COD ratios approximately 0.80 indicating the high degradability of leachate as reported by Quasim & Chiang (1994). The BOD_5/COD ratios decreased to 0.37 from 0.85, to 0.35 from 0.83 and to 0.24 from 0.75 in control, run 1 and run 2 reactors, respectively by days 56. This ratio implies a highly biodegradable leachate. In other words, this level shows the increasing biodegradability of organics due to solubilization of organic substances through methanogenesis. As the organic content biodegradation of MSW occurs, the BOD_5/COD ratio decreased. This decreases indicated that the organic wastes was degraded through fermentation phase which is showing a decreasing biodegradability due to methane formation. The BOD_5/COD ratio of the run 2 reactor was the lowest. This result indicated that, the organic waste in control reactor is converted rapidly to methane via methanogenesis.

TOC give an indication of the amount of organic substrate in the leachate. TOC value of the run 2 reactor was determined as 7850 mg/l on day 14. However, it decreased to 254 mg/l, resulted a TOC removal efficiency of 97 % on day 56. This result indicated that, initially, the co-disposing of sewage sludge with OFMSWs were released organic carbon at high concentrations since the mixture of these wastes biodegraded very rapidly. This hypothesis is supported by the significant deduction in BOD_5/COD ratio as aforementioned.

The accumulation of carbon dioxide in the reactors causes increases in TOC concentrations through anaerobic degradation (Otieno, 1994). In our study, although the initial TOC values were found to be higher, the TOC values determined in the end of incubation day were at lower level. This result indicated that the organic waste converted to methane under anaerobic conditions at the end of 61 days. TOC values measured in all anaerobic reactors exhibit similar trend with the results obtained by Quasim and Chiang (1994).

Table 3.23 BOD_5, COD concentrations, BOD_5/COD ratios and TOC values in the leachate samples of the bioreactors

	Control Reactor			Run 1			Run 2		
	Day 14	Day 30	Day 56	Day 14	Day 30	Day 56	Day 14	Day 30	Day 56
BOD_5 (mg/l)	35005	13056	1896	33596	11270	1616	16874	4521	237
COD (mg/l)	41067	18389	5124	40478	16100	4616	22481	8865	988
BOD_5 / COD ratio	0.85	0.71	0.37	0.83	0.70	0.35	0.75	0.51	0.24
TOC (mg/l)	12525	7050	1668	11415	5960	1110	7850	3019	254

3.7.7 Comparison of the characteristics of the MSW in the anaerobic simulated bioreactors

As can be seen in Table 3.24 the organic matter reduction of MSW in run 2 reactor is the highest level. The percentage of organic matter reduction of MSW in control, run 1 and run 2 reactors are 34 %, 37 % and 56 %, respectively through 61 days of incubation period. In addition, waste settlement in run 2 reactor is the highest level. Similarly, in the study realized by Schmidell et al. (1986); the organic matter reduction decreased, when the sludge quantity was increased. In addition, in the study performed by Çinar et al. (2004), the higher degree of waste settlement observed in sludge containing reactor. A high linear correlation between carbon removal efficiency and waste quantity reduction was observed (R^2= 0.98). It is important to note that, settlement is very important parameter related to landfilling economy. The reductions in C percentage and waste quantity in run 2 reactor was found to be at higher level. The TN, TP and NH_4-N reductions in run 2 reactor is the highest level. The TN, TP and NH_4-N concentrations decreased to 576, 305 and 130 from 11345, 2403 and 640 mg/kg in run 2 while the same parameters decreased to 555, 290 and 115 from 10165, 21464 and 515 mg/kg in run 1. The TN, TP and NH_4-N concentrations in MSW reduced to 545, 284 and 110 from 9895, 2050 and 450 mg/kg in control reactor by day 61. This shows that the methanogenic microorganisms consumed nitrogen and phosphorus through the degradation of carbonaceous compounds.

Table 3.24 Comparison of characteristics of the simulated anaerobic landfilling MSW reactors

	Initial			Final		
	Control	Run 1	Run 2	Control	Run 1	Run 2
Water content (%)	90	88	87	91	90	90
Org. Matter (%) (in DS)	93	92	80	61	58	35
% C (in DS)	52	51	44.4	33.89	32.2	19.4
TN (mg/kg) (in waste)	9895	10165	11345	545	555	576
TP (mg/kg) (in waste)	2050	2164	2403	284	290	305
NH_4-N (mg/kg) (in waste)	450	515	640	110	115	130
Waste Height (cm)	30	30	30	14	13	10
Waste Quantity (g)	1000	1000	1000	315	291	119

3.7.8 Mass balance for C in leachate and solid waste and total C removal efficiency in leachate and solid waste

Carbon removal is important parameter for solid waste treatment. Carbon quantity of leachate and solid waste was calculated before and after of operation periods. High carbon removal means high waste quantity and organic matter reductions. In addition, high carbon removal efficiency supplies economic advantage due to acquire disposal area.

1000 g of solid waste was introduced to the control bioreactor containing 90 % of water and 52 % of carbon. The dry solid and the water content of the solid waste were 100 g and 900 g (0.9 L), respectively. The initial COD value of the leachate was measured as 26230 mg/l in control reactor.

The initial carbon content of solid waste is calculated as follows:

$$100 * 0.52 = 52 \text{ g C} \tag{3.20}$$

By using the equation 3.2, the carbon (C) quantity of the leachate was calculated as follows:

Assume that, the theoretical oxygen demand is equal to the initial COD value.

By taking into consideration the equation 3.2, the carbon (C) quantity in the leachate was calculated as 9.83 g.

The addition of 0.5 L tap water to the control bioreactor was increased the water content of solid wastes to 1.4 L in the control bioreactor.

The initial carbon (C) quantity was calculated as 13.76 g by multiplying the leachate quantity (1.4 L) with the theoretical carbon quantity (9.83 g C).

As a result, the initial total carbon (C) quantity in the solid waste and in the leachate sample was calculated as 52 + 13.76 = 65.76 g.

After 61 days of operation period, the quantity of solid waste containing 91 % of water and 33.89 % of carbon decreased to 315 g from 1000 g. As a result, 28.35 g of solid waste and 286.65 g (0.29 L) of water remained in the control bioreactor.

The final carbon quantity in solid waste was calculated as follows:

$$28.35 * 0.34 = 9.64 \text{ g C} \tag{3.21}$$

The final COD of the leachate was measured as 3214 mg/l, and the final theoretical carbon quantity in the leachate was calculated as 1.2 g C using the equation 3.2.

The final leachate quantity was 0.4 L. The final water quantity of the system was calculated as follows:

$$0.29\ L + 0.4\ L = 0.69\ L \qquad (3.22)$$

The final carbon quantity was calculated as 0.83 g C by multiplying the leachate quantity (0.69 L) with theoretical carbon quantity (1.2 g C).

As a result, the total carbon (C) quantity in solid waste and in the leachate samples of the system was calculated as 9.64 + 0.83 = 10.47 g.

Finally, the carbon removal efficiency of the total system was obtained as 84 % in control reactor.

The total carbon (C) quantities in the solid waste and in the leachate sample were 74.59 g and 9.96 g in run 1 reactor before and after anaerobic operation period. The carbon removal efficiency of the total system was obtained as 87 % in run 1 reactor. Similarly, the carbon removal efficiency of the total system was obtained as 96 % in run 2 reactor.

These calculations showed that carbon removal efficiency in sewage sludge added reactors is significantly higher than the control reactor. Sewage sludge addition has a positive effect on carbon removal from solid waste and leachate.

CHAPTER FOUR

CONCLUSIONS AND RECOMMENDATIONS

4.1 Conclusions

In this study; factors affecting the treatment efficiency of MSWs in simulated landfill bioreactors were investigated. The investigated factors are leachate recirculation, recirculation volume, waste shredding, waste compaction, aeration, alkalinity addition, and industrial and sewage sludge additions.

Initially, experiments were carried out to compare leachate recirculated bioreactor and single-pass (no recirculation) bioreactor and to determine the effects of recirculated leachate volume on waste degradation in simulated anaerobic bioreactors. The results of this study showed that the COD and VFA concentrations in leachate are very high. After 220 days of anaerobic incubation, it was observed that the pH, COD and VFA concentrations, methane gas productions and methane percentages in $Reactor_9$ (recirculation rate = 9 l/day) were better than the single-pass reactor and $Reactor_{21}$ (recirculation rate = 21 l/day). The COD values were measured as 47000, 39000 and 52000 mg/l while the VFA concentrations were 15000, 13000 and 21000 mg/l, respectively, in single-pass, $Reactor_9$ and $Reactor_{21}$ after 220 days of anaerobic incubation. The values of pH were 5.89, 6.44 and 6.16, respectively, after anaerobic incubation. The mean methane percentages of single-pass reactor, $Reactor_9$ and $Reactor_{21}$ were 30 %, 50 % and 40 %, respectively, after 50 days of incubation. It is important to note that the leachate recirculation rates significantly affected the degradation of solid wastes. Organic matter removal efficiency in single-pass, $Reactor_9$ and $Reactor_{21}$ were 16 %, 27 % and 26 %, respectively. The carbon removal efficiencies of these bioreactors were 23 %, 58 % and 23 %, respectively. The removal efficiencies in quantity of the waste were 45 %, 57 % and 49 %, in single-pass, $Reactor_9$ and $Reactor_{21}$, respectively, at the end of 220 days of anaerobic incubation. It was observed that leachate recirculation reduced the waste stabilization time and was effective in enhancing methane gas production and improving leachate. However, leachate recirculation was not effective in removing the ammonia from the leachate. COD mass balance was calculated to evaluate the potential of methane recovery from the reactor. About 24.85, 64.61 and 37.36 l of methane was regenerated from the single pass and the recycled $Reactor_9$ and $Reactor_{21}$, respectively, on day 50. It was found that the maximum mass of COD release were equal to 1404, 948 and 1444 g in single pass, $Reactor_9$ and $Reactor_{21}$, respectively. Using these values, and taking into consideration the methane gas produced, it can be concluded that 4.4 % of COD was removed from the single pass reactor was converted to methane and 16 % and 6.44 % of COD removed were converted to methane in the $Reactor_9$ and $Reactor_{21}$, respectively. The results of this study showed the feasibility of leachate recirculation in reducing the overall leachate loading for treatment and in enhancing the degradation of solid waste. The leachate recirculation should be projected by the landfill managers as an effective measure in increasing the potential filling capacity of a landfill site. For practical purposes the results presented in this study can be extended to continuous-flow anaerobic solid waste pilot bioreactors.

At the second step of the Ph.D. thesis, the effects of shredding and compaction on the anaerobic treatment of domestic solid waste and leachate characteristics were investigated in simulated landfill anaerobic bioreactors. After 57 days of anaerobic incubation, it was observed that the pH, COD, VFA concentrations, and BOD_5/COD ratio in the leachate of shredded reactor were better than the control and compacted reactor. The COD values were measured as 6400, 7700 and 2300 mg/l while the VFA concentrations were 2750, 3000 and 354 mg/l, respectively, in the leachate samples of the control, compacted and shredded reactor after 57 days of anaerobic incubation. The values of the pH were 6.88, 6.76 and 7.25, respectively, after anaerobic incubation in the aforementioned reactors. It was observed that the waste shredding increased the methane percentage in the anaerobic simulated reactor.

Methane percentage of the control, compaction and shredded reactors were 36 %, 46 % and 60 %, respectively. Methane gas generated in the control, compacted and shredded reactors were measured as 13.8 L, 21.5 L and 15.5 L, respectively, at the end of the study. A BOD_5/COD ratio of 0.44 achieved in the shredded reactor indicated that the better solid waste stabilization resulting in a high rate than that of compacted and control reactors. TOC value of the shredded reactor was determined as 10500 mg/l on day 5. However, it decreased to 729 mg/l, resulted a TOC removal efficiency of 93 % on day 47. This result indicated that, initially, the shredding waste was released organic carbon at high concentrations since the shredded wastes biodegraded very rapidly. At the end of the ATA test, it was found that there is no significant toxicity under anaerobic conditions since no decreases in methane gas productions was observed in all reactors. This result can be explained by the no toxic and inhibitor organic chemicals in the reactors since the organic solid wastes taking from the kitchen of the Engineering Faculty Campus does not include any toxic substance. The results of inert COD assays showed that inert COD level was found to be approximately 10 % of the initial COD levels (approximately 250 mg/l) in all reactors. This indicates that the COD of leachate samples could be treated up to 90% which is the maximum COD removal efficiency reached under favorable anaerobic conditions. At the end of the biochemical methane potential (BMP) tests it was found that 225 g/l and 208 g/l COD were converted to methane in leachate samples from the shredded and compacted reactors under anaerobic conditions It was observed that waste shredding reduced the waste quantity, the organic content of the solid waste and the biodegradation time. The removal efficiencies in the quantity of the waste were 70 %, 58 % and 72 % in control, compacted and shredded reactors, respectively. Organic matter removal efficiencies in these bioreactors were 26 %, 23 % and 31 %, while the carbon removal efficiencies were 79 %, 76 % and 86 %, respectively.

The effects of alkalinity on the anaerobic treatment of OFMSW and leachate characteristics were investigated at the third step of the Ph.D. thesis. The results of this study showed that alkalinity addition to solid wastes has a positive effect on the rate of biological degradation in anaerobic simulated recycled reactors through the degradation of organic fraction of solid wastes. After 65 days of anaerobic incubation, it was observed that the pH, COD, VFA concentrations and BOD_5/COD ratio in the leachate, alkalinity added reactors were better than the control reactor. The COD removal efficiencies were 53 %, 87 % and 87 % while the VFA removal efficiencies were 67 %, 88 % and 88 %, respectively, in the leachate samples of the control 3 g/l $NaHCO_3$ and 6 g/l $NaHCO_3$ containing reactors after 65 days of anaerobic incubation. The values of pH were 6.54, 7.19 and 7.31 after 65 days of anaerobic incubation, respectively in the aforementioned reactors. Methane percentages of the control, 3 g/l $NaHCO_3$ and 6 g/l $NaHCO_3$ containing reactors were 37 %, 64 % and 65 %, respectively. Methane gas generated in the control, 3 g/l $NaHCO_3$ and 6 g/l $NaHCO_3$ containing reactors were as measured 12 L, 19 L and 22.6 L, respectively at the end of the study. The BOD_5 values decreased to 9965, 1053, 771 mg/l from initial 32091, 21964, 16019 mg/l at the end of anaerobic incubation in control, 3g/l and 6g/l $NaHCO_3$ containing reactors, respectively. The BOD_5/COD ratio of the 6g/l $NaHCO_3$ containing reactor was the lowest. This result indicated that, the organic waste in alkalinity added reactor is converted rapidly to methane via methanogenesis. It was found that the maximum mass of COD release was equal to 40.1, 30.3 and 22.9 g in control, 3 g/l $NaHCO_3$ and 6 g/l $NaHCO_3$ added reactors, respectively. Using these values, and taking into consideration the methane gas produced, it can be concluded that 28 % of COD was removed from the control reactor was converted to methane and 44 % and 65 % of COD removed were converted to methane in 3 g/l $NaHCO_3$ and 6 g/l $NaHCO_3$ added reactors, respectively. The removal efficiencies in the quantity of the waste in these bioreactors were 79 %, 86 % and 88 %, while the organic matter removal efficiencies were 33 %, 40 % and 47 %, respectively. The carbon removal efficiencies of the control, 3 g/l $NaHCO_3$ and 6 g/l $NaHCO_3$ containing reactors were 82 %, 93 % and 95 %, respectively. Because degradation of MSWs and leachate produced through the degradation of organic substances is most important subjects in terms of pollution emissions, besides cost-effective anaerobic treatment process the additional alkalinity requirement should be kept in mind in terms of economical costs.

The effects of intermittent aeration on the anaerobic treatment of domestic solid waste and leachate characteristics were investigated. 96, 85 and 97 % COD and 86, 77 and 93 % VFA removals were obtained, in the leachate samples of the control (no-aeration), R1 (three days in a week during one hour) and R2 (one day in a week during one hour) reactors, respectively, after 79 days of anaerobic incubation. The values of pH were 6.98, 6.76 and 7.98, respectively in the aforementioned reactors. It was observed that the aeration decreased the methane percentage and the quantity in the simulated bioreactor. The maximum cumulative methane gas production was recorded as 11.2 L, 0.9 L and 3.6 L in control, R1 and R2 reactors, respectively, at the end of 79 days. A BOD_5/COD ratio of 0.23 was achieved in the R2 reactor indicated the better MSW stabilization resulting in a high rate than that of R1 and control reactors. The IC_{50} value based on dilution factor of the R2 reactor is 16 while the IC_{50} value of the control and R1 reactors is approximately 20. It can be concluded that the leachate samples inhibited 50 % light intensity of luminescence bacteria "vibrio fisheri" even diluted 16 and 20 times in R2, R1 and control reactors. It can be showed that intermittent aeration has not a significant effect on toxicity removal from the leachate originated from the anaerobic landfill bioreactors. The final leachate quantities of aerated runs were lower than that of control reactor operated under strictly anaerobic conditions. Organic matter reductions were observed as 37 %, 52 % and 45 % in control, R1 and R2 reactors, respectively. Similarly, the removal efficiencies in the quantity of the waste in these bioreactors were 69 %, 76 % and 72 %, respectively. The carbon removal efficiencies of the control, R1 and R2 reactors were 85 %, 87 % and 86 %, respectively. As a conclusion, it was demonstrated that intermittent aeration of an anaerobic landfilling reactor degrading MSW can significantly increase the rate of waste decomposition and settlement, decrease the methane production and leachate production from the anaerobic reactor. In addition, NO_3-N concentrations of R1 were higher than the others due to extended aeration. NO_3-N concentrations of R1 and R2 reactors were gradually decreased. This could be explained by the partial denitrification of NO_3-N in the non-aerated phase of the aerated bioreactors. NO_3-N was converted to N_2 in aerated bioreactors (R1 and R2) at non-aerated phase.

The effects of co-disposal of dye industry sludge with OFMSW on the anaerobic treatment of domestic solid waste and the leachate characteristics were investigated. after 98 days of anaerobic incubation, it was observed that the pH, COD, VFA concentrations in the leachate samples of the industrial sludge added reactors (especially run 2 –waste/sludge ratio 1:2-) were better than the control reactor (no sludge addition). The COD values were measured as 7128, 5714 and 4205 mg/l while the VFA concentrations were 1605, 1310 and 576 mg/l, respectively, in the leachate samples of the control, run 1 (waste/sludge ratio 1:1) and run 2 reactors after 98 days of anaerobic incubation. Although the control has a high initial BOD_5 rapid decreases in COD was obtained in this reactor. The experimental results indicate that industrial sludge addition not significantly retarded the decreases in BOD_5 concentrations. The values of pH were 6.31, 7.16 and 7.25 in control, run 1 and run 2 reactors, respectively. The maximum cumulative methane gas production was recorded as 12.7 L, 6.7 L and 5.2 L in control, run 1 and run 2 reactors, respectively, at the end of 98 days. Methane percentages of these bioreactors were 31 %, 20 % and 12 %, respectively. The methane yield was found as 0.148 g CH_4-$COD_{removed}$/gVSS add in control reactor while the methane yields were 0.05 CH_4-$COD_{removed}$/gVSS add and 0.04 CH_4-$COD_{removed}$/gVSS add in run 1 and run 2 reactors. It was found that the maximum mass of removed COD was equal to 34.8, 25.5 and 22.6 g in control, run 1 and run 2 reactors on day 98. Using these values, and taking into consideration the methane gas produced, it can be concluded that 93 % of COD was removed from the control reactor and was converted to methane. 67 % and 58 % of COD removed were converted to methane in run 1 and run 2 reactors, respectively on day 98. In addition, ATA test result showed that there is significant toxicity in industrial sludge added reactors (especially run 2) under anaerobic conditions since decreases in methane gas production was observed. The results of inert COD assays in leachate samples showed that inert COD level was found to be approximately 8 %, 10 % and 12 % of the initial COD levels in control, run 1 and run 2 reactors, respectively. Organic matter reductions were observed as 42 %, 16 % and 10 % in control, run 1 and run 2 reactors, respectively. Similarly, the removal efficiencies in the quantity of the waste in these bioreactors were 65 %, 44 % and 34 %, respectively. The carbon removal efficiencies of the control, run 1 and run 2 reactors were 84 %, 64 % and 35 %, respectively.

The effects of co-disposal of mixed industrial (textile, metal plating, electronic, chemistry and plastic industry) sludge with OFMSW on the anaerobic treatment of domestic solid waste and the leachate characteristics were investigated in a shortly period. After 30 days of anaerobic incubation, it was observed that the pH, COD, VFA concentrations in the leachate samples of the mixed industrial sludge added reactors (especially run 2 –waste/sludge ratio 1:2-) were better than the control reactor (no sludge addition). The COD values were measured as 39654, 27160 and 15964 mg/l, respectively, in the leachate samples of the control, run 1 (waste/sludge ratio 1:1) and run 2 reactors after 30 days of anaerobic incubation. The experimental results indicate that mixed industrial sludge addition not significantly retarded the decreases in BOD_5 concentrations. The values of pH were 5.8, 7 and 7.2 in control, run 1 and run 2 reactors, respectively. The maximum cumulative methane gas production was recorded as 13.5 L, 17 L and 17.11 L in control, run 1 and run 2 reactors, respectively, at the end of 30 days. Maximum methane percentages of these bioreactors were 39 %, 46 % and 59 %, respectively. It was found that the maximum mass of removed COD were equal to 4.07, 3.9 and 12.1 g in control, run 1 and run 2 reactors on day 30. Using these values, and taking into consideration the methane gas produced, it can be concluded that 88 % of COD was removed from the control reactor was converted to methane and 91 % and 72 % of COD removed were converted to methane in run 1 and run 2 reactors, respectively on day 30. In addition, ATA test result showed that there is significant toxicity in mixed industrial sludge added reactors (especially run 2) under anaerobic conditions since decreases in methane gas production was observed. The results of inert COD assays in leachate samples showed that inert COD level was found to be approximately 8 %, 13 % and 15 % of the initial COD levels in control, run 1 and run 2 reactors, respectively. Organic matter reductions were observed as 29 %, 10 % and 8 % in control, run 1 and run 2 reactors, respectively. Similarly, the removal efficiencies in the quantity of the waste in these bioreactors were 30 %, 10 % and 8 %, respectively. The carbon removal efficiencies of the control, run 1 and run 2 reactors were 61 %, 10 % and 23 %, respectively.

The effects of co-disposal of sewage sludge with OFMSW on the anaerobic treatment of domestic solid waste and the leachate characteristics were investigated. After 61 days of anaerobic incubation, it was observed that the pH, COD, VFA concentrations in the leachate samples, organic matter reduction, C reduction, and waste quantity and waste settlement in solid waste of the sewage sludge added reactors (especially run 2 –waste/sludge ratio 1:3-) were better than the control reactor (no sludge addition). The COD values were measured as 3214, 2679 and 841 mg/l while the VFA concentrations were 1204, 995 and 705 mg/l, respectively, in the leachate samples of the control, run 1 (waste/sludge ratio 3:1) and run 2 reactors after 61 days of anaerobic incubation. The BOD_5 values decreased substantially as 94, 95 and 99 % in the aforementioned reactors, respectively. The highest BOD_5 decreases occurred in run 2 reactor. The experimental results indicate that, the addition of sewage sludge significantly increased the BOD_5 removals. TOC value of the run 2 reactor was determined as 7850 mg/l on day 14. However, it decreased to 254 mg/l, resulting a TOC removal efficiency of 97 % on day 56. This result indicated that, initially, the co-disposing of sewage sludge and OFMSWs were released organic carbon at high concentrations since the mixing of these wastes biodegraded very rapidly. The values of pH were 7.2, 7.4 and 7.6 in control, run 1 and run 2 reactors, respectively. The maximum cumulative methane gas production was recorded as 12.6 L, 14.9 L and 23.7 L in control, run 1 and run 2 reactors, respectively, at the end of 61 days. Average methane percentages of these bioreactors were 44 %, 50 % and 62 %, respectively. Organic matter reductions were observed as 34 %, 37 % and 56 % in control, run 1 and run 2 reactors, respectively. Similarly, the removal efficiencies in the quantity of the waste in these bioreactors were 69 %, 71 % and 88 %, respectively. The carbon removal efficiencies of the control, run 1 and run 2 reactors were 84 %, 87 % and 96 %, respectively. 55 g C from the solid waste and 9.09 g C from the leachate were removed in run 2 reactor.

4.2 Recommendations

As a result of this Ph.D. dissertation, anaerobic treatment is recommended for the treatment of organic fraction of municipal solid waste and improves the leachate quality due to methane production (energy recovery) and provides predictable stabilization. There are several factors affecting the treatment efficiency of MSWs in simulated landfill bioreactors. Leachate recirculation has a positive effect on solid waste stabilization and reduces the leachate pollution in simulated landfill bioreactors. In addition, 13 percent of reactor volume was recommended as leachate recirculation rate in terms of waste stabilization. Waste shredding, alkalinity addition (6 g/l $NaHCO_3$ alkalinity), intermittent aeration, co-disposal of industrial/sewage sludge with OFMSW (waste/sludge ratio 1:2) were also recommended to treatment the MSWs in simulated landfill bioreactor. These applications supply economical advantages of solid waste and leachate treatment and these parameters can be applied in solid waste sanitary landfill area.

In this study, the experiments were carried out in different seasonal periods and different solid waste content although was used kitchen wastes exhibiting similar organic matter and water content. As a result, although it is very expensive and difficult to operate all the anaerobic bioreactors at different operational mode, all these experiments should be carried out, simultaneously.

CHAPTER FIVE
REFERENCES

5.1 References

Akunna, J.C., Bizeau, C., & Moletta, R. (1992). Anaerobic-aerobic treatment of high-strength ammonium wastewater-nitrogen removal via nitrite. Water Science and Technology, 26, 5-6, 1007-1015.

Anderson, G.K., & Yang, G. (1992). Determination of bicarbonate and total volatile acid concentration in anaerobic digesters using a simple titration. Water Environment Research, 64, 53-59.

Angelidaki, J., & Ahring, B. (1999). Methods for increasing the biogas potential from the recalcitrant organic matter contained in manure. Proceedings of the Second International Symposium of Anaerobic Digestion of Solid Wastes, Barcelona, pp. 375-380.

APHA-AWWA, (1992). Standard Methods for the Examination of Water and Wastewater, 17th edition. American Public Health Association/American Water Works Association/Water Environment Federation, Washington DC, USA.

Bae, J.H., Cho, K.W., Lee, S.J., Bum, B.S., & Yoon, B.H. (1998). Effects of leachate recycle and anaerobic digester sludge recycle on the methane production from solid wastes. Water Science and Technology, 38, 2, 159-168.

Behling, E., Diaz, A., Colina, G., Herrera, M., Gutierrez, E., Chacin, E., Fernandez, E., & Forster, C.F. (1997). Domestic wastewater treatment using a UASB reactor. Bioresource Technology, 61, 239-245.

Beydilli, M.I., Pavlosathis, S.G., & Tincher, W.C. (1998). Decolorization and toxicity screening of selected reactive azo dyes under methanogenic conditions. Water Science and Technology, 38, 4-5, 225-232.

Bolzonella, D., Battistoni, P., Mata-Alvarez, J., & Cecchi, F. (2003). Anaerobic digestion of solid wastes : process behaviour in transient conditions. Water Science and Technology, 48, 1-8.

Braber, K. (1995). Anaerobic digestion of municipal solid waste: a modern waste disposal option on the verge of breakthrough. Biomass and Bioenergy, 9, 1-5, 365-376.

Brunner, D.R., & Keller, D.J. (1972). Sanitary landfill design and operation. USEPA, Report SW-65ts, Washington.

Cecchi, F., Fraverro, P.G., Perin, G., & Vallini, G. (1988). Comparison of codigestion performance of two differently collected organic fractions of municipal solid wastes with sewage sludges. Environmental Technology Letter, 9, 391-400.

Cecchi, F., Mata-Alvarez, J., Pavan, P., Vallini, G., & DePoli, F. (1992). Seasonal effects on anaerobic digestion of the source sorted organic fraction of municipal solid waste. Waste Management & Research, 10, 435-443.

Chan, G.Y.S., Chu, L.M., & Wong, M.H. (2002). Effects of leachate recirculation on biogas production from landfill co-disposal of municipal solid waste, sewage sludge and marine sediment. Environmental Pollution, 118, 393-399.

Cho, J.K., & Park, S.C. (1995). Biochemical methane potential and solid state anaerobic digestion of Korean food wastes. Bioresource Technology, 52, 245-253.

Christensen, T.H., Kjeldsen, P., & Stegmann, R. (1992). Effects of landfill management procedures on landfill stabilization and leachate and gas quality, landfilling of waste. Biogas, 119-37.

Chugh, S., Clarke, W., Pullammanappallil, P., & Rudolph, V. (1998). Effect of recirculated leachate volume on MSW degradation. Waste Management and Research, 16, 6, 564-73.

Chugh, S., Chynoweth, D.P., Clarke, W., Pullammanappallil, P., & Rudolph, V. (1999). Degradation of unsorted municipal solid waste by leach-bed process. Bioresource Technology, 69, 103-115.

Cobb, S.A., & Hill, D.T. (1990). Volatile fatty acid interference with alkalinity measurements in anaerobic fermenters. International Summer Meeting, sponsored by the ASAE.

Çalli, B., Mertoğlu, B., Davutluoğlu, A., Güneş, B., Girgin, E., Tas, N., İnanç, B., & Yenigün, O. (2002). Anaerobic treatment of high ammonia landfill leachate with and without pH control. Symposium of Appropriate Environmental and Solid Waste Management and Technologies for Developing Countries, vol 2, pp 931-938.

Çinar, S., Onay, T.T., & Erdinçler, A. (2004). Co-disposal alternatives of various municipal wastewater treatment-plant sludges with refuse. Advances in Environmental Research, 8, 477-482.

Diamadopoulos, E. (1994). Characterization and treatment of recirculation-stabilized leachate. Water Research, 28, 12, 2439-2445.

Dinamarca, S., Aroca, G., Chamy, R., & Guerrero, L. (2003). The influence of pH in the hydrolytic stage of anaerobic digestion of the organic fraction of urban solid waste. Water Science and Technology, 48, 6, 249-254.

DIN 38412 Part 34. (1993). German Standard Methods for Examination of Water, Wastewater and Sludge, Bio assays (group L). Berlin, Germany.

Donlon, B.A., Razo-Flores, E., Field,J.A., & Lettinga, G., (1995). Toxicity of N-substituted aromatics to acetoclastic methanogenic activity in granular sludge. Applied and Environmental Microbiology, 61, 11, 3889-3893.

Dr. LANGE. (1994). LUMISmini, Operating Manual. Dr. Bruno Lange. Düsseldorf, Germany.

Engelhart, M., Krüger, M., Kopp, M., & Dicht, N. (1999). Effects of disintegration on anaerobic degradation of sewage excess sludge in downflow stationary fixed film digesters. Proceedings of the Second International Symposium of Anaerobic Digestion of Solid Wastes, Barcelona, pp.153-160.

Germirli, B.F., Orhon, D., & Artan, N. (1991). Assestment of the initial inert soluble COD in industrial wastewaters, Water Science and Technology, 23, 1077-1086.

Goel, B., Pant, D.C., & Kishore, V.V.N. (2001). Two-phase anaerobic digestion of spent tea leaves for biogas and manure generation. Bioresource Technology, 80, 153-156.

Gonzalez, J.S., Rivera, A., Borja, R., & Sanchez, E. (1998). Influence of organic volumetric loading rate, nutrient balance and alkalinity/COD ratio on the anaerobic sludge granulation of an UASB reactor treating sugar cane molasses. International Biodet. Biodeg., 41, 127-131.

Gou, B., & Guzzone, B. (1997). State survey on leachate recirculation and landfill bioreactors. Solid Waste Association of North America, Silver Springs, Maryland, USA.

Gönüllü, M.T. (1987). Katı atıklardaki organic maddelerin sızması. VI. İzmir Çevre Sempozyumu, İzmir.

Griffin, M.E., McMahon, K.D., Mackie, R.I., & Raskin, L. (1998). Methanogenic population dynamics during startup of anaerobic digesters treating municipal solid waste and biosolids. Biotechnologic Bioenergy, 57, 342-355.

Hamzawi, N., Kennedy, K.J., & McLean, D.D. (1998). Anaerobic digestion of co-mingled municipal solid waste and sewage sludge. Water Science and Technology, 38, 2, 127-132.

Hoilijoki, T.H., Kettunen, R.H., & Rintala, J.A. (2000). Nitrification of anaerobically pretreated municipal landfill leachate at low temperature. Water Research, 34, 5, 1435-1446.

Hudgings, M., & Harper, S. (1999). Operational characteristics of two aerobic landfill systems. The Seventh Waste Management and Landfill Symposium in Sardinia, Italy.

Iglesias, J.R., Castrillon, L., Maranon, E., & Sastre, H. (1998). Solid-state anaerobic digestion of unsorted municipal solid waste in a pilot-plant scale digester. Bioresource Technology, 63, 29-35.

Iglesias, J.R., Castrillon, L., Maranon, E., & Sastre, H. (2000). Biomethanization of municipal solid waste in a pilot-plant. Water Research, 34, 2, 447-454.

Ilies, P., & Mavinic, D.S. (2001). The effect of decreased ambient temperature on the biological nitrification and denitrification of a high ammonia landfill leachate. Water Research, 35, 8, 2065-2072.

Im, J.H., Woo, H.J., Choi, M.W., Han, K.B., & Kim, C.W. (2001). Simultaneous organic and nitrogen removal from municipal landfill leachate using an anaerobic-aerobic system. Water Research, 35, 10, 2403-2410.

İnanç, B., Çallı, B., & Saatçi, A. (2000). Characterisation and anaerobic treatment of the sanitary landfill leachate in İstanbul. Water Science and Technology, 41, 3, 223-30.

Jokela J, Kettunen RH, Sormunen KM, Rintala JA. (2002). Biological nitrogen removal from municipal landfill leachate: low-cost nitrification in biofilters and laboratuary scale in-situ denitrification, Water Research, 36, 4079-87.

Kennedy, K.J, & Lentz, E.M. (2000). Treatment of landfill leachate using sequenching batch and continuous flow upflow anaerobic sludge blanket (UASB) reactors, Water Research, 34, 14, 3640-3656.

Kettunen, R.H.., Hoilijoki, T.H., & Rintala, J.A. (1996). Anaerobic and sequential anaerobic-aerobic treatments of municipal landfill leachate at low temperatures. Bioresource Technology, 58, 31-40.

Kettunen, R.H., & Rintala, J.A. (1998). Performance of an on-site UASB reactor treating leachate at low temperature, Water Researh, 32, 3, 537-546.

Kiely, G., Tayfur, G., Dolan, C., & Tanji, K. (1997). Physical and mathematical modeling of anaerobic digestion of organic waste. Water Researh, 31, 3, 534-540.

Kim, I.S., Kim, D.H., & Hyun, S.H. (2000). Effect of particle size and sodium ion concentration on anaerobic thermophilic food waste digestion. Water Science and Technology, 41, 67-73.

Kuai, L., De Vreese, L., & Vandevivere, P. (1998). GAC-amended UASB reactor for the stable treatment of toxic textile wastewater. Environ. Technol., 19, 1111-1117.

Kuroda, M. (1988). A study on simultaneous treatment of organic matter and nitrate with a biofilm consisting of methane fermentative bacteria and denitrifying bacteria. Prog. Environ. Sanit. Engng. Res., 24, 231-239.

Laclos, H.F., Desbois, S., & Saint-Joly, C. (1997). Anaerobic digestion of municipal solid organic waste: Valorga full-scale plant in Tilburg, The Netherlands. Water Science and Technology, 36, 6-7, 457-462.

Lay, J.J., Li, Y.Y., & Noike, T. (1998). Developments of bacterial population and methanogenic activity in a laboratory-scale landfill bioreactor. Water Researh, 32, 12, 3673-3679.

Leckie, L.O., Pacey, J.G., & Halvadakis, C. (1979). Landfill management with moisture control. Journal of the Environmental Engineering Division, 105, 337-55.

Ledakowicz, S., & Kaczarek, K. (2002). Laboratory simulation of anaerobic digestion of municipal solid waste. Appropriate Environmental and Solid Waste Management and Technologies for Developing Countries, Turkey, 1139-1146.

Leikam, K., Heyer, K.U., & Stegmann, R. (1997). In-situ stabilization of completed landfills and old sites. Sixth International Landfill Symposium, Cagliari, İtaly, 451-462.

Libanio, P.A.C., Costa, B.M.P., Cintra, I.S., & Chernicharo, C.A.L. (2003). Evaluation of the start-up of an integrated municipal solid waste and leachate treatment system. Water Science and Technology, 48, 6, 241-247.

Lin, C.Y., Chang, F.Y., & Chang, C.H. (2000). Co-digestion of leachate with septage using a UASB reactor, Bioresource Technology, 73, 175-178.

Lin, J.G., Ma, Y.S., Chao, A.C., & Huang, C.L. (1999). BMP test on chemically pretreated sludge. Bioresource Technology, 68, 187-192.

Lu, J.C.S., Eichenberger, B., & Stearns, R.J. (1985). Leachate from municipal landfills production and management, Park Ridge, New Jersey: Noyes Publ.

Malina, J.F., & Pohland, F.G. (1992). Design of anaerobic processes for the treatment of industrial and municipal wastes. Water Quality Management Library, 7, Techonomic Publishing Co.

Manna, L., Zanetti, M.C., & Genon, G. (1999). Modelling biogas production at landfill site. Resources, Conservation and Recycling, 26, 1-14.

Marttinen, S., Kettunen, R.H., Sormunen, K.M., Soimasuo, R.M, & Rintala, J.A. (2002). Screening of physical-chemical methods for removal of organic material nitrogen and toxicity from low strength landfill leachate. Chemosphere, 46, 851-58.

Mata-Alvarez, J., Mace, S., & Llabres, P. (2000). Anaerobic digestion of organic solid wastes. An overwiev of research achievements and perspectives. Bioresource Technology, 74, 3-16.

McCarty, P.L. (1969). Anaerobic waste treatment fundamentals: environmental requirements and control. Public Works, 95-123.

Moosbruger, R.E., Wentzel, M.C., Ekama, G.A., & Marais, G. (1993). Lauterntun waste in UASB systems, feasibility, alkalinity requirements and pH control. Water SA, 19, 41-52.

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

Nopharatana, A., Clarke, W.P., Pullammanappallil, P.C., Silvey, P., & Chynoweth, D.P. (1998). Evaluation of methanogenic activities during anaerobic digestion of municipal solid waste, Bioresource Technology, 64, 169-174.

Official Gazette, (1995). Turkish Hazardous Waste Control Regulations, Appendix 11A.

O'Keefe, D.M., & Chynoweth, D.P. (2000). Influence of phase separation, leachate recycle and aeration on treatment of municipal solid waste in simulated landfill cells. Bioresource Technology, 72, 55-66.

O'Keefe, D.M., Brigmon, R.L., & Chynoweth, D.P. (2000). Influence of methane enrichment by aeration of recirculated supernatant on microbial activities during anaerobic digestion. Bioresource Technology, 71, 217-224.

Otieno, F.A.O. (1994). Stabilization of solid waste through leachate recycling. Waste Management & Research, 12, 93-100.

Owen, W.F., Stuckey, D.C., Healy, J.B., Young, JR. L.Y., & McCarty, P. L. (1979). Bioassay for monitoring biochemical methane potential and anaerobic toxicity, Water Research, 13, 485-492.

Özkaya, B., Baştürk, A., Demir, A., Debik, E., & Bilgili, M.S. (2002). Investigation of leachate recirculation effects in İstanbul Odayeri sanitary landfill. Appropriate Environmental and Solid Waste Management and Technologies for Developing Countries, Turkey, 953-960.

Palmowski, L.M., & Müller, J.A. (2000). Influence of the size reduction of organic waste on their anaerobic digestion. Water Science and Technology, 41, 155-162.

Peavy, H.S., Rowe, D.R., & Tchobanolous, G. (1985). Environmental Engineering. McGraw-Hill Publishing Co. New York.

Pfeffer, J.T. (1992). Solid Waste Management Engineering. Englewood Cliffs, NJ: Prentice Hall.

Plaza, G., Robredo, P., Pacheco, O., & Toledo, A.S. (1996). Anaerobic treatment of municipal solid waste. Water Science and Technology, 33, 3, 169-175.

Pohland, F.G., & Gould, J.P. (1986). Co-disposal of municipal refuse and industrial waste sludge in landfills. Water Science and Technology, 18, 12, 177-192.

Pohland, F.G., & Harper, S.R. (1986). Critical review and summary of leachate and gas production from landfills. PB 86-240181, USEPA.

Purcell, B. (2000). Aerox landfilling: a change of approach. Waste Management, 27-28.

Price, T.J., Probert, S.D., & Manley, B.J.W. (1986). Improving the reliability of LFG-generation assessment tests. Applied Energy, 60, 41-63.

Quasim, S.R. (1965). Chemical characteristics of seepage water from simulated landfills. Ph.D. Dissertation, West Virginia University, Morgantown WV: p 145.

Quasim, S.R., & Chiang, W. (1994). Sanitary Landfill Leachate Generation, Control and Treatment. Tchnomic Publishing Company, USA.

Razo-Flores, E., Luijten, M., Donlon, B.A., Lettinga, G., & Field, J.A. (1997). Complete biodegradation azo dye Azodisalicylate under anaerobic conditions. Environmental Science and Technology, 31, 7, 2098-2103.

Read, A.D., Hudgings, M., & Philips, P. (2001). Perpetual landfilling through aeration of the waste mass; lessons from test cells in Georgia (USA). Waste Management, 21, 617-629.

Reinhart, D. (1996). Full-scale experiences with leachate recirculating landfills: case studies. Waste Management and Research, 14, 347-365.

Reinhart, D., & Al-Yousfi, A.B. (1996). The impact of leachate recirculation on municipal solid waste landfill operating characteristics. Waste Management and Research, 14, 337-346.

Reinhart, D.R., McCreanor, P., & Townsend, T. (2002). The bioreactor landfill: its status and future. Waste Management & Research, 20, 2, 172-186.

Robinson T., McMullan, G., Marchant R., & Nigam P. (2001). Remediation of dyes and in the textile effluent: A critical review on current treatment technologies with a proposed alternative. Bioresource Technology, 77, 247-225.

Samani, Z., Yu, H.W., Hanson, A., & Smith, G. (2002). Energy recovery from grass using two-phase anaerobic digestion. Waste Management, 22, 1-5.

San, İ., & Onay, T. (2001). Impact of various leachate recirculation regimes on municipal solid waste degradation. Journal of Hazardous Materials, B87, 259-71.

Schmidell, W., Craveiro, A.M., Peres, C.S., Hirata, Y.S., & Varella, R.F. (1986). Anaerobic digestion of municipal solid wastes. Water Science and Technology, 18, 12, 163-175.

Shin, H.S., Han, S.K., Song, Y.C., & Lee, C.Y. (2001). Performance of UASB reactor treating leachate from acidogenic fermenter in the two-phase anaerobic digestion of food waste. Water Research, 35, 14, 3441-3447.

Sorgun, K. (1987). Katı atık yönetimi. T.C. Sanayi ve Ticaret Bakanlığı Sınai Eğitim ve Geliştirme Merkezi Genel Müdürlüğü, Mersin.

Sosnowski, P., Wieczorek, A., & Ledakowicz, S. (2003). Anaerobic co-digestion of sewage sludge and organic fraction of municipal solid wastes. Advances in Environmental Research, 7, 609-616.

Souza, M.E., Fuzaro, G., & Polegato, A.R. (1992). Thermophilic anaerobic digestion of vinasse in pilot plant UASB reactor. Water Science and Technology, 25, 213-222.

Speece, R.E. (1996). Anaerobic Biotechnology for Industrial Wastewaters. Archae Press, Nashville Tennessee USA.

Stanforth, R., Ham, R., & Anderson, M. (1979). Development a synthetic municipal landfill leachate. Journal Water Pollution Control Federation, 51, 7, 1965-1975.

Stegmann, R. (1983). New aspects on enhancing biological processes in sanitary landfill. Waste Management and Research, 1, 201-11.

Stessel, R.I., & Murphy, R..J. (1992). A lysimeter study of the aerobic landfill concept. Waste Management & Research, 10, 485-503.

Stroot, P.G., McMahon, K.D., Mackie, R.I., & Raskin, L. (2001). Anaerobic codigestion of municipal solid waste and biosolids under various mixing conditions- I. digester performance. Water Research, 35, 7, 1804-1816.

Tchobanoglous, G., Theisen, H., & Vigil, S. (1993). Integrated solid waste management; engineering principles management issues, New York: McGraw-Hill, Inc.

Tchobanoglous, G., & Burton, F.L. (1979). Wastewater Engineering, McGraw-Hill International Editions.

Veeken, A.H.M., & Hamelers, B.V.M. (2000). Effect of substrate-seed mixing and leachate recirculation on solid state digestion of biowaste. Water Science and Technology, 41, 3, 255-262.

Vieitez, E.R., & Ghosh, S. (1999). Biogasification of solid wastes by two-phase anaerobic fermentation. Biomass and Bioenergy, 16, 299-309.

Wang, Z., & Banks, C.J. (2000). Accelerated hydrolysis and acidification of municipal solid waste (MSW) in a flushing anaerobic bio-reactor using treated leachate recirculation. Waste Management & Research, 18, 215-223.

Wang, Y.S., Odle, W.S., Eleazer, W.E., & Barlaz, M.A. (1997). Methane potential of food waste and anaerobic toxicity of leachate produced during food waste decomposition. Waste Management & Research, 15, 149-167.

Warith, M. (2002). Bioreactor landfills: experimental and field results. Waste Management, 22, 7-17.

Zorpas, A.A., Kapetanios, E., Zorpas, G.A., Karlis, P., Vlyssides, A., Haralambous, I., & Loizidou, M. (2000). Compost produced from organic fraction of municipal solid waste, primary stabilized sewage sludge and natural zeolite. Journal of Hazardous Materials, B77, 149-159.