TREATMENT OF LEACHATE GENERATED FROM BIOREACTOR LANDFILLS

By

Maqsood Ahmed Memon
B.E. (Civil), 1998
Mehran University of Engineering & Technology Jamshoro Pakistan.

A thesis

Presented to Ryerson University

in partial fulfillment of the requirements for the degree of

Master of Applied Science in the program of Civil Engineering.

Toronto, Ontario, Canada, 2006

© Maqsood Ahmed Memon.

UMI Number: EC53608

INFORMATION TO USERS

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleed-through, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

UMI®

Author's Declaration

I hereby declare that I am the sole author of this thesis. I authorize Ryerson University to lend this thesis to other institutions or individuals for the purpose of scholarly research.

I further authorize Ryerson University to reproduce this thesis by photocopying or by other means, in total or in part, at the request of other institutions or individuals for the purpose of scholarly research.

Borrower's Page

Ryerson University requires the signatures of all persons using or photocopying this thesis. Please sign below, and give address and date.

Name of Borrowers	Date	Address	Signature

TREATMENT OF LEACHATE GENERATED FROM BIOREACTOR LANDFILLS
By

Maqsood Ahmed Memon

MASc Ryerson University, 2006

Abstract

Leachate generated from Municipal landfill sites is usually contaminated with organic compounds as well as inorganic pollutants. Leachate needs treatment before being entered to any receiving water body. It is desirable that the leachate should be treated on-site efficiently and cost effectively, particularly for remote and small landfill sites. The existing processes used for the treatment of leachate often exhibit problems related to treatment time, size, and cost. This study focuses on the development of a low cost treatment method to resolve the existing problems related to on-site leachate treatment and handling. The developed method involved the treatment of given leachate in an anaerobic lagoon with Fenton's reagents followed by aerobic lagoon. The leachate used for the treatment was generated from four solid waste bioreactor landfill models (anaerobic and aerobic) that have high moisture content and high organic concentration of solid waste. The effect of pH control and the different concentrations of Ferrous Sulphate ($FeSO_4$) and Hydrogen peroxide (H_2O_2) on anaerobic and aerobic lagoons performance were examined in the treatment process.

It has been observed that the Fenton's reagents with the ratio of 1:1 have a great influence on COD reduction. The maximum COD reductions with pH in the ranges of 6-7 and 3-4 along with Fenton's reagents have been observed to be 6% (39130 mg/l to 36450 mg/l) and 32% (39130 mg/l to 26430 mg/l) respectively. The overall COD concentration

reduction using the proposed treatment was observed to be 50% during the whole

treatment process.

Acknowledgements

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ACRONYMS

AOP	Advance Oxidation Process
BDOF	Biodegradable Organic Fraction
BMP	Biochemical Methane Potential
BOD_5	5-day Biochemical Oxygen Demand
BTX	Benzene, Toluene and Xylene
COD	Chemical Oxygen Demand
EPA	Environmental Protection Agency
$FeSO_4$	Ferrous Sulphate
H_2O_2	Hydrogen Peroxide
LFG	Landfill Gas
MSW	Municipal Solid Waste
NH_3-N	Ammonia Nitrogen
PCP	Pentachlorophenol
TCE	Tetrachloroethylene
TOC	Total Organic Carbon
TS	Total Solids
VFAs	Volatile Fatty Acids

Introduction

1.1 Introduction

Early design of municipal solid waste landfills did not include measures for leachate collection and barrier systems to prevent leakage of contaminants into the surrounding environment. Following major leakage incidents such as the Love Canal incident (Niagara Falls, New York), the importance of waste containment barriers and leachate collection systems was recognized and incorporated into landfill designs. Following these developments, the treatment and disposal of leachate generated from landfills become an important focus of waste management system (Maehlum, 1995).

Leachate is formed precipitation and snowmelt that infiltrates through disposed municipal soil waste. Previous studies indicated that the average BOD_5 (5-day Biochemical Oxygen Demand) and COD (Chemical Oxygen Demand) of leachate solutions are in the range of 60,000 and 40,000 respectively, which is more than 10 times folds of municipal wastewater (Ehrig, 1990; Quasim, 1994). As leachate migrates through the refuse, it accumulates soluble contaminants present in the solid waste and soluble products from anaerobic decomposition reactions.

Engineered landfills are lined with impermeable materials to minimize the migration of leachate into the natural soil beneath the landfill site. A drainage system is usually installed to convey leachate by gravity to low sump or storage tank for further treatment and disposal (Gierlich and Kollbach, 1998; USACE, 1994). Several factors can affect the characteristics of a landfill leachate. Initially, the origin and the nature of the solid wastes are the major factors that influence the quality of leachate. Then as chemical and biological process occurs, the age of the landfill and environmental conditions such as the

amount of precipitation have an important role. A young leachate i.e. in the acidogenic phase contains a high concentration of volatile fatty acids (VFA) due to anaerobic fermentation. On contrary, a leachate in the methanogenic phase is characterized mainly by refractory organic compounds or humic like substances. These latter compounds are formed when the VFA are converted to biogas, composed of methane and carbon dioxide (Gau and Chang, 1996). Consequently, as a leachate ages and organics are being degraded the BOD_5/COD ratio decreases and the pH and ammonia concentrations increase. The latter can reach very high values, 2700 mg/L NH_3-N (Gogate and Pandit, 2004) and if converted to nitrate, could result in eutrophication of the receiving water body. Landfill leachate also contains heavy metals. It is one of the reasons why regulatory bodies do not favor the treatment of leachate with municipal sewage. It is much harder to dispose of sludge from a biological treatment when it cannot be used for agriculture. Another reason to justify separate treatment or on site treatment of leachate is that conventional municipal treatment processes do not efficiently remove many refractory organic compounds (Zenon ,1989). Some of these compounds are hydrophobic and may accumulate in organisms (Gau and Chang, 1996). Many different methods have been investigated for treating leachate generated from municipal solid waste (Marks et al., 1994). Since leachate contains both biodegradable and non-biodegradable components, the methods studies can be divided into two major groups: biological and physical/chemical treatments. Some of the important biological treatment methods include recirculation, activated sludge, sequencing batch reactors, aerobic lagoons and constructed wetlands. Physical/chemical techniques are coagulation / flocculation,

activated carbon, micro filtration, ultra filtration, reverse osmosis and oxidation (Van and Roncken, 1997; Bressi and Favali, 1997).

Due to recent stringent environmental regulations and high potential for soil, surface and groundwater pollution, disposal of landfill leachate has become a problem in numerous solid waste sites in Canada and overseas. Therefore, landfill leachate treatment on-site or off sites are required as an essential part of the solid waste management system. Due to complex nature of leachate characteristics it is difficult to treat the leachate in a single traditional biological treatment process. No single process is capable of complying with leachate treatment requirements (Kettern, 1992). Most landfill leachates could not be treated adequately by just conventional chemical/ physical treatment or conventional biological treatment. Rather a combination of these processes is needed. Researchers combined chemical/physical process and biological treatment units. Chemical/physical processes consist of equalization. Chemical precipitation and coagulation, sedimentation, air stripping, and neutralization. Biological treatment units consist of two aeration tanks and two secondary clarifiers. Overall removal obtained was 99% of BOD_5, 95% of COD, 90% of ammonia, and 57.4% to 99.2% of metals (Keenan et al., 1984). Advanced oxidation processes have seen increased use for the in situ and ex situ chemical oxidation of contaminated soils and ground water. Fenton's reagents is the catalytic decomposition of dilute hydrogen peroxide by iron (II), which results in the generation of hydroxyl radicals (OH); the classic Fenton's reaction is usually conducted by gradually adding dilute hydrogen peroxide to a degassed solution of excess iron (II). This procedure produces hydroxyl radicals (Kotsou et al., 2004).

1.2 Objective of This Study

The present study is developed to address the following issues:

1. Examine the effect of combined biological and chemical process on the efficiency of landfill leachate treatment in on-site lagoons.

2. Investigate various factors affecting on Fenton's oxidation process

3. Optimize the on-site lagoons size for leachate treatment

4. Reduce the time of leachate treatment using on site lagoons

2.0 Literature Review

2.1 Landfill Leachate

The decomposition of the waste in a landfill is mainly due to microbiological processes. The production of landfill gas and leachate are chiefly related to the activity of microorganisms (Senior, 1995). Rainfall is the main contributor to generation of leachate. The precipitation percolates through the waste and gains dissolved and suspended components from the biodegrading waste through several physical and chemical reactions. Other contributors to leachate generation include groundwater inflow, surface water runoff, and biological decomposition (Reinhart and Townsend, 1998). Liquid fractions in the waste will also add to the leachate as well as moisture in the cover material. Moisture can be removed from the landfill by water consumed in the formation of landfill gas, water vapor removed in the landfill gas, and leachate leaking through the liner (Tchobanoglous et al., 1993). Long-term leachate quantity is not as difficult to predict. Leachate quality is also difficult to predict because each landfill is unique and the wastes vary widely (Bagchi, 1990). The major factors that affect leachate quantity and quality are; the type of disposed waste, hydrogeology, climactic conditions, the age of the landfill, the phase of waste decomposition occurring, and the chemical and physical properties of the precipitation (Bagchi, 1990). The removal of organic materials (measured as COD and BOD_5) and ammonia from leachates is the usual prerequisite before discharge the leachates into natural waters (Kettunen et al., 1996). In Figure 2.1, diagram shows leachate quality with time.

Leachate Mound Patterns
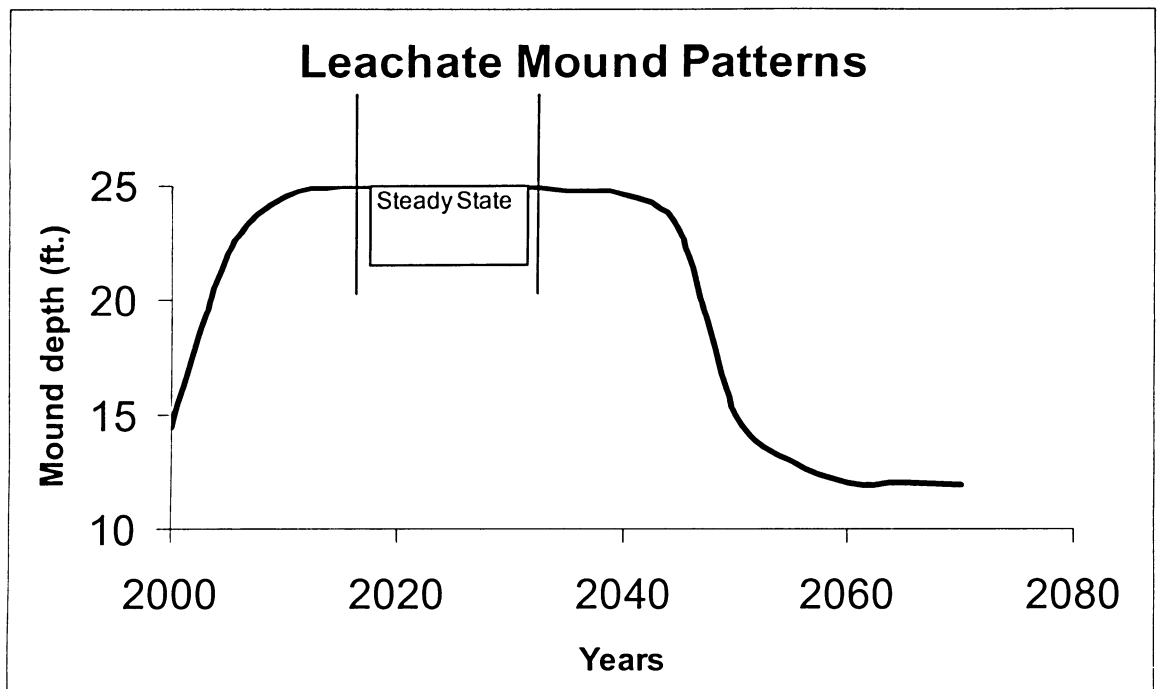
Figure 2.1 Diagram show leachate quality with time (Warith 2004)

2.1.1 Phases of Leachate Generation

Most of the landfill containing domestic waste to have the three phases of decomposition occurs within 15 years. Aerobic decomposition rapidly uses up the oxygen present in the land filled waste during the first phase, which is typically one month. In shallow (< 5 m) deposits of waste or when air is pumped into the waste, a longer period may be possible. Significant quantities of carbon dioxide and hydrogen are produced; particularly if the site is dry (Ham, 1980). The initial phase of land filled waste degradation generates leachates with high organics, Ammonium, Sulphate and Chloride concentrations. Leachates may also have a high concentration of metals and contain some hazardous organics chemicals. During the second phase, anaerobic and facultative organisms

(acetogenic bacteria) hydrolyze and ferment cellulose and other putrescible materials are developed. Simpler and soluble compounds, such as volatile fatty acids with a high 5 days biochemical oxygen demand (BOD when incubated for 5 days, i.e., BOD_5) and ammonia-nitrogen (NH_3-N), are then produced. This phase may last for several years. The leachate produced in that period is characterized by high BOD_5 values (commonly > 10 g L^{-1}) and a high ratio of BOD_5 to chemical oxygen demand (COD) (commonly > 0.7). These indicate that a high proportion of soluble organic materials are readily degradable (McGinley and Kmet, 1984). The reaction produces leachate with an acidic pH (typical 5 or 6) and an unpleasant smell. High concentrations of ammonia assist the dissolution of other components of waste. The leachate also contains high levels of iron, manganese, zinc, calcium, and magnesium. Landfill gas production remains slow and consist of carbon dioxide with lesser quantities of methane and hydrogen (Johansen and Carlson, 1976). Gradually, slower-growing methanogenic bacteria are established. The simple organic compounds released by the continuing acetogenic process start to be consumed in phase III,. A mixture of mainly carbon dioxide and methane is produced and released as landfill gas. At this stage, the landfill is the most active biologically. A dynamic equilibrium is established between acetogenic and methanogenic bacteria, with the wastes continuing to be actively decomposed. The landfill gas is produced until the land filled waste is largely decomposed and atmospheric oxygen can diffuse easily into the waste. The leachate produced in this phase is usually characterized by a relatively low BOD_5 value and low BOD_5/COD ratio. NH_3-N in the leachate, still released by the first stage acetogenic process, is present at high levels (Robinson, 1989). Inorganic substances such as iron, sodium, potassium, sulfate, and chloride dissolve continuously and leach

7

from the landfill for many years. Precipitation of ferrous sulfide reduces concentrations of both iron and sulfate significantly in the leachate. The resulting gas production and leachate parameters are depicted in Figure 2.2.

Phase IV in this phase, the methanogenic bacteria will start to convert the acetic acid and hydrogen into methane (CH_4) gas and carbon dioxide (CO_2). The pH of the leachate is elevated due to the decrease in the concentration of the acetic acid, hydrogen and CO_2 and increases the methane production. In addition, the COD in the leachate is decreased to lower concentrations and the methane gas constitutes to 50 - 60% of the biogas composition (Warith et al., 1998).

Phase V, This is the final stage of decomposition of the municipal solid waste. The rate of methane production and the strength of leachate will decrease to lower values as a result of limited nutrients and organic waste in the landfill (Reinhart 1996; Warith et al., 1998).
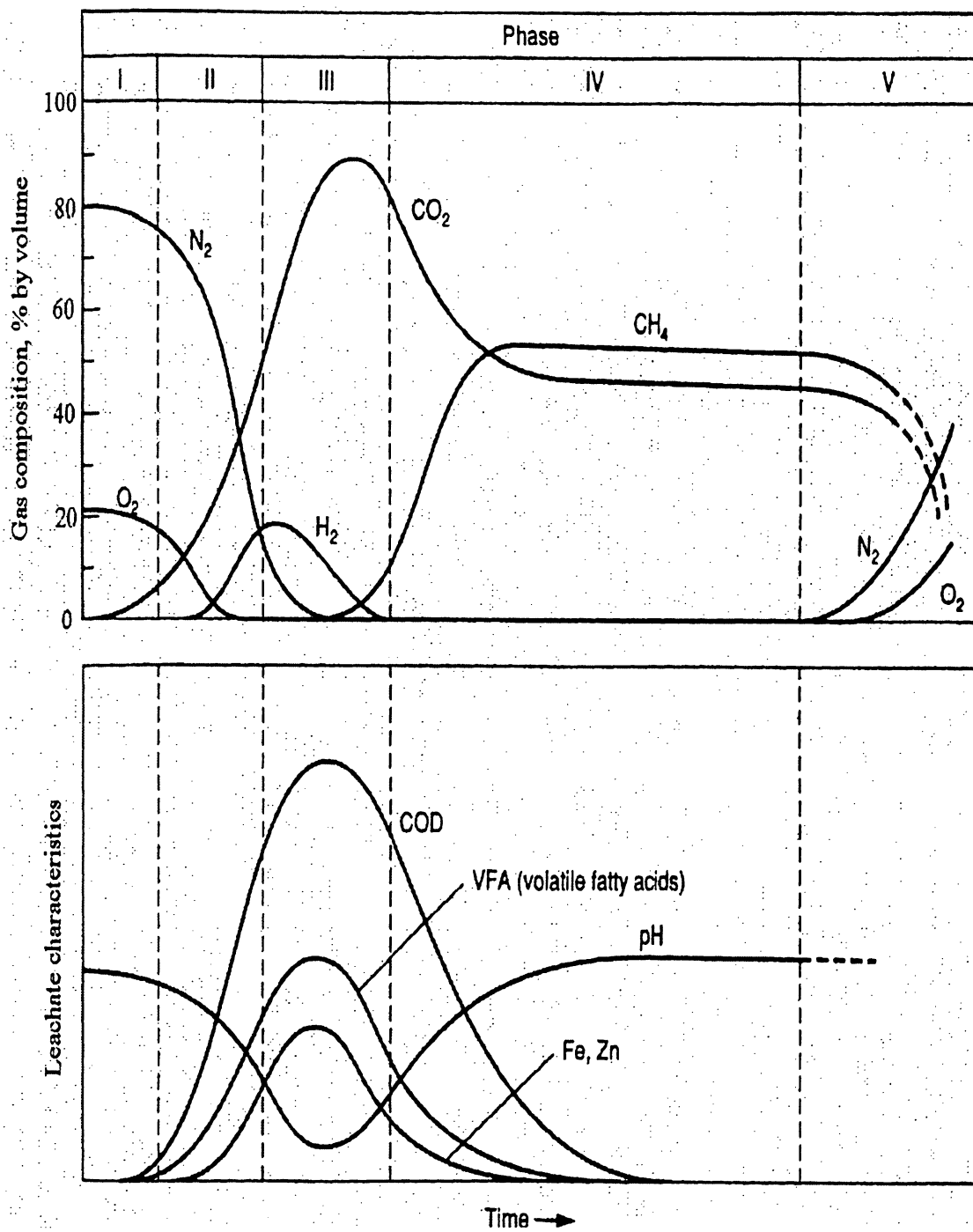
Figure 2.2 Phases of general landfill gas and leachate characteristics (Tchobanoglous et al. 1993)
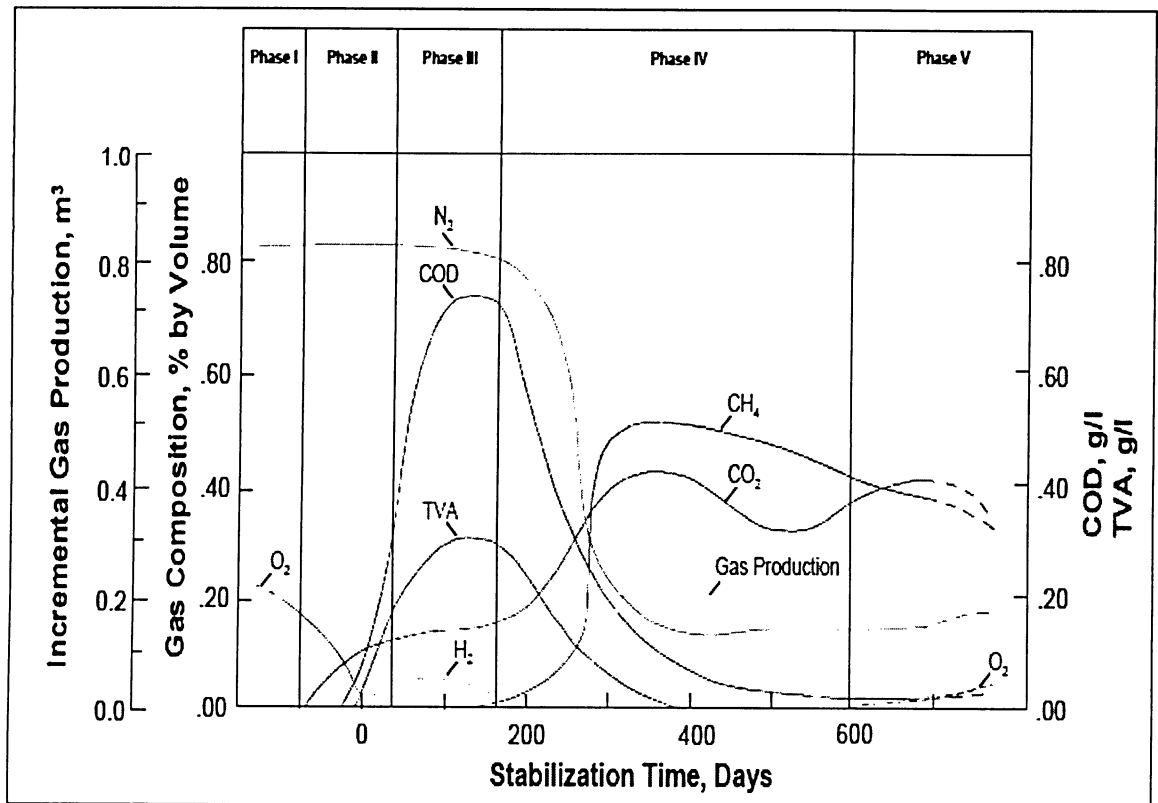
Figure 2.3 Biological decomposition phases in the landfill bioreactor [Pohland, 1996]

2.1.2 Leachate Characterization

It is now known that leachate from sanitary landfill may be an important source of ground water pollution. Many contaminants released from a sanitary landfill, if allowed to migrate, may pose a severe threat to surface and groundwater (Walker, 1969 and Kelly, 1976). It is difficult to define characteristics of leachate because compositions and concentrations of leachate from a landfill depend on various environmental conditions such as compositions of wastes, age of the landfill, geology, temperature, moisture content, and so on. Therefore, a treatment technology for leachate should be considered seriously after fully understanding the compositions and concentrations of the leachate. Conventionally, an anaerobic reactor has mostly been installed in leachate treatment

process for treating high-loading organic compounds discharged from immature landfill area. Since the chemical compositions of leachate differed markedly depending on age and maturity of the landfill site, the influent organic concentration of the immature leachate is decreased rapidly in the following 2–3 years (Jeong, et al., 2001).

2.1.3 Characteristics of Old Landfill Leachate

Landfill leachates from old sites are usually highly contaminated with ammonia (> 400 mg/l of N) resulting from the hydrolysis and fermentation of nitrogen is containing fractions of biodegradable refuse substrates (Carley and Mavinic, 1991). A high content of recalcitrant compounds, and a low biodegradable organic fraction (BOD_5/ COD < 0.1) is also present in it (Diamadopoulos, 1994). Mature leachate contains relatively low concentrations of degradable organic material but high concentrations of ammonia (Knox, 1985). At the middle or end of the landfill, the main leachate organic compounds were refractory long chain carbohydrates, and humic substances. Consequently, a decrease in BOD_5/COD ratios was observed. With age, the refractory high molecular weight compounds were found instead of the degradable organic matter. After 5 to 6 years BOD_5/COD ratios were lower to 0.2 to 0.4 (Paris, 1996).

2.1.4 Characteristics of Young Landfill Leachate

Young leachate is characterized by chemical oxygen demand (COD) contents higher than 5 g/l and by a low nitrogen concentration (< 400 mg/l of N) (Ramirez et al.). Leachates from young landfill are characterized by the presence of substantial amounts of volatile fatty acid (VFA) or their salts, mainly acctate (Ac^-), propionate (Pr^-) and butyrate (Ba^-) (Paula and Foresti, 1992). In general, the leachate concentration, BOD_5 of initial landfill is higher than at any other time and then gradually reduces with increasing landfill age

(Paris, 1996). Higher COD/TOC (total organic carbon) and BOD_5/COD ratios were found in young unstable leachate and about 2/3 of the total organic carbon consisted of short chain fatty acids, which reflect that the rates of anaerobic methane degradation were adequate. Generally, in sanitary landfills up to 2~5 year old, not only the substrates and microbiological contents decreased progressively with age, but also the composition of leachate changed significantly (Chian and DeWalle, 1977). When wastes are disposed in the landfill, microbiological degradation of the organic waste initiates resulting in a leachate with a high concentration of easily degradable components (volatile acids) (Gau et al., 1991). In the young leachate BOD_5/COD ratio vary between 0.6- 0.8 (Paris, 1996). Color of fresh leachate can be dark green and become dark brown upon exposure to the atmosphere. This is caused by chemical oxidation of ferrous iron compounds in the leachate to ferric compounds.

2.2 Leachate Recirculation

In situ treatment of leachate and landfill stabilization can be done by leachate recirculation. One of the most innovative and acclaimed methods of leachate treatment is the circulation of high strength leachate back to the landfill. Leachate recycle not only improves the leachate quality, but also shortens the time required for stabilization from several decades to 2–3 years, (Reinhart and Yousfi, 1996). With leachate recirculation, a landfill can be used as a relatively controlled anaerobic filter to treat leachate, provide accelerated waste stabilization, and reduce the volume of leachate by maximizing evaporative losses during recirculation (Pohland, 1975). Recirculation significantly increases the rate of the disappearance of organic matter in leachate and, by inference, the rate of waste stabilization (Reinhart and Yousfi, 1996). By recirculating the leachate, the

organic component of the leachate can be reduced by the active biological communities within the refuse mass (Quasim and Chiang, 1994). Leachate recirculation stimulated reducing conditions providing for the reduction of sulphate to sulphide, which moderated leachate metals to very low concentrations (Gould et al., 1989). The formation of metal sulphides under anaerobic conditions effectively eliminated the majority of heavy metals in leachate (Chian and DeWalle, 1977). Use of in-situ nitrification, denitrification, anaerobic fermentation and methanogenesis has been proposed to treat leachate, depending on the phase and age of the waste (Pohland, 1995).

2.3 Biological Treatment

Biological methods (Anaerobic and Aerobic) have proved efficient for the treatment for the treatment of municipal landfill leachate.

2.3.1 Anaerobic Treatment

With concentrated leachate, anaerobic could be preferable to aerobic treatment because of its high loading rates; low energy requirement, low excess sludge production, and methane production (Kettunen et al., 1996). The anaerobic treatment of leachate should result in the removal of most of the organic pollutants. A later aerobic treatment should allow a partial removal of biodegradable residual organic pollutants and should also achieve the nitrification of ammonium nitrogen (Hipolito et al., 1994).

2.3.2 Anaerobic Lagoon

An anaerobic lagoon is a deep storage; essentially free from dissolved oxygen that promotes anaerobic conditions. Anaerobic lagoons are typically used for pre treatment of high strength industrial wastewaters, and pretreatment of municipal wastewater to allow preliminary sedimentation of suspended solids as a pretreatment process.

Anaerobic microorganisms in the absence of dissolved oxygen convert organic materials into stable products such as carbon dioxide and methane. The degradation process involves two separate but interrelated phases: acid formation and methane production. During the acid phase, bacteria convert complex organic compound to simple organic compound, mainly short chain volatile organic acid. During this phase, little chemical oxygen demand or biological oxygen demand reduction occurs, because many microorganisms can use the short chain fatty acids, alcohols, etc., and thereby exerts an oxygen demand. The methane production phase involves an intermediate step. First, bacteria convert the short chain organic acids to acetate, hydrogen gas, and carbon dioxide. This process is referred to as methanogenesis. During this phase, waste stabilization occurs, represented by the formation of methane gas. The two major pathways of methane formation are:

(1) $CH_3COOH \longrightarrow CH_4 + CO_2$

(2) $CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O$
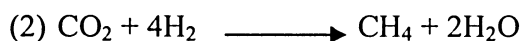
(USEPA, 2002)

2.3.3 Aerobic Lagoon

An aerobic stabilization lagoon contains bacteria and algae in suspension; aerobic conditions (the presence of dissolved oxygen) prevail throughout its depth. There are two types of aerobic lagoons: shallow lagoons and aerated lagoons.

2.3.3.1 Shallow lagoons. Shallow oxidation lagoons obtain their dissolved oxygen via two phenomena: oxygen transfer between air and water surface, and oxygen produced by photosynthetic algae. Although the efficiency of soluble biochemical oxygen demand removal can be as high as 95 percent, the lagoon effluent will contain a large amount of

algae, which will contribute to measure total biochemical oxygen demand of the effluent. To achieve removal of both soluble and insoluble biochemical oxygen demand, the suspended algae and microorganisms have to be separated from the lagoon effluent (USACE, 1998).

2.3.3.2 Aerated lagoon. An aerated lagoon is similar to an oxidation lagoon except that it is deeper and mechanical aeration devices are used to transfer oxygen into the wastewater. The main advantage of aerated lagoon is that they require less area than oxidation lagoons. The disadvantage is that the mechanical aeration devices require maintenance and use energy. Aerated lagoons can be further classified as either complete-mix or partial-mix systems. A complete-mix lagoon has enough mixing energy (horsepower) input to keep all of the bacterial solids in the lagoon in suspension. On the other hand, a partial-mix lagoon contains a lesser amount of horsepower, which is sufficient only to provide the oxygen required to oxidize the biochemical oxygen demand entering the lagoon (USACE, 1998).

2.4 Fenton's Reagents

Fenton's reagents were discovered about 100 years ago, but its application as an oxidizing process for destruction of toxic organics was not applied until the late 1960's (Huang et al., 1993). The Fenton's reagent has been efficiently used as a chemical process for wastewater treatment and pre-treatment. Fenton's reaction essentially depends on three factors: temperature, hydrogen peroxide concentration and Fe^{2+} (Nora et al. 2003). Fenton's reagent is a mixture of H_2O_2 and ferrous iron, which generates hydroxyl radicals according to the reaction (Ruppert and Bauer, 1993; Venkatadri and Peters, 1993) as presented by the following reaction:

15

$$Fe^2 + H_2O_2 \rightarrow Fe^3 + OH^\cdot + OH^- \qquad (1)$$
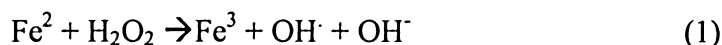
The ferrous iron (Fe^2) initiates and catalyzes the decomposition of H_2O_2, resulting in the generation of hydroxyl radicals. The generation of these radicals involves a complex reaction sequence in an aqueous solution (Pignatello, 1992)

$$Fe^2 + H_2O_2 \rightarrow Fe^3 + OH^\cdot + OH^- \qquad (2)$$

$$OH + Fe^2 \rightarrow OH^- + Fe^3 \qquad (3)$$

$$Fe^3 + H_2O_2 \rightarrow Fe\text{-}OOH^2 + H^+ \qquad (4)$$

$$Fe\text{-}OOH^2 \rightarrow HO_2 + Fe^2 \qquad (5)$$

$$Fe^2 + HO_2 \rightarrow Fe^3 + HO_2^- \qquad (6)$$

$$Fe^3 + HO_2 \rightarrow Fe^2 + O_2H^+ \qquad (7)$$

$$OH + H_2O_2 \rightarrow H_2O + HO_2^- \qquad (8)$$
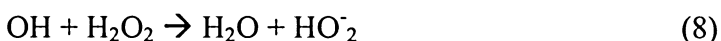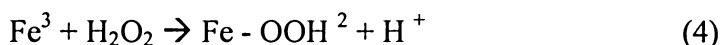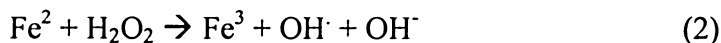
As seen in Equation 8, H_2O_2 can act as an OH^- scavenger as well as an initiator. Due to the formation of Fe^3 during the reaction, the Fenton reaction is normally accompanied by the precipitation of $Fe(OH)_3$. H_2O_2 is one of the most powerful oxidizers known, stronger than chlorine, chlorine dioxide, and potassium permanganate, through catalysis, H_2O_2 can be converted into hydroxyl radicals (OH) with reactivity second only to fluorine, and its application in the treatment of various inorganic and organic pollutants is well established. Oxidation by H_2O_2 alone is not effective for high concentrations of certain refractory contaminants because of low rates of reaction at reasonable H_2O_2 concentrations. Transition metal salts (e.g. iron salts) ozone and UV light can active H_2O_2 to form hydroxyl radicals, which are strong oxidants (Neyens et al., 2002).

When the amount of Fe^{2+} employed exceeds that of H_2O_2, the treatment tends to have the effect of chemical coagulation. However when the two amounts are reversed, the

treatment tends to have the effect of chemical oxidation (Neyens et al., 2002). Concentration of hydrogen peroxide has a critical role in the overall degradation process. Increase the concentration of hydrogen peroxide, causes increases the degradation of the pollutants. Also the rate of degradation increase with an increase in the concentration of ferrous ions (Lin and Lo, 1997). The Fenton's reaction has a short reaction time among the advanced oxidation process; therefore, Fenton's reagent is used when a high COD removal is required (Sarria et al., 2001). The pH is one of the most important parameters of the Fenton's reactions. It has been observed that pH has significant affect on the degradation of the pollutants in the leachate (Sedlak and Andren, 1991). The pH has been affectively between the ranges of 3-4. At lower pH (pH < 2.5), the formation of (Fe (II) $(H_2O))^{2+}$ occurs that reacts more slowly with hydrogen per oxide and, therefore, produces fewer amounts of reactive hydroxyl radicals there by reducing the degradation efficiency (Gallard et al., 1998). At pH > 4, the decomposition rate decreases because of the decrease of free iron species in the solution, probably due to the formation of the Fe (II) complexes with the buffer inhibiting the formation of free radicals and also due to precipitation of ferric oxyhydroxides, which inhibit the regeneration of ferrous ions (Bigda 1995; Lin and Lo 1997, Nesheiwat and Swanson, 2000). Also the oxidation potential of $HO^\cdot$ radical is known to decrease with an increase in the pH (Kwon et al., 1999). It appeared that pH 4 is the optimum for coagulation (Gau and Chang, 1996).

2.5 Application of Fenton's Reagent

Many studies have been done on chemical oxidation by Fenton's reagent. Applicability of Fenton's reagent is well known in various areas such as hazardous waste, wastewater treatment and remediation. Application of advance oxidation process (AOPs) is as follows:

1. Treatment of toxic organic at low concentrations in groundwater.

2. Treatment of low volume high strength wastewaters for detoxification and enhanced biodegradability.

3. Treatment of wastewaters not normally subject to bio oxidation.

4. Detoxification relative to aquatic toxicity following biological treatment (Eckenfelder, 1992).

Advance oxidation process (AOPs) are better alternatives for the treatment of wastewaters containing compounds that are toxic inhibitory or refractory to microorganisms. The most effective application of AOPs targets high strength and low flow rate waste stream (Bowers et al. 1989). Chemical oxidation could be used to remove ammonia to reduce the concentration of residual organics and to reduce the bacterial and viral content of wastewaters (Metcalf & Eddy, 1991). The advantages and liabilities of chemical oxidation by Fenton's reagents are presented in Table 2.1 (Eckenfelder, 1992; Flaherty and Huang, 1992).

Table 2.1 Advantages and liabilities of chemical oxidation by Fenton's reagents (Eckenfelder, 1992; Flaherty and Huang, 1992)

Advantages	Liabilities
▪ Capable of partially or completely oxidizing toxic and refractory chemicals ▪ Toxicity reduction for biological treatment ▪ Low capital cost ▪ Instant start up time ▪ Capable of treatment of low volume strength waste waters for detoxification and enhanced biodegradability	▪ Additional chemical cost ▪ Sludge disposal cost ▪ Potential corrosion problems

Many successful applications of Fenton's reagents in waste and wastewater treatment have been reported. About 50% to 65% of COD removal efficiency was obtained through oxidation of refractory organics in municipal wastewater. Wastewater treated containing a 1.0 mg/ of phenol with Fenton's reagent. The phenol was oxidized to very low concentrations (< 0.005 mg/L) after 30 minutes (Vella and Munder, 1992).

Much effort has gone into treating refractory textile wastewater with Fenton's reagent. The treatment of effluents containing anthropogenic organic compounds those are refractory, toxic, and inhibitory to conventional biological treatment systems, achieved up to 60% of COD removal (Flaherty and Huang, 1994). A significant COD removal up to 90% and color and toxicity reduction was possible cost effectively reported by (Gregor, 1994). Fenton's reagent depends on pH, amount of reagents and temperature.

Effects of these parameters on decolorizing dye wastewater treatment were observed. At the best pH value less than pH 3.5, 90% of COD removal and above 97% of decolorization were obtained (Kuo, 1992). Textile wastewater from a large dyeing and finishing mill has been treated with a combination of Fenton's process and chemical coagulation. COD removal by overall process was up to 80% (Lin and Peng, 1995). More research in depth has been devoted to treating some aromatic compounds that were included on the Environmental Protection Agency (EPA) toxic listing. Benzene, toluene and xylene (BTX), materials frequently found in contaminated groundwater, were treated using Fenton's reagent. BTX were effectively oxidized in a period less than 10 minutes (Lou and Lee, 1995). Three types of AOPs were tested among them Fenton's reagents was most effective to treat chlorophenols (Dong, 1993). Pretreatment of chlorinated aromatics such as chlorophenals followed by methanogenic degradation have attempted. They were decomposed to biodegradable products such as oxalate and formate but further degraded by prolonged oxidation to water and carbon dioxide (Koyama et al., 1994). Highest yield in the oxidation of chlorobenzene was in the pH range of 2 to 3 and the complexes of aromatic intermediate compounds with iron might play a role in regulating reaction pathways found by (Sedlak and Andren, 1991). Removal of pentachlorophenol (PCP) and Tetrachloroethylene (TCE), and pesticide in contaminated soil with Fenton's reagent, respectively tested. The results showed that contaminated soils could be treated more effectively with Fenton's reagent than with hydrogen peroxide alone. Pesticides were reduced from 50 ppm to below detection limits after treating for 30 minutes with 50-ppm ferrous sulfate salt and 200 ppm hydrogen peroxide (Ravi and Gurol, 1994). Pilot plant tests were conducted and confirmed the results of laboratory investigations. Pilot

plant scale experiments with Fenton's reagents showed that 90% of the organophosphorous compounds degraded in about one hour (Munz et al., 1994). Over 80% of TCE could be removed within two minutes founded by (Vella and Veronda, 1994). Landfill leachate treatment using Fenton's reagents were studied by (Kim and Huh, 1997; Bae et al., 1997, and kim et al., 1997). Kim and Huh (1997) studied the potential of Fenton's oxidation process prior to a biological treatment process. Treated old leachate having an average BOD_5/COD ratio less than 0.05, and achieved 68.1 % of COD removal and 92% of decolorization efficiency with 0.044 M of hydrogen peroxide and 0.0035 M of ferrous iron {H_2O_2/Fe (II) mole ratio: 12.57} at pH 3.5 and 2 days of reaction period. Bae et al. (1997) studied the post biological treatment of leachate with Fenton's reagent. After removing ammonia with two stage activated sludge, the leachate was treated with Fenton's reagent, and COD removal by 63% was obtained. Kim et al. (1997) found that the mount of ferrous iron to be added to treat leachate could be remarkably reduced by radiation due to the regeneration of the consumed ferrous iron. A COD removal of more than 70% was obtained, and the optimum conditions found were 10^{-3} M of ferrous iron. pH value of 3, and a 1/1 molar ratio of COD/H_2O_2.

Compared to active research on the application of Fenton's reagent are scarce. A catalyst waste containing 1000 mg/l of phenol and wastewater from a pulp and paper company was successfully treated with Fenton's reagent (Robinson and Monsen, 1992). Final phonel level of the catalyst was below 5 mg/L, and the removals of COD and TOC of wastewater were 70% and 74%, respectively. The landfill leachate pretreated in an anaerobic and an activated biological process was treated with Fenton's reagent to meet

effluent standard for COD (Ahn, 1995). Average removal efficiency of 70% and maximum removal efficiencies of 84-87% were obtained in a full-scale plant.

The COD removal efficiency by oxidation was greatly affected by the pH reaction. The most effective reaction was observed below pH 4.0, but the optimal coagulation pH range to maximize the COD removal efficiency is between 3 and 6.

The dosage of ferrous sulfate over 500 mg/l does not increase the overall COD removal efficiency. The optimum dosage of ferrous sulfate should be determined by considering the capital and operating costs. The efficiency of hydrogen peroxide obtained from the removed COD values by oxidation was observed to be about 45% (Yun and Kyung, 2000). The maximum amount of COD that could be removed by the Fenton's pre-treatment was about 60% of the initial value (i.e., 10540 mg/l). Such a maximum removal was achieved using reagent dosages as high as 10 000 mg /l of H_2O_2 and 830 mg/l of $FeSO_4$ (Antonio et al., 2003). The maximum removal efficiencies of 79% in COD and 98% in color were achieved by Fenton reagent and lime addition at doses of 2,500 mg/L H_2O_2 + 2,500 mg/L $FeSO_4$ (Pala and Erden , 2004) .

3. Materials and Methods

3.1 Overview

An experiment was conducted in order to examine the treatment of leachate generated from bioreactor landfills by Fenton's reagents and leachate recirculation. Four types of chemicals, hydrogen peroxide (H_2O_2), ferrous sulphate ($FeSO_4$), sulfuric acid (H_2SO_4) and Sodium Hydroxide (NaOH) were used in this experiment. The experimental set-up consists of 4 plastic tanks each having capacity of 60 liters. The two plastic tanks were equipped with air bubble system while two have no air supply. 20 liter of leachate was supplied to each tank for every experiment. Two types of synthetic MSW were used: one was consisted of synthetic MSW and the other was mixed with biosolids at the ratio of 4:1 (wet weight). Six bioreactors were designed to simulate bioreactor landfills accepting either MSW with biosolids or MSW without biosolids. Each bioreactor has a volume capacity of 220L and filled with approximately 150L of synthetic MSW (around 70kg in weight). The MSW was broken down by shredding or cutting, weighed on the scale, and then mixed up thoroughly to get uniformity before being put into the bioreactors. The filled MSW was compacted to the required densities in order to reflect typical landfill conditions. The tap water was added into the bioreactor landfills. The leachate produced by bioreactor was pumped back until the synthetic MSW matrices reached field capacity with respect to their moisture contents. The six simulated bioreactor landfills were operated for 102 days in the laboratory. The leachate recirculation was applied to four bioreactors. The daily leachate recirculation rate for each bioreactor in anaerobic stage was 12 % of the matrix volume. Four bioreactors were operated by closed loop leachate recirculations and two single pass bioreactors were connected with lagoons to treat

leachate. Based on their respective operational protocol, matrix components, and replicate number of the bioreactors, the six bioreactors were named as AMF, AMR1, AMR2, ASF, ASR, NMR (A: air; N: no air; M: MSW; S: biosolids; F: flushing; R: recirculation).

3.2 Design and Construction of the Lagoon System

Lagoons are usually large shallow basins or earthen pits, which have been excavated or constructed in an area close to landfill site. They are usually lined with impermeable materials to prevent seepage or migration of the leachate from the impoundment area.

Three types of lagoons are available for leachate treatment depending on the design features and microbial activity: aerobic, anaerobic and facultative. For experimental purpose artificial aerobic and anaerobic lagoons were constructed to simulate the biological treatment of the leachate. Following is the detailed description of the construction of these lagoons.

Anaerobic lagoons were comprised of two air tight transparent plastic tanks each having capacity of 60 liters. A lid was provided at the top of the tank to insure that no air should be dissolved from atmosphere into the leachate. A valve was provided at the bottom of the tank to discharge treated leachate into the aerobic lagoon. The Anaerobic lagoons are shown in the Figure 3.1.

Aerobic lagoons were also comprised of two transparent plastic tanks each having capacity of 60 liters. The plastic tanks (aerobic lagoons) were equipped with three air bubble strips placed at an equal distance to diffuse air into the leachate. The Air bubble strips were connected to the air pump through small tubes. The Aerobic lagoons are shown in the Figure 3.2.
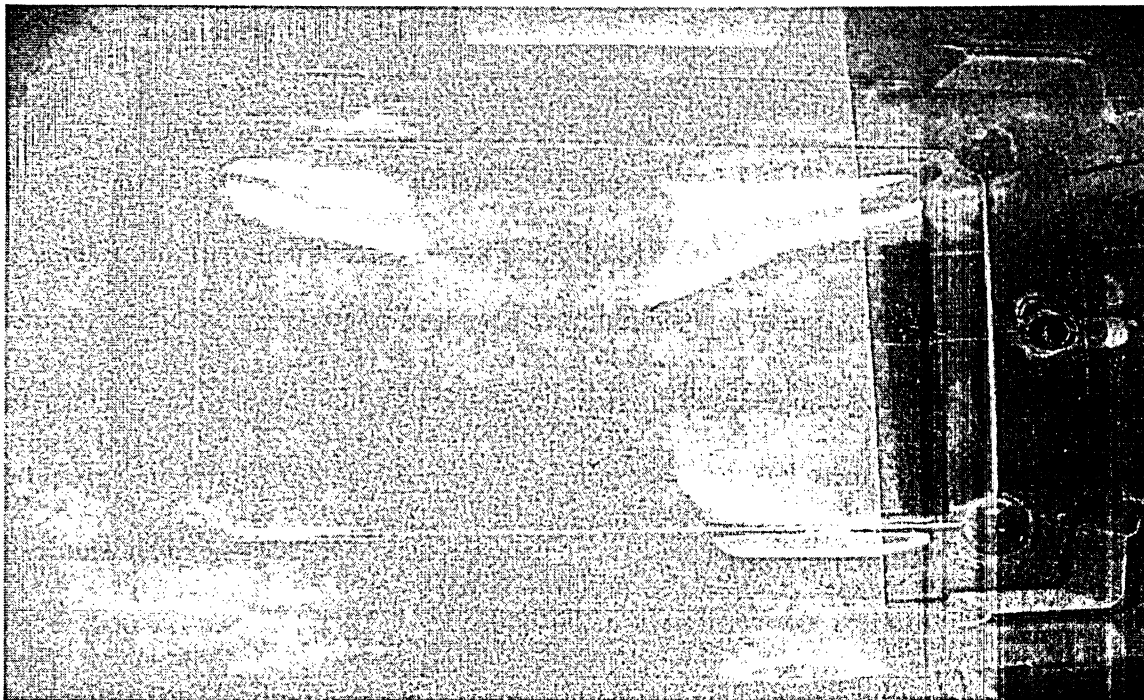
Figure 3.1 Simulated Anaerobic Lagoon
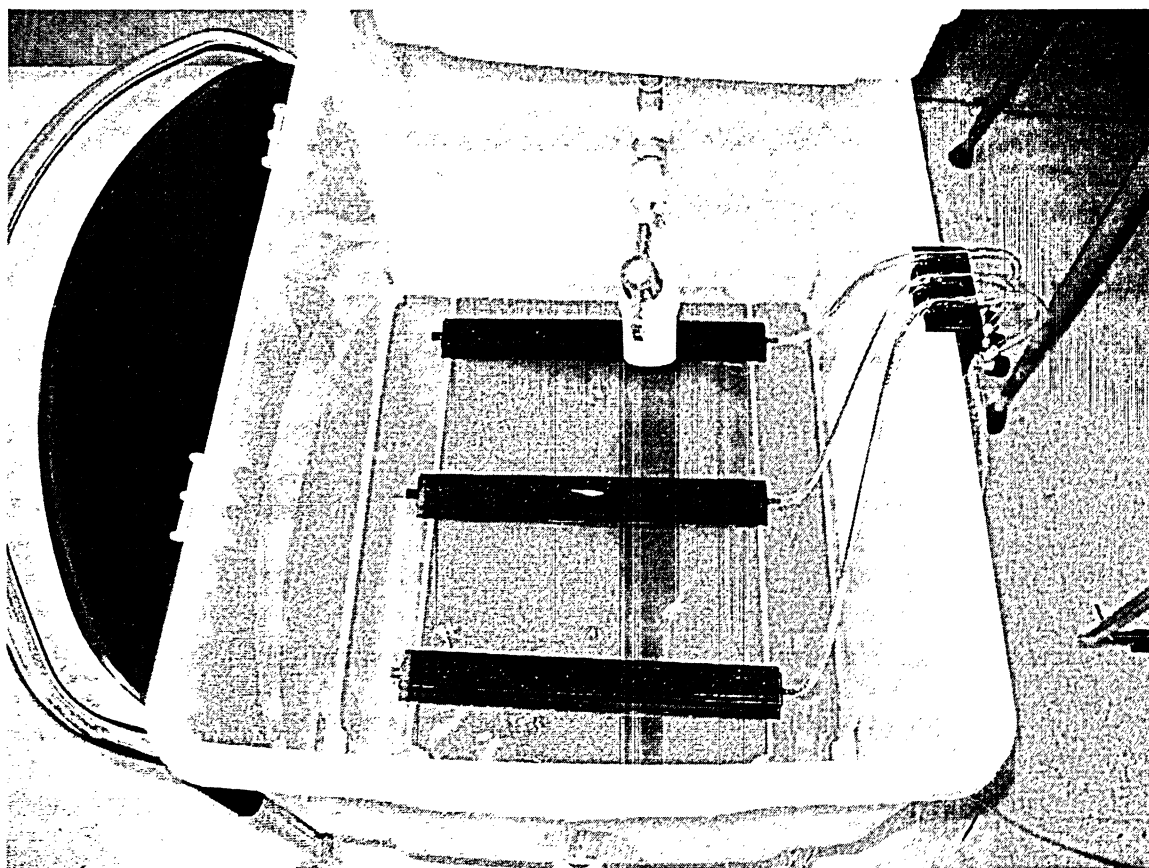
Figure 3.2 Simulated Aerobic Lagoon

3.3 Design and Construction of the Bioreactor Systems

3.3.1 Structural Components and Configuration of the Bioreactor Systems

The structural components and configuration the bioreactor systems are shown in Figure 3.3. Following is the detailed description of the design and construction of the systems.

Bioreactors

Semi-transparent polyethylene cylindrical containers with lid were used as the bioreactors. Each of them has diameter of 0.55 m, height of 0.92m, and total capacity of 220 L. After the air system, leachate recirculation system and sensor wire inside each bioreactor was installed, the wastes were placed inside, and gap between the body of the bioreactor and the lid has been sealed by silicone sealant in order to keep air tight and water tight. There is a ¾" port on the bottom and lid of each bioreactor respectively. Two fittings are installed in the ports. The bottom one is for discharging leachate, and the lid one is for the exhaust gas. A stainless steel sink screen is put onto each bottom fitting in order to prevent clogging or MSW loss. There is a 5cm thick layer of gravel lining the bottom of each bioreactor. The MSW was put on the gravel liner directly.

Leachate Collection Tanks

Each bioreactor was connected to one leachate collection tank with a ¾" x 1 ¼" PVC adaptor and vinyl tube. The capacity of each tank is 20 L. The function of the tank is to collect the leachate discharged from the bioreactor to prevent flooding inside the bioreactor. The generated acidic leachate during the anaerobic can be discharged very quickly, and never accumulated inside the MSW. There is a ½" PVC adjustable ball valve on the sidewall of each tank for sampling and discharging leachate to the leachate recirculation reservoir.

Leachate Recirculation Reservoirs and Pumps

Six transparent polyethylene tanks were used as leachate recirculation reservoirs. Each of them has a capacity of 25 L and graduations. The reservoir served as the "leachate transfer station" where the pH and volume of the recirculated leachate can be measured, and the acidic leachate can be buffered. The submersible pumps (Laguna Statuary Pump 3#) were used for pumping the leachate and makeup water back into the bioreactors.

Leachate Distribution Apparatus

The function of the leachate distribution apparatus is to distribute the recirculated leachate evenly on the top of the MSW matrix, just like raining. The apparatus included a circle with a cross inside, and it is made by connecting a ¾" PVC cross, three ¾" PVC tees, and ¾" vinyl tube. Sixteen holes with 3mm diameter were punched on the vinyl tube. The apparatus was connected to the leachate recirculation pipe outside the bioreactor. A ¾" PVC adaptor was used for the pipe to pass the bioreactor wall. An adjustable PVC ball valve was installed on the recirculation pipe. Every time the recirculation was finished, the valve was closed to keep the bioreactor airtight.

Air Distribution Pipes

Three PVC pipes were installed in each bioreactor to distribute the injected air evenly into the waste matrices. One third of each pipe near the bottom of the bioreactor was perforated. The air pipes were covered by plastic insect screen to prevent MSW getting inside the pipes and clog the pipes. The three pipes were connected together by PVC elbows and tubes, and become one "entity" which also served as a support for the water distribution apparatus. The injected air reached the "entity" through one air pipe that

passed the bioreactor wall by one PVC adaptor. An adjustable PVC ball valve was installed on the air pipe to adjust the airflow.

Air Compressor

Air was supplied from one air compressor (HUSKY, 2.75HP, 8 Gallons, 4.0 SCFM @ 40psi) to aerobic lagoons and the bioreactors. There was also a standby air compressor in the lab (DeVILBISS ® Tradesman Model DAC-7118, DeVILBISS, Canada).

Temperature Sensor and Thermometer

The temperature sensors were placed inside the bioreactors at three different levels: initial, middle and bottom. The sensors were interconnected with the thermometer through wires. The thermometer (EXTECH 421307 thermometer) can read out the internal temperature of the MSW matrix.

Exhaust Gas Discharge System

The lids of each bioreactor were connected with the exhaust gas pipe using tubes and tees. The exhaust gases were discharged outdoor through one ¾" vinyl tube.

3.3.2 Leachate Recirculation Mode

The leachate recirculation system includes leachate collection tank, valves, leachate recirculation reservoir, submersible pump, tubes, and leachate distribution apparatus. It was operated in a closed-loop mode. The mechanism of the leachate recirculation system is presented in Figure 3.4. Arrows in the Figure 3.5 show the leachate flow direction.

3.3.3 Air Injection and Exhaust Mode

The air injection and exhaust system includes air compressor, air supply pipe, gas flow meter, and valve, air distribution pipes, gas exhaust port, and gas exhaust pipe. The movement direction of the injected air is presented by the arrows (Figure 3.6).

3.3.4 The Operation Mode of Single Pass Bioreactors

In the single pass bioreactors, tap water was added into the bioreactors. The generated leachate was transported into the downstream treatment units: aerobic lagoons and anaerobic lagoons. The operation mode is displayed in Figure 3.7.

3.3.5 Bioreactor System Maintenance

The joints and seams were checked often during the study to make sure they were airtight and watertight. Spare parts, leachate tanks and reservoir, and stand-by air compressor and pump were in stock.

3.4 Preparation of Synthetic MSW and Loading of Bioreactors

The synthetic MSW with high organic content and moisture content were prepared and loaded into the six bioreactors. There are two types of synthetic MSW made in this study: one with biosolids; the other one without biosolids. The bioreactors AMF, AMR1, AMR2, and NMR were loaded with synthetic MSW without biosolids. The bioreactors ASF and ASR were loaded with synthetic MSW with biosolids.

3.4.1 MSW Compositions

The synthetic MSW used in this study includes waste foods, waste vegetables, plastics, waste paper, textiles, and biosolids. The percentages of compositions were decided according to the purpose of this study. San and Onay (2001) used synthetic MSW according to the typical MSW Compositions in the city of Istanbul (Table 3.1). Hao (2004) used synthetic MSW according to the typical MSW Compositions in the city of Beijing (Table 3.2). The biodegradable compositions were respectively 95% and 85% of the total MSW weight in the two studies, belonging to high organic content MSW. Based

on these data, the Synthetic MSW compositions and each component percentage in this study were decided (refer to Table 3.3).

Table 3.1 Synthetic Solid Waste Compositions according to the MSW Compositions of Istanbul (Adapted from San and Onay, 2001)

Composition	Percentage (%)
Food	76
Paper	12
Plastics	4
Textiles	4
Yard waste	3
Metal	1
Total	100

Table 3.2 Synthetic Solid Waste Compositions according to the MSW Compositions of Beijing (Adapted from Hao, 2004)

Composition	Percentage (dry weight %)
Food	55
Paper	25
Textiles	5
Plastics and rubber	15
Total	100

Table 3.3 Synthetic MSW Compositions in the Study

Composition	AMF		AMR1		AMR2		ASF		ASR		NMR	
	Kg	%	kg	%	kg	%	kg	%	kg	%	kg	%
Foods	29	42%	31	43%	30	43%	26	35%	26	35%	30	43%
Vegetables	23	33%	22	32%	23	32%	19	26%	19	26%	23	32%
Paper	8	12%	9	12%	8	12%	7	10%	7	10%	8	12%
Plastics	7	10%	6	9%	6	8%	4	6%	4	6%	6	9%
Textiles	3	4%	3	4%	3	4%	2	3%	2	3%	3	4%
Biosolids	0	0%	0	0%	0	0%	15	20%	15	20%	0	0%
Total Wet Weight (kg)	70	100%	71	100%	70	100%	74	100%	74	100%	70	100%
Moisture Content (%)		58%		63%		63%		67%		67%		58%
Total Dry Weight (kg)	29	100%	26	100%	26	100%	24	100%	24	100%	30	100%

3.4.2 Preparation of MSW

Waste foods and vegetables were taken from the nearby restaurant kitchen. When the kitchen wastes were brought in, they were sorted, and only the waste foods and vegetables were used as the main organic components for the simulated bioreactor landfills. Waste foods and vegetables were weighed separately.

The paper, including newsprint, computer printout, office paper, books, and packaging paper, came from the offices at Ryerson University. All the paper was shredded.

New garbage bags were used as plastic component in the synthetic MSW. In the field bioreactor landfills, the plastic bags channeled or blocked the recirculated leachate, as well as encapsulated materials that would readily be biodegraded in the presence of air. Therefore, all the garbage bags in this study were cut to the size of 100-150 mm.

Old clothes were used as textile component in the study. Also, they were cut to the size of 100-150 mm.

Biosolids were taken from Toronto Ash Bridge Bay Treatment Plant. The biosolids were the mixture of primary sludge and secondary activated sludge that have undergone anaerobic digestion process.

3.4.3 Loading of the Simulated Bioreactor Landfills

After all the MSW components were broken down to the suitable size, they were thoroughly mixed up for measuring the initial moisture content of MSW the sample was taken from synthetic MSW. The synthetic MSW was loaded into each bioreactor and compacted. After that, about 39 L of tap water was added into each bioreactor. In the first three days, the leachate was recirculated daily and the volume of the leachate was measured until the MSW in each bioreactor was brought to field capacity.

The moisture content is an essential factor that dramatically affects the waste degradation. On weight basis, moisture content is described as the weight of the water divided either by dry or wet waste weight. On a volumetric basis, moisture content is expressed as the volume of water divided by the volume of wet waste. Generally, the field capacity is used to characterize the moisture content of the MSW matrix. The field capacity is the concept to qualify the internal storage of a landfill, or the moisture content at which the maximum amount of water is held (through capillary forces) against gravity. The addition of more moisture will result in continuous leachate drainage (Reinhart and Townsend, 1998). When the amount of water in the leachate collection tank was approximately equal to the amount of leachate recirculated the previous day, the MSW inside the bioreactors was considered to reach the field capacity.

The range of the field capacity is wide as expected since it is a function of the waste composition, density and porosity, particle sizes, waste overburden, waste age (Yuen et al., 2001; Reinhart and Townsend, 1998).

The characters of the loaded synthetic MSW in each bioreactor are summarized in Table 3.4.

Table 3.4 Physical Characters of Synthetic MSW at the Beginning of the Study

	AMF	AMR1	AMR2	ASF	ASR	NMR
Initial Volume (L)	150	157	160	152	152	173
Initial Height (m)	0.63	0.66	0.67	0.64	0.64	0.73
Initial Field Capacity (%)	65.1%	69.6%	70.4%	70.6%	69.9%	67.0%
Initial Density (kg m^{-3})	563	546	541	545	532	519

Note: final density is the density of synthetic MSW at field capacity; "initial" means at the beginning of the study.

3.5 Operation and Sampling Protocol of the Anaerobic Lagoon, Aerobic Lagoons and Simulated Bioreactor Landfills

3.5.1 Treatment with Fenton's Reagents

The following three experiments were carried out to determine the best method for the maximum COD concentration reduction in Fenton's reagents for given leachate.

1. Leachate volume of 20 liters was treated in an anaerobic lagoon. Its pH values were adjusted to 3, 3.5 and 4 with the addition of H_2SO_4. Dosages of H_2O_2 and $FeSO_4$ were added to the leachate and rapidly stirred for 15 minutes. The stirred leachate was kept in an air-tied lagoon for 6, 12 and 24 hours at each adjusted pH value. Following this stage, the leachate was discharged to an aerobic lagoon and pH value was adjusted to the pH 7 with Sodium Hydroxide. The aerobic lagoons were air supplied from an air pump together with 1 liter of fresh activated sludge collected from a wastewater treatment plant.

2. In this experiment, same type of leachate was treated in another anaerobic lagoon and aerobic lagoon but without chemicals in order to evaluate the performance of experiment with chemicals. The test procedure and conditions were the same as of experiment number 1, except pH value was adjusted to 7 in anaerobic lagoon.

3. Leachate volume of 20 liters was treated in an aerobic lagoon. Its pH value was adjusted to 7. The Air was supplied through air bubble system for 6, 12, and 24 hours. Following this stage, the leachate was discharged to anaerobic lagoon and pH value was adjusted to 3.5 with sulfuric acid. In that leachate, dosage of H_2O_2 and $FeSO_4$ was added and stirred for 15 minutes.

3.5.2 Chemical Oxygen Demand (COD)

The COD of the leachate was analyzed using the potassium dichromate ($K_2Cr_2O_7$) reflux kit for use with accurate Test TM COD # 174-318 and # 174 -326 vials. The potassium dichromate reflux method is an oxidation reduction reaction that estimates the portion of matter in the filtered sample that is susceptible to chemical oxidation.

A SPECTRONIC 20D spectrophotometer set to detect at 600nm was used. Each sample was analyzed in duplicate. Dilution factor was 1/1000, 1/500, 1/100.

3.5.3 5-day Biochemical Oxygen Demand (BOD$_5$)

BOD$_5$ test followed standard method 5210B (APHA et al., 1998). In this study, samples were incubated in a Fisher Scientific ISO temperature Incubator (Model 637D, Fisher Scientific Ltd.), and dissolved oxygen was measured by a YSI model 51B DO Meter (YSI Inc.). After each leachate sample was measured COD value, the BOD$_5$ value can be predicted, and then two dilution factors were selected for each sample according to

Tchobanoglous (2003). Poly seed was used as seed source, each 300 ml BOD bottle was added 5 ml prepared poly seed solution.

3.5.4 pH

pH meter was used to measure the pH values of leachate in the study. Because leachate pH values changed along the time, it is very important to carry out the measurement right after sampling. Commercial standard solutions (including pH 4.0, 7.0, and 11.0) were used for calibrating the pH meter.

3.5.5 Sampling

In anaerobic process, the treated leachate samples were taken at each consecutive hour during the each tested time period (6, 12 and 24 hours) to check the optimum time for the maximum COD concentration reduction. Only three test samples were taken in the aerobic process, at start, middle and at the end of the each tested time period.

During the 102-day study, Anaerobic, Aerobic Lagoons and all the six bioreactors operated according to the proposed protocol based on the purpose of this study. All parameters of the operation were selected from the previous investigators' studies in the literature. Waste samples were collected before and after the operation of the bioreactors. Leachate samples were collected following a timeline.

3.5.6 Treatment with Leachate Recirculation

The function of leachate recirculation is to achieve optimum moisture content and movement inside waste matrices and to treat leachate within bioreactor. The optimum leachate recirculation rate is different for aerobic and anaerobic degradation. The recirculation rate of this study was determined according to the previous researchers' studies. In Hudgins and Harper's study (1999), they kept waste mass moisture contents

above 60% in two aerobic landfills. They also indicated that waste temperatures increased while moisture levels decreased, in some cases to below 40%; as such, leachate flow and air delivery rates should be adjusted based on the field data to keep the waste mass adequately moisturized and aerated. Stessel and Murphy (1992) concluded that waste moisture levels had to be maintained at 75% for the optimum aerobic degradation. The field capacities in this study are in the range of 60% - 70%. To keep the field capacity in the bioreactors, leachate was recirculated daily. At the beginning of the study, the volume of leachate recirculated is approximately equal to 15% of the waste matrix volume in one bioreactor. The volume of leachate generated decreased with time in the aerobic stage because of evaporation and degradation consumption. When the volume of leachate decreased to below 5 L (approximately 4% of the waste matrix in one bioreactor), tap water was added to keep the minimum volume 5 L.

Many researchers conducted studies on the effects of different leachate recirculation rates on anaerobic degradation. Chugh et al (1998) utilized three daily recirculation rates – 2%, 10%, and 30% of initial volume of waste matrices. They concluded that the rate and extent of waste decomposition improved with the increase in moisture flow. However, the results of Sponza and Agdag's study (2004) contrasted the previous study. Their recirculation rates are 9 L d^{-1} (13% of the reactor volume) and 21 L d^{-1} (30% of the reactor volume) respectively. After 220 days of anaerobic incubation, they observed that the pH, COD, VFAs concentrations, methane gas productions and methane percentages in 9 L d^{-1} bioreactor were better than in 21 L d^{-1} bioreactor. They indicated that high recirculation volumes might deplete the buffering capacity and remove the activity of methanogens. Warith (2002) used 15% of the total volume of solid waste in each waste

cell and recirculated three times a week. Based on these previous studies, daily recirculation rate was determined as 12 % of the total waste matrix volume in each bioreactor for the anaerobic stage in this study.
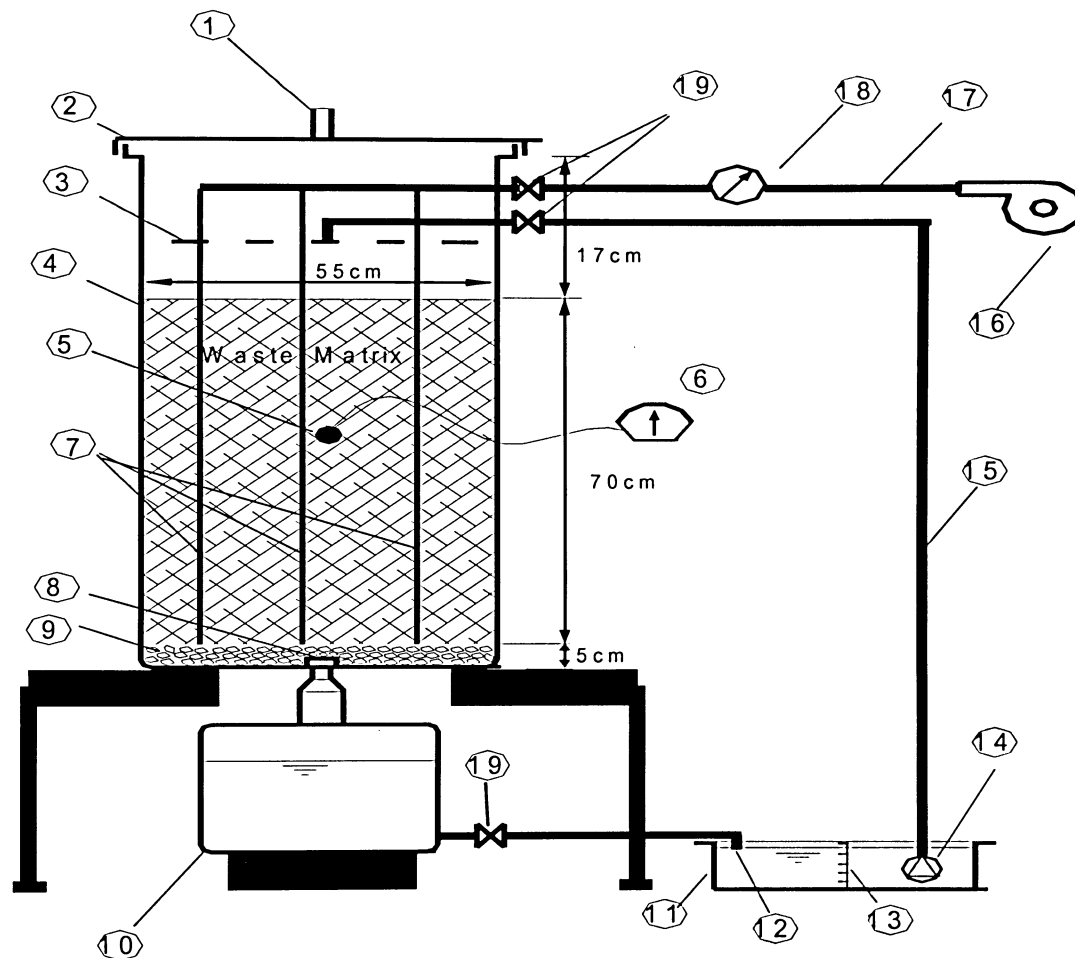
1	Gas Exhaust Port	11	Leachate Recirculation Reservoir
2	Lid of Bioreactor	12	Leachate Sampling Port
3	Leachate distribution Apparatus	13	Graduation
4	Body of Bioreactor	14	Leachate Recirculation Pump
5	Temperature Sensor	15	Leachate Recirculation Pipe
6	Thermometer	16	Air Compressor
7	Air Distribution Pipes	17	Air Supply Pipe
8	Screen	18	Gas Flow Meter
9	Gravel	19	Adjustable Valve
10	Leachate Collection Tank		

Figure 3.3 Dimensions, Components, and the Configuration of the Simulated Bioreactor Landfill

1	Gas Exhaust Port	11	Leachate Recirculation Reservoir
2	Lid of Bioreactor	12	Leachate Sampling Port
3	Leachate distribution Apparatus	13	Graduation
4	Body of Bioreactor	14	Leachate Recirculation Pump
8	Screen	15	Leachate Recirculation Pipe
9	Gravel	19	Adjustable Valve
10	Leachate Collection Tank		

Figure 3.4 Operation Mode of Leachate Recirculation System
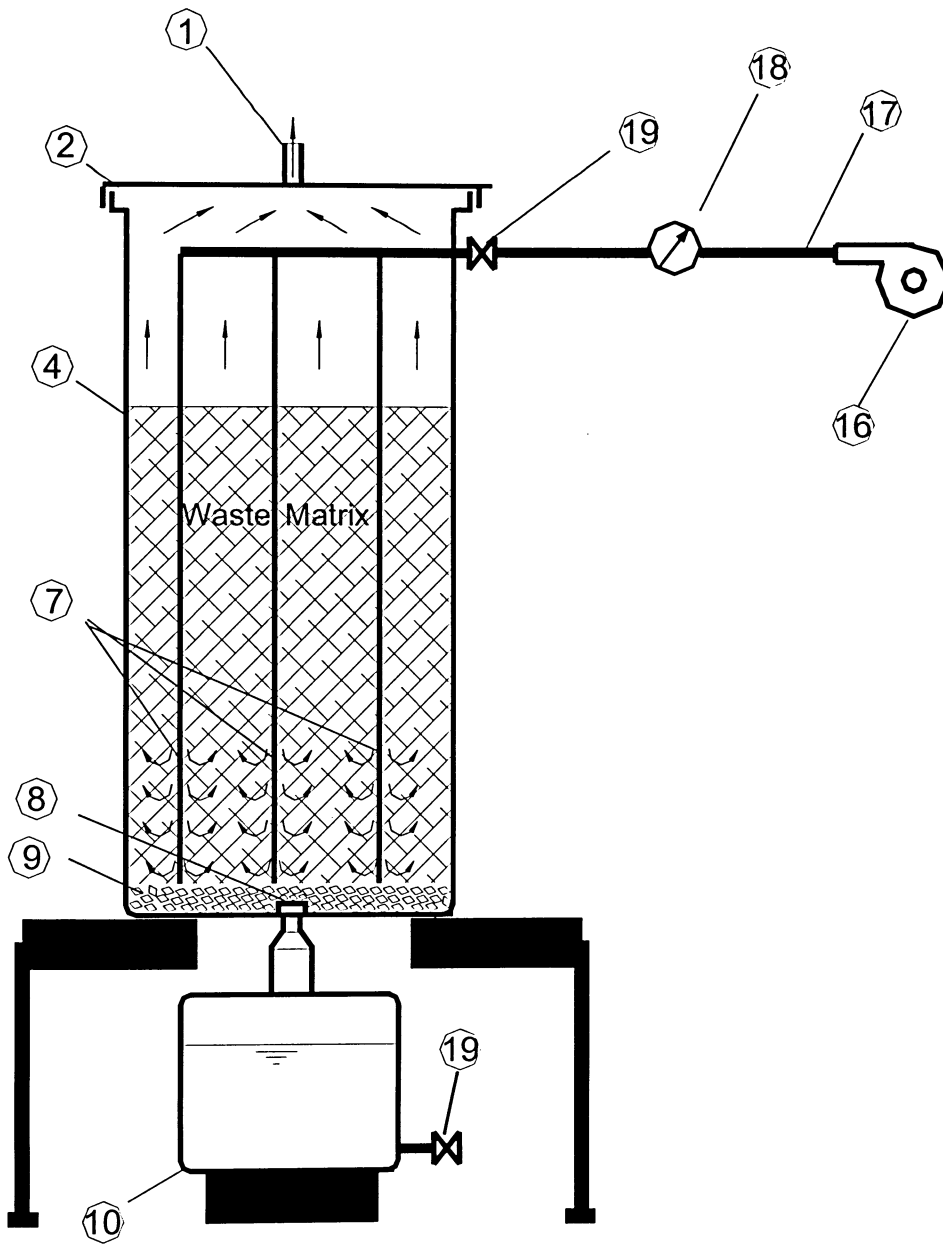
1	Gas Exhaust Port	10	Leachate Collection Tank
2	Lid of Bioreactor	16	Air Compressor
4	Body of Bioreactor	17	Air Supply Pipe
7	Air Distribution Pipes	18	Gas Flow Meter
8	Screen	19	Adjustable Valve
9	Gravel		

Figure 3.5 Operation Mode of Air System
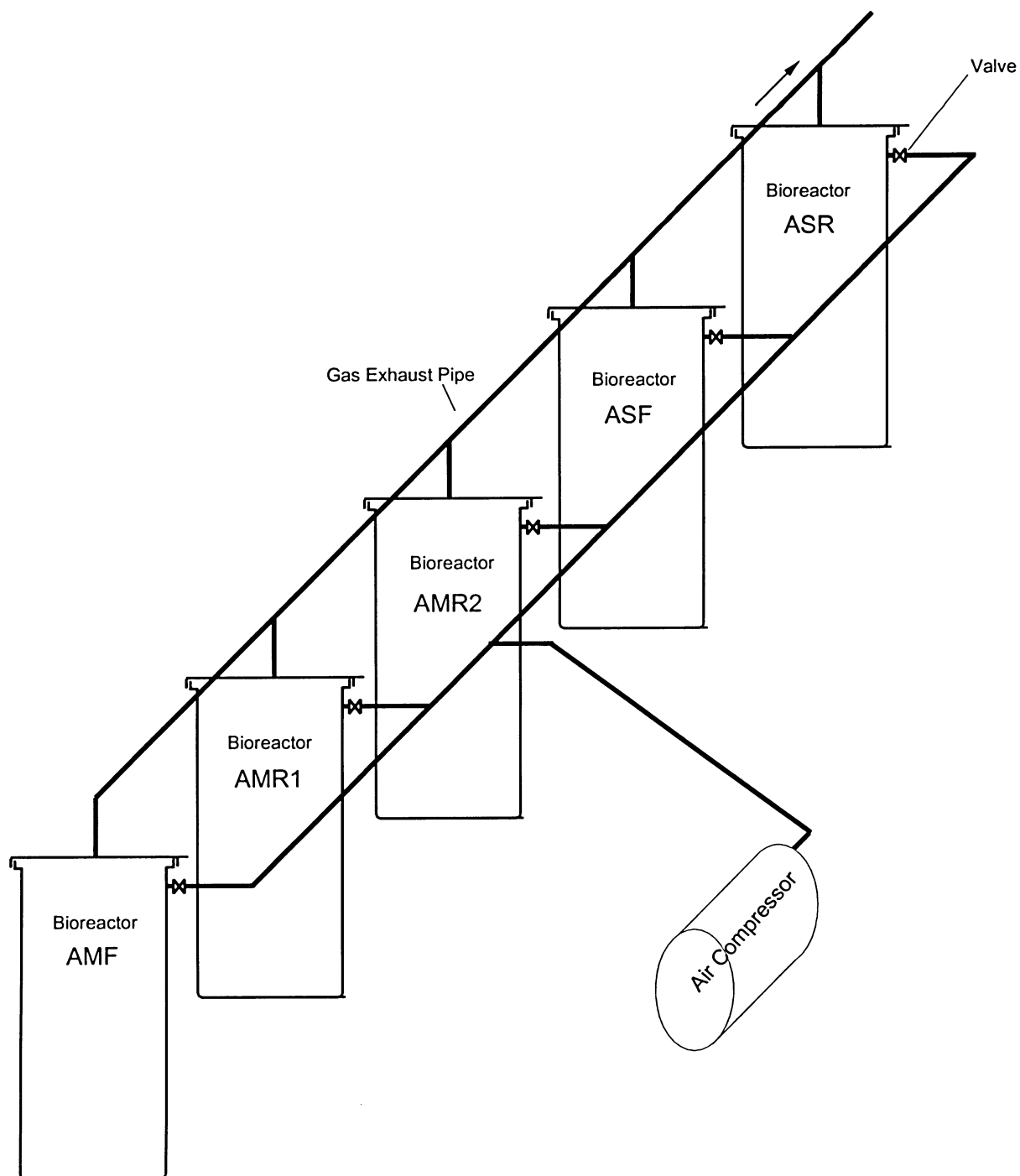
Figure 3.6 Connections of the Air Compressor and the Five Bioreactors

1	Gas Exhaust Port	10	Leachate Collection Tank
2	Lid of Bioreactor	11	Leachate Recirculation Reservoir
3	Leachate distribution Apparatus	13	Graduation
4	Body of Bioreactor	14	Leachate Recirculation Pump
8	Screen	15	Leachate Recirculation Pipe
9	Gravel	19	Adjustable Valve
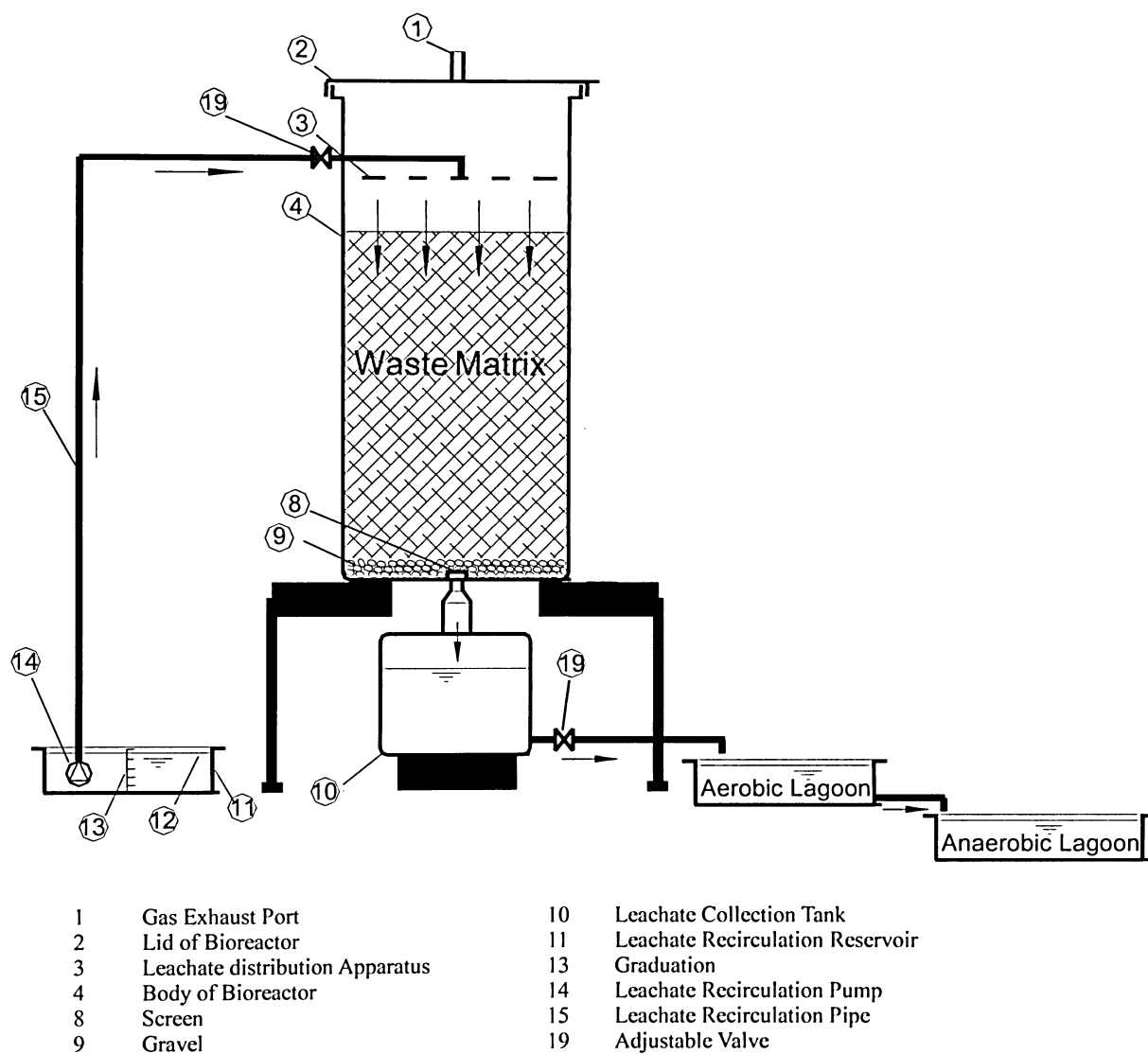
Figure 3.7 Operation Modes of Single Pass Bioreactors

4 Experimental Results and Discussion

4.1 Leachate Quality from Different Bio- Reactors

Leachate was collected from four bioreactor landfill models. The municipal solid waste compositions and operational protocol of each bioreactor landfill was different. That's why leachate quality was different from each bioreactor landfill. Quality of leachate from each bioreactor is discussed below.

Bioreactor # 1: In this bioreactor operational protocol was 18 days aerobic and followed by anaerobic condition until the end of the experiment. Initially COD concentration was about 37,600 mg/l and BOD_5 was 18,800 mg/l. On the 18th day of aerobic stage, COD concentration decreased and it reached a concentration of 15,800 mg/l. The pH value of leachate was initially measured as 4.4 and finally pH 7.0 was noted. The BOD_5/COD ratio decreased from initially 0.5 to finally 0.34.

Figure 4.1 Variation in COD with time

Figure 4.2 Variation in BOD₅ with Time
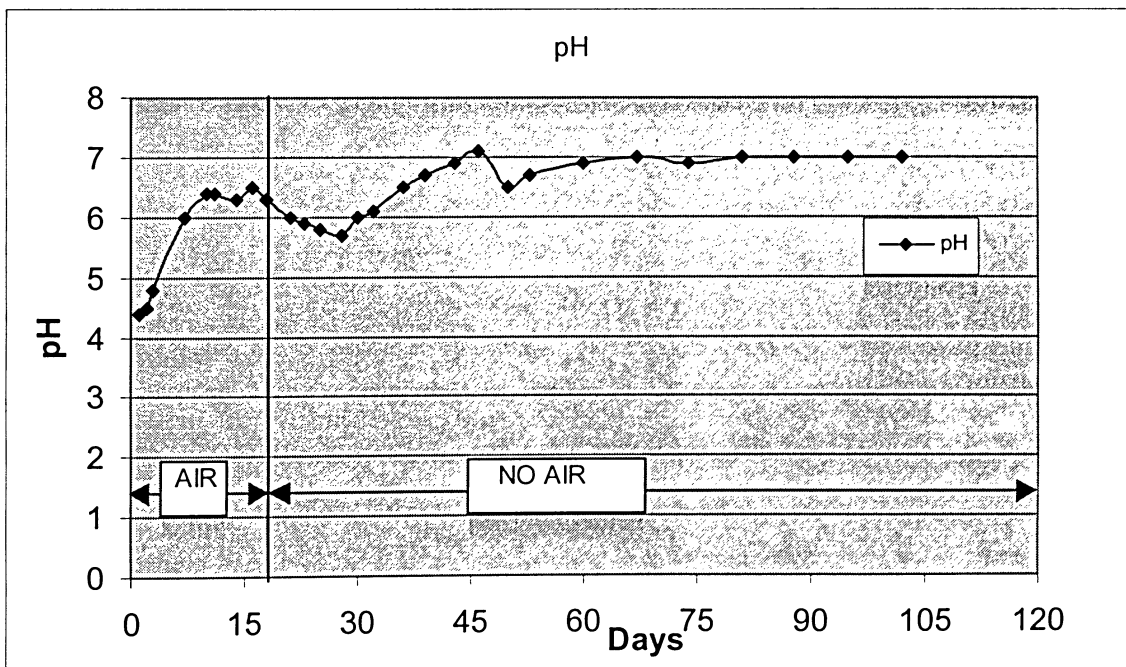
Figure 4.3 Variation in pH with Time

Bioreactor # 2: In this bioreactor, operational protocol was anaerobic. Initial COD concentration was 33,000 mg/l and the initial BOD_5 concentration was 19,000 mg/l. The peak COD concentration was 63,000 mg/l and the peak BOD_5 concentration was 30,000 mg/l (these values were noted after 15 days of anaerobic stage). It was noted that, at the end of this experimental run, COD concentration was still high in this bioreactor and it was 45,000 mg/l and BOD_5 was 21,000 mg/l (compared to BIO-1). The BOD_5/COD ratio decreased from initially 0.58 to finally 0.48. Comparisons between BIO-1 and BIO-2, it is clearly observed that initially aerobic stage has significantly effect on the leachate quality of municipal solid waste.

Figure 4.4 Variation in COD with Time

Figure 4.5 Variation in BOD₅ with Time

Figure 4.6 Variation in pH with Time

Bioreactor # 3: Municipal Solid wastes along with biosolids (Digested Sludge from waste water treatment plant) were used in this bioreactor. The operational protocol was 18 days aerobic followed by anaerobic stage. Initial COD concentration was 30,000 mg/l and initial BOD_5 concentration was 14,000 mg/l. Peak COD and BOD_5 concentrations were 37,000 mg/l and 19,000 mg/l, respectively. Final COD concentration was 21,000 mg/l and final BOD_5 concentration was 7,000 mg/l after 102 days of operation. The BOD_5/COD ratio decreased from initially 0.58 to finally 0.48. The pH value of leachate was initially 4.5 after 18 days of aerobic stage it was reached 6.7, and finally 7.2 was observed.
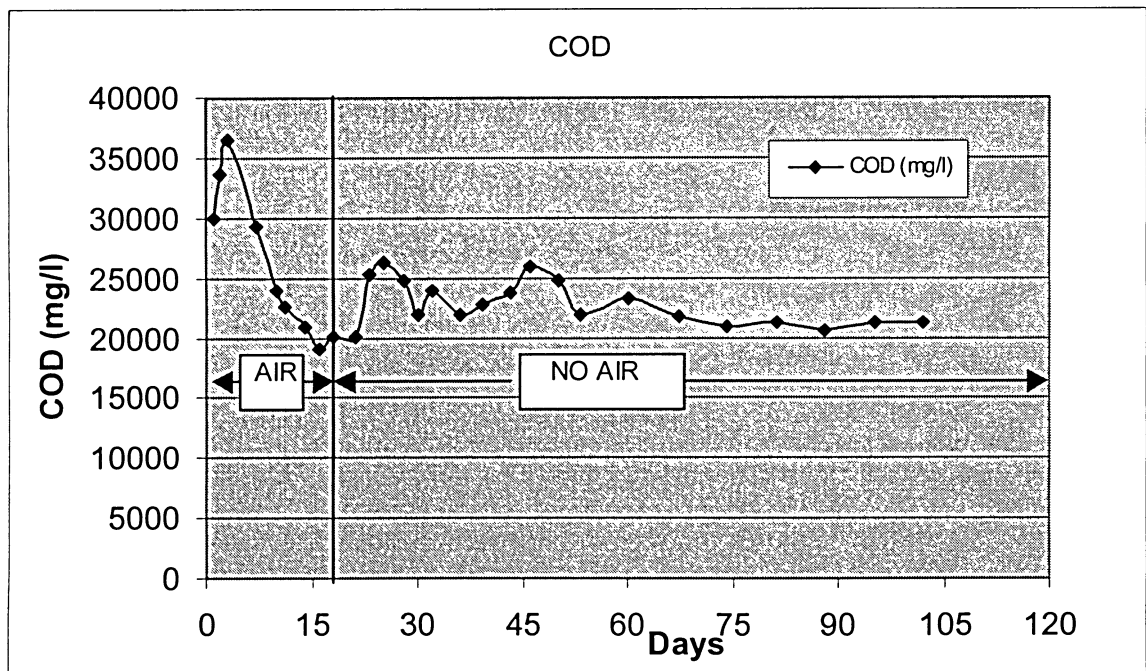
Figure 4.7 Variation in COD with Time
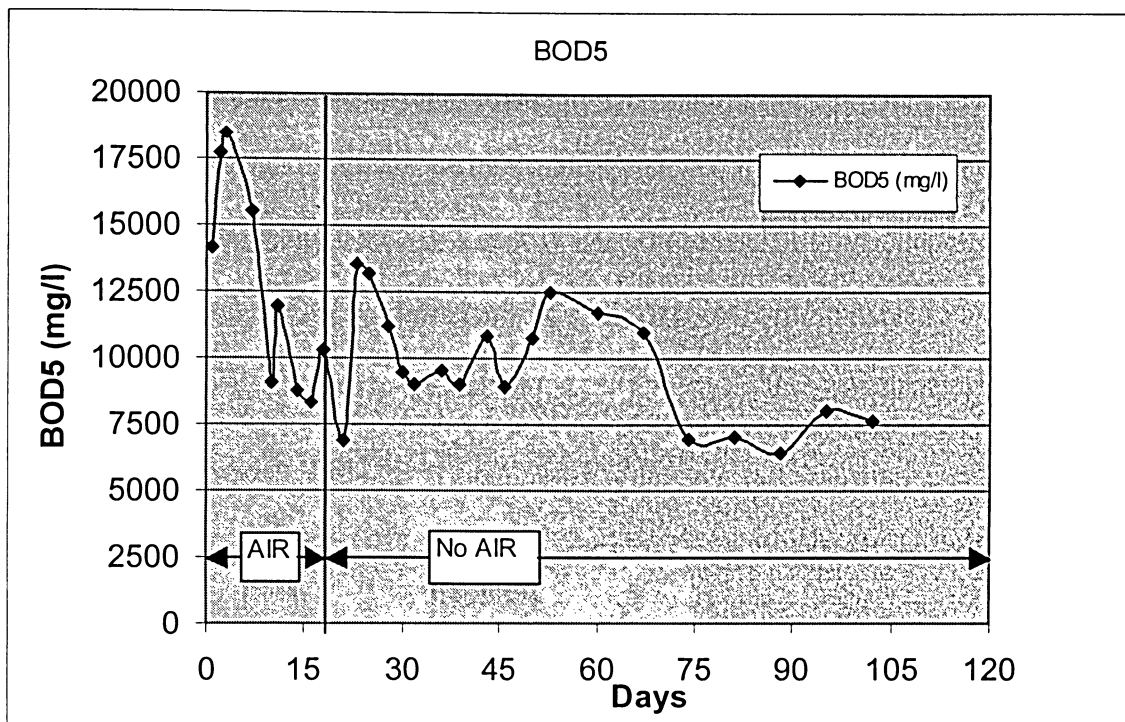
Figure 4.8 Variation in BOD₅ with Time
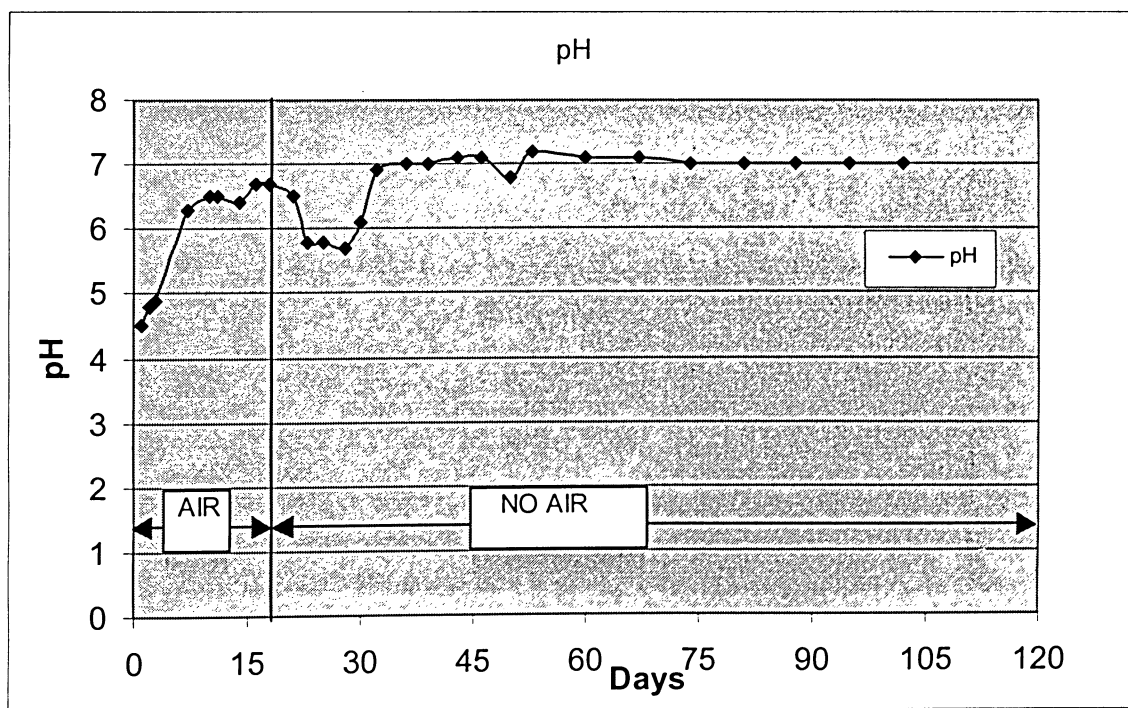
Figure 4.9 Variation in pH with Time

Bio-Reactor landfill # 4: In this bioreactor landfill, leachate was not recirculated within bioreactor landfill but it was discharged to the lagoons directly for the leachate treatment. Tap water was used instated of leachate to make a leachate in bioreactor. For this reason every time the quality of leachate was less polluted and COD and BOD_5 concentration was less in every pass.
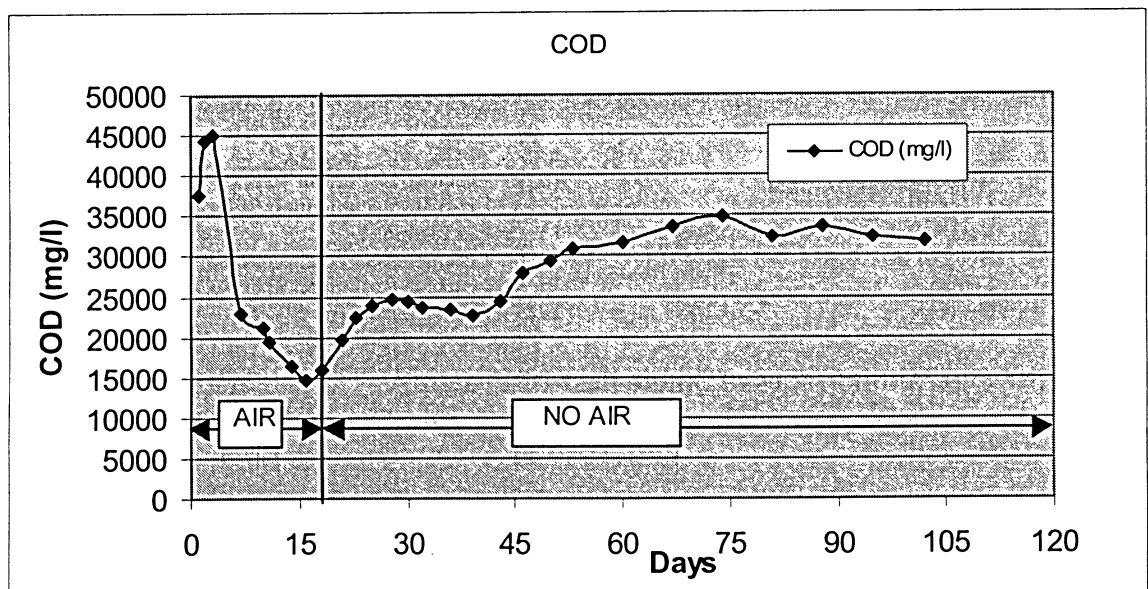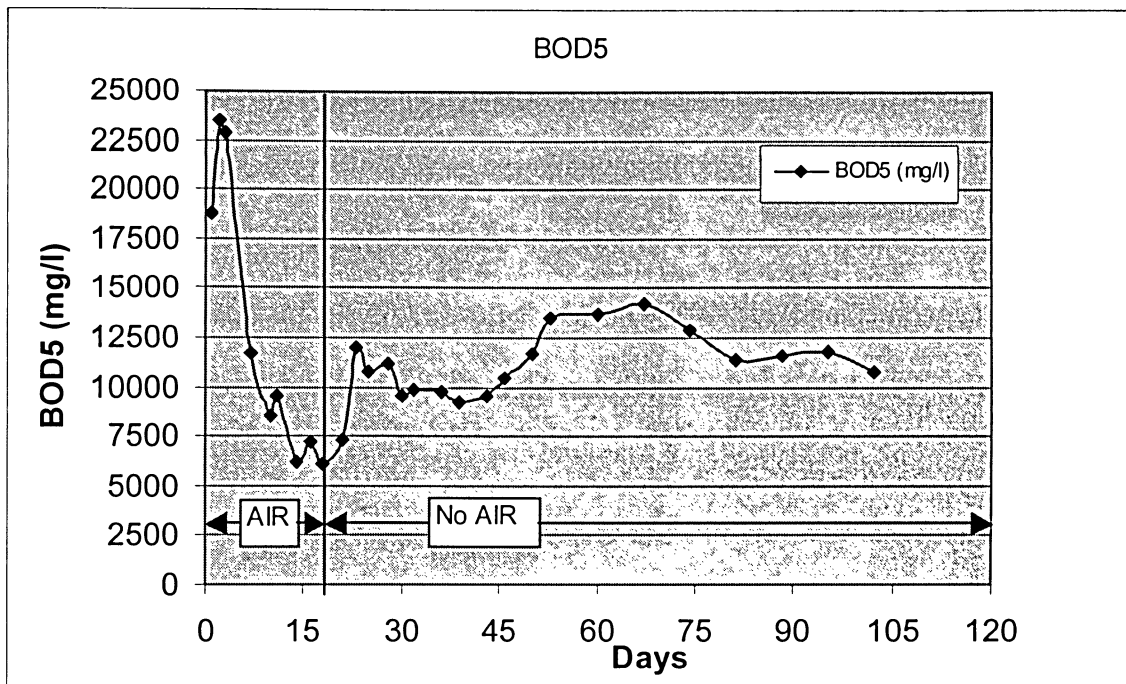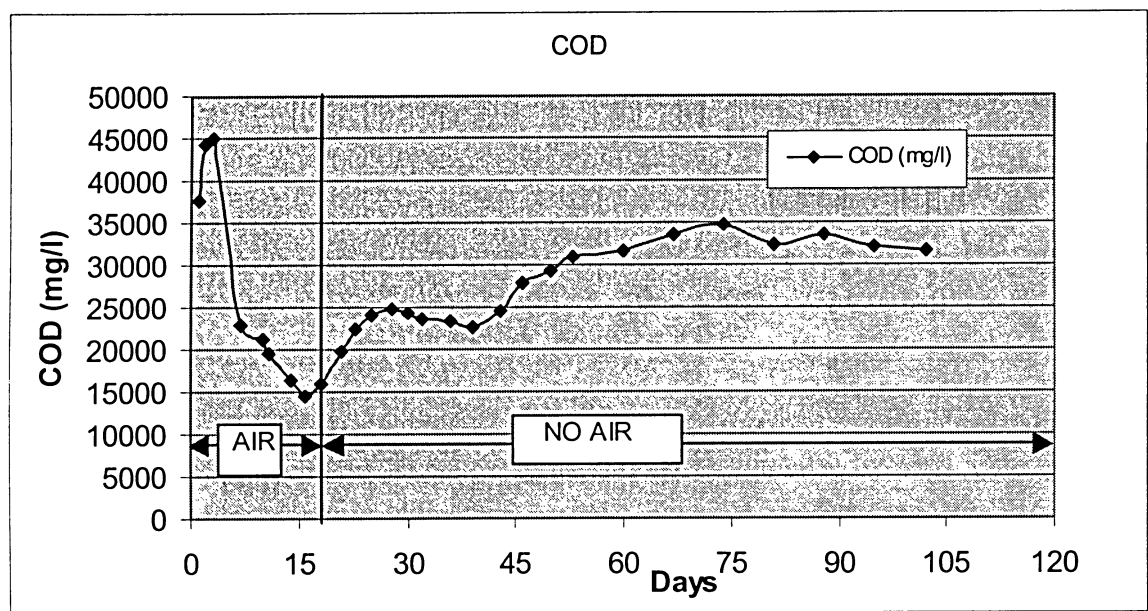

Figure 4.10 Variation in COD with Time
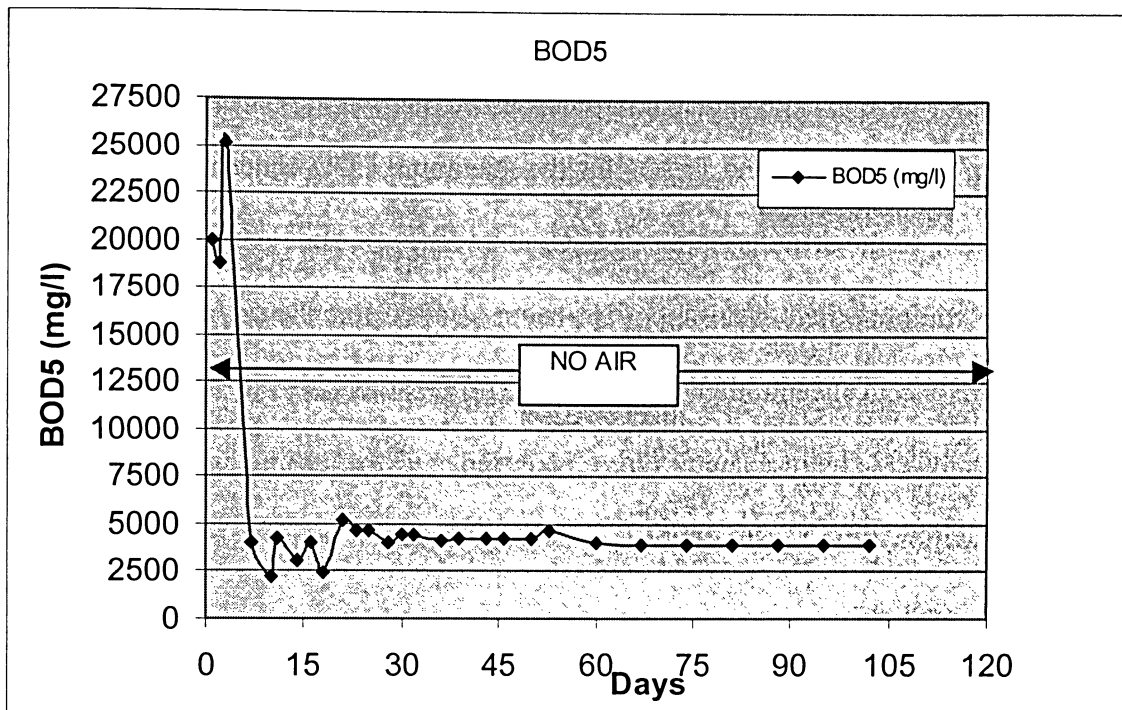
Figure 4.11 Variation in BOD₅ with Time

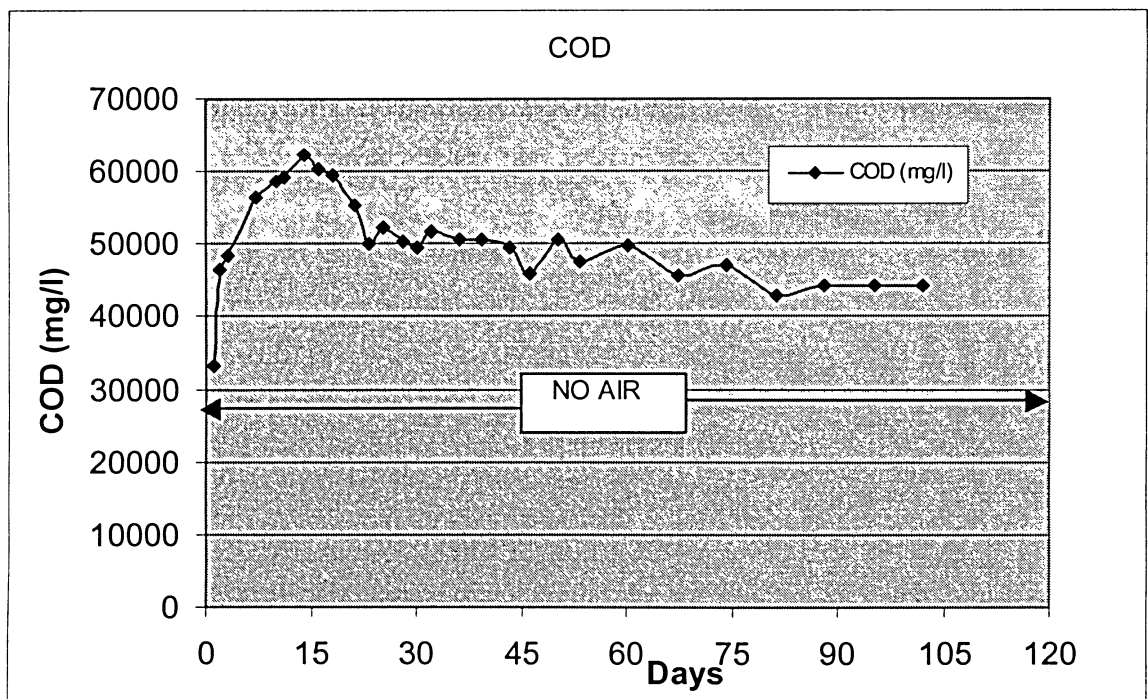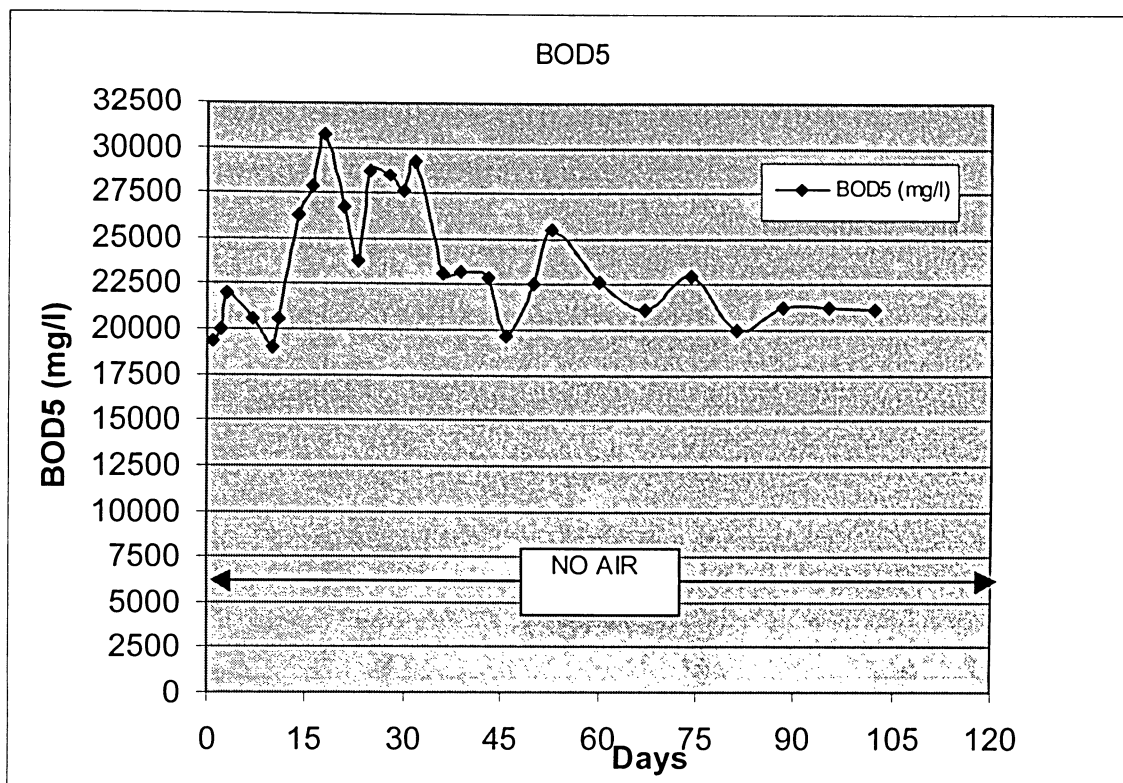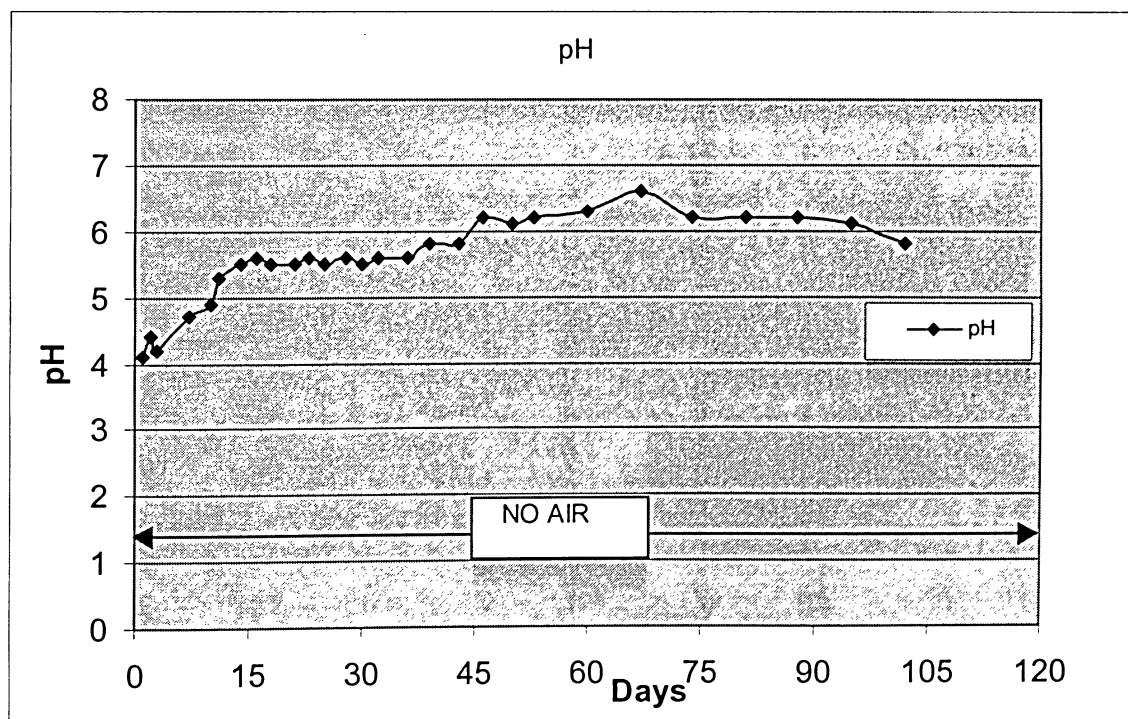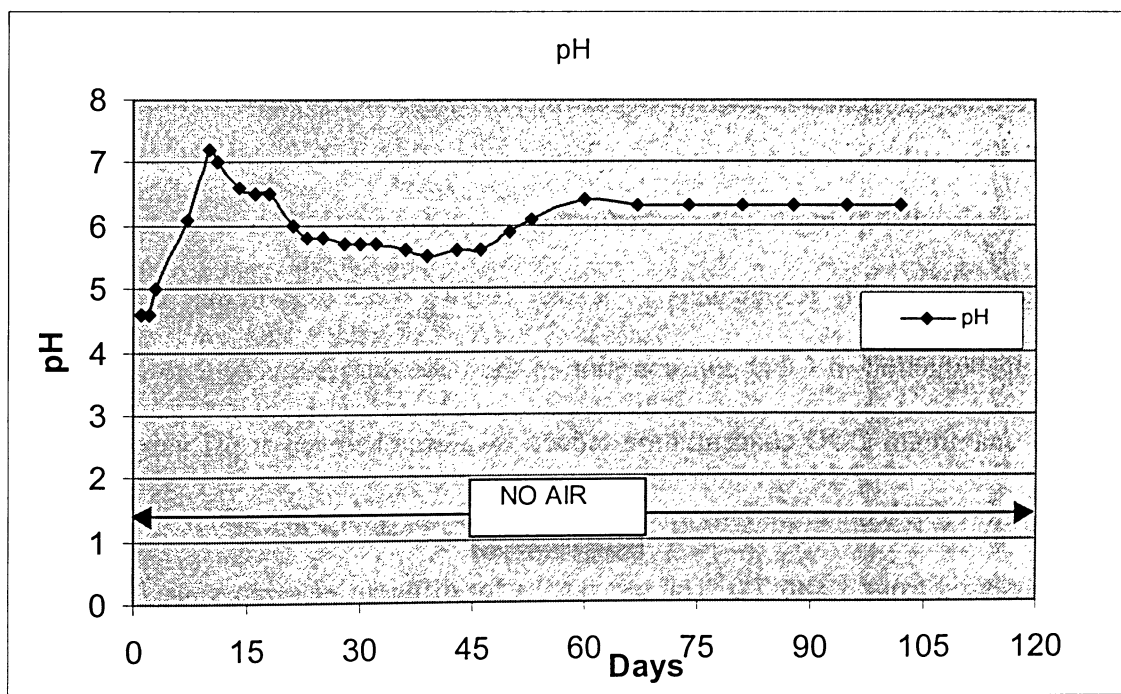**Figure 4.12 Variation in pH with Time**

Fenton's reaction depends on pH, concentrations of hydrogen peroxide and Ferrous Sulphate, and oxidation time. Various batch reactor tests were carried out to determine the optimum ratio of H_2O_2 and $FeSO_4$ for the maximum COD concentration reduction. The test results for the different ratios of H_2O_2 and $FeSO_4$ are shown in Figures 4.14, 4.16 and 4.17. In addition, there is an important factor to determine the optimum pH level for the maximum COD concentration reduction. The different levels of pH were examined as shown in Table 4.1. The test samples were collected at different time intervals to find out the best oxidation time. Test results for each experimental series are discussed in the following subsections.

4.2.1 Effect of pH Changes at Constant Fenton's Reagent Concentration

The pH of raw leachate was adjusted to different values ranging from 2.0 to 7.0 to determine the optimum value of pH for the maximum COD concentration reduction in presence of Fenton's reagents. The supernatant in each treatment lagoon was used to measure the COD concentration. The initial COD concentration of the leachate was approximately 39,129 mg/l. The concentrations of H_2O_2 and $FeSO_4$ were used as 3,500 mg/l and 3,500 mg/l, respectively. The test results were shown that there was no significant reduction in COD concentration at the pH values between 2 to 2.5 and 6 to 7.0. The maximum COD concentration reductions were observed at pH values from 3.0 to 5.0. The COD concentration was started to increase gradually when the pH values were increased from 3.5 to 7.0. The test results for different pH values are illustrated in Table 4.1.

Table 4.1 Test Results at Different Values of pH

pH	H$_2$O$_2$ (mg/l)	FeSO$_4$ (mg/l)	COD Concentration (mg/l)	% COD Reduction
7.4 Initial	0.0	0.0	39,129	0.0
2.0	3,500	3,500	37,240	5.0
2.5	3,500	3,500	36,494	6.7
3.0	3,500	3,500	30,000	23.0
3.5	3,500	3,500	26,433	32.0
4.0	3,500	3,500	26,710	31.0
5.0	3,500	3,500	29,630	24.0
6.0	3,500	3,500	36,456	6.0
7.0	3,500	3,500	38,930	0.5

Based on the above-mentioned experimental results, a statistical analysis was conducted. It was observed that the COD concentration could be predicted as a function of pH value using a quadratic regression equation. The quadratic regression analysis was done using statistical analysis software called SPSS. The developed quadratic regression model is as follows,

$$COD = 61253 - 15519 \, pH^2 + 1803 \, pH$$

The r-square value (goodness of fit) for the observed model is 0.813. The graph between predicted and observed values is shown in Figure 4.13.
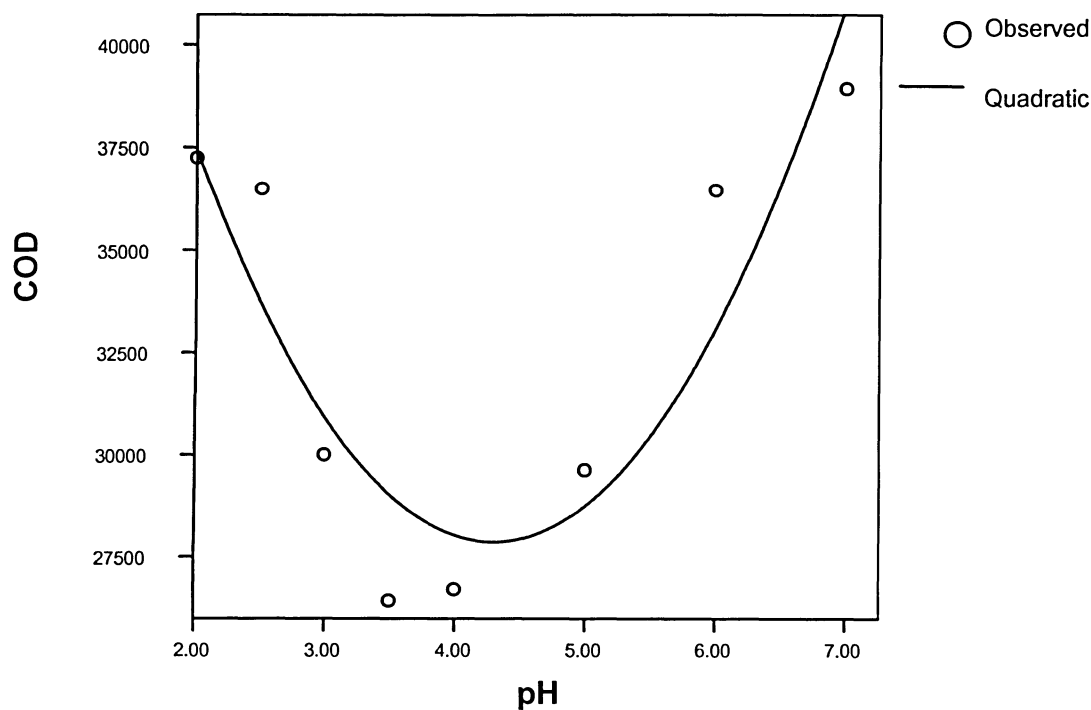
Figure 4.13 Predicted and observed values of COD regression

4.2.2 Effect of Different Ratios of Fenton's Reagent on COD Concentration reduction

Three batch reactor tests were conducted to determine the suitable ratio between H_2O_2 and $FeSO_4$ for the maximum COD concentration reduction. The initial COD concentration in first test was 1,744 mg/l and adjusted pH was 3.5. In this first batch reactor test, the COD concentration reduction was observed at different ratios of H_2O_2 and $FeSO_4$ (Figure 4.14). It was observed that the ratios of 1:1/2 and 1:1 have the maximum COD concentration reduction. These ratios were further analyzed independently for a very high initial COD concentration. The initial COD concentrations used for the ratios of 1:1/2 and 1:1 were 10,763 mg/l and 11,674 mg/l, respectively. At

the ratio of 1:1/2, the maximum COD concentration reduction was observed to be 16% with 4000 mg/l of H_2O_2 and 2000 mg/l of $FeSO_4$ (Figure 4.16). The maximum COD concentration reduction for the ratio of 1:1 was observed to be 28% with 3,000 mg/l of H_2O_2 and 3,000 mg/l of $FeSO_4$ as shown in Figure 4.17.

It is evident from this experiment that the addition of Fenton reagents has a positive influence on COD concentration reduction under anaerobic conditions.

Series Number	H_2O_2 (mg/l)	$FeSO_4$ (mg/l)	COD concentration (mg/l)
1	0	0	1,744
2	2000	133	596
3	2000	200	596
4	2000	400	151
5	2000	1000	151
6	1500	1000	151
7	2000	2000	62
8	3000	2000	62
9	6000	4000	151
10	1000	2000	62
11	1500	2000	62
12	1000	3000	107
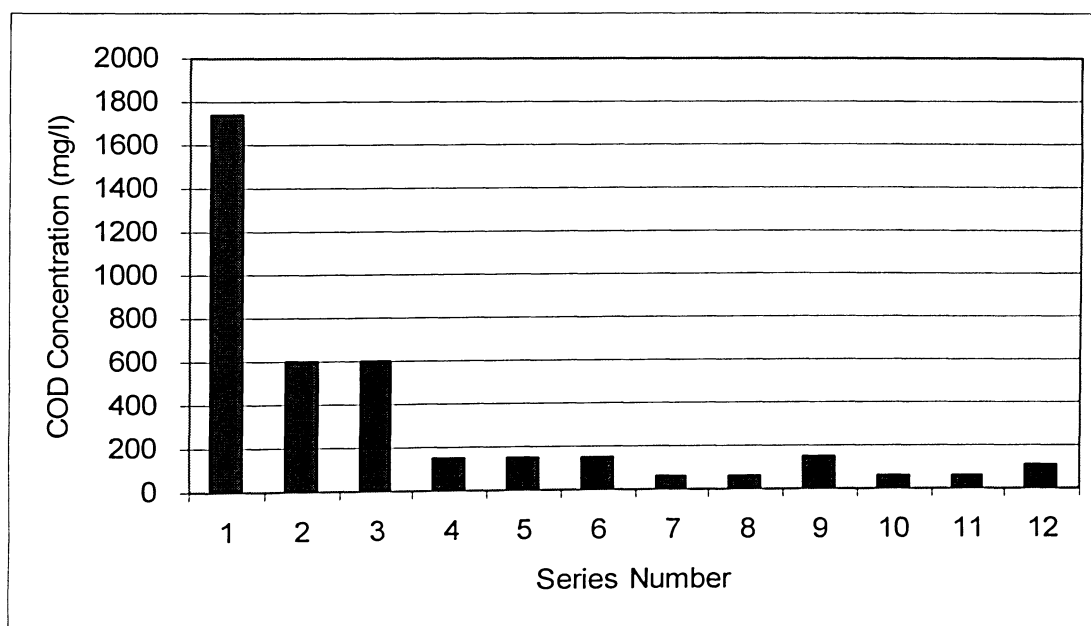
Figure 4.14 COD Concentration Results for Different Ratios of H_2O_2 and $FeSO_4$

In this experiment the concentration of COD is predicted based on different concentrations of H_2O_2 and $FeSo_4$. The statistical analysis of the experimental results was conducted using SPSS. The multiple linear regression analysis was done using H_2O_2 and $FeSo_4$ as independent variables and COD concentration as dependent variable. The developed multiple regression models for the given experimental results is as follows,

$COD = 285 + 0.058 \, H_2O_2 - 0.134 \, FeSO_4$.

The r-square values for the observed multiple regression models is 0.49.The graph between predicted and observed cumulative probabilities is displayed on Figure 4.15.
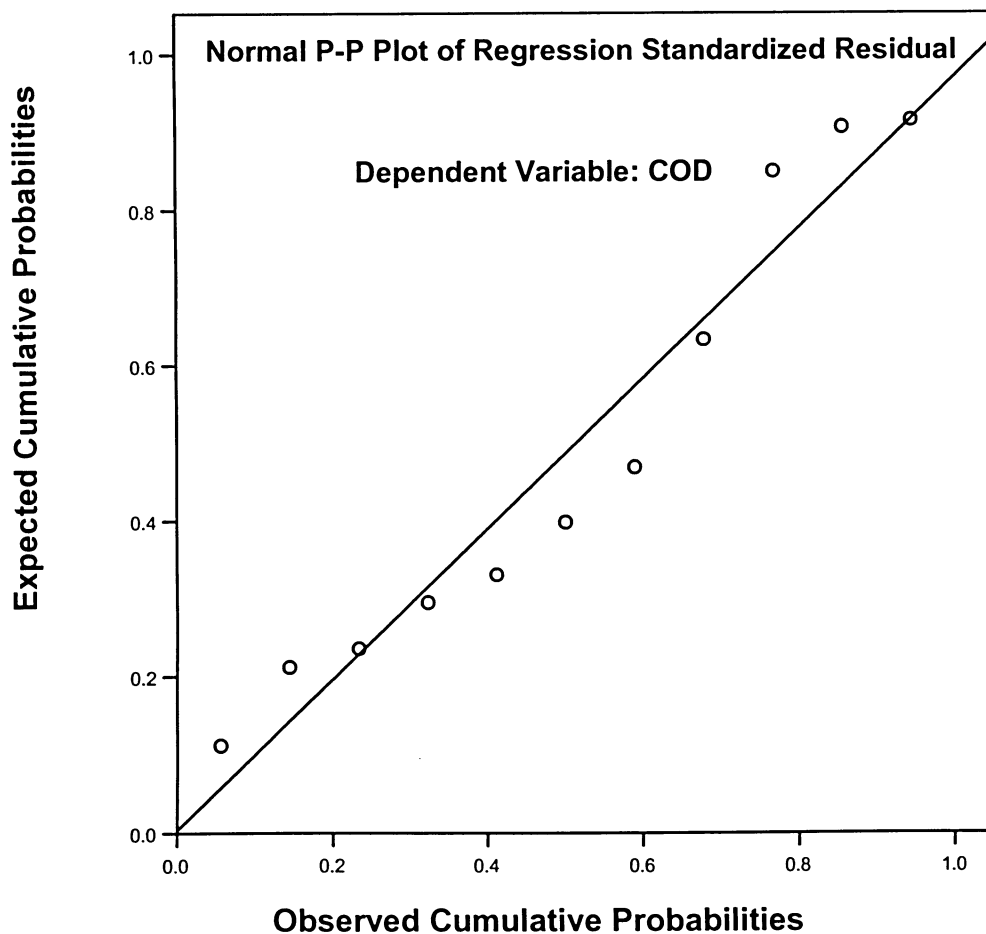
Figure 4.15 Predicted and observed cumulative probabilities

Series Number	H_2O_2 (mg/l)	$FeSO_4$ (mg/l)	COD concentration (mg/l)
1	0	0	10763
2	1000	500	10628
3	2000	1000	10166
4	3000	1500	9711
5	4000	2000	9008
6	5000	2500	9539
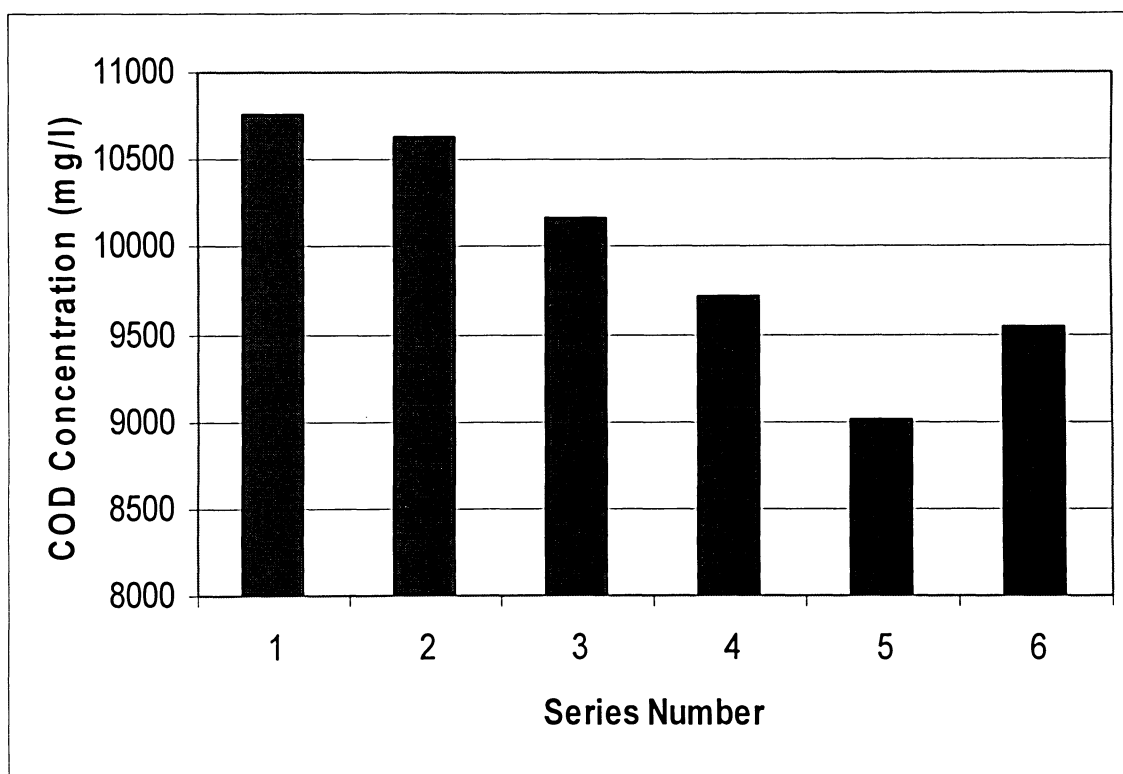
Figure 4.16 COD Concentration Results for 1:1/2 Ratio of H_2O_2 and $FeSO_4$

Series Number	H$_2$O$_2$ (mg/l)	FeSO$_4$ (mg/l)	COD concentration (mg/l)
1	0	0	11674
2	1000	1000	8693
3	2000	2000	8547
4	3000	3000	8381
5	4000	4000	8797
6	5000	5000	8423
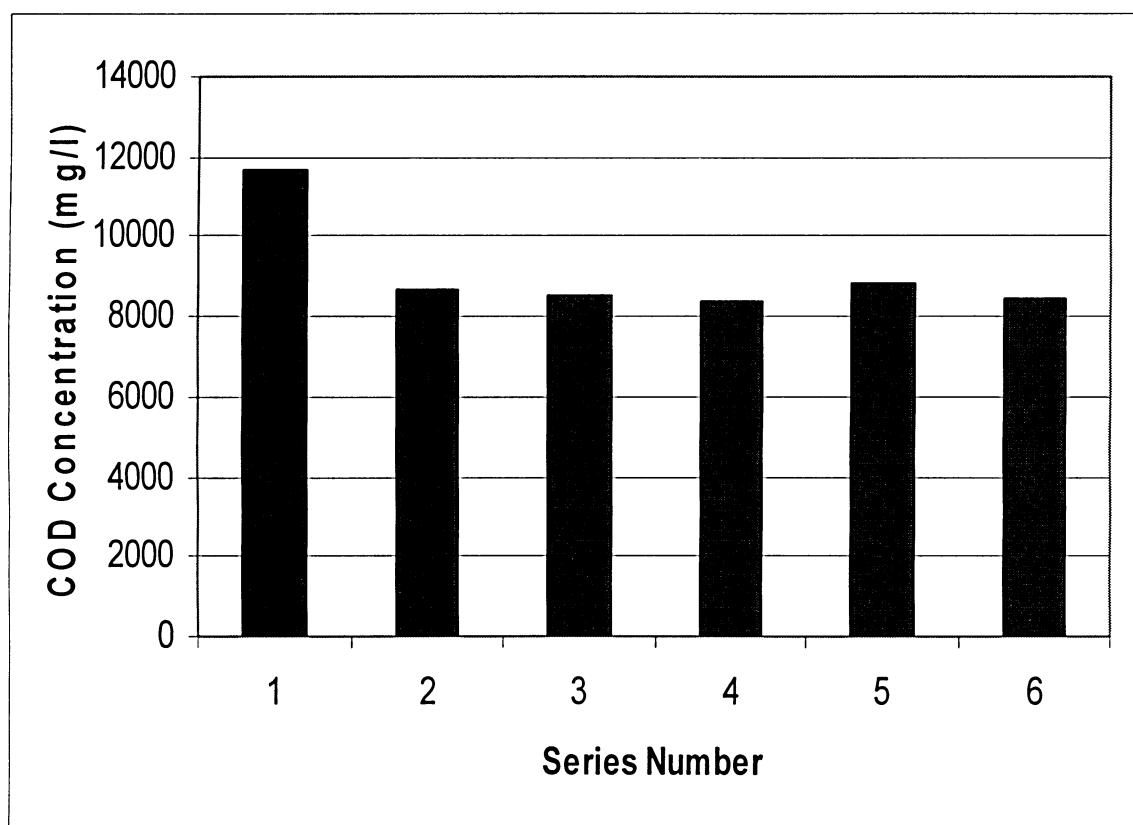
Figure 4.17 COD Concentration Results for 1:1 Ratio of H$_2$O$_2$ and FeSO$_4$

4.3 The Effect of Oxidation Time

The effect of oxidation time on the COD concentration reduction was observed at 2,500 mg/l and 2,500 mg/l concentrations of ferrous sulphate and hydrogen peroxide, respectively (Figure 4.18). The initial COD concentration and adjusted pH value were 17,514 mg/l and 3.50, respectively. The experimental results indicated that only 15% of

COD concentration was removed after 30 minutes of oxidation time. When the oxidation time was increased to 1 hour, the COD removal was increased to 24%. When oxidation time was further increased to 7 hours, the COD concentration removal was observed to be 37%. However further increase of oxidation time from 7 hours to 24 hours showed an increase in COD concentration rather than a decreasing trend. From these experimental results it was noted that oxidation time should not exceed 7 hours for optimum COD concentration reduction. It should also be noted that an increase in oxidation time would proportionally affect the size of the leachate treatment lagoons.
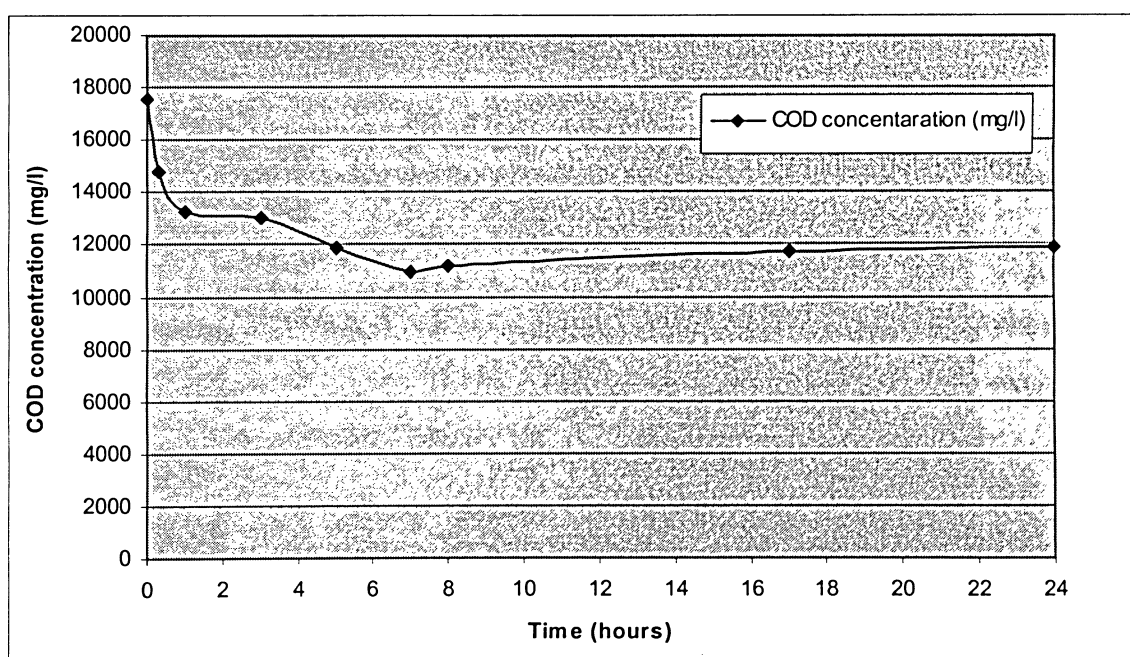
Figure 4.18 Effect of Oxidation Time for COD Concentration Reduction

4.4 Effect of Aeration and Oxidation on a Different Kind of Leachate

For the COD concentration reduction, the effect of oxidation on the leachate with and without bio-solids was observed to be same. The COD concentration reduction for both types of leachate was observed to be in the range of 32 %. The COD concentration

reduction in aeration was noted to be 10 % more in leachate without bio-solids compared to the leachate with bio-solids. It is concluded that with bio-solid leachate effect of oxidation was less because of lubrication of biosolids. The cumulative COD reductions in oxidation and aeration were noted to be 46% for leachate with bio-solids and 50% for leachate without bio-solids. These test results are shown in Figure 4.19.
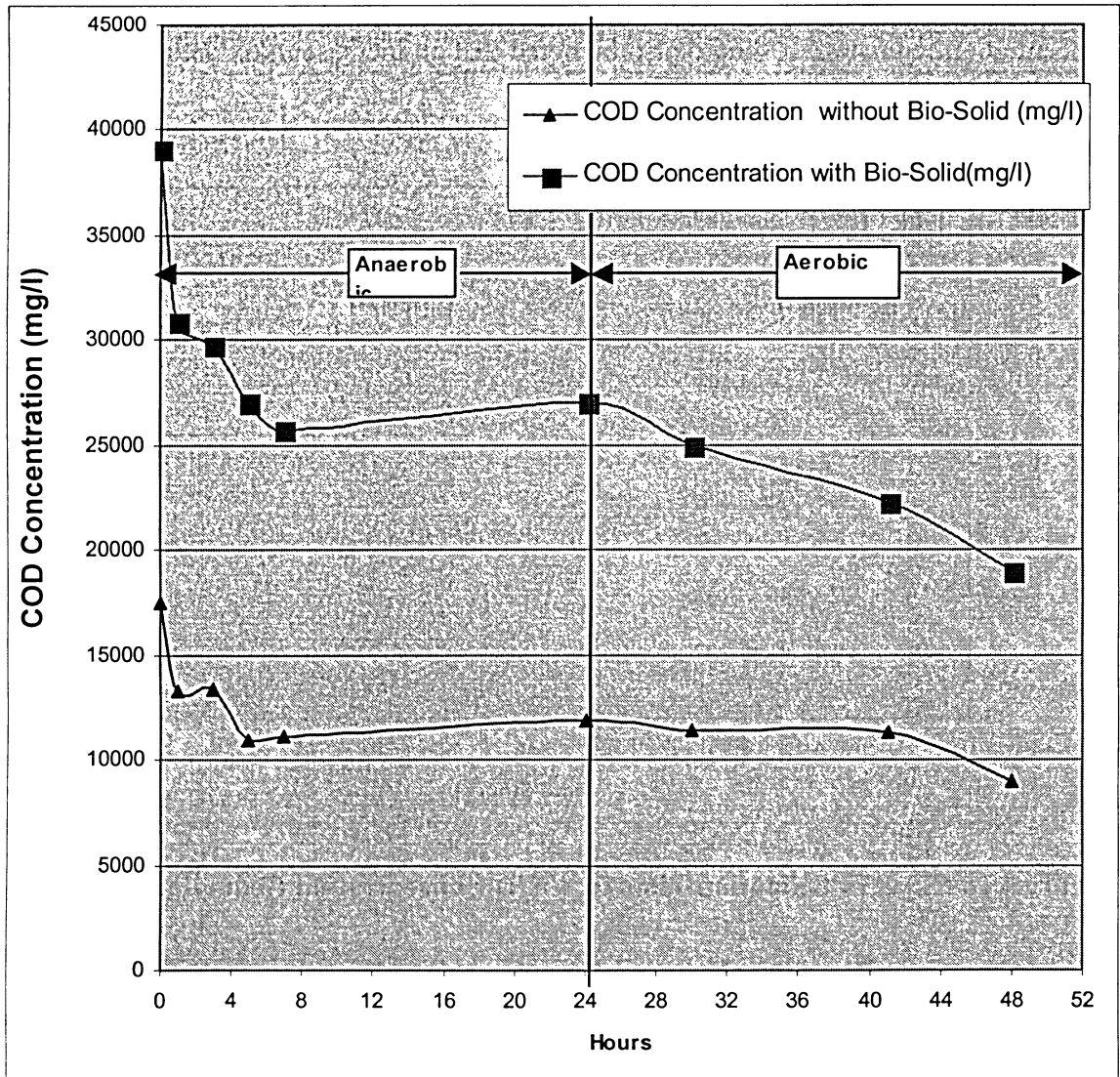
Figure 4.19 COD Concentration Reduction in Aerobic and Anaerobic Lagoons with Bio Solid and without Bio Solid type of Leachate

4.5 Field Applications of the Chemical and Biological Treatment Process

It is desirable that the leachate produced by landfills should be treated on-site efficiently and cost effectively, particularly for remote and small landfill sites. Presently, the leachate treatment process used at the landfill sites is time consuming and costly. Usually, on-site landfill leachate treatment process is based on lagoons system. The lagoons system is either aerobic or anaerobic based on leachate contamination. The lagoons system takes larger area for their operation. Besides, their maintenance cost is also very high. The anaerobic lagoons are also not environment friendly because of bad odor produced during the leacahte treatment process. The land cost is a prime factor in the design of landfill leachate treatment system. It is not desirable to spend so much money to buy a large area for lagoons construction. This study provides an alternate leachate treatment process in which treatment time is reduced to 7 hours as compared to months taken by existing anaerobic lagoons. The accomplishment in treatment time reduction will reduce the size of lagoons and odor problem in future landfill designs. The developed leachate treatment process is described in detail in the previous sections. This chemical and biological leachate treatment process can be applied to wastewater and landfill leachate treatment as described below,

1. Capable of treatment of low volume strength waste waters for detoxification and enhanced biodegradability

2. For wastewater treatment where COD concentration is less, there will be no need to construct aerobic lagoon and wastewater will be treated in anaerobic lagoons with Fenton's reagents

3. Treatment of leachate in remote and small landfill sites

Conclusion and Recommendations

5.1 Conclusions

Strict environmental rules prohibit the treatment of non-organic recycling materials into the landfills. The municipal solid waste MSW containing the high organic and moisture contents (80% -90% of the total weight of the MSW) is treated in the landfills. Leachate from municipal landfills causes potential environmental problems to the nearby groundwater and surface water. It is necessary to treat the landfill leachate with a proper treatment system. Typical characteristic of leachate is that the quantity and quality of leachate fluctuate so seriously that they cause difficulties in leachate treatment. It is desirable to treat the leachate onsite rather than haul to the wastewater treatment plants. The existing problems with the treatment of leachate onsite are lagoon size and treatment time. This study focuses on the development of a low cost treatment method to resolve the existing problems related to on-site leachate treatment and handling. The developed method involved the treatment of given leachate in an anaerobic lagoon with Fenton's reagents followed by aerobic lagoon.

Based on the analysis of the experimental results of the developed method, the following conclusions are accomplished:

1. It is evident from the previous research (Bae et al., 1997), that the leachate in acidic form has great influence on COD concentration reduction in the chemical oxidation process. Different tests were conducted to identify the optimum value of pH. It has been observed that pH of 3.5 is an optimum level in which maximum COD concentration reduction could be achieved.

2. As indicated previously, the leachate treatment time is also an important criterion in developing the treatment method. The existing anaerobic lagoon leachate treatment method is time consuming and requires large area for treatment. The Fenton's reagent was employed to accelerate the anaerobic leachate treatment process. After 30 minutes of the Fenton's reagent reaction, COD concentration started to decrease and reached its minimum reduction after 6 to 7 hours of contact time. However, after the maximum reduction has occurred, COD concentration exhibited an increasing trend. It has been concluded that maximum time for Fenton's reaction should not exceed 6 hours.

3. In addition to Fenton's Reagent reaction time, concentrations of H_2O_2 and $FeSO_4$ used in the experiments have also great influence on the COD concentration reduction. Different ratios of H_2O_2 and $FeSO_4$ (e.g. 1:1/2, 1:3) were tested to identify the optimum ratio between these two chemicals. The test results show that the ratio between H_2O_2 and $FeSO_4$ should be 1:1, which exhibit high effect on COD concentration reduction in the treated leachate.

4. After the Fenton's reagent reaction stage, the leachate was further treated under aerobic conditions. The aerobic process further helped to reduce the COD concentration. It was observed that the minimum 24 hours of aeration time has a significant effect on COD concentration reduction.

5. The leachate used in this experiment had high concentrations of COD (47000 mg/l). It was observed that more than 50% reduction in COD concentration could be achieved in the overall treatment process developed in this study. This process

can improve the efficiency of the exciting landfill leachate treatment in several landfills.

5.2 Recommendations

Based on this study the following points are recommended for further research in landfill leachate treatment:

1. It was observed that during Fenton's reagent reaction the COD concentration was started to increase after 7 hours in anaerobic lagoon. It should be further investigated to identify the cause of this increase and why Fenton's reagents are not effective after 7 hours.

2. Due to time limitation the aerobic leachate treatment was conducted about 24 hours. Further research can be done at different aerobic treatment time intervals along with recommended Fenton's reagents reactions process developing in this study. This might help to increase the further COD concentration reduction.

Reference:

Alexander, M. (1961) Introduction to soil microbiology. New York ,NY ; John Wiley & sons.

Ahn M.S. (1995) Advanced Treatment of Landfill Leachate by Fenton's Oxidation and Membrane, PhD Dissertation, University of Hanyang, Republic of Korea.

American Public Health Association (APHA), American Water Works Association (AWWA), Water Environment Federation (WEF), (1998) Standard Methods for the Examination of Water and Wastewater. 20th Edition. Clesceri, L. S., Greenberg, A. E., Eaton, A. D. Washington, DC.

Antonio L., Michele P., Angela V., Appio C. D. P. (2003) Fenton's pre-treatment of mature landfill leachate. Chemosphere 54, 1005–1010.

Bae B.U., Jung E.S., KimY.R. and Shin H.S. (1999) Treatment of landfill leachate using activated sludge process and electron beam radiation. Water Research 33(11), 2669-2673.

Bae J.H., Kim S.K. and Chang H.S. (1997) Treatment of landfill leachate: Ammonia Removal via Nitrification and Denitrification and further COD reduction via Fenton's Treatment Followed by Activated Sludge. Water Science and Technology, 36 (12), 341-348.

Bagchi A. (1990) Design, Construction, and Monitoring of Sanitary landfill. John Wiley & Sons: NewYork ,NewYork .

Bigda R.J. (1995) Consider Fenton's chemistry for wastewater treatment. Chemical Engineering 91, 62-66.

Bowers A.R., Eckenfelder W.W., Gaddipati P., and Monsen, R.M. (1989) Treatment of Toxic or Refractory wastewaters with Hydrogen Peroxide Water Science Technology 21, 477-486.

Bressi, G. and Favalia (1997) Use of MBR in leachate Treatment. In Leachate and Landfill gas Management ,Proceedings of the Sixth International Landfill Symposium, Sardinia, Vol:2, 260-274.

Carley B.N. and Mavinic D.S. (1991) The Effects of External Carbon Loading on Nitrification and Denitrification of a High Ammonia Landfill Leachate. Water Environment Research 63(1), 51-59.

Chian E.S.K. and Dewalle F.B. (1977) Evaluation of leachate treatment , Vol:1: Characterization of Leachate. U.S. Environmental Protection Agency, Cincinnati, Ohio, USA. EPA, 600/2-77-186a.

Chugh, S., Pullammanappallil, P.and Rudolph, V. (1998) Effect of recirculated leachate volume on MSW degradation. Waste Management and Research. 16 (6), 564-573.

Diamadopoulos E. (1994) Characterization and Treatment of Recirculation Stabilized Leachate. Water Research, Vol: 28, (12), 2439-2445.

Dong C. (1993) Destruction of hazardous organic contaminants by advanced Oxidation process. PhD. Dissertation University of Delaware.

Eckenfelder,W.W (1992) The Role of Chemical Oxidation in Waste Water Treatment Process. Proceedings of the First International symposium on Chemical Oxidation Technology for the Ninetees, Technomic Publishing Co.Inc., Lancaster, P.A., 1-10.

Ehrig H.J. (1983) Quality and quantity of Sanitary Landfill Leachate. Waste Management and Research, 1, 53-68.

Forgie D.J.L. (1998) Selection of the most appropriate leachate treatment methods. Part 1: A review of potential biological leachate treatment methods .Water Pollution Research Journal of Canada, 23 (2),308-328.

Flaherty K.A. and Huang C.P. (1994) Continuous Flow Applications of Fenton's Reagent for Oxidizing Chlorinated Phenols. Proceedings of the Second International symposium on Chemical Oxidation Technology for the Ninetees, Technomic Publishing Co.Inc., Lancaster, P.A., 45-57.

Gallard H., Laat J. and Legube B. (1998) Influence pH on the speed of oxidation of organic compounds by Fe_2/HO_2. Reactional mechanisms and modeling. New Journal of Chemistry, 263-268.

Gau S.H., Chang P.C. and Chang F.S. (1991) Study on the Procedure of Leachate Treatment by Fenton Method. International Proceedings 16th Conference on Wastewater Treatment Technology in Republic of China, Taiwan, ROC; 527-537.

Gau S.H. and Chang F.S. (1996) Improved Fenton's Method to removed Recalcitrant organics in Landfill Leachate. Water Science and Technology Vol: 34(7-8), 455-462.

Gierlich H. and Kollbach J. (1998) Treating Landfill Leachate in Europen Countries. Pollution Engineering International.

Gogate P.R. and Pandit A.B. (2004) A review of imperative technologies for wastewater treatment I: oxidation technologies at ambient conditions. Advances in Environmental Research 8,501-551.

Gould J.P., Cross W.H. and Pohland F.G. (1989) Factors influencing mobility of toxic metals in landfills operated with leachate recycle, in Emerging Technologies in

Hazardous Waste Management. D.W.Tedder and F.G. Pohland, Eds.; ACS Symposium Series 422.

Gregor K.H. (1994) Oxidative Decolorization of Textile Waste Water with Advanced Oxidation. Proceedings of the Second International symposium on Chemical Oxidation Technology for the Ninetees, Technomic Publishing Co.Inc., Lancaster, P.A., 161-169.

Hagerty,D.J., Pavoni J.L. and Heer J.E.(1973) Solid Waste Management, New York, NY: John Wiley & sons.

Ham,R.(1980) Decomposition of Residential Solid Waste in test Lysimeters. SW-190C. Washington, DC: US environmental Protection Agency.

Hao X. (2004) Personal communication.

Hipolito G., Jose, L.R. and Pedro A.G. (1994) Comparison of Anaerobic Treatment of Leachates From an Urban Solid Waste Landfill at Ambient Temperature and at 35 C. Bioresourse Technology 58, 273-277.

Huang C.P, Dong C.and Tang Z. (1993) Advanced chemical oxidation: its present role and potential future in hazardous waste treatment. Waste Management 13, 361-377.

Hudgins M. and Harper S. (1999) Operational characteristics of two aerobic landfill systems. 7th International Waste Management and Landfill Symposium in Sardinia, Italy.

Irene M.C.L. (1996) Characteristics and Treatment of Leachates from Domestic Landfills. Environment International Vol: 22 (4), 433-442.

Jae.H. B., Sang K.K. and Hyun S.C. (1997) Treatment of Landfill Leachates Ammonia removal via nitrification and denitrification and further COD reduction via Fenton's Treatment followed by activated sludge. Water Science and Technology Vol: 36 (12), 341-348.

Jeong H.I., Hae-J.W., Myung W.C., Ki-B. H. and Chang-W.K. (2001) Simultaneous Organic and Nitrogen Removal from Municipal Landfill Leachate using Anaerobic-Aerobic System. Water Resource Vol: 35 (10), 2403–2410.

Johansen, O.J. and Carslon, D.A. (1976) Characterization of sanitary landfill leachates. Water Resource 10, 1129-1134.

Keenan,J.D.,Steiner,R.L.,and Fungaroli, A.A. (1983) Chemical-Physical Leachate Treatment Jounral of Environmental Engineering 109 (6), 1371-1385.

Kelly, W.E. (1976) Groundwater Pollution near a Landfill. Journal of the Environmental Engineering Division, ASCE, 102(EE6), 1189-1199.

Kettunen R.H., Hoilojoki T.H. and. Rintala J.A. (1996) Bioresource Technology Vol: 58, 31-40.

Kettern, J.T. (1992) Biological or Chemical-Physical Landfill Leachate Purification-an Alternative or a Useful Combination. Water Science Technology 26(1-2), 137-145.

Kim Y.K. and Huh I.R. (1997) Enhancing biological treattability of landfill leachate by chemical oxidation. Environmental Engineering Science, 14(1), 73-79.

Kim S.M. and Vogelpohl A. (1998) Degradation of organic pollutants by the photo-Fenton –process. Chemical Engineering and Technology 21(2), 187-191.

Kim S.M., Geissen S.U. and Vogelpohl A. (1997) Landfill leachate treatment by a photoassisted Fenton reaction. Water Science and Technology, 35(4), 239-248.

Knox K. (1985) Leachate treatment with nitrification of ammonia. Water. Resource. 19(7), 895–904.

Kotsou M., Kyriacou A., Lazaridi K. and Pilidis G. (2004) Integrated aerobic biological treatment and chemical oxidation with Fenton's reagents for the processing of green table olive wasterwater. Process Biochemistry 39, 1653-1660.

Koyama O. and Nakamura K. (1994) Degradation of chlorinated aromatics by Fenton oxidation and methanogenic digester sludge. Water Resource 28, 895-899.

Kuo W.G. (1992) Decolorizing dye Wastewater with Fenton's Reagents Water Resource 26, 881-886.

Kwon, B.G., Lee, D.S., Kang, N. and Yoon, J., (1999) Characteristics of p-chlorophenol oxidation by Fenton's reagent. Water Research 33, 2110-2118.

Lin S.H. and Peng C.F. (1995) A continuous Fenton Process for Treatment of Textile Wastewater. Environmental Technology 16, 693-702.

Lin, S.H. and Lo, C.C., (1997) Fenton process for treatment of desizing wastewater. Water Research, Vol: 31, 20-50.

Lou J.C. and Lee, S.S. (1995) Chemical Oxidation of BTX using Fenton's Reagents , Hazardous Waste & Hazardous Materials, 12(2) 185-193.

Maehlum T. (1995) Treatment of Landfill Leachate in on site lagoons and constructed wetlands. Water Science and Technology, Vol: 32 (3), 129-135.

Marks, A.L., Luthy, R.G. and Diwekar U.M. (1994) Semi-Continuous Evaporation Model for Leachate Treatment Process Evaluation Environmental Progress, Vol.13 (A), 278-288.

McGinley, P.M. and Kmet, P. (1984) Formation, Characteristic, treatment and disposal of leachate from Municipal Solid Waste Landfills. Special Report, Department of National Resources, The University of Wisconsin, Madison, WI.

Metcalf and Eddy. (1991) Wastewater Engineering: Treatment, Disposal, and Reuse. 3rd Edition McGraw-Hill, Inc., New York.

Munz C., Galli R., Scholtz R. and Egli S. (1994 a) Oxidative Treatment ofprocess water in a soil Decontamination plant I, Laboratory studies. Proceedings of the Second International Symposium on chemical oxidation Technology for the Nineties, Technomic Publishing Co.Inc., Lancaster, P.A., 247-263.

Munz C., Galli R., Scholtz R. and Egli S. (1994 b) Oxidative Treatment of process water in a soil Decontamination plant II, Pilot Plant and Large Scale Experiences. Proceedings of the Second International Symposium on chemical oxidation Technology for the Nineties, Technomic Publishing Co.Inc., Lancaster, P.A., 264-277.

Nesheiwat, F.K. and Swanson, A.G. (2000) Clean contaminated sites using Fenton's reagent. Chemical Engineering. Progress ,96 (4), 61-66.

Neyens E. and Baeyens J. (2002) A review of classic Fenton's peroxidation as an advanced oxidation technique. Journal of Hazardous Materials, B98, 33-50.

Nora S.M., Josep F.F., Xavier F.S. and Antoni S.F. (2003) Pre oxidation of an extremely polluted industrial wastewater by the Fenton's reagent. Journal of Hazardous Materials, B101, 315-322.

Onay T.T. and Pohland F.G. (2001) Nitrogen and sulfate attenuation in simulated landfill bioreactors. Water Science and Technology. 44 (2), 367-372.

Paris H. C. (1996) Assessment of Leachates From Sanitary Landfills: Impact of Age, Rainfall, and Treatment. Environment International, Vol: 22, (2), 225-237.

Pala A. and Erden D. (2004) Chemical Pretreatment of Landfill Leachate Discharged into Municipal Biological Treatment Systems. Environmental Engineering Science, Vol. 21 (5), 549-557.

Paula D. and Foresti C. (1992) Kinetic Studies in a USAB Reactor Subjected to Increasing COD Connection. Water Science Technology 25(1), 103-111

Pignatello J.J. (1992) Dark and photo assisted Fe^{III} catalyzed degradation of chlorophenoxy herbicides by hydrogen peroxide Environmental Science and Technology 26, 944-951.

Pohland F.G. (1975) Sanitary Landfill Stabilization with Leachate Recycle and Residual Treatment, US Environmental Protection Agency-600/2-75-043, 67–80.

Pouliot J.M, Yanful E. K .and Bassi A.S. (2000) Biological Treatment of Landfill Leachate. Water Quality Research Journal of Canada, 201-217.

Quasim S.R. and Chiang W. (1994) Sanitary landfill leachate. USA: Tchonomic Publishing Company. ISBN 1-56676-129-8.

Ramirez Z.R.M., Duran Moreno A., Orta de V.M.T.and Monje R.I. (2000) Treatment of landfill leachate by comparing advanced oxidation and coagulation- flocculation processes coupled with activated carbon adsorption, Water Science & Technology, 41, (1), 231–235.

Ravi K.J.X. and Gurol M.D. (1994) Fenton's Reagents as Chemical Oxidant for Soil contaminants. Proceedings of the Second International Symposium on Chemical Oxidation: Technology for the Nineties, Tehnomic Publishing Co. Inc., Lancaster, P.A., 206-229.

Reinhart D, and Al-Yousfi AB. (1996) The impact of leachate recirculation on municipal solid waste landfill operating characteristics. Waste Management Resource 14, 337–46.

Reinhart, D.R. and Townsend T.G. (1998) Landfill Bioreactor Design & Operation.

Ruppert G. and Bauer R., (1993) Mineralization of cyclic organic water contaminants by the photo Fenton reaction: influence of structure and substituents. Chemosphere, Vol: 27, 1339-1347.

Robinson S.F. and Monsen R.M. (1992) Hydrogen per Oxide and Environmental Immediate Response Proceedings of the First International symposium on Chemical Oxidation Technology for the Ninetees, Technomic Publishing Co.Inc., Lancaster, P.A., 51-77.

Sarria V., Parra S., Invernizzi M., Peringer P.and Pulgarin C. (2001) Photochemical-Biological Treatmentof a real industrial biorecalcitrant wastewater containing 5-amino-6-methyl-2-benzimidazolone, Water Science Technology 44, 93-101

Sedlak, D.L. and Andren, A.W., (1991) Oxidation of chlorobenzene with Fenton's reagent. Environmental Science and Technology, Vol: 25, 777-782.

Senior, E. (1995) Microbiology of Landfill Sites, Second Edition Chelsea, Mi:Lewis Publishers.

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

Shyh F.K. and Huey M.C. (1997) Coagulation of textile secondary effluents with Fenton's reagent. Water Science and Technology, Vol: 36 (12), 215-222.

Sponza D. T. and Agdag O. N. (2004) Impact of leachate recirculation and recirculation volume on stabilization of municipal solid wastes in simulated anaerobic bioreactors.

Process Biochemistry. 39, 2157-2165.

Tchobanoglous G., Theisen H. and Vigil S. (1993) Integrated Solid Waste Management: Engineering Principles and Management Issues. McGraw-Hill, Inc New York, New York.

VanDijk L. and Roncken G.C.G., (1997) Membrance Bioreactor for Waste Water Treatment. The State of the art New Development Water Science and Technology, 35(10), 35-41.

Vella, P.A, and Munder, J.A. (1992) Use of KM_nO_5, H_2O_2, CIO_2 in Waste Water Application. Proceedings of the First International symposium on Chemical Oxidation Technology for the Ninetees, Technomic Publishing Co.Inc., Lancaster, P.A., 22-238

Venkatadri R. and Peters R.W. (1993) Chemical oxidation technologies: ultraviolet light/hydrogen peroxide,Fenton's reagent and titanium dioxide-assisted photocatalysis. Journal of Hazardous Materials, Vol: 10, 107-149.

Vella P.A. and Vernoda B. (1994) Oxidation of Trichloroethylene:A comparison of Potassium Permanganate and Fenton's Reagents. Proceedings of the Third International Symposium on Chemical Oxidation: Technology for the Nineties, Tehnomic Publishing Co.Inc., Lancaster, P.A., 62-73.

Walter Z.T. and Stephanie T. (2001) Oxidation kinetics and Mechanisms of Trihalomethanes by Fenton's reagents. Water Research, Vol: 31 (5), 1117-1125.

Warith, M. A. and Sharma, R. (1998) Technical review of methods to enhance biological degradation in sanitary landfills. Water Quality. Research. Journal. Canada 33 (3), 417-437.

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

Warith, M. A. (2003) Solid waste management: new trends in landfill design. Emirates Journal of Engineering Research. 8 (1), 61-70.

Wink D., Nims R., Saavedra J., Utermahlen W. and Forde P. (1994) The Fenton oxidation mechanism :Reactivities of biologically relevant substrates with two oxidizing intermediates differ from those predicted for the hydroxyl radical. Proceedings of the National Academy of Sciences USA. Chemistry, Vol: 91, 6604-6608.

www.**usace**.army.mil

www.epa.gov

Yuen S. T. S., Wang Q. J., Styles J. R. and McMahon T. A. (2001) Water balance comparison between a dry and a wet landfill—a full-scale experiment. Journal of Hydrology. 251, 29-48.

Yun W. K. and Kyung Y. H. (2000) Effects of Reaction Conditions on the Oxidation Efficiency in the Fenton Process. Water Recourse Vol: 34 (10) 2786-2790.

Zaloum R. and Abbott M. (1997) Anaerobic pretreatment improves single sequencing batch reactor treatment of Landfill Leachates. Water Science and Technology, Vol: 35 (1), 207-214.

Zenon Environmental Systems Inc. (1989) Technical and economic assessment of reverse-osmosis for treatment of Landfill leachate. Prepared for Waste Management Branch, MOE, RAC Project NO 303 RR.

APPENDIX A – EXPERIMENTAL DATA

Results of Leachate pH Analysis

Initial Data   Unit: pH

Date	Day No.	AMF	ASF	ASR	NMR	AMR1	AMR2	AMR
6-Sep-04	1	4.6	4.9	4.5	4.1	4.3	4.5	4.4
7-Sep-04	2	4.6	5.0	4.8	4.4	4.4	4.6	4.5
8-Sep-04	3	5.0	5.5	4.9	4.2	4.9	4.8	4.8
12-Sep-04	7	6.1	6.3	6.3	4.7	6.0	6.0	6.0
14-Sep-04	9	7.2	6.9	6.5	4.9	6.5	6.4	6.4
16-Sep-04	11	7.0	7.1	6.5	5.3	6.4	6.4	6.4
19-Sep-04	14	6.6	7.3	6.4	5.5	6.2	6.5	6.3
21-Sep-04	16	6.5	7.7	6.7	5.6	6.4	6.6	6.5
23-Sep-04	18	6.5	7.6	6.7	5.5	6.2	6.4	6.3
26-Sep-04	21	6.0	7.1	6.5	5.5	5.9	6.2	6.0
28-Sep-04	23	5.8	7.0	5.8	5.6	5.8	5.9	5.9
30-Sep-04	25	5.8	6.9	5.8	5.5	5.7	5.8	5.8
3-Oct-04	28	5.7	6.8	5.7	5.6	5.6	5.7	5.7
5-Oct-04	30	5.7	6.9	6.1	5.5	6.0	6.1	6.0
7-Oct-04	32	5.7	6.7	6.9	5.6	6.0	6.2	6.1
11-Oct-04	36	5.6	6.6	7.0	5.6	6.5	6.6	6.5
14-Oct-04	39	5.5	6.5	7.0	5.8	6.7	6.6	6.7
18-Oct-04	43	5.6	6.8	7.1	5.8	6.9	6.8	6.9
21-Oct-04	46	5.6	6.8	7.1	6.2	7.1	7.1	7.1
26-Oct-04	51	5.9	6.5	6.8	6.1	6.6	6.5	6.5
28-Oct-04	53	6.1	6.8	7.2	6.2	6.7	6.6	6.7
4-Nov-04	60	6.4	6.6	7.1	6.3	6.9	6.9	6.9
11-Nov-04	67	6.3	7.1	7.1	6.6	7.0	7.0	7.0
19-Nov-04	75	6.3	6.9	7.0	6.2	6.9	7.0	6.9
24-Nov-04	80	6.3	6.9	7.0	6.2	7.0	7.0	7.0
2-Dec-04	88	6.3	6.9	7.0	6.2	7.0	7.0	7.0
9-Dec-04	95	6.3	6.9	7.0	6.1	7.0	7.0	7.0
16-Dec-04	102	6.3	6.9	7.0	5.8	6.9	7.0	7.0

Results of Leachate COD Analysis

Initial Data   Unit: mg/l

Date	Day No.	AMF	ASF	ASR	NMR	AMR1	AMR2	AMR
6-Sep-04	1	37992	25539	30000	33142	35753	39510	37632
7-Sep-04	2	36867	25204	33560	46390	41050	47439	44245
8-Sep-04	3	35753	29301	36494	48346	41050	49097	45074
12-Sep-04	7	8102	32838	29301	56458	21255	24536	22896
15-Sep-04	10	7795	32838	23872	58549	20525	21701	21113
16-Sep-04	11	6882	29301	22555	59251	17509	21306	19408
19-Sep-04	14	7855	23755	21000	62319	17408	15567	16488
21-Sep-04	16	8348	21466	19088	60201	14623	14623	14623
23-Sep-04	18	8515	20291	20001	59499	16113	15567	15840
26-Sep-04	21	11909	26533	20022	55323	20395	18918	19657
28-Sep-04	23	16010	26323	25289	50215	23874	20960	22417
30-Sep-04	25	15794	31812	26323	52332	25701	22300	24001
3-Oct-04	28	15741	31931	24743	50485	23907	25591	24749
5-Oct-04	30	15701	34893	21874	49647	23907	24743	24325
7-Oct-04	32	14344	32414	23907	51755	23701	23495	23598
11-Oct-04	36	13546	21361	21966	50572	23650	23000	23325
14-Oct-04	39	14166	15842	22782	50739	22577	22782	22680
18-Oct-04	43	10508	15698	23770	49610	24395	24605	24500
21-Oct-04	46	13524	14637	25882	45887	26098	29443	27771
25-Oct-04	50	8054	15226	24843	50700	27428	31079	29254
28-Oct-04	53	9136	16115	21974	47700	27428	34488	30958
4-Nov-04	60	8380	13288	23253	49828	28346	34963	31655
11-Nov-04	67	8274	15980	21778	45725	32144	34788	33466
18-Nov-04	74	8274	15980	20876	47158	34602	34850	34726
25-Nov-04	81	8274	15980	21223	42753	32380	32283	32332
2-Dec-04	88	8274	15980	20600	44354	34650	32600	33625
9-Dec-04	95	8274	15980	21250	44354	33039	31444	32242
16-Dec-04	102	8274	15980	21215	44154	32549	30902	31726

Results of Leachate BOD$_5$ Analysis

Initial Data   Units: mg/l

Date	Day No.	AMF	ASF	ASR	NMR	AMR1	AMR2	AMR
6-Sep-04	1	19950	10950	14160	19350	16200	21360	18780
7-Sep-04	2	18825	14700	17760	19995	22050	24960	23505
8-Sep-04	3	25200	14760	18450	21960	20760	24960	22860
12-Sep-04	7	4080	15343	15557	20600	11280	12180	11730
15-Sep-04	10	2280	16200	9128	18997	9342	7680	8511
16-Sep-04	11	4280	13450	11950	20598	8040	11040	9540
19-Sep-04	14	3117	13251	8751	26327	6390	6057	6224
21-Sep-04	16	4071	12167	8333	27900	6107	8375	7241
23-Sep-04	18	2400	10500	10312	30750	6000	6250	6125
26-Sep-04	21	5203	9159	6909	26787	6009	8559	7284
28-Sep-04	23	4640	13839	13539	23802	13908	10000	11954
30-Sep-04	25	4657	13832	13149	28725	12285	9285	10785
3-Oct-04	28	4029	13500	11250	28500	11325	11100	11213
5-Oct-04	30	4487	14332	9458	27600	9708	9332	9520
7-Oct-04	32	4507	13830	9025	29256	9650	10093	9872
11-Oct-04	36	4159	10813	9573	23100	9675	9879	9777
14-Oct-04	39	4208	6021	9025	23250	9128	9380	9254
18-Oct-04	43	4300	5649	10833	22916	9720	9345	9533
21-Oct-04	46	4224	4570	8957	19666	9432	11535	10484
25-Oct-04	50	4287	5750	10750	22500	10429	12905	11667
28-Oct-04	53	4714	6500	12535	25500	13392	13660	13526
4-Nov-04	60	4035	6200	11750	22698	13750	13750	13750
11-Nov-04	67	3950	6300	10999	21165	15082	13451	14267
18-Nov-04	74	3950	6000	7000	22998	12750	13125	12938
25-Nov-04	81	3950	5900	7042	20000	11214	11535	11375
2-Dec-04	88	3950	5700	6428	21250	11500	11600	11550
9-Dec-04	95	3950	5600	7999	21250	11856	11749	11803
16-Dec-04	102	3950	5600	7678	21150	10892	10583	10738

Leachate Treatment by Lagoons

Batch # 01

- **Leachate type** C

- **Time** 12 h N/A—12 A---- 12 h N/A---- 24 h A

- **Chemicals** NO
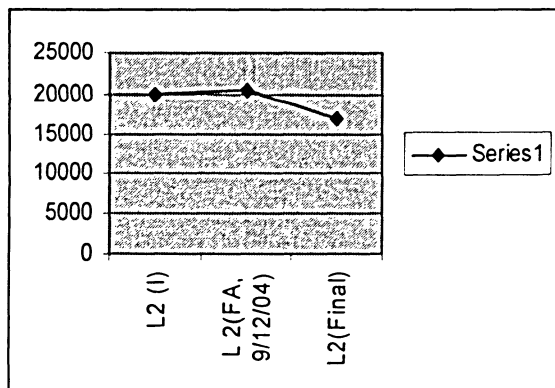
- **Cycle** No Air---- Air

- **Ph** No Adjusted
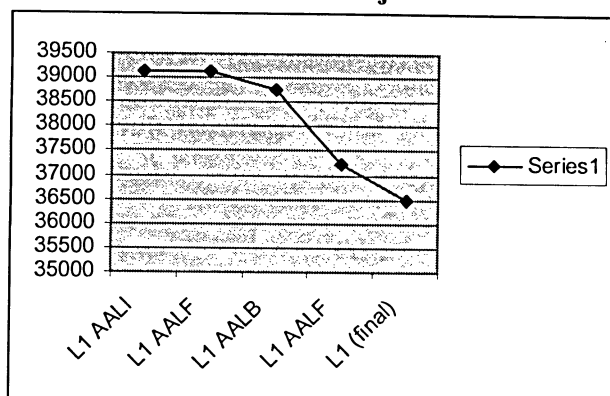
	COD	
	mg/l	%
IN N/A	39129	
12 N/A	39129	0
12 A	37240	4.82
12 N/A+ 24 A	36494	2.00
final		6.73

Batch # 02

- **Leachate type** C

- **Time** 12 h N/A---- 12 A

- **Chemicals** 2000 mg H_2O_2 + 1000 mg FeSo4 + digested sludge 1 L

- **Cycle** N/A---- A
- **Ph** No Adjusted

	COD	
	mg/l	%
IN	19970	
OUT	16823	15.76

Batch #   03

- **Leachate type**   C

- **Time**   12 h N/A---- 12 A

- **Chemicals**   2000 mg H_2O_2 + 1000 mg FeSo4 + fresh Activated sludge 1 L

- **Cycle**   N/A---- A

- **Ph**   No Adjusted

	COD	
	mg/l	%
Initial	7929	
N/A 12 h	6542	17.5
A / sludge	8120	
A 12 h out	3697	52.3
Air stage		54.4

Batch #   04

- **Leachate type**   C

- **Time**   12 h N/A---- 12 A

- **Chemicals**   2000 mg H_2O_2 + 1000 mg FeSo4 + old Activetd sludge 1 LL

- **Cycle**   N/A---- A

- **Ph**   No Adjusted

	COD	
	mg/l	%
N/A in	7640	
N/A out	6157	19.4
A out	5604	26.0

Batch #   05

- **Leachate type**   S

- **Time**   12 h N/A---- 12 A

- **Chemicals**   2000 mg H_2O_2 + 1000 mg FeSo4 + Activated sludge 1 L

- **Cycle**   N/A---- A

- **Ph**   Adjusted 3.5 N/A--------7 A

|	COD	
	mg/l	%
N/A In	26433	
12 N/A	17570	33.53
12 A out	15734	40.36

Batch #   06

- **Leachate type**   S

- **Time**   24 h N/A---- 24 A

- **Chemicals**   2000 mg H_2O_2 + 1000 mg FeSo4 + fresh Activated sludge1 L

- **Cycle**   N/A---- A

- **Ph**   Adjusted 3.5 N/A--------7 A

	COD	
	mg/l	%
N/A In	21885	
24 N/A	19313	11.75
24 A out	17917	18.13

Batch #   07

- **Leachate type**   S

- **Time**   24 h N/A---- 242 A

- **Chemicals**   2000 mg H_2O_2 + 1000 mg FeSo4 + fresh Activated sludge 1 L

- **Cycle**   N/A---- A

- **Ph**   Adjusted 3.5 N/A--------7 A

	COD	
	mg/l	%
N/A In	11521	
24 N/A	10646	07.59
24 A out	9113	20.90

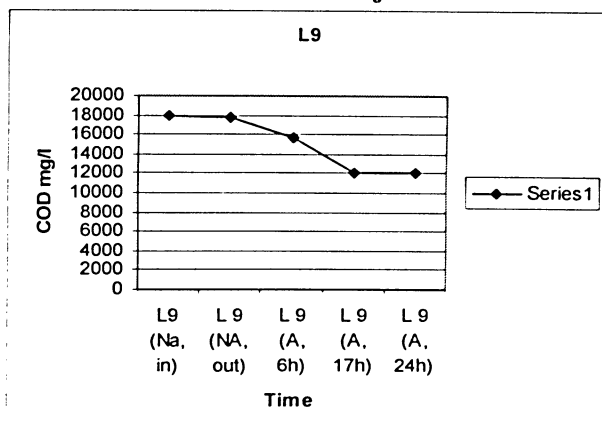**Batch #**   08

- **Leachate type**   S

- **Time**   24 h N/A---- 24 A

- **Chemicals**   2500 mg H_2O_2 + 2500 mg FeSo4 + digested sludge 1 L

- **Cycle**   N/A---- A

- **Ph**   Adjusted 3.5 N/A--------7 A

Lagoon Batch 8
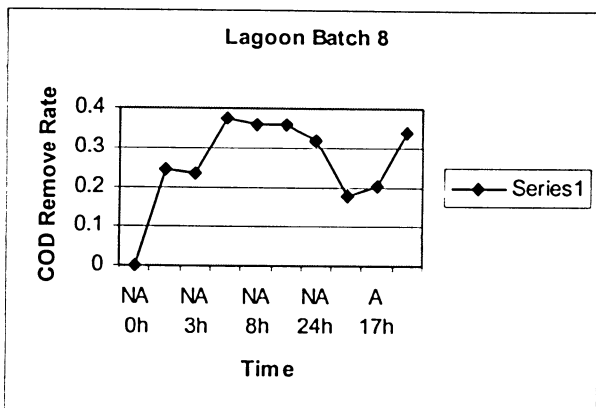
	COD	
	mg/l	%
N/A in	17514	
N/A 1 h	13279	24.18
N/A 3 h	13403	23.47
N/A 5 h	10955	37.45
N/A 8 h	11180	36.17
N/A 17 h	11180	36.17
N/A out	11893	32.09
A 6 h	14407	17.74
A 17 h	13997	20.08
A 24 h	11598	33.78

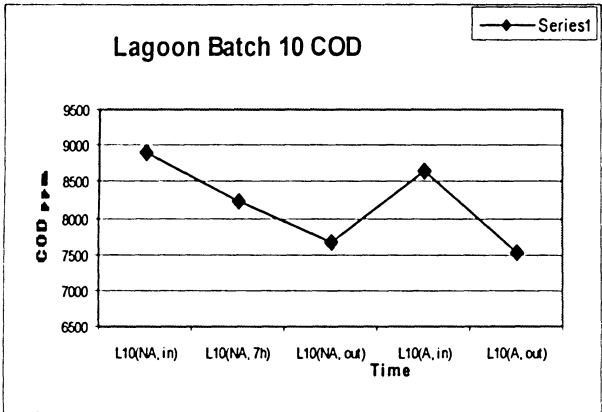**Batch #**   **09**

- **Leachate type**   **S**

- **Time**   **24 h N/A---- 24 A**

- **Chemicals**   **No**

- **Cycle**   **N/A---- A**

- **Ph**   **No Adjusted**

L9

	COD	
	mg/l	%
N/A in	17885	
N/A out	17678	1.16
A 6 h	15758	11.89
A 17 h	12124	32.21
A 24 h	12008	32.86

Batch #   **10**

- **Leachate type**   **C**

- **Time**   **24 h N/A---- 24 A**

- **Chemicals**   **2500 mg H$_2$O$_2$ + 2500 mg FeSo4 + fresh Activated sludge 1 L**

- **Cycle**   **N/A---- A**

- **Ph**   **Adjusted 3.5 N/A--------7 A**

	COD	
	mg/l	%
N/A in	8896	
N/A 7 h	8242	7.35
N/A 24	7663	13.86
A in	8663	2.62
A out	7507	15.61

Batch #   **11**

- **Leachate type**   **C**

- **Time**   **24 h N/A---- 24 A**

- **Chemicals**   **No**

- **Cycle**   **N/A---- A**

- **Ph**   **No Adjusted**

	COD	
	mg/l	%
N/A in	8176	
N/A out	8076	1.22
A in	9054	-10.74
A out	4848	40.45
A		46.45

Lagoon Batch 11
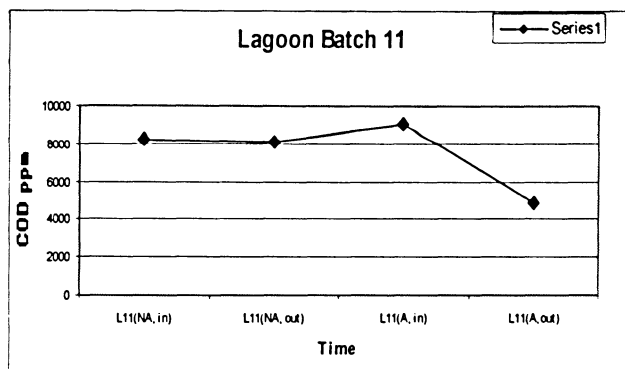
Batch #   **12**

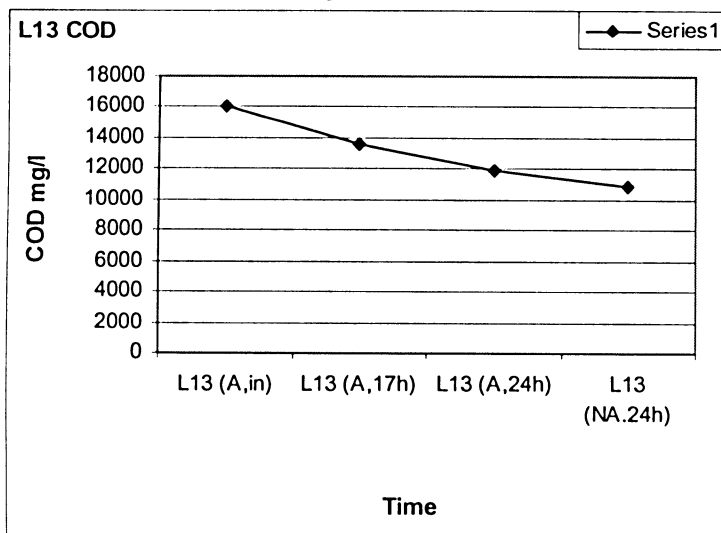- **Leachate type**   **S**

- **Time**   **24 h A---- 24 N/A**

- **Chemicals**   **2500 mg H2O2 + 2500 mg FeSo4 + fresh Activated sludge 1 L**

- **Cycle**   **A---- N/A**

- **Ph**   **Adjusted 3.5 N/A--------7 A**
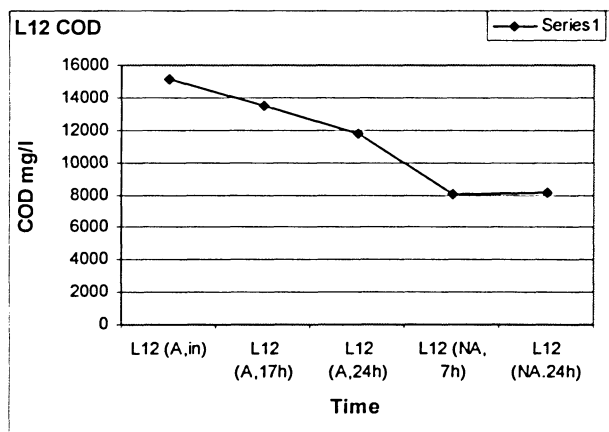
	COD	
	mg/l	%
A in	15100	
A 17 h	13551	10.3
N/A 24	7663	21.9
N/A in	8663	46.8
N/A out	7507	45.9

Batch #   **13**

- **Leachate type**   S

- **Time**   24 h A---- 24 N/A

- **Chemicals**   2500 mg H_2O_2 + 2500 mg FeSo4 + fresh Activated sludge 1 L

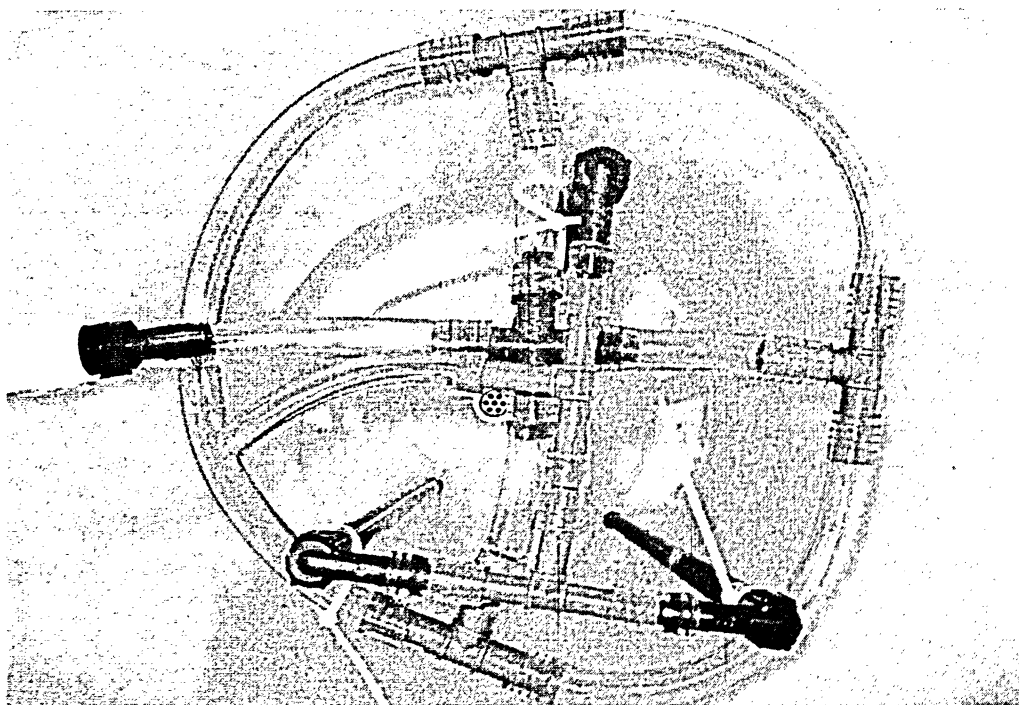- **Cycle**   A---- N/A

- **Ph**   Adjusted 7 A

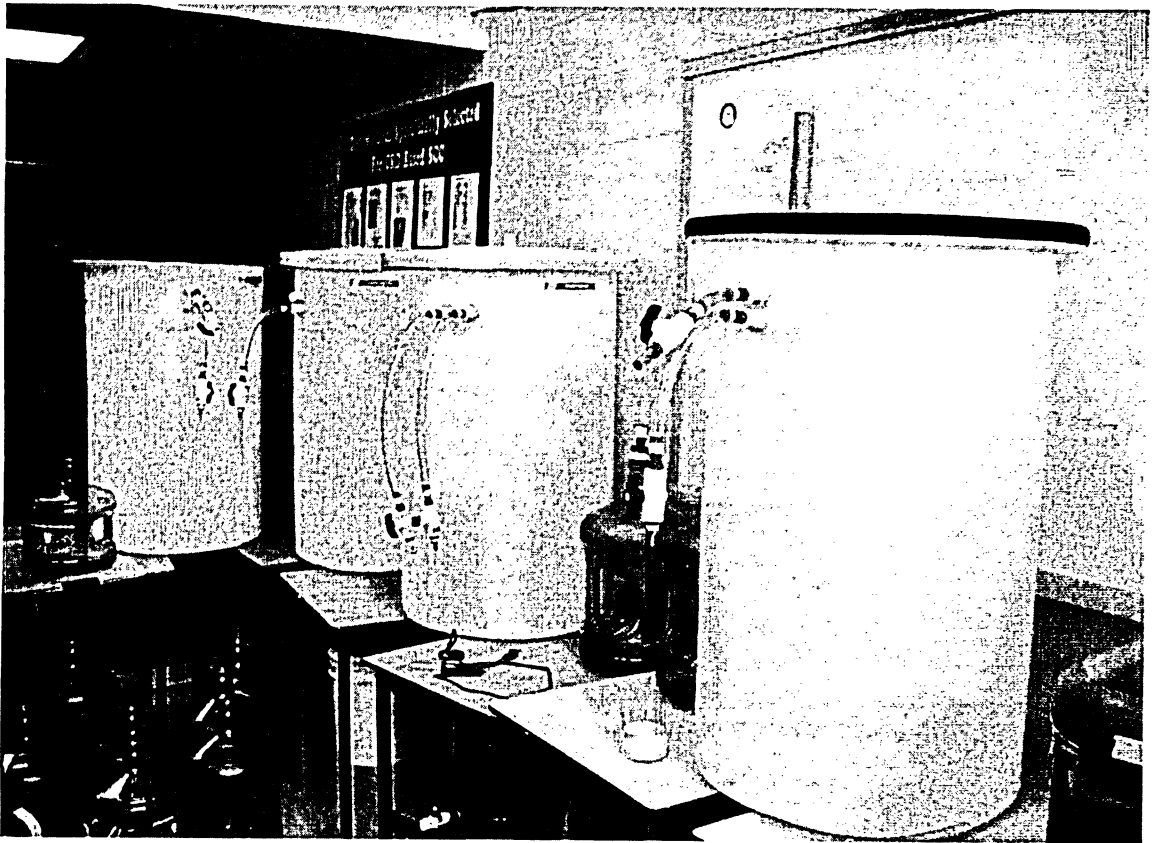|	COD	
	mg/l	%
A in	16086	
A 17 h	13551	10.3
N/A 24	11904	21.9
N/A out	10891	46.8

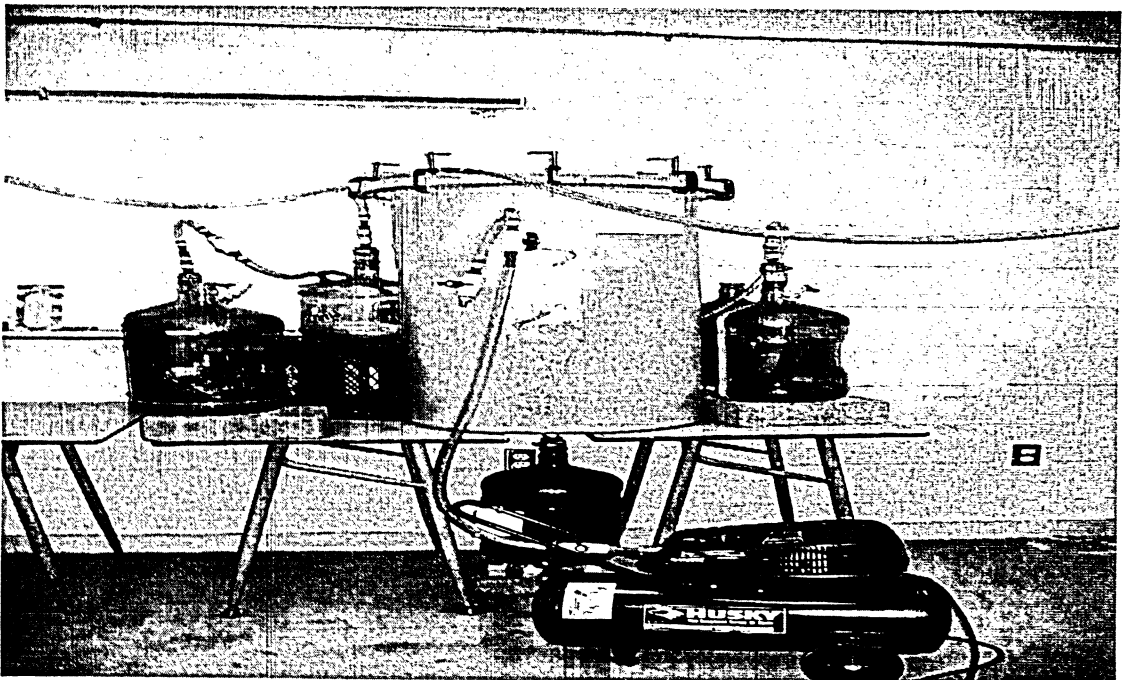# APPENDIX B – SUPPLEMENTARY PHOTOGRAPHS
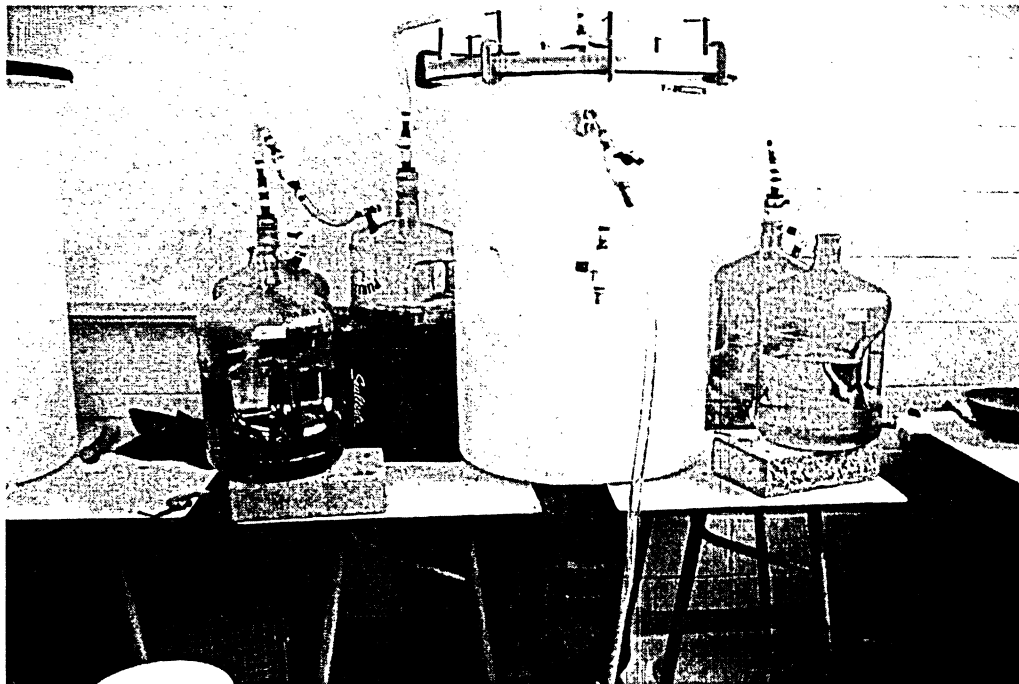
Bio Reactor with air, leachate recirculation and methane disposal unit
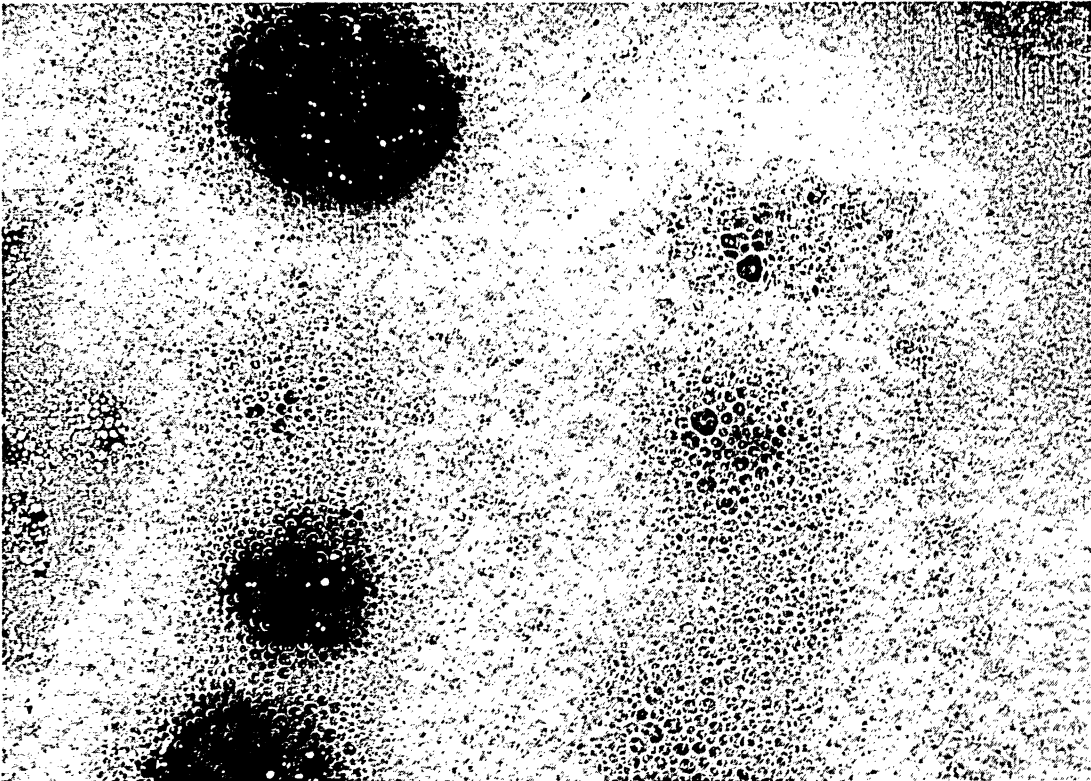

Air and Leachate recirculation system

Bio reactors

Leachate treatment with Fentons Reagents and Air

After Treatment