ABILITY OF DISSOLVED ORGANIC CARBON FROM SIMULATED LEACHATE TO EXTRACT Pb FROM MINE TAILING

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ความสามารถของสารละลายอินทรีย์ในน้ำชะขยะสังเคราะห์ในการสกัดตะกั่วออกจากหางแร่

นางสาวศิรินดา ลาภเจริญ

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ศิรินดา ลาภเจริญ : ความสามารถของสารละลายอินทรีย์ในน้ำชะขยะสังเคราะห์ในการสกัดตะกั่วออกจากหางแร่. (ABILITYOF DISSOLVED ORGANIC CARBON FROM SIMULATED LEACHATE TO EXTRACT Pb FROM MINE TAILING) อ.ที่ปรึกษาวิทยานิพนธ์หลัก : ผศ. ดร. พิชญ รัชฎาวงศ์, อ.ที่ปรึกษาวิทยานิพนธ์ร่วม : รศ.ดร. มาร์ค แนนนี่ 170 หน้า.

เนื่องจากขยะจำพวกผักและผลไม้ในประเทศไทยมีเป็นจำนวนมาก โดยเฉพาะขยะที่ทิ้งโดยตรงจากตลาดซึ่งขยะจำพวกนี้นอกจากย่อยสลายได้เร็วแล้วยังมีการปนเปื้อนน้อย ดังนั้นจึงได้ทำการศึกษาเพื่อนำน้ำชะขยะที่ได้จากขยะประเภทนี้ไปใช้ประโยชน์อย่างอื่นได้ต่อไป จากที่น้ำชะขยะโดยทั่วไปมีคุณสมบัติในการชะโลหะหนัก น้ำชะขยะที่ได้จากขยะประเภทผักและผลไม้อาจสามารถใช้ประโยชน์ในการสกัดโลหะหนักโดยเฉพาะตะกั่วออกจากหางแร่

ในการทดลองนี้มีการสร้างน้ำชะขยะขึ้นจากถังทดลองที่ใส่ผักและผลไม้ และมีการวัดค่าคุณสมบัติต่าง ๆ ของน้ำชะขยะเป็นระยะเพื่อสังเกตุการเปลี่ยนแปลงคุณสมบัติของน้ำชะขยะ พบว่าขยะจำพวกผักและผลไม้มีค่าความเป็นกรดสูงมาก จนไม่เหมาะสมสำหรับแบคทีเรียไม่ใช้อากาศในระบบ จึงต้องมีการปรับค่าความเป็นกรด-ด่างร่วมกับการเวียนกลับของน้ำชะขยะเพื่อเร่งอัตราการย่อยสลาย และเมื่อนำน้ำชะขยะที่ได้ในระยะเวลาต่าง ๆ มาสกัดตะกั่วออกจากหางแร่ พบว่าน้ำชะขยะในช่วงสัปดาห์แรก ๆ มีความสามารถในการสกัดตะกั่วได้ดีถึง 60-70% ซึ่งเป็นน้ำชะขยะที่มีค่าความเป็นกรดต่ำกว่า 4 แต่เมื่อน้ำชะขยะมีอายุมากขึ้นและมีค่าความเป็นกรดเพิ่มขึ้นอยู่ในช่วง 5-8 ความสามารถในการสกัดตะกั่วลดลงเรื่อย ๆ จนไม่สามารถสกัดได้เลยจนกระทั่งค่าความเป็นกรดมากกว่า 8.5 และเริ่มเข้าสู่มีเทนเฟส จึงสามารถสกัดตะกั่วออกจากหางแร่ได้เล็กน้อย แต่ยังคงต่ำกว่า 10% จนสิ้นการทดลอง หลังจากนั้นนำน้ำชะขยะมาแยกส่วนเป็นกรดฮิวมิค กรดฟูลวิคและไฮโดรฟิลิค พบว่ากรดฮิวมิคที่ได้มีปริมาณต่ำมากโดยมีเพียง 0.48% และ 0.92% เท่านั้น กรดฟูลวิคมีปริมาณ 15%-29% อย่างไรก็ตามผลการตรวจวัดด้วยเครื่อง FTIR และเครื่อง UV-visible พบว่าองค์ประกอบทางเคมีก็มีส่วนคล้ายคลึงกับกรดฮิวมิคจากแหล่งกำเนิดอื่น

สาขาวิชา การจัดการสิ่งแวดล้อม ลายมือชื่อนิสิต
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4789709920 : MAJOR ENVIRONMENTAL MANAGEMENT
KEYWORDS : LEACHATE / DOC / EXTRACTION / Pb / HUMIC

SIRINDA LAPCHAROEN : ABILITY OF DISSOLVED ORGANIC CARBON FROM SIMULATED LEACHATE TO EXTRACT Pb FROM MINE TAILING. THESIS ADVISOR: PICHAYA RACHADAWONG, Ph.D., THESIS CO-ADVISOR: MARK A. NANNY, Ph.D., 170 pp.

Food waste such as fruits and vegetables (waste from market) are the vast majority waste in Thailand. These kinds of waste are rich in organic matter and have a high water content resulting in higher biodegradation. This leachate should be used further for any valuable purpose such as environmental remediation. It has been known from previous researcher that landfill leachate has an ability to extract heavy metal. It may be used as extraction agent to separate heavy metal especially lead from mine tailings.

In this study, simulated leachate was generated from biodegradation reactor of fruit and vegetable wastes. Simulated leachate was collected and many parameters were measured to investigate the properties of leachate and also degradation phases. The results showed that the very low pH of the system was not appropriate for anaerobic bacteria The system had insufficient buffering capacity. Therefore, alkalinity addition and also leachate recirculation were necessary for this system to enhance the degradation rate. Simulated leachate was used for extraction of Pb from mine tailings. The comparison of extraction ability of leachate with different ages and properties were conducted. Simulated leachate from first few weeks which had pH lower than 4 could extract Pb as high as 60-70%. When the leachate increased same time as increasing of its pH to 5-8, its extraction ability decreased dramatically until no extraction ability at all. However, it showed some extraction ability again when it came to methane phase with pH more than 8.5 but the extraction ability was still lower than 10% until the end of experiment. Then simulated leachate was fractionated into three fraction; humic acids(HA), fulvic acids(FA) and hydrophilic fraction(HyI). Leachate contained very low content of humic acids (0.48% and 0.92%) and fulvic acids(15-29%). However from Fourier Transform Infrared Spectroscopy and UV-visible results, its functional groups were similar to humic acids from other sources.

Field of Study : Environmental Management Student's Signature ....
Academic Year : 2008 Thesis Advisor's Signature ....

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Finally, I especially want to dedicate my dissertation to my family members, my mother and my husband for their unconditional love, encouragement, understanding and help. With out their help, I will not have been successful as today, and for that I will be endlessly grateful

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LIST OF ABBREVIATIONS

AHA = Aldrich Humic Acid
AMD = Acid mine drainage
AP = Acid-precipitated
AS = Acid-soluble
BMA = Bangkok Metropolitan Area
BOD = Biochemical oxygen demand
CEC = Cation exchange capacity
cm = Centimeter
COD = Chemical oxygen demand
DOC = Dissolved organic carbon
DOM = Dissolved organic matter
DTPA = Diethylenetriamine pentaacetic acid
EDTA = Ethylenediaminetetraacetic acid
FA = Fulvic acids
FAAS = Flame atomic absorbance spectroscopy
FTIR = Fourier Transform Infrared Spectroscopy
g = Gram
g/kg = Gram per kilogram
GC-MS = Gas chromatography-mass spectrometry
HA = Humic acids
HMBC = Heavy metal binding capacity
hr = Hour
HS = Humic substance
HyI = Hydrophilic fraction
ICP-OES = Inductively coupled plasma optical emission spectroscopy
K = Stability constant
kg/capita/day = Kilogram per capita per day
km = Kilometer
LFG = Landfill gas
M = Molar
m^2 = Square meter
m^3/kg = Cubic meter per kilogram
mg/kg = Milligram per kilogram
mg/L = Milligram per litre
min. = Minute
MNRE = Ministry of Natural Resources and Environment
mol/L = Mol per litre
MSW = Municipal solid waste
mV = Millivolt
N = Normal
NMR = Nuclear magnetic resonance spectroscopy
NTA = Nitrilotriacetic acid
OM = Organic matter
ORP = Oxidation reduction potential
PCD = Pollution Control Department
ppm = Part per million

LIST OF ABBREVIATIONS

rpm = Round per minute
SOM = Soil organic matter
SRFA = Suwannee river fulvic acid
TMAH = Tetramethylammonium hydroxide
TOC = Total organic carbon
VFA = Volatile fatty acids
VOCs = Volatile organic carbon
v/v = Volume by volume
WHAM = Windermere Humic Aqeous Model
w/v = Weight by volume
µ = Ionic strength
µmhos/cm = Micro mhos per centimeter
µg/L = Micro gram per litre

CHAPTER I

INTRODUCTION

1.1 Rationale

Landfilling is the most common disposal method for municipal solid waste (MSW) that cannot be recycled in Thailand and also many countries. Considering Thailand circumstance, high humidity and high temperature suit for biodegradation process. In 2005, the amount of MSW generated in Thailand was approximately 40,000 tons per day or 14 million tons per year, of which 21.1% of total MSW quantities were generated from Bangkok Metropolitan Area (BMA), 32.2% from municipalities and Pattaya City and 46.6% from rural areas or sub-district administrative organization areas. Some typical solid wastes found in Thailand are: food waste, paper, textiles, rubber and wood. One major kind of Thailand MSW is food waste such as fruits and vegetables (especially waste from market). This kind of waste contains high content of organic carbon and they can also create a large volume of leachate. They also contain no hazardous waste and also no accumulation of heavy metal as MSW. Therefore, they have been studied for use in enhancing biogas production rate in an anaerobic digestion process. Because of high moisture content, vegetable and fruit wastes not only give a high yield of biogas but also give large volume of leachate. This leachate should be used further for any valuable purpose such as environmental remediation.

It has been known from previous researcher (Christensen et al., 1996) that landfill leachate has an ability to extract heavy metal. Leachate can be acidic and often contains a high concentration of dissolved organic carbon (DOC). The reaction in landfill can generate many kinds of chemicals and in the maturation phase which is the last phase of landfill contains high content of DOC. The organic material presented in leachate has been studied by many researchers who concluded that organic material has high affinity for complexation of heavy metals (Baun et al., 2003). DOC can be fractionated as humic acids (HA) fraction, fulvic acids (FA) fraction which are hydrophobic fractions and last fraction is hydrophilic (HyI) fraction. These three fractions may play a major role for metal extraction of leachate. However, it was questioned that how the chemical characteristic of landfill leachate changes with time and affect the metal extraction ability.

Although, there are many research on metal extraction of leachate exists (Christensen et al., 1996; Conte et al., 2005), there is no research on extraction ability of simulated landfill leachate, especially from fruit and vegetable waste. Therefore, this research is aimed at studying the ability of simulated landfill leachate to extract heavy metal from contaminated matrix correlate to landfill ages. Moreover, the characteristic of each fraction of DOC in leachate was studied.

1.2 Objectives of the study

The main objective of this research is to utilize leachate from simulated landfill reactor to remove heavy metal from contaminated solid matrix such as soil, mine tailing etc. The sub objectives are as follows:

1. To study the ability of simulated landfill leachate to extract and solubilize metal ions correlated with landfill ages.
2. To evaluate the extraction ability of dissolved organic carbon (DOC) fractions (e.g. HA fraction, FA fraction and HyI fraction) for heavy metal extraction.
3. To study the chemical characteristic of the highest extraction ability simulated landfill leachate.

1.3 Hypotheses

1. The extraction ability of leachate changes with landfill ages.
2. DOC in simulated landfill leachate has ability to form complex with metal.
3. Artificial leachate can be produced and used for metal extraction to remove metal from solid metric such as soil or mine tailing.

1.4 Scope of the study

This study can be divided into three phase; phase I: leachate simulation, phase II: Pb extraction and the last phase, phase III: leachate characterization. In part I, leachate was generated from fruit and vegetable wastes in composition of Si-Mum Muang Market, Thailand (Chewha, 2003). The experiment was conducted in pilot scale bioreactor column with anaerobic condition. Artificial leachate produced from simulated landfill reactors was collected regularly from the beginning of experiment to the last phase of experiment. Reactor adjustment with NaOH addition and leachate recirculation were also operated due to high acidic property of our leachate; otherwise maturation phase may not be reached. Factors affecting the degradation rate of solid waste consist of leachate recirculation, recirculation volume, waste shredding, pH adjustment and alkalinity additions. The leachate was monitored in many parameters such as chemical oxygen demand (COD), volatile fatty acids (VFA), etc. to study the changes of leachate property in correlation with time. All parameter could clarified the changes of stabilization phase in the reactor and they might affect to Pb extraction ability in the next phase.

In phase II, leachate generated from phase I was used as extracting agent to extract Pb from mine tailing (Akra Mining, Thailand). Metal extraction ability of each leachate sample was investigated by mixing portion of mine tailing with leachate sample and shaking until equilibrium. Then leachate was centrifuged and separated from mine tailing. The quantity of extracted Pb was analyzed. Percentage of Pb extracted was plotted with leachate ages, pH, DOC and VFA. Some of these factors might have a correlation with Pb extraction ability of simulated leachate. This experiment answers the first objective. After the extraction part, leachate extraction ability correlated with their ages was clarified.

According to second and third objectives, in phase III, leachate samples of different extraction ability and different stabilization phase were fractioned into three fraction of HA, FA and HyI. The fractionation process was done by passing filtered leachate through DAX-8 resin column. All these fractions were then investigated by Fourier Transform Infrared Spectroscopy (FTIR), UV-visible and Elemental analyzer to study the relation between their structure and their Pb extraction ability. These analyses gave some information of chemical structure and elemental composition. The characterization and Pb extraction ability of leachate will be discussed.

CHAPTER II

LITERATURE REVIEWS

2.1 Introduction

Because of economic growth, population growth and development of new technology, there is a rapid increase of product consumption which will be disposed of finally. Among many disposal methods used presently, landfilling is one of the common method in most countries for disposal. Same as many countries, most of MSW in Thailand goes to landfill because of lower operation cost compared with other methods such as incineration. There are also other advantages of landfilling for Thailand, for example, lower construction cost, easier operation, etc. In year 2005, Thailand MSW production was up to approximately 40,000 tons per day or 14 million tons per year. The amount of total MSW were generated from BMA 21.2%, 32.2% from municipalities and Pattaya city and 46.6% from rural areas or sub district administrative organization areas as shown in Table 2.1

Table 2.1 MSW quantities generated in 2005. (Ministry of Natural Resources and Environment, MNRE)

Area	**MSW quantities in 2005 (tons per day)#**	**% of total MSW**
1. Bangkok Metropolitan Area (BMA)	8,340*	21.2
2. Municipalities and Pattaya City	12,635†	32.2
3. Sub-district Administrative Organizations (rural area)	18295‡	46.6
Total	39,270	100.0

Note: #include 3% of household hazardous waste

Sources: *Public Cleansing Bureau, BMA

†Pollution Control Department’s Questionnaire

‡Calculation based on waste generation rate of 0.4 kg/capita/day

It was also found that waste generation rates were approximately 1.0 – 1.4 kg/capita/day in major cities and tourism areas, 0.7 – 1.0 kg/capita/day in municipal areas and 0.4 – 0.6 kg/capita/day in Sub-district Administrative Organizations (SOAs) areas. The composition of MSW was shown in Table 2.2. It can be seen from Table 2.2 that food waste has the highest composition ranging from 29.25% in Chiangmai to 42.68% in Bangkok.

Table 2.2 Average Physical Composition of MSW in Thailand major cities.

Province	Wastes composition (%)									
	Food waste	Paper	Plastic	Glasses	Metal	Rubber	Clothes	Wood	rock	etc
Bangkok	**42.68**	12.09	10.88	6.63	3.54	2.87	4.68	6.9	3.93	6.11
ChiangMai	**29.26**	12.17	18.33	6.75	3.86	3.09	4.01	14.32	4.44	3.48
Phatum-thanee	**41.75**	17.08	16.58	4.99	3.96	3.10	3.06	8.53	0.54	0.43
Samutpra-kran	**38.14**	14.96	15.88	4.51	3.57	3.82	4.67	5.82	3.62	5.01

Source: Pollution Control Department. (2005)

According to the high productivity of fruits and vegetables in a tropical country like Thailand, the majority of market waste is fruit and vegetable waste. This kind of waste is rich in organic matter and has a high water content resulting in higher biodegradability. Therefore, high amount of leachate from landfill can be produced easily and rapidly. This leachate should be used further for any valuable purpose such as environmental remediation. It has been known from previous researcher (Christensen et al., 1996) that landfill leachate has an ability to extract heavy metal. The reaction in landfill can generate many kinds of chemicals and also DOC. DOC can be fractionated as HA fraction, FA fraction which are hydrophobic fractions and another fraction is HyI fraction. These three fractions may play a major role for metal extraction of leachate. However, it may be questioned that how the chemical characteristic of landfill leachate changes with time and affect the metal extraction ability.

2.2 Landfill

MSW is approximately 75 to 80% organic matter, composed mainly of proteins, lipids, carbohydrates (cellulose and hemicelluloses), and lignin. Approximately two-thirds of this material is biodegradable. The biodegradable portion can be further divided into a readily biodegradable fraction (food and garden waste) and a moderate biodegradable fraction (paper, textiles, and wood).

A solid waste landfill can be classified as a biochemical reactor because of solid waste and water as the inputs and landfill gas and leachate are generated as output. Solid wastes deposited in landfill decompose by a combination of chemical, physical and biological process. Physical decomposition of solid waste occurs from the breakdown of the refuse components by physical degradation and also by the rising and flushing action of water movement. Chemical processes resulting in refuse decomposition include the hydrolysis, dissolution/precipitation, sorption/desorption, and ion exchange of refuse components. Chemical decomposition generally results in altered characteristics and greater mobility of refuse components, thereby enhancing the rate at which the landfill becomes more chemically uniform (Chian and De Walle, 1997). Biological decomposition is resulting from natural bacteria. This is a complex process in landfill site which refuse is decomposed to various end products. The reaction starts with the beginning of the landfill and continuously occurs through the life time of landfill though the reaction and composition changes with landfill ages.

The landfill ecosystem is quite diverse due to the heterogeneous nature of waste and landfill operating characteristics. The diversity of the ecosystem promotes stability; however, the system is strongly influenced by environmental conditions, such as temperature, pH, moisture content, and the oxidation-reduction potential (ORP). The landfill environment tends to be rich in electron donors, primarily organic matter. The dominant electron receptors are carbon dioxide and sulfate.

2.2.1 Phases of landfill stabilization

A number of landfill investigation studies have suggested that the stabilization of waste proceeds in five sequential and distinct phases. During these phases, the rate and characteristics of leachate produced and gas generated from a landfill are not only dissimilar, but also reflect the microbial mediated processes taking place inside the landfill. Most landfills are influenced by different climatologically conditions, landfill environment (Pohland et al., 1994). The changes to solid wastes depend on the processes in the landfill and could indicate the phase of landfill stabilization. These events can be observed by monitoring leachate and gas production. Landfill degradation could be divided into 5 phases as follows (Tchobanoglous et al., 1993) and shown in Figure 2.1 and Figure 2.2.

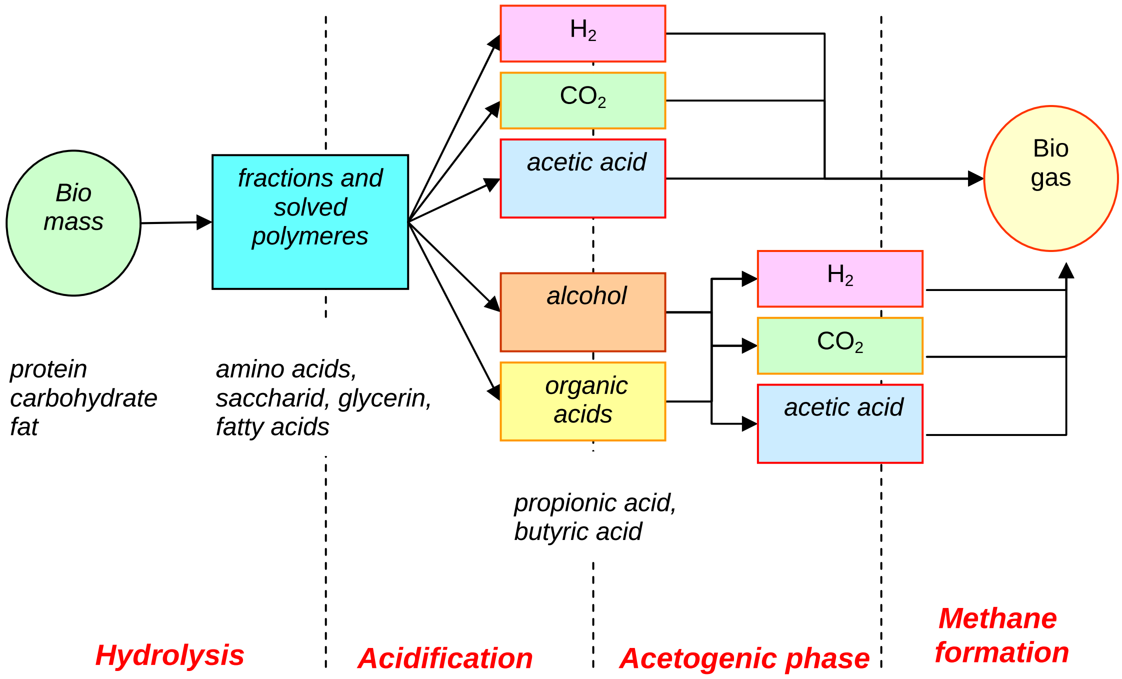


Figure 2.1 Phases of landfill stabilization

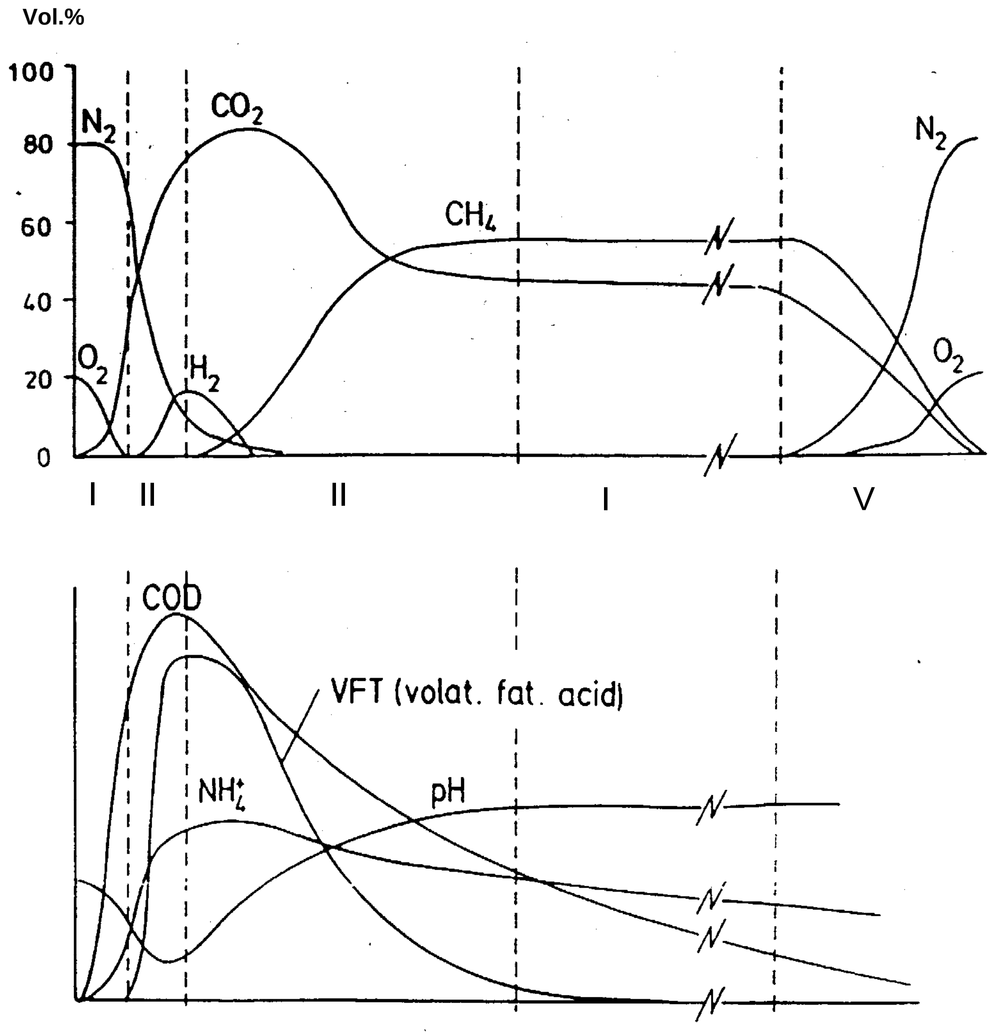


Figure 2.2 Changes in selected indicator parameters during the phases of landfill stabilization (Pohland and Harper, 1985)

Phase I: **Initial adjustment Phase**

This period predominates from the initial waste placement to the closure of the landfill segment. In this stage, the aerobic decomposition consumes oxygen available in landfill and generates carbon dioxide. The source of aerobic and anaerobic organisms occurring in landfill is from the daily cover that is applied which includes soil, including the sludge from waste treatment plants and the recirculation of leachate. Preliminary changes in environmental components occur in order to create favorable conditions for biochemical decomposition. Organic fractions of MSW can be converted to a stable organic residue known as compost and represented by the following equation.

Organic matter + O_2 + nutrients --------> new cells + resistant organic matter + CO_2 + H_2O + NH_3 + SO_2^{2-} + heat

Phase II: Transition Phase

In this transition phase, the field capacity is often exceeded and aerobic decomposition is gradually changed to an anaerobic phase by the depletion of oxygen in landfill. Therefore, the electron acceptor shifts from oxygen to nitrate and sulfate. Under anaerobic conditions, organic fraction is converted to carbon dioxide and methane. The conversion can be represented by the following equation.

Organic matter + H_2O + nutrients ----> new cells + resistant organic matter + CO_2 + H_2O +NH_3 + H_2S + heat

This anaerobic condition can be monitored by measuring the ORP of the waste. In this phase, the pH of the landfill decreases due to the conversion of complex organic material to organic acids, including the effect of the generation of carbon dioxide. By the end of this phase measurable concentration of chemical oxygen demand (COD) and volatile fatty acids (VFA) can be detected in the leachate.

Phase III: Acid Formation Phase

In the acid phase, microorganisms transform higher molecules such as lipids, polysaccharides, proteins, and nucleic acids into lower molecules such as acetic acid and small concentrations of organic acids. The continuous hydrolysis of solid waste, followed by the microbial conversion of biodegradable organic content, results in the production of intermediate volatile fatty acids at high concentrations throughout this phase. There is also a metal species mobilization observed. Carbon dioxide and hydrogen gas increase as a result of the anaerobic process. The presence of organic acids and also carbon dioxide drop the pH of landfill. During the acid phase, BOD, COD, and the conductivity of the leachate will increase significantly due to the dissolution of organic acids.

Phase IV: Methane Fermentation Phase

In this phase, intermediate acids are consumed by methanogenic bacteria and converted into methane and carbon dioxide. Sulfate and nitrate are reduced to sulfides and ammonia, respectively. The pH of leachate increases to neutral, in the range of 6.8 to 8 with the decreasing amount of organic acids. The pH is controlled by the bicarbonate buffering system, and consequently supports the growth of methanogenic bacteria. COD, BOD and total organic carbon (TOC) in leachate all decrease as the result of organic acids consumption. In the methanogenic phase, ORP is highly negative and indicative of highly reducing conditions (Stratakis, 1991). Heavy metal release from solid waste is precipitation and complexation with sulfide and carbonate anions proceed and appear in leachate. The highest volume of methane is produce during this phase.

Phase V: Maturation Phase

During the final state of landfill stabilization, nutrients and available substrate become limiting and the biological process in this phase is low including the removing of nutrients with the leachate. Gas production dramatically drops and reappearance of oxygen and oxidized species may slowly be observed. The ORP will rise slowly and the more resistant organics will slowly degrade an influence mobility of other species. The predominant gases evolving in this phase are methane and carbon dioxide and small amounts of nitrogen and oxygen may also be found. During maturation phase, the slow degradation of resistant organic fractions may continue with the production of humic-like substances.

The progress toward final stabilization of landfill solid waste is subject to the physical, chemical and biological factors within the landfill environment, the age and characteristics of landfill waste, the operational and management controls applied, as well as the site-specific external conditions. Table 2.3 shows landfill constituent concentration ranges as a function of the degree of landfill stabilization.

Table 2.3 Landfill Constituent Concentration Ranges as a Function of the Degree of Landfill Stabilization (Tchobanoglous et al., 1993)

Parameter	Transition	Acid formation	Methane fermentation	Maturation
Chemical oxygen demand (COD), mg/l	480-18,000	1,500-71,000	580-9,760	31-900
Total volatile fatty acids, mg/l as acetic acid	100-3,000	3,000-18,800	250-4,000	0
pH	6.7	4.7-7.7	6.3-8.8	7.1-8.8
Conductivity, µS/cm	2,450-3,310	1,600-17,100	2,900-7,700	1,400-4,500

2.2.2 Landfill Leachate

Leachate can be defined as liquid that has percolated through solid waste and has extracted, dissolved or suspended materials. Normally, leachate is composed of liquid that has entered the landfill from external sources, such as surface water, rainfall and the liquid produced from the decomposition of the wastes. When water percolate through solid wastes in landfill that are during the decomposition process, both biological materials and chemical composition of leachate will be vary on the age of landfill, the composition of waste and the time of sampling.

2.2.2.1 Leachate Generation

Within a landfill, a complex sequence of physically, chemically, and biologically mediated events occurs. As a consequence of these processes, waste is degraded or transformed. As water percolates through the landfill, contaminants are leached from the solid waste. Mechanisms of contaminant removal include leaching of inherently soluble materials, leaching of soluble biodegradation products of complex organic molecules, leaching of soluble products of chemical reactions, and washout of fines and colloids. All layers of a mixture of soil or refuse in the compacted landfill also have a field capacity, or the ability to retain moisture. If the field capacity of this mixture is exceeded, the leachate will drop to the next lower refuse layer. A refuse mixture that does not attain field capacity discharges essentially no water to the deeper layer.

The characteristics of the leachate produced are highly variable, depending on the composition of the solid waste, precipitation rates, site hydrology, compaction, cover design, waste age, sampling procedure, interaction of leachate with the environment, and landfill design and operation. Some of the major factors that directly affect leachate composition include the degree of compaction and composition of the solid waste, climate, site hydrogeology, season, and age of the landfill. Organic containment of leachate is primarily soluble effuse components or decomposition products of biodegradable fractions of waste.

The capacity for leachate polluting streams and lakes is expressed by the BOD which estimates the potential for using oxygen. Another means for expressing pollution potential is COD. COD is always greater than BOD. Leachate tends to contain a large variety of organic and inorganic compounds at relatively low concentration that can be of concern if groundwater and surface water contamination occurs.

Organic compounds in landfill include organic acids, ketones, aromatic compounds, chlorinated aromatic compounds, ether, phthalates, halogenated aliphatic compounds, nitro-aromatic compounds, phenols, heterocyclic compounds; pesticides sulfur substituted aromatic compounds, polyaromatic hydrocarbons, polychlorinated biphenyls, and organophosphate (Brown and Donnelly, 1988)

The HA, FA and the hydrophilic fraction which are called ‘humic substances (HS)’ can be isolated and purified from landfill leachate. These fractions play an important role to form complexes with heavy metals presented in leachate. The molecules of HS consist of hydrophilic and hydrophobic groups, charge sites encounter ions, the identity and proportion of which vary from molecule to molecule (Swift, 1996)

2.2.2.2 Characteristics of Leachate

In landfill leachate, material is removed from the waste mass via mechanism that include leaching of inherently soluble material, leaching of soluble material, leaching of soluble products of biological and chemical transformation, and wash out of fines and colloids. The characteristics of the leachate are highly variable depending on the composition of the waste, rate of water infiltration, refuse moisture content, and landfill design, operation, and age.

Organic contaminants of leachate are primarily soluble refuse components or decomposition products of biodegradable fractions of waste. Organic compounds detected in many researches of MSW landfill leachate or contaminated groundwater plumes from landfills include organic acids, ketones, aromatic compounds, chlorinated aromatic compounds, ethers, phthalates, halogenated aliphatic compounds, alcohols, amino aromatic compounds, nitro-aromatic compounds, phenols, heterocyclic compounds, pesticides, sulfur substituted aromatic compounds, polyaromatic hydrocarbons, polychlorinated biphenyls, and organophosphates.

The class of organic compounds found at highest concentration in leachate is generally VFA produced during the decomposition of lipids, proteins, and carbohydrates. Aromatic hydrocarbons, including benzene, xylene, and toluene, are also frequently found at lower concentrations. These compounds were considered to be constituents of gasoline and fuel oils.

The dominant organic class in leachate shifts as the age of the landfill increases due to the ongoing microbial and physical/chemical processes within the landfill. An investigation of leachate obtains from landfills operated from one to 20 years found that the relative abundance of high molecular weight humic-like substances decrease with age, while intermediate-sized fulvic materials showed significantly smaller decreases (Kang et al., 2002). The relative abundance of organic compounds present in this leachate was observed to decrease with time in the following order: free VFA, low molecular weight aldehydes and amino acids, carbohydrates, peptides, humic acids, phenolic compounds, and fulvic acids.

2.2.2.3 Leachate and its ages

Because landfill is the long-term method of waste disposal for solid waste, the biological and chemical processes occurring in landfill will change with respect to the age of landfill. Recent studies reported that HS which were isolated and purified from leachate play an important role in the complexation with heavy metals as the landfill ages. Aromatic components and molecular size of HS increased with landfill age which suggests that the degree of humification increases as the landfill age increased (Kang et al., 2002)

In evaluation of the data published on speciation of metal species in landfill leachate, many researchers (Christensen et al., 1996; Christensen et al., 2000) have studied the distribution of heavy metals between colloidal and dissolved fractions in landfill leachate. In spite of the limited database and the different definitions of the dissolved fraction (<0.45 µm or <0.001 µm), the results indicated that a large fraction of heavy metals was found in the colloidal fractions which are organic materials, but inorganic colloids have also been found in landfill leachate. For dissolved species, dissolved organic complexes were found to be an important complexation with metals (Baun et al., 2004)

2.2.3 Landfill Gas

Landfill gas resulted from biological decomposition of organic material in the solid waste stream. Approximately 50% to 70% of MSW is composed of biodegradable materials. In a landfill, microorganisms act to degrade this material. For most of the landfill life anaerobic conditions dominate, and the primary end products of anaerobic waste decomposition are methane and carbon dioxide. These two gases, along with minor amounts of water and trace components, are termed landfill gas. Landfill gas creates a number of problems because methane is explosive, many of the trace components have toxic and odor-causing characteristics, and methane serves as a greenhouse gas. On the other hand, landfill gas presents a resource recovery opportunity because of the energy value of methane. As a result, landfill gas must be managed properly.

2.2.3.1 Gas Generation

Because of the prevailing anaerobic conditions within a biologically active landfill, these sites produce large quantities of gas composed of methane, carbon dioxide, water, and various trace components such as ammonia, sulfide, and nonmethane volatile organic carbon compounds (VOCs). The lag period prior to methane generations may range from a few weeks to a few years, depending on landfill conditions. The duration of gas production is also influenced by environmental conditions within the landfill. Table 2.4 shows constituents of MSW landfill gas.

Table 2.4 Constituents of MSW Landfill Gas (Tchobanoglous et al., 1993)

Component	% by volume
Methane	45 – 60
Carbon Dioxide	40 – 60
Nitrogen	2 – 5
Oxygen	0.1 – 1.0
Ammonia	0.1 – 1.0
Hydrogen	0 – 0.2

2.2.3.2 Characteristics of Landfill Gas

As previously stated, when solid waste decomposed, significant portions of organic wastes are ultimately converted to gaseous end-products. The rate of gas production is a function of refuse composition, climate, moisture content, particle size and compaction, nutrient availability, and buffering capacity. Reported production rates vary from 0.12 to 0.41 m^3/kg dry waste (Tchobanoglous et al., 1993). Production rates and gas composition also follow typical stabilization phases, with peak flow rates and methane content occurring during the methanogenic phase. LFG is typically 40 to 60 percent methane, with carbon dioxide and trace gases such as hydrogen sulfide, water vapor, hydrogen, and various volatile fatty acids comprising the balance.

2.2.4 Landfills as Bioreactors

Leachate is generated in a landfill as a consequence of the contact of water with solid waste. Leachate may contain dissolved or suspended material associated with wastes disposed of in the landfill, as well as many byproducts of chemical and biological reactions. Leachate from MSW landfills varies in strength as a result of the biological activity occurring as the solid waste degrades. Leachate from young landfills has both high dissolved solids content as well as a high concentration of organic matter relative to domestic wastewater. Leachate also may contain a trace amount of hazardous constituents found in the waste stream.

Under proper conditions, the rate of MSW biodegradation can be stimulated and enhanced. Environmental conditions that most significantly impact biodegradation include pH, temperature, nutrients, absence of toxins, moisture content, particle size, and ORP. One of the most critical parameters affecting MSW biodegradation has been found to be moisture content. Moisture content can be most practically controlled via leachate recirculation. Leachate recirculation provides a means of optimizing environmental conditions within the landfill to provide enhanced stabilization of landfill contents as well as treatment of moisture moving through the fill. The numerous advantages of leachate recirculation include distribution of nutrients and enzymes, pH buffering, dilution of inhibitory compounds, recycling and distribution of methanogens, liquid storage, and evaporation opportunities at low additional construction and operating cost. It has been suggested that leachate recirculation can reduce the time required for landfill stabilization from several decades to two to three years.

2.2.4.1 Landfill Bioreactor

Many laboratory scale studies (Sponza and Agdag, 2004; Wang et al., 2006) have been conducted to investigate the effects of leachate recirculation on leachate quality, waste stabilization, waste settlement, gas production, attenuation of heavy metals and other factors.

Moisture content, pH, temperature, availability of macro- and micro- nutrients and the presence of suitable microorganisms are the main parameters controlling the process of landfill stabilization and, therefore, are the parameters typically manipulated in the laboratory studies. Moisture content can be controlled by the addition of regulated quantities of water or leachate. The pH can be controlled by adding buffering compounds. Macro- and micro-nutrients are usually present in sufficient quantities in the waste and do not act as limiting factors in the stabilization process, hence nutrients usually are not added. Presence of suitable microorganisms responsible for stabilization can be ensured by adding anaerobically digested sludge in which acclimated anaerobic and facultative microorganisms are present.

2.2.4.2 Leachate Recirculation

Landfill can be used as readily available biological reactors for the treatment of leachate. The landfill can be essentially transformed into an engineered reactor system by providing proper management such as leachate recirculation. Such landfills are capable of accelerated biochemical conversion of wastes and effective treatment of leachate.

Most landfills are traditionally constructed so the leachate is collected and removed. The rate of stabilization in dry landfills may require many years, thereby extending the acid formation and methane fermentation phases of waste stabilization over long periods of time. Under these circumstances, decomposition of biodegradable fractions of solid waste may be incomplete, or preventing commercial recovery of methane gas and delaying closure and possible future reuse of the landfill site. In addition, during single-pass operations, the leachate must be drained, collected, and treated prior to final discharge.

In contrast, leachate recirculation may be used as a management alternative that requires the containment, collection, and recirculation of leachate back through the landfill waste. This option offers more rapid development of active anaerobic microbial populations and increases reaction rates of these organisms. The time required for stabilization of the readily available organic constituents can be compressed to as little as two to three years rather than the usual 15 to 20 years period. This accelerated stabilization is enhanced by the routine and uniform exposure of microorganisms to constituents in the leachate, thereby providing the necessary contact time, nutrients, and substrates for efficient conversion and degradation. Thus leachate recirculation essentially converts the landfill into a dynamic anaerobic bioreactor that accelerates the conversion of organic materials to intermediates and end products.

The advantages of leachate recirculation have been well documented. Application of leachate recirculation to full-scale landfills has occurred with increasing frequency in recent years. Leachate is returned to the landfill using a variety of techniques, including wetting of waste as it is placed, spraying of leachate over the landfill surface. To optimize bioreactor operations, the waste moisture levels must be controlled by the rate of leachate recirculation, which are a function of waste hydraulic conductivity and the efficiency of the leachate introduction technique. The quantity of liquid supplied is a function of such waste characteristics as moisture content and field capacity. In some cases the infiltration of moisture resulting from rainfall is insufficient to meet the desired waste moisture content for optimal decomposition, and supplement liquid may be required. The most efficient approach to reach field capacity is to increase moisture content through wetting of the waste at the working face and then uniformly to reach field capacity through liquid surface application or injection.

2.2.4.3 Impact of Leachate Recirculation

Result from many studies has shown that moisture control permits rapid stabilization of waste enhances gas production, and improves leachate quality. This reduces long-term environmental consequences and liability of waste storage and improving the economics of landfills. Leachate characteristics of recirculating landfills follow a pattern similar to that of conventional landfills, such as moving through phases of acidogenesis, methanogenesis, and maturation (although few recirculating landfills have reached maturation). Actually, the overall magnitudes of various leachate components, during the consecutive phases of landfill stabilization, are quite comparable in both types of landfills. However, the acidogenic phase tends to be more pronounced in recirculating landfills as opposed to conventional landfills, forming a plateau with consistently high concentration of leachate constituents. Such a phenomenon can be explained by the fact that uniform, high moisture contact opportunities exist in the leachate recycling landfills. On the other hand, dryness in areas of conventional landfills, accompanied by fewer chances of moisture contact and availability, minimize the leaching opportunity in such landfills, and results in rapidly peaking leachate histograms. Even in the case where recycled leachates are somewhat stronger than single-pass leachates, they primarily are treated inside the landfill utilizing its storage and degradation capacity as an effective bioreactor.

The conversion of organic pollutants was enhanced in the recirculation columns due to reduced ORP and simulated methanogenesis. The primary removal mechanism for metals in conventionally operated landfills appears to be washout, although limited chemical precipitation may occur. In leachate-recirculating landfills, the primary removal mechanism appears to be metal sulfide and hydroxide precipitation and subsequent capture within the waste matrix by encapsulation, sorption, ion-exchange and filtration. Chian and Dewalle (1977) reported that the formation of metal sulfides under anaerobic conditions effectively eliminated the majority of heavy metals in leachate. In addition, metal hydroxide precipitation is enhanced under neutral or above neutral leachate conditions, which are promoted by leachate recirculation. With time, moderate to high molecular weight humic-like substances are formed from waste organic matter in a process similar to soil humification. These substances tend to form strong complexes with heavy metals. In some instances, a remobilization of precipitated metals can result from such complexation once the organic content has been stabilized and aerobic conditions begin to reestablish. Landfill constituent concentration ranges as a function of the degree of landfill stabilization are presented in Table 2.5 and 2.6.

Table 2.5 Landfill Constituent Concentration Ranges as a Function of the Degree of Landfill Stabilization in Phase II and III (Reinhart and Townsend, 1998)

Parameter	**Phase II**		**Phase III**	
	Transition		**Acid Formation**	
	Conventional	**Recirculation**	**Conventional**	**Recirculation**
BOD, mg/l	100-10,000	0-6,893	1,000-57,000	0-28,000
COD, mg/l	400-18,000	20-20,000	1,500-71,000	11,600-3,550
TVA, mg/l as Acetic Acid	100-3,000	200-2,700	3,000-18,800	1-30,730
BOD/COD	0.23-0.87	0.1-0.98	0.4-0.8	0.45-0.95
pH	6.7	5.4-8.1	4.7-7.7	5.7-7.4
Conductivity, µmhos/cm	2,450-3,310	2,200-8,000	1,600-17,100	10,000-18,000

Table 2.6 Landfill Constituent Concentration Ranges as a Function of the Degree of Landfill Stabilization in Phase IV and V (Reinhart and Townsend, 1998)

Parameter	**Phase IV**		**Phase V**	
	Methane Formation		**Final Maturation**	
	Conventional	**Recirculation**	**Conventional**	**Recirculation**
BOD, mg/l	600-3,400	100-10,000	4-120	100
COD, mg/l	580-9,760	1,800-17,000	31-900	770-1,000
TVA, mg/l as Acetic Acid	250-4,000	0-3,900	0	-
BOD/COD	0.17-0.64	0.05-0.8	0.02-0.13	1.05-0.08
pH	6.3-8.8	5.9-8.6	7.1-8.8	7.4-8.3
Conductivity, µmhos/cm	2,900-7,700	4,200-16,000	1,400-4,500	-

2.2.4.4 Simulated landfill reactor

Simulated landfill reactor has been constructed by many researchers (Wang et al., 2006; Warith., 2002; Agdag and Sponza., 2005) to study factors that affect the process in landfill. The accelerated landfill can reduce the biodegradation and stabilization time and also improve the leachate quality. Factors affecting the treatment efficiency of MSW in bioreactors are leachate recirculation, recirculation volume, waste shredding, waste compaction, pH adjustment, aeration, and nutrient and alkalinity additions (Reinhart et al., 1996).

The study carried out by San and Onay (2001) showed that a four times per week recirculation strategy with a pH control provided the highest degree of stabilization. The study by Warith (2002) showed that the highest pH was observed in the pH buffered and nutrient added reactor. It was reported that COD, VFA, and BOD/COD ratios in the leachate samples produced from the alkalinity added reactors were lower than the control reactor while the pH values were higher than the control reactor (Agdag et al., 2005). Sanphoti (2005) studied the effect of leachate recirculation with supplement water addition on methane production and waste decomposition in simulated tropical landfill. The result indicated that anaerobic digestion with leachate recirculation and supplemental water addition showed the highest performance in terms of cumulative methane production and the stabilization period time required.

2.3 Dissolved organic carbon

DOC is organic material from plants and animals broken down into such a small size that it is “dissolved” into water. Some DOC molecules have a recognizable chemical structure that can easily be defined (such as fats, carbohydrates, and proteins) however most have no readily identifiable structure and are lumped under the term humic or tannin substances. These humic or tannin substances also often have natural acids associated with them (which can influence pH levels).

DOC is generated from organic waste in landfill and is a product of anaerobic degradation processes. DOC was defined as the fraction of TOC that passes through a

0.45 μm filter. Christensen et al. (1996), Christensen et al. (1998), and Christensen and Christensen (2000) studied the effect of DOC complexing with Cd, Cu Ni, Pb and Zn in leachate samples. The degree of complexation was determined and the results demonstrated that the organic material has high affinity for complexation of heavy metals. Moreover, this ability was increased by the increasing of DOC concentration. In addition, the complexation ability of DOC is primarily related to its content of functional groups (e.g. carboxylic and phenolic groups) because of their acid-base behaviors. The complexation capacity of DOC with respect to metals depends on the pH of the system (Christensen et al., 2000) including the solubilization behavior of heavy metals. Therefore, pH of the leachate could be the predominant parameter that should be considered.

A significant amount of research has examined the role of DOC on the behavior of trace metals. Studies on HA metal relationships have provided information on a wide range of subjects including sorption characteristics, kinetics, stability constants, bonding mechanisms and modeling. Some researchers (Christensen et al., 2000; Kang et al., 2002) have also examined the effects of pH on the nature of DOC. Karlik (1995) found an increase in humic compounds with increasing pH. Temminghoff et al. (1994) found that the humic/fulvic ratio increases from pH 4.4 to pH 5.7. Many researches have applied the relationships between increasing DOC with increasing pH to the mobilization and speciation of metals in environmental systems. Temminghoff et al. (1997) found increased Cu mobility at both low and neutral pH values in a Cu contaminated sandy soil. They found that at pH 3.9, only 30% of Cu in solution was bound by DOC, whereas 99% of the Cu was bound by DOC at pH 6.6. Naidu and Harter (1998) related Cd mobility to organic ligands. Increasing equilibration time and temperature reduced the mobility of Cd caused by organic matter. Almas et al. (1997) and Jordan et al. (1997) also examined the increased mobility of Pb in the presence of natural organic matter in a sandy soil. They found that peat HA had a higher binding affinity for Pb than peat FA. They also showed the decreased binding of Pb to the sandy soil when DOC was present in column and batch sorption studies.

2.3.1 Characteristic of DOC in landfill leachate.

Christensen et al.(1998) characterized DOC in landfill leachate-polluted groundwater at Vejem landfill, Denmark. They found that FA fraction was about 60% of total DOC with molecular weight 1800 Da, hydrophilic fraction was 30% of total DOC with molecular weight 2100 Da and the humic acid fraction was 10% of total DOC with molecular weight 2600 Da. The O/C ratio for all three fractions was similar. For HA, the O/C ratio indicated a high content of carboxylic group, phenolic groups or carbohydrates. For FA and HyI fraction, carboxylic acids were the dominating functional group, representing about 6 meq/g. The weakly acidic groups in FA and the HyI represented about 1 and 3 meq/g, respectively. The total acidity in FA and HyI fraction accounted for 48-57% of the O/C ratio. In HA, carboxylic groups made up of about 3 meq/g and the weakly acidic groups made up of about 1.5 meq/g. The total acidity was accounted for 29-32% of the O/C ratio. From these results that HyI resembles HA and FA so the distinction between the fractions may be related to the methods only and be of little practical value

Gondar et al. (2005) studied characterization and acid-base properties of FA and HA isolated from two horizons of an ombrotrophic peat bog by using chemical methods and spectroscopic techniques. Comparison of the E4/E6 ratios showed that in the deeper horizon the peat HS remained practically unchanged, whereas the o-alkyl-C content of HA decreased with depth. No variation with depth in the ionization constants of the carboxylic groups or of the phenolic groups was observed. The values of the ratios of the carboxylic/phenolic contents were similar to previous researches.

Gonzalez (2001) studied comparison of the information gained by pyrolytic techniques and Nuclear Magnetic Resonance Spectroscopy (NMR) spectroscopy on the structural features of aquatic HS. The molecular composition of FA and HA fractions from a German natural lake have been characterized by solid state ^{13}C-NMR spectroscopy and on-line Curie-point pyrolysis at 510 ^{o}C both in the presence and the absence of tetramethylammonium hydroxide (TMAH) followed by the separation and identification of the compounds released similar by gas chromatography-mass spectrometry (GC-MS). The results showed that FA fraction does contain less aromatics and more aliphatics than the HA fraction, whereas the content in O-alkyl structures is similar in the two fractions.

Kang et al. (2002) characterized HA and FA fraction from landfill leachate with different landfill ages. The elemental analysis and spectral features obtained from UV/visible, FTIR, and ^{1}H and ^{13}C NMR showed that the aromatic character in the leachate HS was relatively lower than that of commercial HA (Aldrich Co., AHA), and higher in the HS of older landfill leachate. Their fluorescence spectra indicated that HA had a relatively higher content of condensed aromatic compounds than the FA obtained from the same sources, and the spectrum of AHA showed that aromatic compounds may be present in a much more condensed and complex form. Molecular size distribution data revealed that the leachate HA contained a higher percentage of smaller molecules of <10,000 Da, compared with that of the AHA (45-49% vs 33%), and molecular size of the leachate HS had a tendency to increase as landfill age increase. They found that the aromatic character in the leachate HS was lower than the AHA and higher in the HS of older landfill leachate. The degree of humification increased as the landfill age increased.

Nanny and Ratasuk (2002) studied the characteristic of hydrophobic neutral and hydrophobic acid DOC isolated from municipal landfill leachate. The results showed that the acid-precipitated and acid-soluble fraction of hydrophobic neutral and hydrophobic acid DOC are highly aliphatic, with linear and branching moieties, and less oxidized than most terrestrial and aquatic HS.

Persson et al. (2006) studied transformation of DOM in a landfill leachate-A size exclusion chromatography/mass spectrometric approach. It was concluded that the leachate DOM underwent substantial qualitative changes along the investigated gradient at the Vejen landfill, Denmark. The molecular weight decreased, the polydispersity increased, and the aromaticity varied with the lowest values found in the middle of the gradient. The high aromaticity in the end of the gradient may explain the higher DOM binding capacity towards hydrophobic compounds seen earlier in these samples. The DOM seemed to become more similar to FA present in uncontaminated groundwater with respect to molecular weight and polydispersity along the gradient.

Calace et al. (2001) characterized two kinds of municipal landfill leachates derives from ‘old’ and ‘young’ municipal waste landfills on the basis of the molecular weight distribution of the constituents. In the old leachate, the constituents were distributed over a wider range of molecular weights; high molecular weight fractions were present. In young leachate, the fraction is narrower at the lower molecular weight. The results showed that the high molecular weight fractions of old leachates are found to be complex structures formed by condensed nuclei of carbons substituted by functional groups containing nitrogen, sulfur and oxygen atoms; the low molecular weight fractions of leachates are, instead, characterized by linear chains substituted by oxygenated functional groups such as carboxyl and/or alcoholic groups.

2.3.2 Correlation of DOC with metal ions.

Christensen et al.,(1996) investigated the ability of DOC from landfill leachae polluted groundwater to form complexes with the heavy metals cadmium (Cd), nickel (Ni) and Zinc (Zn). The DOC samples originated from the leachate pollution plume at Vejen Landfill, Denmark were studied. The experiments were performed as batch sorption experiments and the metal distribution between the aquifer material and the solution (K_d) was determined. The result showed that DOC from landfill leachate polluted groundwater has the ability to form complexes with Cd, Ni and Zn. The effect of DOC on the mobility of Cd, Ni and Zn had lower importance for the environmental. The constants for complexes increased slightly in the following order Zn < Cd < Ni. At high metal concentration (level of mg/L), the complex formation was lower than at low metal concentrations (level of µg/L)

Christensen et al. (2000) studied the complexation of Cd, Ni and Zn by DOC in leachate-polluted groundwater. The metal-DOC complexation at different DOC concentrations over a range of pH values was measured. The results showed that the complex formation of Cd, Ni and Zn by DOC from landfill leachate polluted groundwater increased with increasing pH.

Impellitteri (2002) studied the correlation of DOM fractions with the desorption of Cd., Cu, Ni, Pb and Zn from 18 Dutch soils. Eighteen Dutch soils were extracted in aqueous solutions at varying pH and analyzed for heavy metals. Extracted

DOC was also fractionation into three operationally defined fractions: HyI, HA and FA. The result showed that Cu and Pb concentrations in solution as a function of extract equilibrium pH are greatest at low and high pH resulting in parabolic desorption/dissolution curves. While processes such as proton competition and proton promoted dissolution can account for high solution metal concentrations at low pH, these processes cannot account for higher Cu and Pb concentration at high pH. DOC increases with increasing pH, concurrently with the increase in Cu and Pb solution concentrations. While the absolute concentrations of FA and HA generally increase with increasing pH, the relative proportional increase is greatest for HA. They also found that HA plays a major role in increasing the concentration of solution Cu and Pb with increasing pH in the 18 soils studies. They also found that in more acidic environment, FA may play a lower role than HA in governing organo-metallic interaction. For Cd, Ni and Zn the desorption/dissolution pattern showed high metal solution concentration at low pH with slight increase in solution concentration at extremely high pH value (pH>10). However, high pH environment would rarely occur in natural.

Weng (2002) studied the complexation of Cu, Cd, Zn, Ni and Pb with DOM in the soil solution at pH 3.7-6.1. The results showed that the DOM complex species are generally more significant for Cu and Pb than Cd, Zn and Ni. The solubility of the metals depends mainly on the metal loading over soil, pH, and the concentration of inorganic ligands and DOM in the soil solution.

2.4 Humic Substances

Organic matter in the environment (soil, sediment and natural water) can be divided into two classes of compounds: non-humic material (e.g. protein, polysaccharides, nucleic acid and small molecules which are sugar, and amino acids), and HS. HS are colloidal macromolecules systems, heterogeneous, polydisperse complex that are poorly understood. They have a yellow to black appearance, and they are believed to be formed from plant and animal residues by microbial decay by the process of humification, which occurs in soils, sediments.

Humic substances was defined by Stevenson, 1994 as ' *A series of relatively high molecular-weight, brown to black-colored substances formed by secondary synthesis reactions; the term is used as a generic name to descrito colored material or its fractions obtainedon the basis of solubility characteristics; thee materials are distinctive to the soil environment in that they are dissimilar to the biopolymers of microorganisms and higher plants*'. This definition provides very little information about the chemical nature, properties and environmental role of HS. However, it clearly sets the view that HS are macromolecule (high-molecular-mass), formed naturally, and structurally similar to microbial and plant biopolymers, but derived by the re-polymerization of the byproducts of biopolymer decomposition.

There is more recent definition of HS by MacCarthy, 2001 as '*Humic substances comprise an extraordinarily complex, amorphous mixture of highly heterogeneous, chemically reactive yet refraction molecules that serve a key role in the Earth's ecological system, produced during early digenesis in the decay of biomatter, and formed ubiquitously in the environment via processes incolcing chemical reaction of specie randomly chosen from a pool of diverse molecules and through random chemical alteration of precursor molecules*'. HS are partitioned into three main fractions; HA, FA, and humin. These classes of HS are operationally defined by their differential aqueous solubility in acidic and alkalinity solutions, not by their structural or chemical characteristics.

Last phase of landfill contains high content of DOC which can be divided in any fractions. DOC can be fractionated as HA, FA and HyI fraction. HA and FA are the part of HS that is a naturally occurring biogenic, that can generally be characterized as being yellow to black in color of high molecular weight. HA and FA can be separated by solubility principle. HA is soluble in alkali (base) and insoluble in acid while FA is soluble in both alkali and acid.

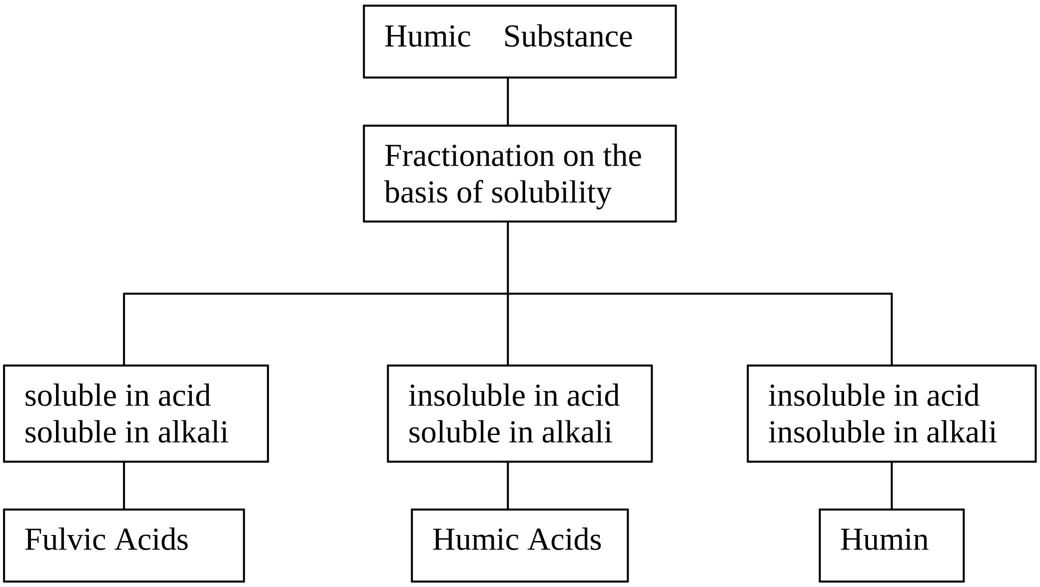


Figure 2.3 Humic substances diagram

2.4.1 Genesis of Humic Substances

Several mechanisms, or pathways, have been proposed to describe the genesis of HS. These are two categories of pathways: (1) those that are purely biological and involve the enzymatic decomposition of biopolymers and the enzymatic recombination of the microbial byproduct; and (2) those that involve the biotic decomposition of biopolymers and the abiotic assemblage of macromolecular structures or aggregates. In the pathway described above, HS are presumed to comprise of macromolecular, polymeric structure. These substances result from condensation reactions that form numerous cross-linkages that involve strongly covalent bonds, such as C-C and C-N bonds. The unaltered portion of the unit will contain aromatic and aliphatic structures and will be relatively non polar or hydrophobic; whereas, that portion of the molecule containing the carboxyl group will be polar or hydrophilic.

2.4.2 Chemical and Structural Characteristics of Humic Substances

HS are most often studied after they have been isolated and purified. Within this framework, a considerable amount of chemical information, such as elemental and functional group composition, has been accumulated. However, the macro structural characteristics of HS remain unknown.

2.4.2.1 Elemental Content

One of the most common means of characterizing HS is to determine the total elemental content. This involves the determination of C, H, O, N and S concentrations in the isolates. The comprising of the HS tends to differ in their elemental characters. Relative to FA, HA generally have greater C and lower O content. The disparity between C and O concentration also results in differences in the O/C mole ratios between the two fractions, with FA having a greater O/C ratio than the HA. The greater oxygen content an O/C ration of the FA is related to the higher concentrations of oxygen containing functional groups, such as the carboxyl group (R-COOH), and to the higher concentrations of carbohydrates in the FA materials. Another distinguishing characteristic of the FA and HA is the H/C mole ratio. The relative magnitude of the H/C mole ratio is used to indicate the degree of aromaticity and unsaturation of carbon chains. Relatively small H/C mole ratios suggest that the HS have a high degree of aromaticity; whereas, larger values indicate a greater abundance of aliphatic structures. Typically, H/C mole ratio for the FA is greater than those of the HA, indicating that the FA have greater aliphatic character than the HA (or that the HA have greater aromatic character than FA). The FA differed from the HA within respect to their mean C, N and O concentrations and O/C and H/C ratios. On average, the FA contain less C than HA, more O, and less N. The O/C mole ratio of FA is also greater than that of the HA.

Table 2.7 Mean Elemental Content (g/kg), O/C and H/C Mole Ratios (mole/mole) of Soil HA and FA Collected from Around the World (Aiken et al., 1985)

Element	HA		FA	
	Mean	Range	Mean	Range
C	562	536 - 587	457	407 - 506
H	47	32 - 62	54	38 - 70
O	355	328 - 383	448	397 - 498
N	32	8 - 43	21	9 - 33
S	8	1 - 15	19	1 - 36
O/C	0.51		0.74	
H/C	1.00		1.42	

2.4.2.2 Functional Groups and Structural Components

The major functional group in HS are oxygen containing and include carboxyl, alcoholic and phenolic, hydroxyls, carbonyls and methoxyls. The HA and FA differ relative to their compositions of oxygen functional groups. As shown on Table 2.8, HS contain approximately equal contents of carboxyl and phenolic groups. Although the carboxyl and phenolic groups appear to dominate, the abundance of alcoholic and carbonyl groups are also highly significant. FA is dominated by carboxyl groups, followed by alcoholic. As a result of the greater carboxyl content, the FA have greater acidity than the HA.

The molecular mass values for the HA ranged from approximately 2000 to 1,300,000 Da. Approximately 75% of the HA had molecular masses in the 20,000 to 50,000 Da range. Less than 20% of the substances were > 100,000 Da in mass. FA is quite small in comparison to the HA. Their masses tend to fall in a very limited range; from approximately 300 to 2000 Da.

Table 2.8 Mean Total Acidity and Functional Group Content (mol/kg) of Soil Humic and Fulvic Acids Collected from around the World (Aiken et al., 1985)

Funtional Group	HA		FA	
	Mean	Range	Mean	Range
Total Acidity	67	56 - 89	103	64 - 142
Carboxyl	36	15 – 57	82	52 – 112
Phenolic-OH	39	21 – 57	30	3 – 57
Alcoholic-OH	26	2 – 49	61	26 – 95
Carbonyl	29	1 – 56	27	12 – 42
Methoxyl	6	3 - 8	8	3 - 12

2.4.3 Humic substance complex formation

A wide variety of organic compounds in natural waters and wastewater can act as complexing agents for metal ions. The nature and extent of metal ion complexation by natural water organics is not well-defined, probably because of the poorly defined nature of these organic compounds and also because of the staggering complexity of these multimetal, multiligand systems.

HS undoubtedly have the ability to combine with considerable quantities of metal ions. For instant, many metals can be enriched into peat from soil waters so that the concentration of the metal in the peat is up to 10,000 times that of its concentration in the water. For this reason, there is no question about the ability of humic materials to combine with metals; it is the nature of the association that is open to question. Two modes of binding appear to be significant. These are (1) the formation of complexes or chelates between the functional groups of the HS and the metal, and (2) an association between the HS and a colloidal particle of metal hydroxide (possibly through sorption on the surface of the particle). The formation of one or another of these associations between humic material and metals may depend on the initial states of HS and metal and their absolute and relative concentrations.The nature of the complexes formed between HS and metals are not known unequivocally. By the blocking various functional groups on the HS and then exposing the modified humic material to metals in solution, it is possible to obtain an idea of which functional groups are important in the complexation of metals. Schnitzer and Khan (1972) reported that at pH 3.5, 75% of the complexed Fe(III), 66% of the Al(III), and 50% of the Cu(II) reacted simultaneously with strongly acidic carboxyl groups and with phenolic groups. A further 8% of the Fe(III), 20% of the Al(III), and 32% of the Cu(II) reacted with more weakly acidic carboxyl groups alone. The experiments also indicated that the alcoholic OH groups were not involved in forming metal complexes.

2.4.4 Humic acid

HA is a typical HS which has high molecular weight and it is not possible to define a detailed molecular structure for HA as it is consisting of non-uniform distribution of functional groups joined by a variety of aliphatic and aromatic units. The stronger acid group was classified as carboxylic to phenolic on aromatic ring. These carboxylic groups (strong and weak) and hydroxyl groups (aromatic and aliphatic) are capable of complexing metal ions.

2.4.4.1 Interaction of trace elements in acid mine drainage solution with HA

Suteerapataranon et al. (2006) studied the release of metal ions from a coal mining area, Lumphun, Northern Thailand by leaching test. Considerable amounts of Mn, Fe, Al, Ni and Co are dissolved in both simulated rain water (pH 4) and 10 mg/L AHA solution (pH7). Due to the presence of oxidizing pyrite and sulfide minerals, the pH in both leachates decreases down to approximately 3 combined with high sulfate concentration typical to acid mine drainage (AMD) water composition. Interaction of the acidic leachates upon mixing with ground and surface water containing natural organic matter is simulated by subsequent dilution (1:100, 1:200, 1:300, 1:500) with a 10 mg/L HA solution (ionic strength: 10^{-3} mol/L). The experiment indicated that metal ions dissolved in AMD may experience either retention or mobilization when released from the source. When diluted in near neutral natural water, metal ions can be kept to a certain degree in solution by HS through complexation. Agglomeration to larger HA aggregates and thus precipitation, sedimentation or attachment to surfaces can predominate under conditions where polyvalent metal ions as Fe(III) and Al(III) saturate the complexing functional HA groups. At very high metal ion concentrations, co-precipitation of Fe-oxy-hydroxide/humic acid may also become relevant.

2.4.4.2 Humic acids and heavy meal binding or complexing capacity.

Madronova et al. (2001) measured the ion exchange properties of HA prepared from oxidized young coals of the North-bohemia coal field. An experiment was done for metals in columns packed with activated HA. Solution containing only one metal (Pb^{2+}, Cd^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+}, Ca^{2+}, Mg^{2+}, Co^{2+}, Mn^{2+}) and solutions containing two and more metals were tested. The penetrating capacities are related to the strength of the bonds measured under static conditions. The results showed that the penetrating capacities of all metals were in these series: $Pb > Cu > Cd > Ni > Co \geq Zn > Mn \geq Ca \geq Mg$. The sorption efficiency of Pb is 100% for this experiment

Ward et al. (2005) investigated heavy metal binding capacity (HMBC) of MSW landfill leachates. MetPLATE was used to determine the HMBC of MSW leachates collected from 14 sites in Florida, with a wide range of chemical and physical characteristics. The potential for MSW leachate to bind with heavy metal was investigated with Cu, Zn and Hg. The HMBC values obtained ranged from 3 to 115, 5 to 93 and 4 to 101 for HMBC-Cu^{+2}, HMBC-Zn^{+2}, HMBC-Hg^{+2}, respectively. In addition, the high strength leachates displayed the highest binding capacities, although the landfills sampled represented a wide range of characteristics.

Brown et al. (1999) studied the simultaneous determination of Ca, Cu, Ni, Zn and Cd binding strengths with FA fractions. The equilibrium binding of Ca^{2+}, Ni^{2+}, Cd^{2+}, Cu^{2+} and Zn^{2+} with unfractionated Suwannee river fulvic acid (SRFA) and an enhanced metal binding subfraction of SRFA was measured using Schubert's ion-exchange method at pH 6.0 and at an ionic strength of 0.1 ($NaNO_3$). Schubert' ion exchange method was rigorously tested by measuring simultaneously the conditional stability constant of citric acid complexed with the five metals at pH 3.5 and 6.0. The log K of SRFA with Ca^{2+}, Ni^{2+}, Cd^{2+}, Cu^{2+} and Zn^{2+} determined simultaneously at pH 6.0 follow the sequence of $Cu^{2+} > Cd^{2+} > Ni^{2+} > Zn^{2+} > Ca^{2+}$ while all log K values increased for the enhanced ,metal binding subfraction and followed a different sequence of $Cu^{2+} > Cd^{2+} > Ca^{2+} > Ni^{2+} > Zn^{2+}$. Both FA samples and citric acid exhibited a 1:1 metal to ligand stochiometry under the relative low metal loading conditions used here. Quantitative ^{13}C NMR showed increases in aromaticity and ketone content and decreases in aliphatic carbon for the elevated metal binding fraction while the carboxyl carbon, and elemental nitrogen, phosphorus, and sulfur content did not change. The more polar, elevated metal binding fraction did show a significant increase in molecular weight over the unfractionated SRFA.

Baker et al. (2005) investigated the complexation of HA from AZraq Oasis with two heavy metal ions Cd(II) and Zn(II) at pH 4 and 5 under constant ionic strength of 0.1 and at different temperatures (25, 35, 45, 55 and 65^{o}C). This investigation was done by using Schubert’s ion-exchange equilibrium method, and its modified version. The result revealed that Azraq HA has a high affinity to form stable complexes with heavy transition metal ions because of the highly oxygenated nature of AZraq HA. The stability constants derived for Cd-humate and Zn-humate were observed to increase with temperature and pH. The metal ion-humate complexation reaction overall was found to be endothermic. The values indicate spontaneous change (ΔG negative) with a large favorable entropy change (ΔS positive) at the two different pHs.

It can be concluded from previous researches that there are three possibilities of binding of humic acid with metal ions:

1. By chelation between carboxyl and phenolic hydroxyl groups.
2. By chelation between two carboxyl groups.
3. By complexation with carboxyl group.

2.4.5 Fulvic acids

The binding or complexing of metal ions by FA in natural water and soils are an important factor in metal toxicity, bioavailability and transport. Complexation can drastically change the biological and physicochemical properties of the trace metal species (Brown et al, 1999). Due to the ubiquitous nature of FA in soils and water, they are important natural complexing agents of metal ions. The molecular functional groups responsible for the observed metal binding have been the subject of many studies and several functional group assembles have been suggested including citric acid, weakly acidic, salicylic acid, and aromatic o-dicarboxylic acids.

2.4.6 Comparison of Humic and Fulvic Acids

Lagier, T. et al., 1999 studied fate of heavy metals trapped in landfill under sulphur species: effects of oxidant and complexant macromolecules by extracting molecule of HA and FA from leachate of municipal landfill according to Thurman and Malcom’s method and characterized by analytical techniques (elemental analysis, NMR ^{13}C, ultrafiltration, UV-visible and FTIR spectrometry). Results of the elemental analysis of HA and FA from leachate can be compared to results found in the bibliography and synthesized by Rice and MacCarthy (1991). Results indicated that HA extracted from leachate have less carboxylic, alcoholic and phenolic groups than FA (O/C smaller so they are more hydrophobic). In saturation degree, H/C denotes a weaker aromaticity for HA. When compare their HA and FA materials extracted from leachate and those extracted from natural origins (Table 2.9).

The analysis of HA and FA from leachate showed similarities between these substances and humic materials of different origins. But some differences can also be noticed: the HS isolated from leachate have higher sulphur and aliphatic carbons content, lower quantities of phenolic, carboxylic and alcoholic groups. The humic like acids from leachate have a high molecular weight (Lagier, 1999)

Table 2.9 Elemental composition of humic like substances extracted from leachate compared to humic substances from different origins (Rice and MacCarthy, 1991)

	Humic Acids			Fulvic Acids			
Origins	leachate	terrestrial	aquatic	leachate	Sewage sludge	terrestrial	aquatic
Samples	1	214	56	1	3	127	63
C%	48.7	55.4	51.2	50.8	40.8	45.3	46.7
H%	5.9	4.8	4.7	6.1	6.6	5.0	4.2
N%	6.3	3.6	2.6	2.5	2.8	2.6	2.3
O%	32.8	36.0	40.4	37.6	42.3	46.2	45.9
S%	7.1	0.8	1.9	2.5	8.1	1.3	1.2
O/C	0.51	0.5	0.6	0.55	0.78	0.78	0.75
H/C	1.47	1.04	1.12	1.43	1.93	1.35	1.10
N/C	0.111	0.055	0.043	0.059	0.059	0.049	0.042

2.5 Mine Tailing

Metal mining, smelting, and processing throughout the world have soils contaminated with heavy metals in the excess of the background concentrations. These processes introduce metal contaminants into the environment through gaseous and particulate emissions, waste liquids, and solid wastes (Dudka and Adriano, 1997). In addition to the soil contamination from these pathways, many mining and smelting sites have considerable surface water and groundwater contamination from heavy metals released and transported from contaminated soil. This contamination endangers water supply resources as well as the economic and environmental health of surrounding communities.

Mine tailings are large piles of crushed rock that are left over after the metals of interest like lead, zinc, copper, silver, gold and others, have been extracted from the mineral rocks that contained them. The mineral separation process, especially in older mining operations, is only partially efficient. As a result, after the crushing and grinding (milling) processes, some of the metal-containing minerals are left behind as small tailings particles.

It is also known that tailings in mining areas are composed of various kinds of mineral containing high amount of heavy metals. Residual waste crushed rock from mining activities represents a major source for metal rich AMD water. The tailing minerals can release metal ions over long time period due to oxidation of sulfide minerals leading to the production of sulfuric acid. Metals in the waste rock can be released by the low pH AMD and possibly be transported by rain water and surface water away from the source. Figure 2.4 shows major stages of mineral production.

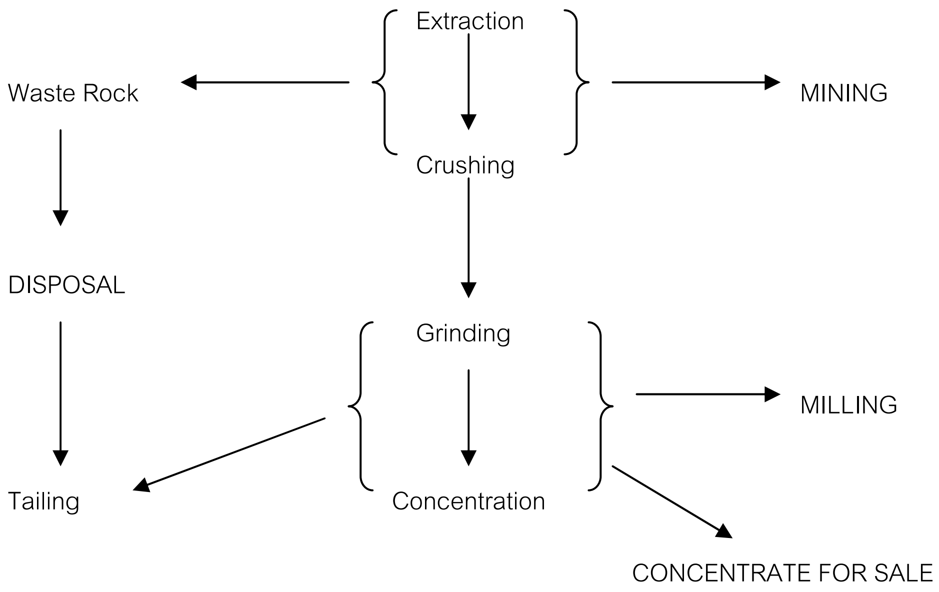


Figure 2.4 Major stages in the production of non-ferrous concentrates

2.5.1 Contamination Problems

Many researchers have studied the contamination problems associated with the presence of metals in soils and aquifers caused by mining activities in various locations (McGregor et al., 1998; Dold and Fontbote, 2001; Al et al., 2000; Romero et al., 2007). The type of contaminants and their concentration in the environment depend on their initial concentrations and, in mining areas, on the nature of the mineral deposit in question. When mine waste (waste rock dumplings, tailings and slags) are disposed of without any environmental control, mining activities may cause greater soil or groundwater contamination. Organic amendments such as biosolids can contribute to the rehabilitation of mineral sand mines and do not constitute a heavy-metal contamination treat to soils or plants (Rate et al., 2004)

The use of column experiments and the application of organic amendments such as cattle manure on mine tailing have also shown the mobilization of heavy metals (Zn, Cd, Pb) by the leaching of Pb-Zn mine waste (Schwab et al., 2007). Laboratory studies with composted sludge have shown that this material has a high affinity of heavy metals such as Pb, with a retention capacity of 15 wt% (Urasa and Macha, 1997). Basta et al. (2001) investigated the effectiveness of lime-stabilized biosolids at reducing the extracability and bioavailability of Cd, Pb and Zn from smelter contaminated soils, and showed that alkaline organic treatments reduced metal extracability and phytoavailability. Also, the use of municipal sewage sludge compost with $CaCO_3$ and red fescue and (*Festuca Rubra*) can stabilize metals in acidic and phytotoxic mine spoils (Simon, 2005).

In the treatment of AMD, laboratory column experiments have proven useful for simulating the effect of biosolids on the reduction of contaminant mobilization. Santibanez et al. (2006) showed the reduction of and NO_3 concentration in a percolate of biosolids mixed with tailing. Waybrant et al. (2002) demonstrated a reduction in Fe (1200-300 to <0.01 mg/L), Zn (0.06-0.01 mg/L), Ni (0.8-12.8 to<0.01 mg/L) and sulfates in pyrite wastes amended with a mixture of wood chips, sawdust, composted municipal sewage sludge and leaf compost.

Similar column experiments, based on a mixture of municipal compost and calcite percolated by mine water simulating the contaminated groundwater resulting from the Aznalcollar mine tailing dam failure, showed the removal of Fe, Al, Zn and Cu. The metal removal was attributed to the precipitation, co-precipitation and sorption of metal oxyhydroxides and carbonates onto the biosolid surface (Gibert et al., 2005). The use of biosolids composed of woodchips and pulp waste as a reactive layer has shown a decreasing in sulfate, Fe and Zn in water in tailing impoundments (Hulshof et al., 2006).

When biosolids are used as reactive layers or permeable reactive barriers, the redox reactions catalyzed by biological processed may remove many inorganic cations or inorganic anions by means of the indirect precipitation resulting from the oxidation or reduction of inorganic cations. Thus, Ag, Cd, Co, Cu, Fe, Ni, Pb and Zn are removed by the precipitation/coprecipitation of these metals as sulfides (Ludwig et al., 2002; Blowes et al., 2000; Mc Govern et al., 2002).

In one current treatment techniques, an organic carbon reactive material is used to stimulate sulfate reduction and the subsequent metal sulfide precipitation (Amos et al., 2004). The H_2S generated in the sulfate reduction, the Fe(II), and other metallic species such as As, Cd, Co, Cu, Ni, Pb and Zn may precipitate, thereby producing sulfide minerals.

2.5.2 Cleanup of contaminated site

The mining industry has to expand continuously to meet the demands of the ever-increasing economic growth. However, contamination of soil by heavy metals, especially those in mine-tailing areas, poses a serious threat to the environment. These heavy metals may adversely affect the soil ecology, agricultural productivity, food chain and water quality. Thus, soil remediation of the mining area is very important nowadays.

In general, the feasible techniques that aim to remove heavy metals from contaminated soils include phytoremediation, microbial remediation and physical-chemical remediation. In the physical-chemical remediation methods, chelating agents are always used to enhance heavy metal removals. These chelating agents remove heavy metals with less impact on soil properties than other decontamination systems, thus show a significant potential to extract heavy metals from the contaminated soils.

Cleanup of contaminated site and disposal of metal-laden wastes are costly endeavor. Many remediation methods involve soil excavation, or in situ treatment including immobilization, mobilization, burial, washing, etc. Although highly effective at lowering risk, remediation technologies based on the excavation, transport, and landfilling of metal contaminated soils and wastes are expensive. More cost-effective techniques treat contaminants in place; however, some of these methods may temporarily exacerbate environmental risks. Soil washing increases metal solubility and mobility to remove metals from contaminated soil profiles. Increasing metal mobility for soil washing of contaminants may also increase the risk for transport and redistribution of contamination to underlying soil and groundwater. Other in situ techniques, such as verification, are often not feasible cleanup methods due to the high costs of energy needed to complete the process.

2.5.2.1 Reduction in Metal Solubility from Inorganic Chemical Treatments

Several types of inorganic chemical treatments have been used to reduce metal solubility in soils. These treatments have been evaluated predominantly using chemical partitioning and mineralogical methods. Alkaline materials used as chemical immobilization treatments include calcium oxides, calcium and magnesium carbonates (limestone), and industrial by-products such as cement kiln dust and alkaline fly ash. Alkaline amendments can reduce heavy metal solubility in soil by increasing soil pH and metal sorption to soil particles (Filius et al., 1998; McBride et al., 1997). Increased sorption of metals to soil colloids can decrease mobile metals in solution and reduce metal transport in contaminated soils. Additionally, increased soil pH and carbonate buffering can allow the formation of metal-carbonate precipitates, complexes, and secondary minerals (Chlopecka and Adriano, 1996). Metal-carbonate minerals formed with addition of carbonate-rich limestone can decrease heavy metal solubility and reduce metal mobility and transport. Phosphate chemical addition to contaminated soils has proven to extremely effective for reducing metal solubility. Experiments involving treatment of metal contaminated soils with rock phosphates have shown that formation of metal-phosphate precipitates and minerals reduced heavy metal solubility.

Reduction in metal solubility or concentration of soluble metal species from chemical amendments through increased sorption or precipitation of insoluble metal minerals are effective means of decreasing metal transport from smelting wastes, mine tailing, and contaminated soils.

2.5.2.2 Reduction in Metal Transport from Chemical Treatments

Most studies investigating chemical immobilization treatments have focused on reducing bioavailability, solubility, or extractability such as sequential extraction. Results from these studies may show reduced solubility and potential decreased metal transport, but few studies have measured reductions in metal transport from chemical amendments to contaminated soils.

Among the chemical treatments, mixed rock phosphate treatment were the least effective for reducing total Cd, Pb, and Zn elution from the contaminated soil. Limestone, although moderately effective for reducing Cd and Pb (45% and 54.8% reduction) was less effective for decreasing Zn in effluent solution. Poor efficiency of the limestone treatment ascribed to the soil system being prebuffered at a near neutral pH, and the slight increase in pH creating modest effects on metal solubility in the contaminated soil. Rock phosphate layered at 180 g/kg was the most effective for reducing Pb transport with a 99.9% reduction over the untreated control. The improved efficiency of the layered RP treatment over mixed treatments was attributed to greater effective surface area that allowed for immobilization of Pb within the rock phosphate matrix. However, DAP was superior to all other treatments for reducing Cd and Zn elution. The 10 g DAP/kg treatment was the most effective for immobilizing heavy metals transported from the contaminated soil, with only 5.4% of Cd, 1.1% of Pb, and 4.2% of the Zn eluted compared with the untreated soil. Increasing DAP from 10 to 90g/kg released As via ligand exchange and elevated total As eluted from 0.13 to 29.5 mg/kg. Peryea and Kamereck (1997) reported similar phosphate-arsenate ligand exchange reaction when investigating the release and movement of As from addition of phosphate fertilizers to arsenate-contaminated orchard soils.

2.5.3 Study of sequential extraction

The use of chemical partitioning or sequential fractionation to determine the concentration of metals present is specific soil chemical fractions has been used to determine plant availability (Chlopecka and Adriano, 1996), plant and human availability (Basta and Gradwohl, 2000), and heavy metal movement in soil profile (Li and Shuman, 1996). In many sequential fractionation schemes, the strength of salts and acids increase incrementally for successive extractions of the same soil sample. Often the fraction referred to as “potentially mobile” is the solution obtained from a weak salt or deionized water extraction. Other fractions are often operationally defined as organic, oxide-bound, or residual fractions. These fractions are typically considered immobile unless specific environmental conditions are induced in the soil environment.

Chemical partitioning of metal fractions to determine metal release and transport from mine- and smelter-waste has been studied by many researchers. Li and Shuman (1996) used a sequential extraction procedure to investigate the movement of metal fractions from a steel production waste into the soil profile. There scheme divided the sequential extractions into five phases: exchangeable, organic, Mn-oxide, amorphous Fe-oxide, crystalline Fe-oxide, and residual. Soils were sampled at incremental depths within the profile and subjected to the sequential fractionation scheme. For the distribution of metal in the soil profile below 30 cm, the exchangeable Zn fraction became the dominant fraction. Furthermore, soil samples at 100 cm, which indicated that Zn, Cd and Pb movement in the soil profiles was minimal. This minimal movement was attributed to Cd and Pb sorption to the organic fraction, which prevented excessive downward movement into the soil profile.

Abdel-Saheb et al. (1994) also used a sequential extraction scheme to understand the plant availability and runoff loss potential of heavy metals mine tailing. Their research attributed the exchangeable (0.01 M $CaCl_2$) and sorbed (water soluble) fractions as being the most susceptible to plant uptake and leaching. Their results indicated that Zn was relatively immobile near the tailing piles but increased in mobility with distance away from the tailing piles. This phenomenon was attributed to the high pH present in the tailing piles that buffered the system decreased in soil pH with distance from the tailing piles. Greatest concentrations of Cd, Pb, and Zn were found in the sulfide fraction, indicating that a large percentage of these metals were present as sulfide minerals with little weathering or oxidation since extraction as ore.

2.5.4 Heavy metal leaching from mine tailing as affected by organic amendments.

Andres and Francisco (2008) conducted the column experiments to investigate the removal of heavy metals from two mine tailing (El Arteal and Jaravias) using sewage sludge as a reactive material. Sewage sludge is used as reactive material on the El Arteal tailings, Fe, Mn, Zn and Pb are removed and Cu and Ni are mobilized. The experiments carried out on the Jaravias tailing give similar results, showing the retention of Cu, Pb, Fe and Mn the mobilization of Ni and Zn. An analysis performed using the PHREEQC numerical code suggests that the retention of Fe in the sewage sludge may be caused by the precipitation of $Fe(OH)_{2.7}Cl_{0.3}$ and possibly pyrite, and that the retention of Pb at high pH may be caused by the formation of stable phase minerals such as $Pb(OH)_2$ and PbS in these conditions. Ni mobilization in the column experiments with the two tailings samples may be caused by the presence of significant amounts of leachable Ni in the sewage sludge. The complexation of metals with DOM, calculated with the MinteQ model, may be moderate.

Schwab et al. (2007) conducted a column experiments to investigate Zn, Cd and Pb leaching from mine tailings as affected by the addition of organic amendments. Composted yard waste, composted cattle manure, and cattle manure aged for one month increased heavy metal leaching from mine tailings when compared to an unamended control. They found that aged cattle manure and composted cattle manure significantly increased Zn concentration in the leachate. The maximum Zn concentration in leachate from the manure-amended treatments was as high as 3.7 mg/L, where as Zn concentrations from the control were less than 0.7 mg/L. All organic amendments increased Cd leachate concentrations. The presence of aged cattle manure greatly increased Pb concentrations in the leachate from less than 10 µg/L for the control treatment to higher than 60 µg/L. Lead concentration in leachate was positively correlated with inorganic carbon, total organic carbon, total carbon and bicarbonate. An increase in Pb leaching due to the addition of aged cattle manure may be due to:(1) complexation between Pb and water soluble organic matter and (2) increase in solution pH accompanying the addition of the manure.

2.5.5 Soil washing by various agents

The clean-up of soils contaminated with heavy metals is one of the most difficult tasks for environmental engineering. Many techniques have been developed that try to remove heavy metals from contaminate soil, including ex-situ washing with physical-chemical methods (Anderson, 1992) and in-situ phytoextraction. In the ex-situ washing methods chelating agents of acids are used to enhance heavy metals removals. Ethylenediaminetetraacetic acid (EDTA) is the most commonly used chelate because of its strong chelating ability for heavy metals. Laboratory studies have shown that EDTA is effective in removing Pb, Zn, Cu and Cd from contaminated soil, although extraction efficiency depends on many factors such as the ability of heavy metals in soil, ionic strength of EDTA, electrolytes , pH and soil matrix (Sun et al., 2001). After soil washing, EDTA may be recovered and reused through reactors of metal-EDTA complexes. Most of these studies used bath extractions with rather high solution-to-soil ratios whereas in large scale operations it would be more practical and economical to use soil column or heap leaching.

Apart from ex-situ washing techniques, some of the in-situ phytoremediation methods also use chelating agents to enhance heavy metals availability in soils. For, example, the use of EDTA has been shown to increase the concentration of soluble Pb in Pb contaminated soils and subsequently enhance Pb uptake by plants with high biomass production, such as Indian mustard or maize (Huang et al., 1997). On the other hand, chelate agents produce side effects in the assisted phytoextraction caused by the slow biodegradation in soil. Their action persists after plants harvesting, including toxic effects in the new crop and contributing to the dispersion of metals in soil profile.

2.6 Heavy Metal

Unlike organic chemicals and plastics, metals generally cannot be degraded chemically or bacteriologically into simpler constituents, such as carbon dioxide and water, which are relatively neutral environmentally. Metals occur naturally in a wide range of economic concentrations in the ground from approximately 0.05% for uranium, through 0.5 – 1 % for copper, to approximately 60% - 70% iron, and invariably occur in admixture with a wide range of minor and trace metals.

Heavy metals can be toxic to soil microorganisms if present in high concentrations. Heavy metal pollution was negatively correlated to microbial population and activity (Baath, 1989). Observed effects include reduced microbial activity, decreased litter decomposition and reduced nitrogen transformation.

Adsorption/desorption and precipitation/dissolution reactions control heavy metal accumulation in the soil profiles, metal transport to the groundwater, and bioavailability for plant uptake. Quantifying sorption is a critical aspect of predicting chemical behavior of a metal is soils. Adsorption can be affected by many factors such as pH (Stahl and James, 1991), cation exchange capacity, insoluble organic matter and clay content, competition from other metal ions, and soluble organic and inorganic ligands. The presence of soluble organic ligands in soil may significantly influence metal adsorption through the formation of stable complexes.

Schwab (2005) studied the influence of organic ligands on the retention of lead in soil by studying the effect of citrate and salicylate on the leaching of lead in soil in a laboratory experiment. Adsorption of Pb to soils can be affected by the presence of citrate and salicylate due to formation of metal-ligand complexes either on the soil surface or in the solution phase. Lead adsorption decreased with increasing citrate concentration because formation of surface complexes of Pb-citrate could not compete with stable solution complexes. In contrast, increasing concentrations of salicylate complex in solution resulted in increased sorption to the soil. Considering the extreme conditions required to induce Pb leaching, it is likely that Pb will remain relatively immobile in soil even in the presence of a strong complexing agent such as citrate

In vegetated soil, the effects of soluble organic ligands on the adsorption of heavy metals to soil may be important because plant roots and soil microorganisms continually produce organic acids throughout their life cycles. Some of these organic acids are very strong complexing agents for metals, but the influence of the organic ligands on heavy metal adsorption is not completely understood. In heavy metal-contaminated soil, vegetation can significantly affect metal adsorption and hence mobility. If a ligand strongly complexes with Pb in solution, the presence of this ligand has the potential to reduce sorption to soil and increase leaching (Benyahya and Garnier, 1999). Ligands that sorbed to soil may increase ternary soil-ligand-metal complexes. Organic ligands do not always reduce adsorption of heavy metals to soil (Schwab et al., 2005). Adsorption of organic anions can increase the negative charge on soil surfaces providing more sites for metal adsorption. In some cases, organic ligands have increased heavy metal adsorption to soils.

When complexing organic ligands are presented in metal-contaminated soil, a number of reactions are possible. The net impact on metal retention will depend upon the relative strength of the solution and the surface complexes formed. The first reaction is the solid phase that controls metal concentrations in solution. Lead is known to form sparingly soluble, discreet solid phases. Therefore, if an organic complexing agent is to have a significant impact on the total Pb in solution, Pb^{2+} must bind strongly with the ligand.

2.6.1 Lead (Pb)

Lead is a common contaminant of soil and considered to be a risk to human health when soil concentrations exceed 400-500 mg Pb/kg soil. Lead may contaminate soil through vehicle exhausts, sewage-sludge biosolids, mining, and smelting. Highly contaminated soils may have Pb concentrations> 10000 mg/kg. Toxicity from Pb-contaminated soils primarily occurs from direct ingestion. Symptoms of lead poisoning in adults include irritability, poor muscle coordination, nerve damage, increased blood pressure, hearing and vision impairment, and reproductive disorders. In children, lead poisoning can cause brain damage, mental retardation, behavioral problems, anemia, liver and kidney damage, hearing loss, hyperactivity, development delays, and other physical and mental problems.

Jing (2004) studied lead leachability in stabilized/solidified soil samples evaluated with different leaching tests. The results showed that: (1) the main factor controlling the Pb concentration in the leachate is the final pH ;(2) the final pH is a function of the leachate acidity; and (3) for a given final pH, the type of leachant has a relatively minor effect on leachability. The diffuse layer adsorption model, aqueous and precipitation reactions were employed in the MINTEQA2 program to describe the Pb leaching behavior. Both leaching tests and model simulations indicate that the Pb leaching behavior can be divided into three stages based on the leachate pH: a high alkalinity leaching stage at pH>12, where Pb formed soluble hydroxide anion complexes and leached out; a neutral to alkaline immobilization stage in the pH range of 6-12, which was characterized by low Pb leachability caused by adsorption and precipitation; and an acid leaching stage with pH<6, where the acid neutralizing capacity of the stabilization/solidification materials was totally consumed and therefore free Pb-ion leached out.

2.6.2 Factors affecting metal partitioning in soils

The most important variables affecting metal partitioning in soils in nature are the same factors that affect desorption/dissolution of metal in soils. Metals on soil solids may enter the soil solution by desorption or dissolution. Metal precipitates, which may be present at higher concentrations of metal in soil, will dissolve to maintain equilibrium concentrations in the solution phase. Desorption processes primarily depend on the characteristics of the solid, complexation of the desorbing metal, system pH, the ionic strength of solution, the type and species of possible exchanging ions in solution, and kinetic effects.

2.6.2.1 pH

Soil pH is considered the master variable concerning metal behavior in soil systems and is the most important factor affecting metal speciation is soils. Generally, desorption of metals is increased as pH decreases. Thus, metals tend to be more soluble in more acidic environments. Solubility of metals may increase at higher pH due to binding with dissolved organic matter (DOM). The solubility of soil organic matter (SOM) increases with pH increase.

Soil solids with pH-dependent charge tend to deprotonate with increasing pH. Metals in solution can then react at these negatively charged, deprotonated sites.

There is also less proton competition for fixed charge sites at higher pH values. Both of these factors contribute to increasing desorption of metals with decreasing pH.

2.6.2.2 Ionic Strength

Increased ionic strength in solution generally decreases sorption of cations in soil systems, assuming that surfaces are negatively charged. This results in an inverse relationship between ionic strength and K_d. Egozy (1980) found that Co distribution coefficients decreased as soil solution salt concentration increased. Theoretically, as ionic strength increases, the reactive layer for cation sorption decreases in thickness. Di Toro et al.(1986) found the same results, but the ionic strength effects were overshadowed by high particle concentrations in the batch extractions of quartz.

2.6.2.3 Kinetic Effects

Rarely do rates of adsorption equal rates of desorption for metals on soil surfaces. Usually, rates of desorption are much slower than rates of adsorption. This phenomenon could result from a number of processes. The reverse reaction would theoretically require high activation energy (E_a) to occur and may not be thermodynamically favorable. Sorbed metals may undergo rearrangement on the sorbing surface. Backers et al. (1995) suggested that desorption of Cd and Co from Fe-oxides slowed with time due to the movement of the sorbed metals to sites exhibiting slower desorption reactions.

2.6.2.4 Soil Solid Characteristics

Primary minerals such as quartz, feldspar, secondary minerals such as clay minerals, metal oxides (which may be primary or secondary minerals), and organic matter compromise the majority of soil solids. Desorption of metals from clay minerals may be governed by system pH for minerals with predominantly pH dependent charge, such as kaolinite. System pH will be less important for clay minerals. The location of the sorbed metal on or in the clay mineral also plays a role in desorption. Backes et al. (1995) found that Cd and Co desorption occurred much more readily on Fe-oxides compared with Mn-oxides. Metals incorporated into the structure of recrystallized oxides may reduce the desorption of metal from solid to solution. SOM can sorb or chelate metals. Desorption of metals from organic matter is pH dependent as the main functional groups (carboxylic and phenolic) on SOM exhibit pH-dependent charge (Sparks, 1995). SOM may have a greater impact on soils with low inorganic cation exchange capacity (CEC). Elliot et al. (1986) found that removal of SOM from soils reduced sorption of Pb, Cu, Cd and Zn but only sorption of Cu and Cd were reduced upon removal of SOM from a soil with high inorganic CEC.

2.6.3 Heavy Metal Extraction

Several chemical reagents such as EDTA, nitrilotriacetic acid (NTA) and diethylenetriamine pentaacetic acid (DTPA), are widely used in soil science for different purposes. The complexing ability of these reagents has been involved for the solubilisation of heavy metals from contaminated soils in soil cleaning procedures. Of course, EDTA has broadly been used as a predictor of heavy metal bioavailability and in soil remediation processes. In soil-cleansing procedures, many investigators revealed its application in an increase of metal solubility. Moreover, the ion exchanger resins, could be used as ion sinks for collecting the metals once they are extracted in the soil solution by EDTA.

2.6.3.1 Correlation of heavy metal and Landfill Leachate

Leachate can play an important role in the complexation of heavy metals. Fractionation of this effluent by different techniques (ultrafiltration and XAD resins) shows that high molecular weight molecules are the most important for two reasons. Firstly, they represent more than 50% of organic carbon in leachate (in landfill which are more than 10 years old). Secondly, they have high complexant capacities; and they are able to play an important role on other environmental questions namely the transfer of inorganic pollutants.

The second variable which can play an important role in the remobilization of metal is the redox potential. The introduction of oxidant species avoids the oxidation of reduced sulphur species (as the pyrite) and the solubilization heavy metals. The oxidation of pyrite is also well known to generate AMD.

2.6.3.2 Correlation of metal ions with humic acids extracted from other sources.

Martyniuk (2003) studied the adsorption of metal ions on humic acids extracted from brown coals in solid and gel forms. The result showed that both type of humic acids selectively adsorbed lead ions, whereas gel forms of humic acids were selective adsorbers of Cr^{+3} and Al^{+3}. At, higher pH solutions, there was a sharing of COOH groups in metal ions bonding. The Pb, Ag, Hg, and Cu ions are exceptional because even at low pH reaction of the solution (<5) they are bounded with phenolic groups as well. Only these metal ions were able to form complex with carboxylic and phenolic groups of humic acids.

Sarathy and Allen (2005) studied the complexation of Cu by DOM from surface water and wastewater effluent and compared with the Windermere Humic Aqeous Model (WHAM) version VI. They found that DOM from both sources has ligands with similar proton binding. The concentration of weak proton binding ligands was around 15 times higher in the wastewater than in surface water. There is an existing of non-humic materials in wastewater effluent that bind to copper.

Plaza (2005) studied the complexation by HA and FA from pig slurry and amended and non-amended soils. The results showed that the Cu(II) binding affinity of HA is generally larger than that of the corresponding FA. Comparing to control soil HA, pig-slurry HA and FA had a much smaller binding capacity and stability constant. Therefore, pig-slurry application to soil decrease the Cu(II) binding affinity of soil HA and FA.

Janos et al. (2002) studied the leachability of some metals (Al, As, Ba, Ca, Cr, Cu, Fe, K, Mg, Mn, Ti, Zn) from fly ashes in the present of EDTA and naturally occurring complexing agents, HA. The study showed that the leaching of metals from granular solid wastes is a relatively quick process, in which equilibrium is attained within several hours. Complexing agents strongly influence the leachability of metals from fly ashes and, in most cases, increase significantly the amounts of pollutants released into the environment. This is also true for naturally occurring complexing agents such as HS. The presence of HS usually increases the mobility of metals in environment.

2.7 EDTA

EDTA is one of the major chemical reagent used to extract trace elements from soils samples in order to predict their bioavailability or mobility (Ure, 1996; Shuman, 1985; Lake et al., 1984). EDTA has also been used for many years as a chelating agent for supplying micronutrient cations for plants. Lastly, this species may also be used to remediate contaminated soil. On the other hand, EDTA is one of the most widely used industrial complexing agents (photographic industry, textile and paper manufacturing, industrial cleaning) and persists as a major pollutant in rivers and groundwaters (Novack et al., 1996). The unusual property of EDTA is its ability to chelate or complex metal ions in 1:1 metal-to-EDTA complexes.

The clean-up of soils contaminated with heavy metals is one of the most difficult tasks for environmental engineering. A number of techniques have been developed that aim to remove heavy metals from contaminated soil, including ex-situ washing with physical-chemical methods and in-situ phytoextraction. In the ex-situ washing methods, chelating agents or acids are used to enhance heavy metals removal. EDTA is the most commonly used chelate because of its strong chelating ability for different heavy metals. Previous researches (Elliot and Brown, 1989; Brown and Elliot, 1992, Heil et al., 1999) have shown that EDTA is effective in removing Pb, Zn, Cu and Cd from contaminated soils, although extraction efficiency depends on many factors such as the lability of heavy metals in soil, the strength of EDTA, electrolytes, pH and soil matrix.

In comparison with other chelating agents, EDTA presents the following advantages: a low degree of biodegradability in soil and moreover a high level of complexing capacity with respect to heavy metals. The chelating agent EDTA not only can form soluble complexes with metals but may also influence the distribution of metals in the fractions by moving metals from less water soluble fractions to more soluble fractions.

EDTA was patented in Germany in 1935 by F. Munz. The molecule is a substituted diamine usually marketed as its sodium salts. It is a powerful complexing agent of metals and a highly stable molecule, offering a considerable versatility in industrial and household. EDTA is a chelate ligand with a high affinity constant to form metal-EDTA complexes, being deliberately added to sequester metal ions.

EDTA is a novel molecule for complexing metal ions. It is a polyprotic acid containing four carboxylic acid groups and two amine groups with lone pair electrons.

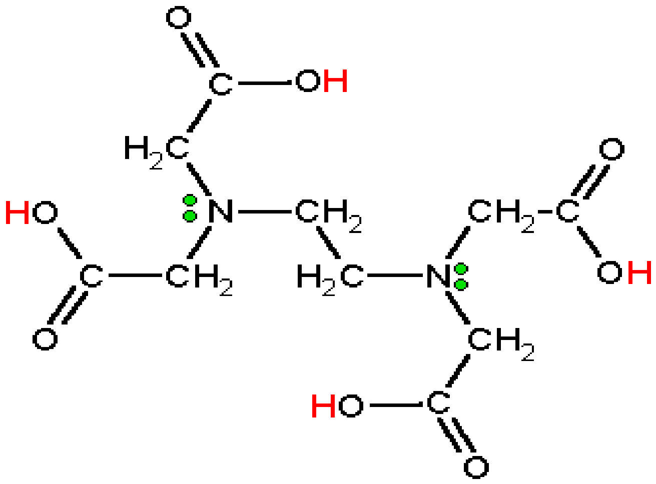


Figure 2.5 EDTA chemical structure

The extraction efficiency of heavy metals by EDTA has been reported to be strongly dependent on the source of heavy metal contamination in the soil and on metal distribution among the soil fraction. The release of metals from contaminated soils depends not only on the extraction conditions (such as, pH, reagent concentration), but also on the modes of metal retention within the soil. Consequently, metal reactivity and behavior towards the extracting solution also depend on the nature of the metal fixation on the soil particles, which can be operationally measured by application of sequential extraction procedures. Weakly sorbed fractions (i.e., exchangeable and carbonate) could be readily extracted, but an effective extraction of strongly sorbed metals in oxide and residual fractions was not always guaranteed within different soil types and contamination sources.

Garrabants and Kosson (2000) recently studied using EDTA s a leaching agent to determine the metal availability from soils and solid wastes. The leachability of As, Cd, Cu, Mn and Pb was compared with the availability test at pH 7 and 4. Various chelating agent such as EDTA, NTA and DTPA were suggested for a pretreatment and detoxification of fly ashes (Hong et al., 2000). The leaching tests on the residues after the treatment with the chelating agents showed that the fly ashes were successfully detoxified to meet the guideline for landfilling.

Barona and Romero (1996) extracted Pb contaminated soil with EDTA and observed that the amount of Pb that was removed correlated with the amount of Pb associated with the Fe and Mn-oxide and organic matter soil fraction. Wasay et al. (1998) studied speciation of metals in polluted soils and found that most of the heavy metals were found to be bound to Fe-Mn oxides and the organic fraction (30-40%) except for Cd and Zn, which were mainly present on the exchangeable fraction (63-87%). Li and Shuman (1996) also found that the concentration of Zn in the Fe and Mn oxide fractions was not affected by EDTA probably because of the high association of Zn with the oxides. Basta et al. (1993) concluded that Cd complexation by organic matter was important for Cd retention.

Sun et al.(2001) studied the extraction of Zn, Cd, Cu and Pb from four contaminated soils by using EDTA in batch and column experiments. They found that EDTA extracted the four heavy metals with similar efficiency. In contrast, different elution patterns were obtained for Zn, Cd, Cu and Pb in the column leaching experiment using 0.01 M EDTA. Cu was either the most mobile or among the most mobile of the four heavy metals, and its peak concentration corresponded with the arrival of full strength EDTA in the leachate. The mobility of Zn and Cd was usually slightly lower than that of Cu. Pb was the least mobile. It is likely that the lability of metals in soil played a more important role in determining the elution pattern. Pb is usually the least labile in soils among the four heavy metals studied, and this is reflected by its slowest elution. In contrast, the proportion of soil total Cu that is associated organic matter is usually higher than for other heavy metals. Organically bound metals may be more labile than mineral bound metals. The other explanation for the different elution patterns between the four heavy metals may be the differences in the kinetics of metal desorption/dissolution. They also found that the ratio of heavy metals leached to the EDTA added decreased when the molar ratio of EDTA to total heavy metals in soil increased. This means that the heavy metals extraction efficiency of EDTA decreases with increasing ratio of EDTA to total heavy metals in soil.

Xia et al.(2008) found that the high extractable efficiency of heavy metals in soil samples by EDTA suggested that EDTA have the potential to remediate tailing soils. This is likely to be related to the strong complexing capacity of EDTA with respect to heavy metals and the formation of the stable 1:1 metal-EDTA complexes. Percentage extractabilities of metal followed the sequence of Cd > Zn > Cu > Pb. Previous studies showed that pH influenced the extraction of heavy metals by EDTA only in the acidic range (pH<5). The removal of greater amounts of toxic metals has most often been observed at lower pH levels. The formation of complexes in soil is controlled by the kinetic of all complexation reactions, adsorption in soil solid phases, mineral dissolution and the possible degradation of the chelating agent or its metal complexes. These interactions are difficult to predict and depend on the contaminants and soil conditions.

CHAPTER III

EFFECT OF ALKALINITY ON PERFORMANCE OF SIMULATED BIOREACTOR OF FRUIT AND VEGETABLE WASTES

Abstract

The purpose of this study is to simulate leachate from market waste (fruit and vegetable waste) and investigate the leachate properties changes with degradation phases. Pilot scale bioreactor was conducted and filled with fruit and vegetable waste. Interested parameters, for example, pH, ORP, COD, biogas production, biogas composition etc. were measured. When the degradation process in the reactor proceeded, the degradation time was longer than expected because of unsuitable circumstance for anaerobic bacteria. Therefore, alkali addition and leachate recirculation was introduced to enhance degradation process. The results showed significant changes for many parameters such as methane production, COD indicated methanogenesis was reached. The remarkable positive effect of alkalinity was observed with all parameters of the system. There was no methane production before alkali addition.

Keywords: Alkalinity, Anaerobic, Bioreactor, Leachate

3.1 Introduction

Thailand generates over 39,240 tons/day of municipal solid waste of which more than 40% is food waste (PCD, MNRE, Thailand, 2003). Most of MSW goes to landfill disposal or open dumping which seems to be suitable and less expensive for Thailand’s situation. One majority of organic waste is fruit and vegetable waste especially waste from markets which are normally disposed of on site. Fruit and vegetable wastes are relatively free of contaminants as compare to street collection waste, household or industrial waste. Furthermore, fruit and vegetable waste contains a high content of organic carbon. Therefore, fruit and vegetable waste were used as a source to study enhancing biogas production rate in an anaerobic digestion process. Because of high moisture content, vegetable and fruit waste not only give a high yield of biogas but also provide a large volume of leachate. This high volume of leachate should be used further to enhance the bioreactor’s performance and also to reduce the environmental impact of food wastes. Therefore this study was part of leachate production for leachate utilization in our other experiment.

Anaerobic digestion is a preferred treatment method for degrading highly putrescible waste streams such as food waste due to its high methane potential (Dearman et al., 2006). Anaerobic digestion of the organic solid waste, especially the organic fraction of MSW, is very important in the field of landfill management. The landfill can be converted into a controlled bioreactor system by using leachate containment, collection and circulation. Compare to conventional sanitary landfills, landfill bioreactors could provide the potential for more rapid, complete and predictable attenuation of solid waste constituents, enhance the recovery and utilization of gas and reduce environmental pollution (Pohland and Al-Yousfi, 1994). Food waste has a high potential for methane production depending on the type of food used (Lay et al., 1997). It can be digested rapidly making it a good source of material for anaerobic digestion (Bouallagui et al., 2004; Lay et al., 1997). However, acid production lowers reactor pH inhibiting the methanogenic system and limiting the generation of significant amounts of methane (Vavilin et al., 2006). Although fruit and vegetable waste can generate high yield of biogas, the large amount of organic acid production can inhibit the methanogenesis phase in landfilling process.

Generally, anaerobic digestion of landfill can easily become imbalanced, which is called ensiling problem, even with the most advanced leachate management practice (Pohland and Al-Yousfi, 1994, Delia and Osman, 2004). The ensiling problem is caused by inhibited anaerobic microbial activity which leads to inhibitory fermentation products consisting primarily of VFA (Pohland, 1980). The imbalance between acidogenesis and methanogenesis in the landfill is the main reason for this ensiling problem. The anaerobic landfill of leachate circulation only would accelerate organic matter hydrolysis and convert them into organic acids without solving the imbalance perfectly. VFA, mainly composed of acetic acid, propionic acid and butyric acid in landfill bioreactor, are the important intermediates of the anaerobic biological process, which result in a decrease of pH, eventually leading to the ensiling problem. Therefore, an important parameter to cause the imbalance problem in an anaerobic digester is either the high concentration of VFA or high acidification percentage (Weiland and Rozzi, 1991).

Factors affecting the treatment efficiency of MSW in bioreactors are leachate recirculation, recirculation volume, waste shredding, waste compaction, pH adjustment, aeration, and nutrient and alkalinity additions (Reinhart et al., 1996). The alkalinity of water is a measure of its capacity to neutralize acids and is due primarily to the salts of weak acids (Agdag and Sponza, 2005). If the acid concentration exceeds the available alkalinity, the landfilling bioreactor will sour. This will be severely inhibiting the microbial activity, especially the methanogens. When methane production ceases, the VFA may continue to accumulate. Methanogens prefer nearly neutral pH conditions with a generally accepted optimum range of approximately 6.5-8.2 (Anderson and Yang, 1992). In the study realized by Warith (2002), it was shown that the highest pH was observed in the sludge added reactor and a highly reduced COD was observed in the pH buffered and nutrient added reactor. The study carried out by San and Onay (2001) showed that a four times per week recirculation strategy with a pH control provided the highest degree of stabilization. Dinamarca et al. (2003) studied the influence of pH on the anaerobic digestion of the organic fraction of the urban solid waste in a two phase anaerobic reactor. The higher degradation of total suspended solid and volatile suspended solid was obtained in the reactors operated at pH 7 and 8

The continuous hydrolysis of solid waste, followed by the microbial conversion of biodegradable organic content result in the production of intermediate VFA at high concentrations. In the methane fermentation phase, the pH value is elevated, being controlled by the bicarbonate buffering system (Reinhart and Al-Yousfi, 1996). A balance between acid production and acid consumption is essential for a stable anaerobic process running at the highest possible rate. Plaza et al. (1996) showed that, pH was controlled by the addition of sodium bicarbonate as a buffer at a minimum buffer/substrate ratio of 0.06 kg/kg total solid. Adequate alkalinity, or buffer capacity, is necessary to maintain a stable pH in the digester for optimal biological activity. An alkalinity level ranging from 1,000 to 5,000 mg $CaCO_3$/L was recommended by Tchobanoglous and Burton (1979). Alkaline pretreatment in the anaerobic digestion of co-mingled MSW significantly increases the biodegradability of the waste mixture (Hamzawi et al., 1998)

There are many studies on increasing the degradation rate of waste by leachate recirculation and alkalinity addition but there are limited literatures on alkalinity addition of fruit and vegetable waste in simulated bioreactor. The purpose of this study is to simulate leachate from fruit and vegetable waste with pilot scale bioreactor. In addition, the study of alkalinity addition affect to the waste degradation rate was also conducted. This study monitored parameters such as pH, VFA, oxidation reduction potential (ORP), gas production and methane yield.

3.2 Material and methods

3.2.1 Lab-scale simulated landfill bioreactor

Two reactors used in this study were cylindrical and made from PVC. These reactors had a diameter and length of 0.25 m and 0.5 m, respectively. The reactors were operated in batch mode at room temperature (30–38 ^{o}C) under anaerobic condition. The top of the reactors were covered with PVC plate and rubber seal to prevent flow of air to create anaerobic condition inside the reactors. A leachate drainage, leachate collection system, leachate recirculation pumps and gas collection system were utilized to simulate landfill bioreactors. The leachate was collected from the bottom part of the reactor and the effluent was recycled back to the top of the reactor with a peristaltic pump. There are three separate ports on the top of each reactor for measurement of gas production, for recirculation of the leachate and for gas sampling. Before filling with wastes, 5 cm thick layer of coarse gravel was placed at the bottom of each reactor. A circular nylon screen with 5 mm diameter holes was placed on the top of the gravel layer to prevent loss of solid waste through bottom pipe and also prevent clogging the collecting pipe. The gas produced from the reactors was collected and its volume measured by using the inverted cylinder technique. The diagram of simulated bioreactor is shown in Figure 3.1. The picture of reactors is presented in Figure 3.2.

3.2.2 Fruits and vegetables waste preparation

Fruit and vegetable wastes were prepared the same composition as the representative of Si-Mum Muang Market, Thailand (Chewha, 2003). The waste composition is shown in Table 3.1. The fruit and vegetable wastes were shredded in small pieces by hand into 1-2 cm and mixed together to enhance the homogeneity of waste. The shredded waste was mixed with 1 L of anaerobic digested sludge obtained from wastewater treatment plant of Utility Business Alliance Co., Ltd. to enhance the rate of stabilization, degradation and gas production.

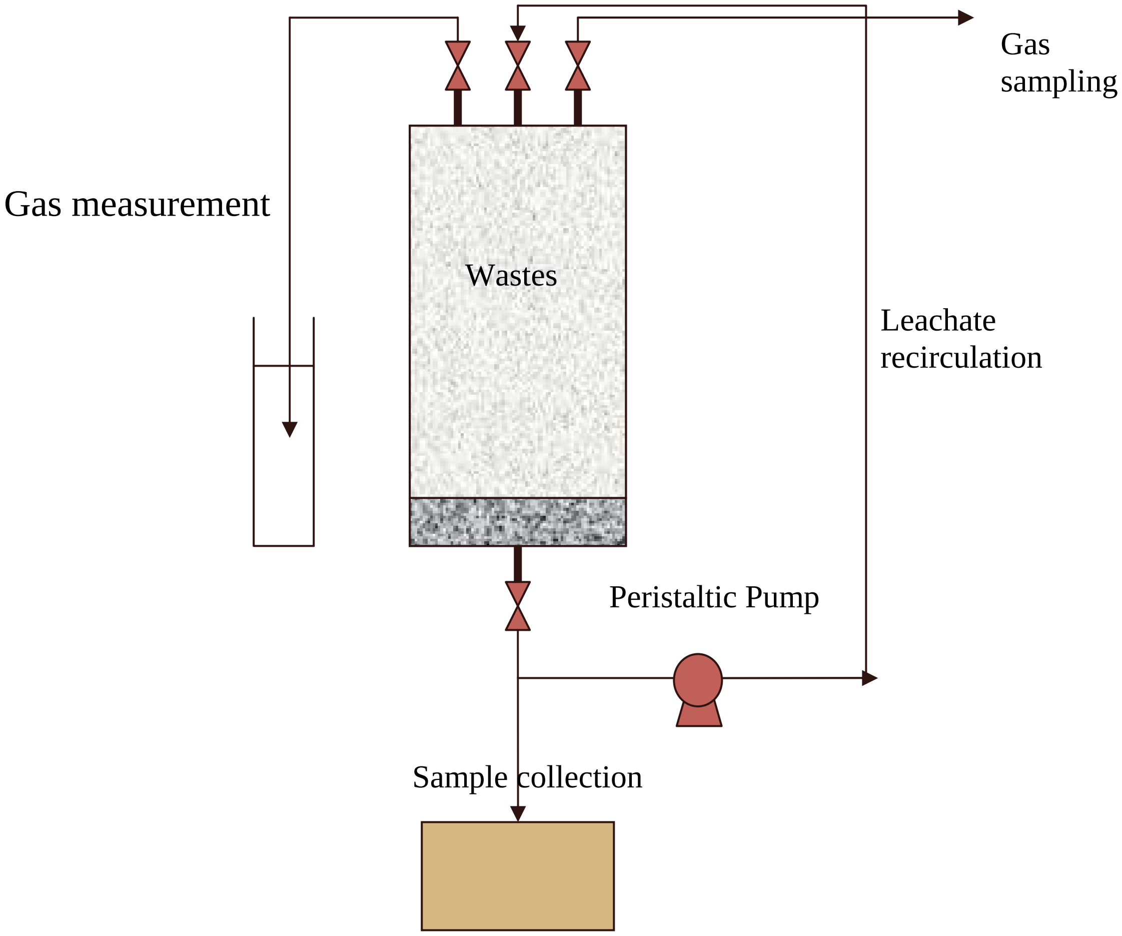


Figure 3.1 Diagram of simulated bioreactor

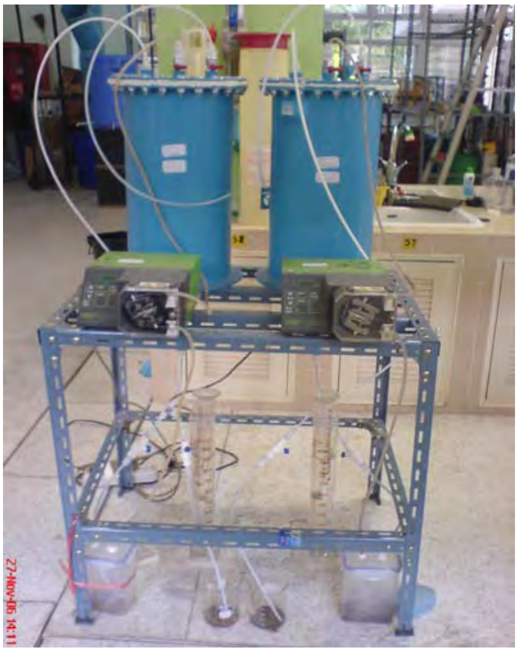


Figure 3.2 Reactors of the experiment

Table 3.1 Synthetic waste composition

Fruits and vegetables	Total weight (wet/kg)	Percentage (wet weight)
Chinese White cabbage	0.937	12.5
Morning Glory	0.8625	11.5
Egg plant	2.3625	31.5
Kale	0.75	10.0
Cow Peas	0.9375	12.5
Water mimosa	0.225	3.0
Cabbage	0.225	3.0
Chinese Cabbage	0.15	2.0
Bitter Cucumber	0.1875	2.5
Banana	0.375	5.0
Orange	0.4875	6.5
Total	7.5	100.0

Si-Mum Muang Market waste composition (Chewha, 2003)

3.2.3 Simulated anaerobic landfill reactor operation

The experiment could be divided in two operational phases, no alkalinity addition phase and alkalinity addition phase. Each simulated anaerobic landfill reactor was filled with 7.5 kg of fruit and vegetable wastes as the composition shown in Table 3.1. Two replicate reactors were operated under identical conditions. From the beginning of the experiment, the effluent collected from the bottom of each reactor was recycled back to the reactors. After packing the reactor, 1 L of deionized water and all leachate collected from the bottom of the reactor were added on the top of the reactors. This step was repeated for several days until the amount of liquid added in each day was equal to the amount of liquid collected on the next day which means the full capacity of waste was reached (Chewha, 2003). This day will be defined as “Day 0”. After “Day 0”, the wastes will be allowed to cure without any recirculation or addition of alkali solution. Then 300 mL of leachate from both reactors were collected and recycled back to reactors three times a week as an attempt to enhance the activity of the methanogens and enhance the stabilization rate of reactor. The recirculation was operated regularly in two phases experiment. After 200 operation days the degradation process was not as expected, therefore, 5 N NaOH was used as alkali solution to adjust pH of leachate to 7.0 before recycled back to the reactor to increase the alkalinity of the system (Chewha, 2003). The leachate from both reactors was collected and measured their parameters frequently as shown in Table 3.2.

Table 3.2 Parameters monitoring frequency.

Parameters	**Frequency**
pH	Twice a week
ORP	Twice a week
Gas production	everyday
%CH4	Once a week
COD	Once a week
DOC	Once a week
VFA	Once a week
Alkalinity	Once a week

3.2.4 Analytical methods

Leachate collected from both reactors was analyzed for pH, ORP, COD, gas production, gas composition, VFA and alkalinity. COD concentrations in leachate samples were detected by using closed reflux colorimetric method following standard method. The pH in leachate samples were measured by using pH meter. ORP in leachate was determined immediately after sampling, using ORP meter. ORP is very sensitive to sample storage time. The reading may rise fairly rapidly and become a lot more positive when it is measured only hours after sampling. Thus, ORP measurement was done immediately at the time of sampling. Gas production was measured by liquid displacement method by passing it through a inverted volumetric cylinder column containing 5 %(v/v) H_2SO_4 and 20% (w/v) Na_2SO_4. Biogas generated from reactors was collected by 1 L Tedlar gas sampling bag through sampling port on the top of reactor. Then, percentage of methane in gas produced was determined by Gas Chromatography (GC) 19091P-MS4 equipped with a Thermal Conductivity Detector (TCD). The column is HP-PLOT Q Agilent Technologies 30m x 0.32 mm ID. VFA concentrations in leachate samples were measured by using standard method for water and waste water examination. Alkalinity was measured using standard methods for water and waste water examination #4500-P (Titration method).

3.3 Results and discussion

3.3.1 pH

The pH values of the leachate from both replicate reactors are shown in Figure 3.3. Since the beginning of the operation, pH of both reactors tended to increase rapidly during the first 30 days from pH 3.5 to pH 4.5. Initially the fruit and vegetable wastes produce a low pH leachate at the beginning of the experiment. After that, pH increased gradually from 4.5 on Day 30 to 4.6-4.9 on Day 81. It can be seen obviously that after pH reached 4.9 on day 81, pH value of both reactors were stable for a long period of time until starting of alkali addition on Day 200. This caused an extension of the time required for the stabilization of organic fraction of the waste to stabilize since methane forming anaerobes are known to be very sensitive to low pH (Bolzonella et al., 2003). Because methanogenic bacteria prefer nearly neutral pH, therefore there was no methanogenesis occurred at this pH. It is shown that the pH of the reactors was not favorable for the development of an active methanogenic population despite recirculation of leachate and the initial addition of activated sludge. At the period of the experiment, reactors were in acidogenesis phase. Lens et al. (2003) found that the lack of bicarbonate delayed the conversion of organic solid wastes to methane resulting in low methane productions and percentages of methane in biogas in control reactor.

Stable pH around 5.0 mean the system had not enough capability to buffer the system itself because of very high organic acid from wastes. These results were accompanied with the gas production and gas composition because until Day 200, there was no generation of methane gas. The major gas production was CO_2 at about 80-90 %. After Day 200, alkali addition, pH value of both reactors increased gradually from 5.0 and reached 6.2 for reactor A and 6.5 for reactor B on Day 382. The gradual increase occurred because of VFA released which made pH of the system increase gradually during the initial alkali addition. The conversion of fatty acids to methane gas caused an increase in the pH levels within the alkalinity supplemented reactors. Then, pH values tended to increase more rapidly to 8.9 and 9.2 for reactor A and B on Day 509, respectively. After Day 382, methanogenesis phase was observed in all parameters: methane gas production and a dramatic decrease in VFA and COD. The result of San and Onay (2001) study showed a similar sudden increase in the pH of the recycle reactor from 5.92 on Day 250 to 7.3 on Day 257.

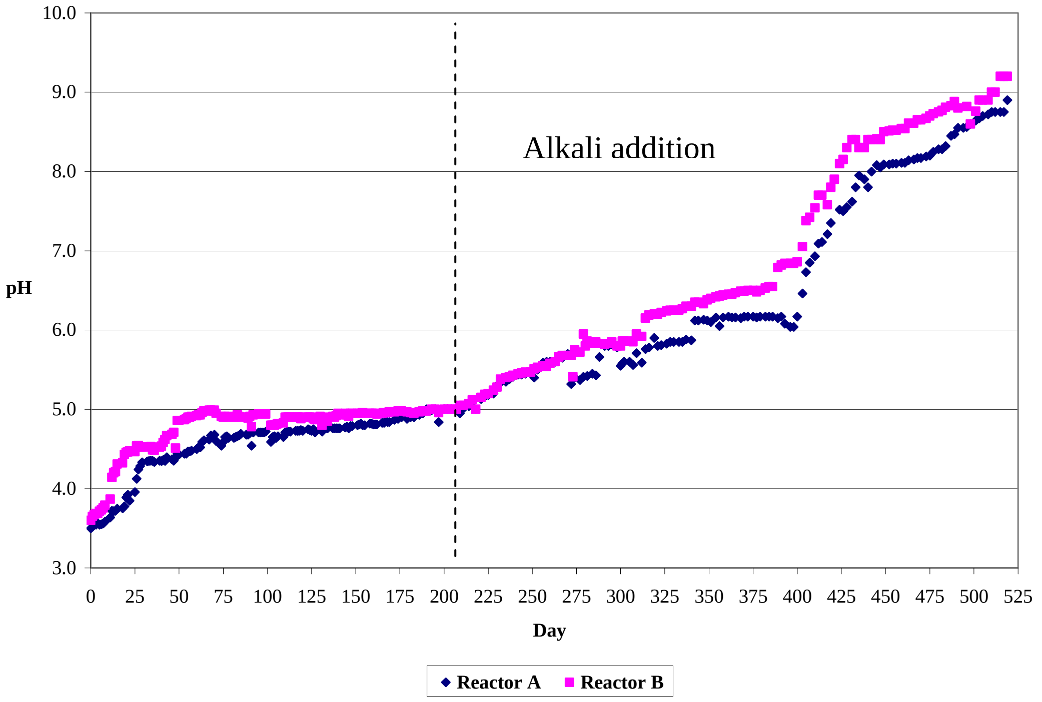


Figure. 3.3 pH of leachate from anaerobic landfill reactors during phase I and II

3.3.2 Oxidation-reduction potential (ORP)

The ORP values of the leachate collected from bottom of both reactors are given in Figure 3.4. Up to approximately Day 70 the ORP values are positive are positive indicative that oxygen was still present in the reactors. ORP values were slightly dropped from the beginning at 150 - 180 mV and reached approximately -70 to -75 mV on Day 140, indicating the anaerobic environmental condition had formed. The ORP values for both reactors seem stable after Day 140 with some fluctuation until alkalinity addition phase on Day 200. After Day 200, ORP started to drop gradually again and reached -183.7 mV for reactor B and -125.4 mV on Day 386 for reactor A. Then they showed a highly drop to -389 mV for reactor A and -420 mV on for reactor B on Day 519. The decreasing ORP shows the positive effect of pH neutralization of leachate. Though the ORP values for both reactors are not exactly the same they show the similar trends in both phases. After the consumption of the available oxygen in anaerobic reactors, ORP value began to decrease indicating the degradation shifting from acidogenic phase to methanogenic phase.

The redox potential within a landfill identifies the mechanism of waste degradation. Generally, high redox potential (aerobic conditions) causes accelerated degradation of waste. It has been suggested in the literatue (Farquhar, 1973) that there is an optimum ORP requirement for methanogenesis, which generally ranges from -100 to -300 mV. With this regard, these bioreactors did not start methanogenesis phase until day 386 onward when ORP reached approximately -120 to -190 mV. The results showed the same correlation with other parameters.

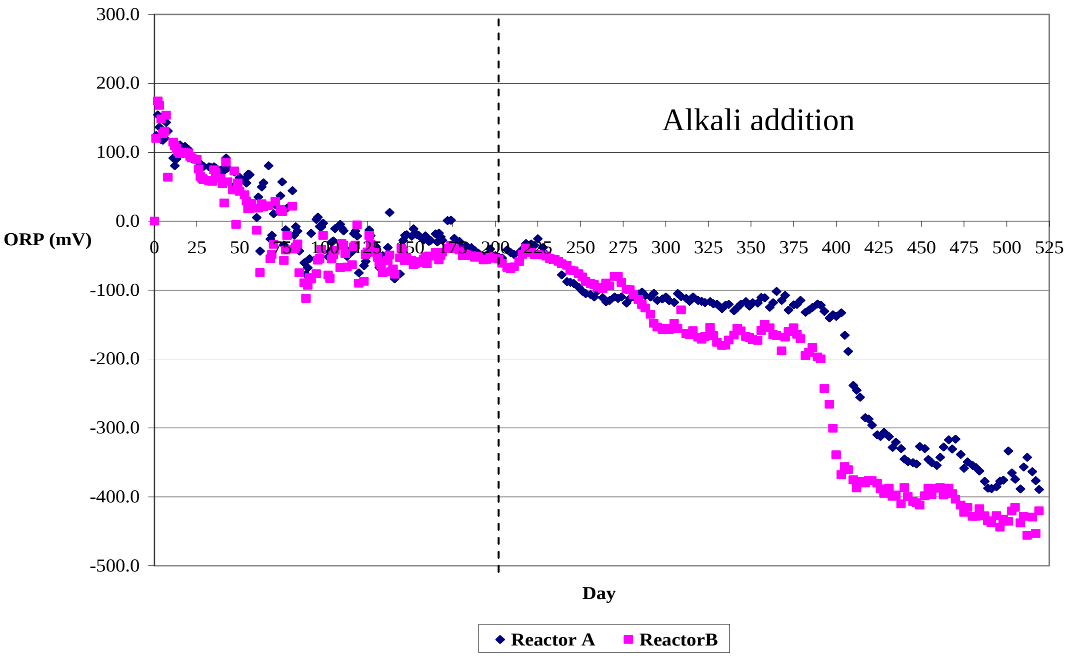


Figure 3.4 ORP of leachate from anaerobic landfill reactors phase I and II

3.3.3 Gas production and gas composition

The cumulative gas production from both reactors is given in Figure 3.5. The cumulative gas rapidly increased during the first 45 days and then slightly increased until alkali addition. The reason for high cumulative gas production for the first 45 days is the high production of carbon dioxide in acidification process. The slower rate of cumulative gas production between Day 45 and Day 200 indicated that anaerobic degradation had terminated. After Day 200, cumulative gas production started to increase again. The maximum cumulative gas production for no alkali addition was 40 L and for alkali addition was 105-112 L. It is important to note that the increase percentage of gas production was lower in phase I while the increase in the percentage of gas production was higher in phase II between day 200 and the end of experiment. The reason for the high cumulative gas production and high methane production in alkali phase is the faster degradation of wastes through rapid methanogenesis.

The biogas composition is given in Figure 3.6. From Figure 3.6, there was no methane production in phase I. In phase II, methane production started from day 396 in alkali addition phase. Methane production increased from approximately 20% methane to 70% for reactor B and from 20% to 60% for reactor A while carbon dioxide decreased from 65% to approximately 25 - 35%. The biogas composition obtained in this study is comparable to those obtained by Wang et al. (2005) who studied the anaerobic batch digestion of food waste. Their results showed that the methane contents of the biogas produced was 71%. Moreover, these results were also similar to Zhang et al.(2007) who studied characterization of food waste as feed stock for anaerobic digestion. Their biogas composition was 73% in average.

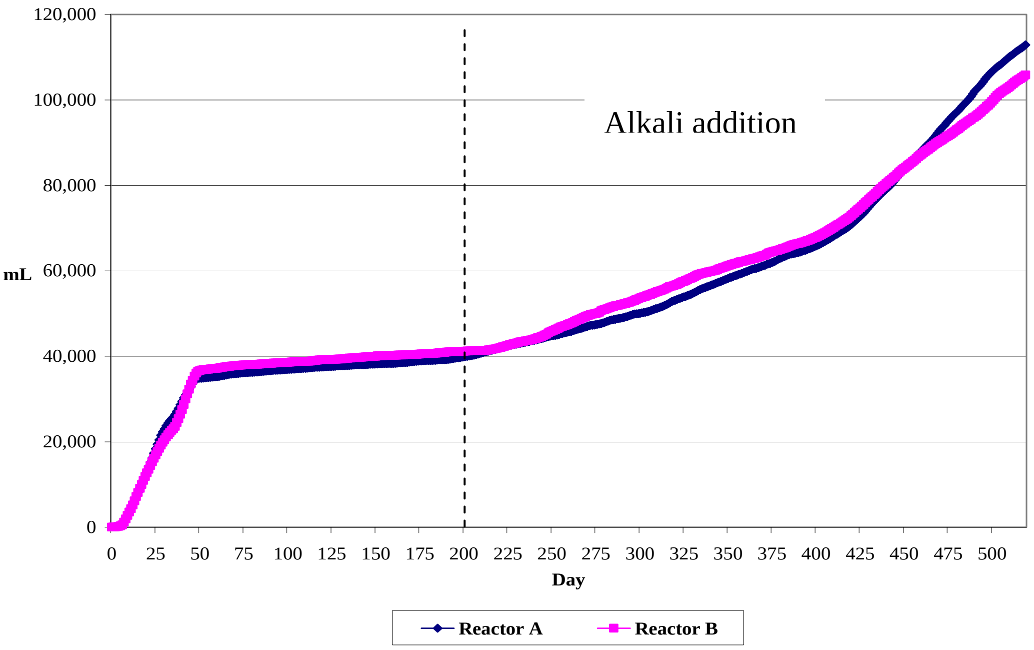


Figure 3.5 Cumulative gas production for anaerobic landfill reactors phase I and II

Methane gas productions and cumulative gas production in simulated anaerobic bioreactors show that the alkalinity addition has a positive effect on biodegradation of fruit and vegetable wastes in simulated bioreactors due to high methane gas production. The biodegradation rate was higher in alkali addition phase. Without alkali addition, there was no methane production due to lack of buffering capacity of the system and unsuitable pH for methanogenic bacteria. There was also a strong association between pH and methane generation rate. There was no methane production in no alkali phase until pH reached 6.5 or nearly neutral at Day 386, where upon methane production increased dramatically. This indicated that there was a threshold limit for methane generation rate round 6.5. Therefore, alkalinity addition is recommended for biodegradation of fruit and vegetable kind of wastes. The production of methane gas indicated that reactors were shifted to methanogenesis phase after a long period in acidogenesis phase.

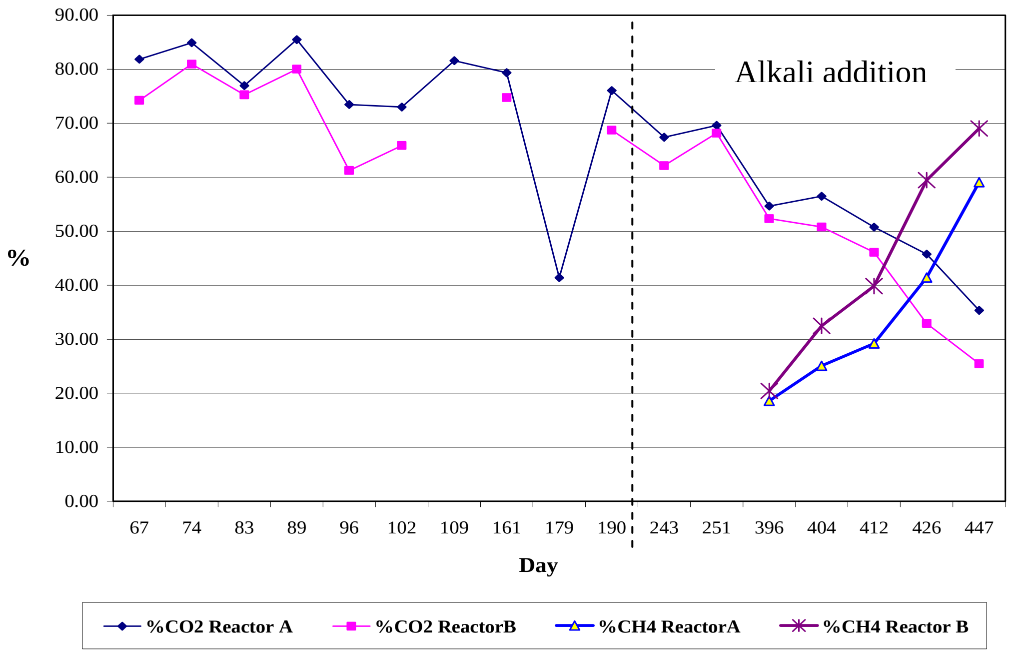


Figure 3.6 Gas composition for landfill reactors phase I and II

3.3.4 Chemical Oxygen Demand (COD)

The COD concentrations of collected leachate from bottom of both reactors are given in Figure 3.7. The initial COD concentrations from both reactors were approximately 32,000 and 36,000 mg/L. The COD of leachate increased to 44,571 and 49714 mg/L on Day 76 and then decrease and stable around 30,000 – 40,000 mg/L until alkalinity addition phase. After the alkali was added on Day 200, COD concentration was slightly decreased with some fluctuation to approximately 30,000 35,000 mg/L. The stability of COD in the absence of alkali and during the initial portion of alkali addition may result from leachate recirculation. Then, COD of both reactors drop more sharply at nearly the end of experiment from Day 399 onward. Finally, COD values of reactor A and reactor B are 6,400 and 1,600 mg/L respectively on Day 509. The reason for this decrease in COD value was the positive effect of alkalinity addition on anaerobic degradation.

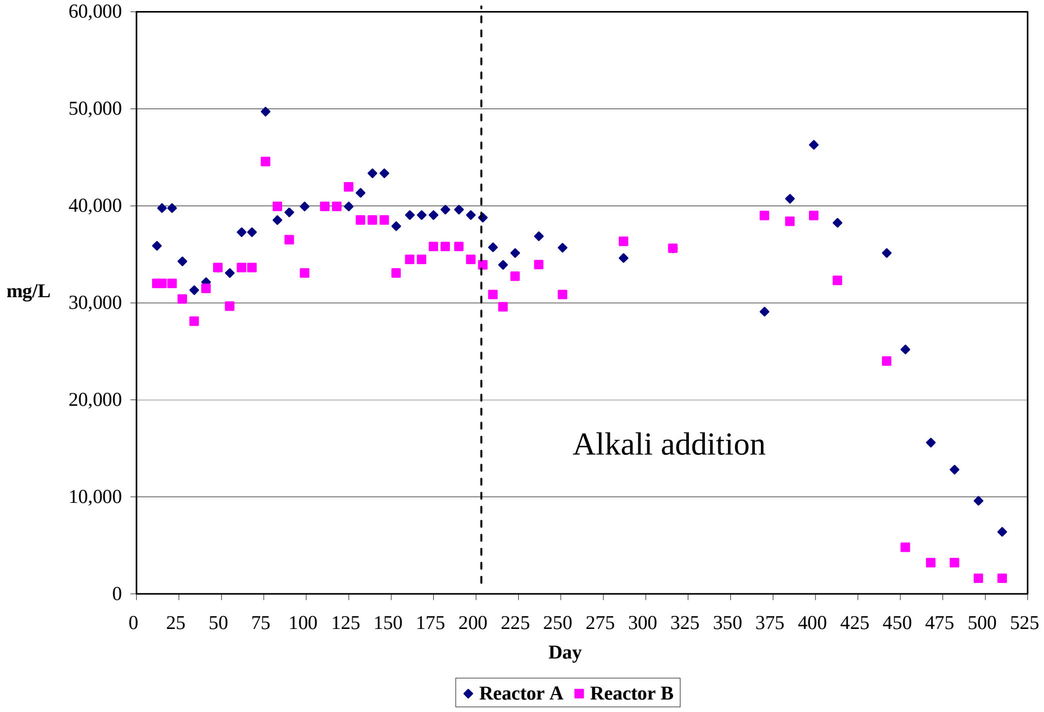


Figure 3.7 COD concentration anaerobic landfill reactors phase I and II

This indicates that the addition of alkalinity to the fruit and vegetable wastes simulated bioreactor has a positive effect on the anaerobic degradation of this kind of waste. The organic matter can convert to methane through the methanogenesis. However, the degradation process was stable in phase I and occurred quite slowly in phase II, because of very low pH of leachate which unsuitable for methanogen bacteria. Inadequate alkalinity/leachate COD ratio in the anaerobic reactors may cause minimum pH in he anaerobic reactor to fall below 6.2 which can lead to failure of the system. Methanogens prefer nearly neutral pH conditions with a generally accepted optimum range of approximately 6.5-8.2. Souza et al. (1992) found that an alkalinity/COD ratio 0.5 in the influent decreased the pH to 6.6, which is considered as the lower limit value recommended for anaerobic digestion processes. In this study, this ratio reach approximately 0.3 on Day 375 and started to increase at the same time as decreasing of COD. Therefore, without alkalinity addition this system would not have enough buffering capacity to convert COD to methane or VFA. The ratio proposed by Gonzales et al. (1998) is 0.4. Anderson and Yang (1992) reported that if the acid concentration exceed the available alkalinity, a drop in pH could occurs. When methane production becomes ceases the VFA may continue to accumulate. Alkalinity addition was used in numerous studies to neutralize the pH the anaerobic treatment of MSW (San and Onay, 2001; Warith, 2002).

The results show the same trend as Agdag and Sponza (2005). They compared alkalinity effect of organic solid waste with 3 g/L and 6 g/L $NaHCO_3$ addition and without alkalinity adition. From their experiment, the COD value of the leachate in the control reactor increased to 40,700 mg/L until day 21, and then started to decrease. The COD values of the leachate taken from the 3 g/L and 6 g/L NaHNO3 containing reactors increased to 30,000 and 23,000 mg/L until day 7. Then, the COD concentrations started to decrease. They confirmed the positive effect of alkalinity on anaerobic degradation. The time require for stabilization of COD was shortened by the addition of alkalinity. They can shorten the time required for stabilization of COD values more quickly than this experiment because they started alkalinity addition at the beginning of their experiment and their original wastes are not fruit and vegetable wastes. Besides high degradation rate or high methane production yield, this kind of wastes can also produce very low pH leachate.

3.3.5 Volatile fatty acid (VFA)

The concentrations of VFA in the leachate of both reactors are given in Figure 3.8. The concentrations of VFA start to measure from Day 182 onward. The initial VFA concentrations in both reactors were approximately 8,000 mg/L and remain nearly stable until Day 223, 23 days after alkali addition. The VFA measurement showed that without alkali addition, fruit and vegetable wastes degraded very slowly. Adequate alkalinity was necessary to maintain a stable pH in the digester for optimal biological activity. Then VFA concentrations slightly increased from 8,425 mg/L for reactor A and 8,325 mg/L for reactor B on Day 223 to nearly 13,000 mg/L on Day

385. Increase in VFA concentration in leachate showed that the reactors remained predominantly in the acidogenesis phase. However, the presence of methane generation showed that the methanogens activity still occurs. The increase in VFA concentration indicated the organic acids that have been produced more after inhibition period of very low pH. However, after Day 390, VFA decreased rapidly to 290 mg/L for reactor B and 160 mg/L for reactor A. As the VFA concentrations decreased, the methane generation rate started and increased, beginning at Day 396. Elevated VFA concentrations were inhibitory for methane generation, but as VFA was removed in the leachate exchange process, conditions became conductive to methane generation. This result agrees with other investigations (Pullammanappallil et al., 2001).

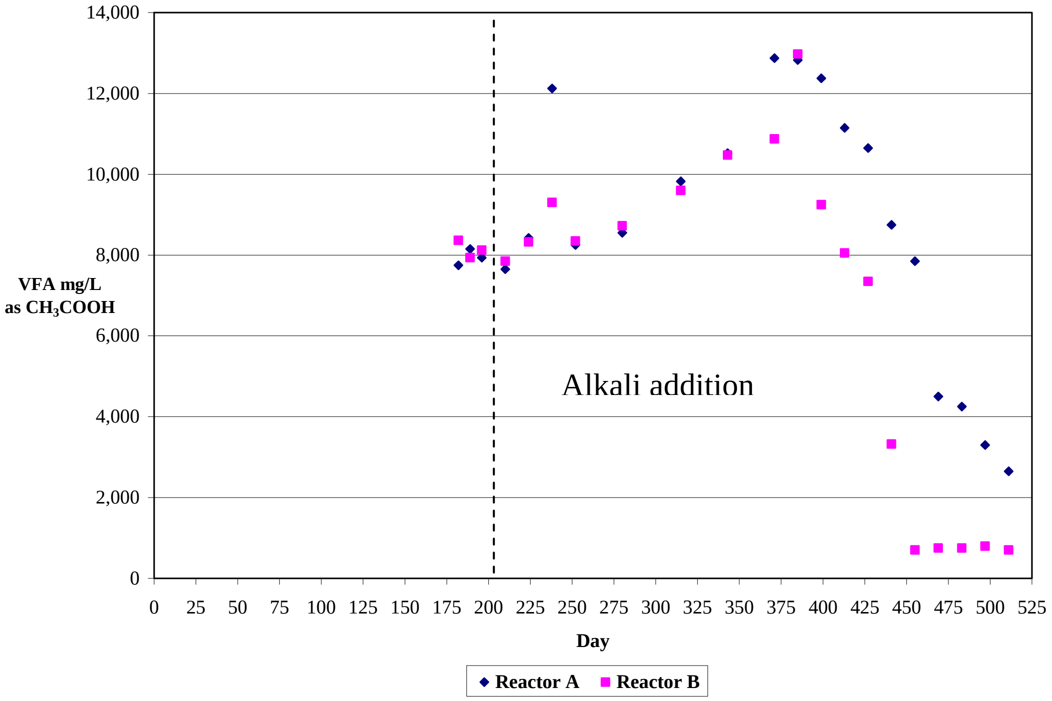


Figure 3.8 VFA of leachate collected from anaerobic landfill reactors phase I and II

Agdag and Sponza (2005) reported similar result to confirm the requirement of adequate alkalinity. From their experiments, VFA values of the reactors containing 3 g/L and 6 g/L $NaHCO_3$ increased to 30,000 and 23,000 mg/L on Day 7 and then they were down to about 14,000 and 1,300 mg/L in Day 65. Their results showed a strong linear correlation between COD and VFA concentrations.

3.3.6 Alkalinity

The alkalinity of the leachate from the bottom of both reactors is given in Figure 3.9. The alkalinity values of both reactors started to measure from Day 182 onward also. The initial alkalinities of both reactors were approximately 4,000 mg/L and then slightly decrease until alkali addition phase. After the alkali addition, alkalinity values were gradually increased from approximately 3,000 – 3,800 mg/L to 12,000 mg/L on Day 385. Farquhar and Rovers (1973) suggested that a system would need an alkalinity of at least 2,000 mg/L to maintain an optimum methanogenesis. From the results, both reactors showed high alkalinity that should be adequate for the degradation process.

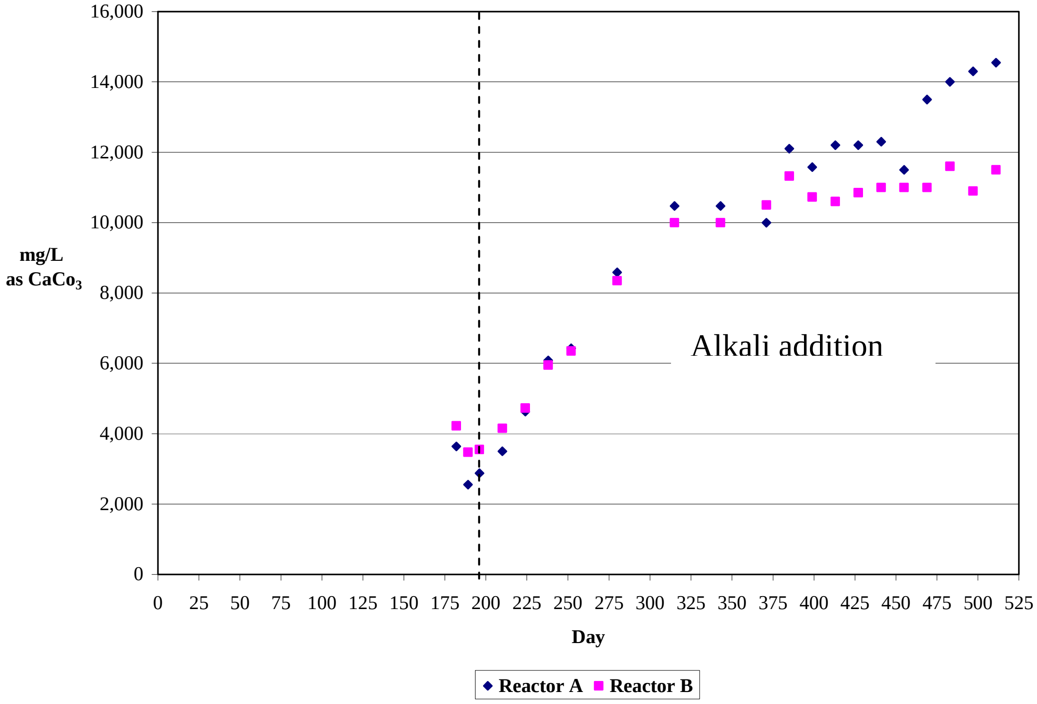


Figure 3.9 Alkalinity of leachate collected from anaerobic landfill reactors phase I and II

With this regards phase II with alkali addition shows the high buffering capacity as reflect by the increasing of alkalinity. Though alkalinity in no alkali addition was above 2,000 mg/L, there is not enough buffering capacity for this system due to high amount of organic acids. However, it could be seen that there is adequate alkalinity buffering capacity after alkali addition. Interested parameters, for example, pH, ORP, COD, biogas production, biogas composition etc. were measured from Day 200 reflects by increasing of alkalinity values.

An alkalinity varying between 1,000 and 5,000 mg $CaCO_3$/L, was recommended for anaerobic treatment depending on COD and VFA produced (Tchnobanoglous and Burton, 1979). Traditionally, the total alkalinity in an anaerobic digester includes all the bicarbonate alkalinity and approximately 80% of the VFA (Anderson and Yang, 1992). When the system is inbalance, the methanogens could be inactivated by unfavorable environmental conditions, e. g., pH drop, accumulation of VFA and toxicity of aromatic amines due to their toxic properties (Kuai et al., 1998)

3.4 Conclusion

The alkalinity addition to anaerobic landfill reactors has a positive effect on the rate of biological degradation of fruit and vegetable wastes which generate high amount of organic acids. Leachate recirculation might have not enough effect to enhance the gas production and stabilization process during the first phase because of unsuitable pH. The alkali addition has shown the acceleration of fruit and vegetable wastes stabilization and also enhance gas production. Increase of methane gas after alkalinity addition was indicative of the presence of methanogens in the reactors. These methanogens were unable to active under low pH value or high concentration of volatile acids. Because of fruit and vegetable wastes can generate very low pH leachate that can inhibit methanogenesis process therefore alkalinity addition is recommended for landfill of this kind of waste.

The degree of waste stabilization and efficiency of COD removal were dependent on the operational phases. Leachate recirculation with pH control further enhanced landfill stabilization and treatment efficiency. Buffering the leachate prior to its recirculation is an important operational parameter for the maintenance of the desired pH values in the system.

CHAPTER IV

LEACHING OF Pb FROM MINE TAILINGS USING FRUIT AND VEGETABLE WASTE LEACHATE AND EDTA

Abstract

The Pb extraction ability of simulated fruits and vegetables waste leachate with different leachate ages from mine tailing was investigated. Leachate was produced in reactor from columns containing fruit and vegetable waste. The results show high extraction ability with some fluctuation for leachate from the first 50 days with pH lower than 5.0 while the leachate from Day 364 to Day 434 showed no extraction ability. In methanogenesis phase or last phase of experiment presented some extraction ability but still much lower than the initial phase leachate. Low pH and high DOC of leachate might have effect to extraction ability. EDTA showed very high extraction ability from 61 to 75 % which was higher than most of simulated leachate.

Keywords: EDTA, Extraction, Leachate, Pb

4.1 Introduction

Mining creates potential risk to the environment because of the potential release of heavy metals. When mine waste (waste rock dumps, tailings and slags, mainly) are disposed of without any environmental control, mining activities may cause greater soil and groundwater contamination. The type of contaminants and their concentration in the environment depend on their initial concentration and, in mining areas, on the nature of the mineral. This environmental problem and its effect on human health are highly concerned. Heavy metals such as zinc (Zn), lead (Pb) and cadmium (Cd) are highly persistent in soil, with residence time of thousands of years. Excessive accumulation of heavy metals can have serious effects on soil fertility, affect ecosystem functions and constitute a health risk to animals and human beings. Lead (Pb) is one of the most common contaminant in the environment and has chronic toxicity. Previous studied show that leachate pH is the major factor in controlling Pb leachability (Cocke, 1990). Low Pb concentrations increase when pH changes to an extremely low or high value.

The clean-up of contaminated sites with heavy metals is one of the most difficult tasks for environmental engineering. A number of techniques have been developed that aim to remove heavy metals from contaminated sites, including *ex-situ* washing with physical-chemical methods (Anderson, 1993) and *in-situ* phytoextraction. In the *ex-situ* washing methods, chelating agents or acids are used to enhance heavy metals removal. EDTA is the most commonly used chelate because of its strong chelating ability for different heavy metals. Despite chelating chemicals, organic carbon in leachate also has shown the ability to complex with heavy metals. Besser and Rabeni (1987) illustrated a significant increase in heavy metal leaching from mine tailing when leaves were used as cover material. The addition of anaerobically digested liquid sewage to the soil led to a decrease in the sorption of Cd to the soil across the pH range of 5 and 7 (Lamy et al., 1993). Water soluble organic matter may play a significant role in enhancing heavy metal leaching to the ground water (Ward et al., 2005; Khodadoust et al., 2005).

Thailand generates over 39,240 tons/day of MSW and more than 40% of those is food waste (PCD, MNRE, 2003). Most of MSW goes to landfill disposal or open dumping. One majority of organic waste in Thailand is fruit and vegetable waste especially waste from markets which is normally disposed on site. The source of this waste mean that fruit and vegetable waste are relatively free of contaminants compare to street collection waste, household or industrial waste. This kind of waste contains high content of organic carbon. Therefore, they have been studied to use for enhancing biogas production rate in an anaerobic digestion process. These kinds of waste are rich in organic matter and have a high water content resulting in higher biodegradation. Because of high moisture content, vegetable and fruit waste not only give a high yield of biogas but also give large volume of leachate.

In landfilling, waste can produce leachate containing DOC which is a product of the anaerobic degradation process in landfill. Several years after landfilling, waste still produces leachate containing DOC in the g/L level (Ehrig, 1983). At this stage, the easily degradable organic compounds, e. g. the volatile fatty acids, are no longer present. Water soluble organic matter is a complex mixture with FA as an important group of constituents (Sposito et al., 1982; Schnitzer, 2000). The degradation process significantly affects water soluble organic matter, water soluble C, organic N, carbohydrate, and low molecular weight organic acid contents (Tiquia, 2005). This process not only altered material composition, but also pH, CEC and other chemical properties. Aoyama (1996) studied the chemical composition of water soluble organic matter during decomposition of different types of plant residues, and noted that organic carbon in the extract tended to decrease with time, with decreases in FA fractions but increases in HA fractions. Natural litter decomposition and composting produces molecules of increasing polarity and decreasing molecular weight (Wershaw et al., 1996). Although the heavy metals are less soluble in neutral pH phase, the heavy metals can solubilize in an acidic leachate and DOC. The complexion ability of DOC is primarily related to its content of functional group such as carboxylic and phenolic groups.

The complex-forming equilibrium significant affects the solubility and mobility of heavy metals. Note that a number of common inorganic anions (carbonates, sulfates) exhibit non-negligible complexing ability. The commercial and commonly used complexing agent is EDTA because of its strong chelating ability for different heavy metals (Norvell, 1991). Laboratory studies have shown that EDTA is effective in removing Pb, Zn, Cu and Cd from contaminated soils, although extraction efficiency depends on many factors such as the lability of heavy metals in soil, the strength of EDTA, electrolytes, pH (Elliot and Brown, 1989; Brown and Elliot, 1992; Heil et al., 1999). Recently, Garrabants and Kosson (2000) used EDTA as a leaching agent to determine the metal availability from soils and solid wastes. The leachability of As, Cd, Cu, Mn and Pb was compared with the availability test at pH 7 and 4. Despite EDTA, DOC from landfill leachate also shows complexing ability. Probably the most important naturally occurring complexing agents are HS (HA and FA) (Stevenson, 1994). The complexing ability of DOC is primarily related to its content of functional groups (such as carboxylic and phenolic groups) (Livens, 1991). Because these groups exhibit acid-base behavior, the complexation capacity of the DOC with respect to metals depends on the pH of the system. Janos (2002) studied leaching of metals from fly ashes in the presence of complexing agent by using EDTA and HA.

According to leachate extraction or complexation ability for heavy metals, this natural occurring substances may be used substantial EDTA for heavy metal extraction in remediation purpose. There are studied on leaching of heavy metals from mine tailings or soil using DOC from many sources. However, there is no investigation of leaching of Pb from mine tailings by using simulated leachate from fruit and vegetable waste. Due to vast majority of fruit and vegetable waste in Thailand and also their degradation properties, simulated leachate can be generated in bioreactor same time as biogas production. The objectives of this experiment are to study the ability of simulated landfill leachate to extract metal ions with different ages of leachate. In addition, the comparison between heavy metal extraction ability of simulated leachate and other complexing agents, especially EDTA were studied.

4.2 Material and methods

4.2.1 Mine Tailing Preparation

Akra mine tailing was collected from Akra Gold Mining, Phichit province, Thailand. Akra mining site is located at Phichit province, in northern region of Thailand and 280 km from Bangkok. The mining site comprised of two open pits, a processing plant to crush and mill the ore before passing to carbon in the leaching technology to extract gold. A tailing storage area is approximately 320,000 m^2 and located on the southern part of the area. The mine tailing was contaminated with Zn Cd, Cr and Pb in varying concentration due to geology and mining activities.

After collection, mine tailing was air dried, then grinded and sieved through 10 mesh sieve. EPA Method 3051 (EPA 1994) was used to analyze metal contents in mine tailing samples. A tailing sample of 0.5 g was transferred into a fluorocarbon microwave digestion vessel with 10 mL nitric acid and digested for 10 minutes. The sample was cooled and the supernatant diluted with 50 mL deionized water. The supernatant was then filtered through Whatman filter paper (No. 42). Then it was analyzed using an inductively coupled plasma optical emission spectroscopy (ICP-OES). The sand, silt and clay contents were characterized using sieve and sedimentation method (Allen, 1974). Mine tailing pH was measured in distilled water at 1:1 ratio of mine tailing to water (adapted from Reeuwijk, 1995). Cation exchange capacity (CEC) was determined using 1M NH_4OAc (pH 7) solution extraction method (Thomas, 1982), and the organic matter content was estimated by the Walkley and Black method (Walkley and Black, 1934). The results were shown in Table 4.1. All glassware used for dilution, storage and experiments were cleaned with non-ionic detergent, thoroughly rinsed with tap water soaked overnight in a 10% (v/v) HNO_3 solution and finally rinsed with ultrapure quality water prior to use.

Table 4.1 Physical and Chemical properties of Akra mine tailing

Properties	Akra mine tailing	
pH		5.5
Texture	Sand (%)	54.8
	Silt (%)	34.0
	Clay(%)	11.2
OM (%)		1.04
CEC (cmol/kg)		1.9
Metal content (mg/kg)	Pb	59.83
	Zn	209.24
	Cd	2.16
	Mn	1583
	Cr	54.83
	Ni	9.27

4.2.2 Batch metal extraction procedures

4.2.2.1 Simulated leachate

Simulated leachate samples collected from part I experiment were used as extracting agent in this part. Their ability to extract Pb from mine tailing was investigated. Some of leachate samples were the representative of the same landfill phase but had different properties and also extraction ability. Prior to extraction ability measurement, leachate samples were filtered through 0.45 µm membrane filter and defined as DOC. The mixing ratios (1:20, 1.5:30 and 2:20) between mine tailing and leachate solutions were studied: 1:20 ratio of mine tailing: leachate solution was chosen because of highest extraction capability. Mine tailings were suspended in each leachate samples in ratio of 1:20 and shaken for 24 hours in a shaker at 200 rpm at room temperature (Manouchehri, N. and Bermond, A., 2006; Sun et al., 2001; Conte et al., 2005). After that, suspensions were centrifuged in polypropylene tubes at 10,000 rpm for 10 minutes in order to separate solid residues from leachate. The extraction experiments were done triplicate. Deionized water was used as blank agent in metal extraction step and also analyze step. Supernatant was then filtered through

No.42 Whatman filer paper before further analysis. Besides our simulated leachate, EDTA, AHA and also deionized water were examined their extraction ability. In addition, Zn extracted from this extraction procedure was analyzed also to compare with Pb extraction.

4.2.2.2 Ethylenediaminetetraacetic Acid

Extraction of metals from mine tailing was performed using EDTA solution, as extracting reagent also. EDTA was prepared by dissolving the reagent grade in deionized water. EDTA solutions were prepared in two concentrations of 0.04 and 0.1 M. The extraction ability experiment followed the same mixing ratio and extraction time of simulated leachate in order to compare their extraction ability. In all extractions, 1 g of mine tailing sample was weighted and mixed with 20 mL EDTA solution, then shaken for 24 hr in a shaker at 200 rpm at room temperature. Then, mine tailing-EDTA solutions were centrifuged in polypropylene tubes at 10,000 rpm for 10 minutes in order to separate solid residues from leachate. Supernatant was then filtered through Whatman No.42 filer paper before further analysis.

4.2.2.3 Commercial Humic Acid

DOC can be experimentally fractionated into HA, FA and HyI , therefore the extraction ability measurement of AHA was conducted to compare with our simulated leachate. The solution of AHA was prepared by dissolving HA in deionized water. Similar to simulated leachate, 1 g of mine tailing was extracted with 20 mL of 1000 mg/L and 500 mg/L with varying pH (adjusted with HNO_3) of AHA. The mixture was shaken for 24 hours in a shaker. After extraction the suspension was centrifuged at 10,000 rpm for 10 minutes and the supernatant filtered through Whatman No. 42 filter paper before Pb analysis with Flame Atomic Absorption Spectrometry.

4.2.3 Chemical and data analysis

Before Pb concentration measurement, leachate solution from 4.2.2.1 was digested with HNO_3 to eliminate effect of organic carbon. Pb and Zn concentrations in the extract were determined by Flame Atomic Absorption Spectrometry. Deionized water with pH adjustment using 0.1 M HNO_3 to same pH as leachate was also done Pb extraction from mine tailing with the same method as leachate to compare. EDTA solution and also HA solution from 4.2.2.2 and 4.2.2.3 were also analyzed for Pb extracted by Flame Atomic Absorption Spectrometry

4.2.4 Sequential extraction method

The sequential extraction procedure of Tessier et al. (1979) was employed. This method partitions the heavy metals into four operationally defined chemical fractions: acid-soluble fraction, reducible fraction, oxidizable fraction and residual fraction.

4.2.4.1 Step 1 (acid-soluble fraction-bound to carbonates)

Three 0.5 g dry sediment replicates were placed into 50 mL of polypropylene centrifuge tubes. Twenty milliliters of 0.11 mol/L of acetic acid was added to the tube which was shaken for 16 hr at 35°C and a speed of 30 rpm. The extract was separated from the solid phase by centrifugation at 3000 rpm for 20 min. The supernatant liquid was decanted into a 50 mL polypropylene centrifuge tube and stored in a refrigerator at 4 °C prior to analysis. The residue was washed with 10 mL of deionized water and shaken again for 15 min and then centrifuged for 20 min at 3000 rpm. The supernatant was decanted and removed carefully to avoid loss of the solid residue.

4.2.4.2 Step 2 (reducible fraction-bound to Fe and Mn oxides)

Twenty milliliters of 0.5 mol/L hydroxylamine hydrochloride (adjusted to pH of around 1.5 by adding of 2 mol/L HNO_3) was added to the residue from Step 1 in the centrifuge tube. Again, the tube was shaken for 16 hr at room temperature at speed of 30 rpm. The extract was separated from the solid phase by centrifugation and decantation as described for Step 1 and stored at 4 °C. The solid residue was washed as in Step 1 before proceeding in Step 3.

4.2.4.3 Step 3 (oxidizable fraction-bound to organic matter and sulfides)

In this step, 5 mL of 8.8 mol/L H_2O_2 (pH of 2-3) was added carefully, in small aliquots, into the residue from Step 3 in the centrifuge tube. The tube was covered loosely and digested at room temperature for 1 hr with occasional shaking. The tube was then continuously digested for 1 hr at 85 ^oC in a water bath with occasional shaking for the first 30 min, and the volume was then reduced to around 2-3 mL by further heating of the uncovered tube. Another 5 mL of 8.8 mol/L H_2O_2 was added. Again, the covered tube was heated to 85 ^oC and digested for 1 hr before the volume in the uncovered tube was reduced almost dryness. After cooling, 25 mL of 0.1 mol/L ammonium acetate (adjusted to pH 2 by adding of concentrated HNO_3) was added to the residue and the tube was shaken for 16 hr at room temperature. The extract was separated from the solid phase by centrifugation and decantation as described above and stored at 4 ^oC.

4.2.4.4 Step 4 (residual fraction-strongly associated to the crystalline structures of the minerals)

The residue from Step 3 was digested in a mixture (3:1) of concentrated HNO_3 and HF. The metal content of the residue from Step 3 was determined using a microwave-assisted acid digestion procedure (US EPA, Method 3052, 1996). Three replicates of 0.5 g of samples were analyzed by digestion with a mixture of acid (9 mL concentrated HNO3 and 3 mL concentrated HF). Samples were heated in the microwave unit. The temperature of samples rose to 180 ^oC in 10 min and remained at 180 ^oC for 9.5 min. Digests were centrifuged at 3000 rpm for 10 min to clear the supernatant which was then analyzed by ICP-OES.

4.3 Results and discussion

4.3.1 Pb extraction ability and simulated leachate ages

The amount of Pb extracted from mine tailing using simulated leachate from reactor A and B with different ages of leachate are presented in Figure 4.1. Referring to Table 4.1, the initial concentration of Pb in Akra mine tailing was 59.83 mg/kg. It can be seen from Figure 4.1 that Pb extracted from mine tailing by simulated leachate ranges from 0% to nearly 70%. The extraction ability of leachate is very high during first 140 days of bioreactors. The leachate showed almost 70% extraction ability in the first 50 days of experiment and then decrease rapidly to 20% in leachate sample of Day 196. Leachate from reactor A and reactor B showed the same trend. The highest Pb extracted by leachate A was in Day 42 sample with value 39 ppm while Pb extracted by leachate B was highest in Day 7 sample with value 41 ppm. During these days, pH value was very low (<4.5) and DOC of leachate was very high (> 11,000 mg/L) comparing to other periods of experiment.

There was an acidic condition during this phase, therefore Pb could be extracted by proton induced of leachate. At low pH, the activity of H^+ is high and H^+ tends to displace metals from the binding sites. Though DOC was very high at this range, but at very low pH, acetic acid was protonated and a weaker complexing agent (Jensen, 2003). Then the extraction ability of leachate decreases gradually from Day 140 to no extraction of Pb at all in Day 363. The pH values range between 5.0 and 6.5. The system remained in acidogenesis phase until Day 396. The leachate showed no extraction ability from Day 363 (pH 6.16-.45) to Day 433 (pH 7.8-8.4). At this pH range, there might be precipitation of Pb. The extraction ability of leachate started to increase from no Pb extracted of Day 433 sample to 7% - 9% Pb extracted in the last phase of the experiment Day 518). Phase of leachate moved from acidogenesis phase to methanogenesis phase in Day 396. However, pH system did not reached 6 until Day 342 for reactor A and Day 314 for reactor B and reached 7 in Day 403 for reactor A and Day 412 for reactor B. The extraction ability of leachate started to increase again in Day 447 which pH was approximately 8.0-8.5 and DOC was 7,906 mg/L for reactor A and 1,976 mg/L for reactor B but the extraction ability is still low. At this range, there was higher generation of HS (Chapter V) which is naturally occurring ligands with strong complexing ability. FA and HA are large molecular weight materials with many acidic functional groups that can form complex with heavy metals (Jensen, 2003). The extraction ability of this leachate is not comparable with the extraction ability of the first period of bioreactors. Though the bioreactors were studied for a long period of time, the degradation process did not reach maturation phase at the end of the experiment. This may required a longer time for degradation process or sooner buffering addition to the system.

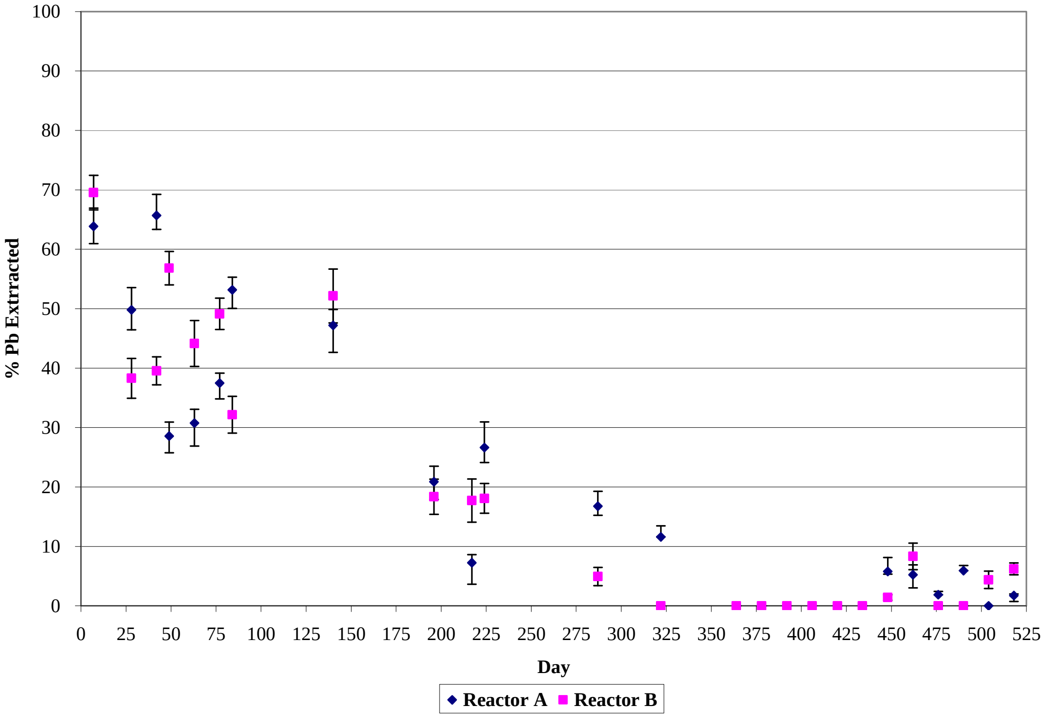


Figure 4.1 % Pb Extracted from mine tailing using leachate with different landfill ages

However, leachate of Day 7 (pH < 3.8) from both reactors showed the highest extraction ability of leachate. The extraction ability experiment of deionized water was also performed and it showed no ability to extract Pb from mine tailing though it was adjusted pH by HNO_3.

4.3.2 Zn extraction ability and simulated leachate ages

In comparison with Pb, % Zn extracted from the same samples as Pb were also studied and the results were presented in Figure 4.2. The initial concentration of Zn in mine tailing was 209.24 mg/kg. From Figure 4.2, % Zn extracted by different leachate ages shows similar trend as Pb in Figure 4.1. The % Zn extracted are range from 0 – 36%. The highest Zn extracted was in the initial phase of leachate. The graph tended to decrease from Day 7 until Day 315 that show very low % Zn extracted. Then started to increase from Day 455 which was the methanogenesis phase to the end of experiment. Though % extraction of Pb and Zn showed different results but they showed the same trend of extraction ability of leachate. From this experiment, initial phase leachate presented the highest extraction ability.

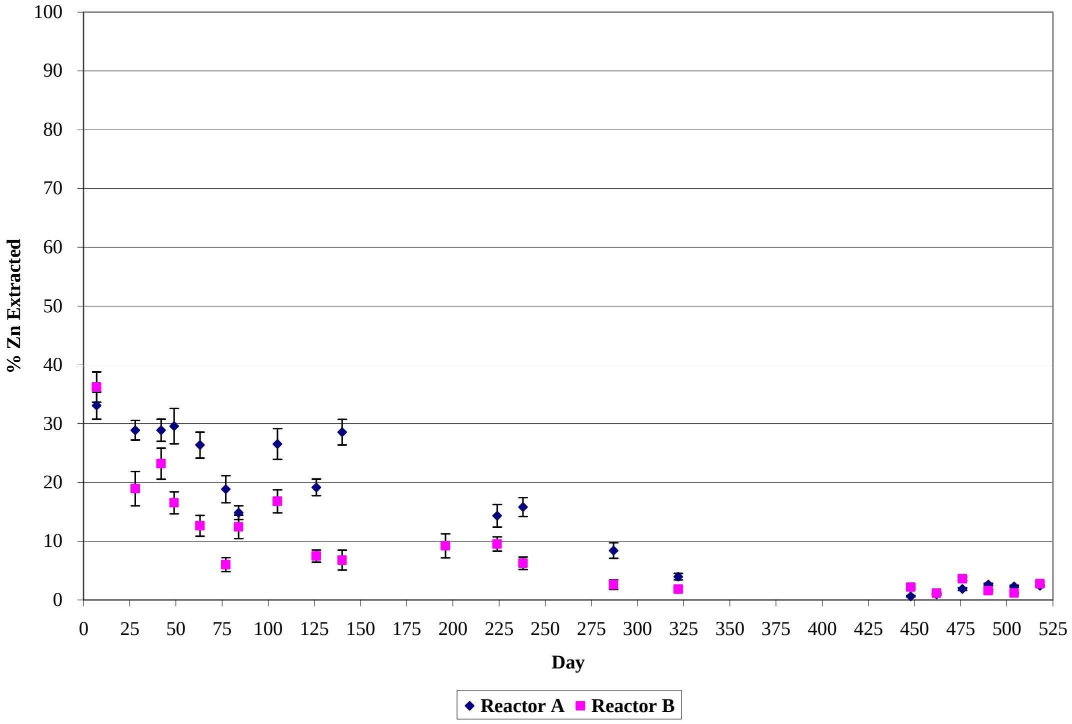


Figure 4.2 % Zn Extracted from mine tailing using leachate with different landfill ages

4.3.3 Pb extraction ability and simulated leachate DOC

After collection, leachate was filtered through 0.45 μm membrane filter and measured for TOC. These TOC values of filtered leachate were defined as DOC. DOC values of both reactors were measured and the results are presented in Figure 4.3. It can be seen that there was not much different between both reactors. DOC value of leachate A was ranged from 11,338 to 14,000 mg/L (Day 7 to Day 210) while DOC of leachate B was ranged from 8,615l to 12,550 mg/L (Day 7 to Day 210). DOC values of both reactors remained stable at approximately 12,000 – 14,000 mg/L for the first 200 days of reactor experiment. Then after alkali addition, DOC slightly increased from 12,000-14,000 mg/L in Day 200 to 14,000 to 16,168 mg/L in Day 385. The highest DOC is 16,168 mg/L in Day 385. After that DOC decreased dramatically from 16,168 mg/L in Day 385 to 1,662 mg/L in Day 509 until the end of experiment. There was a generation of methanogenesis phase and there was a high production of methane gas in this phase so DOC in leachate had been changed to methane gas through degradation process.

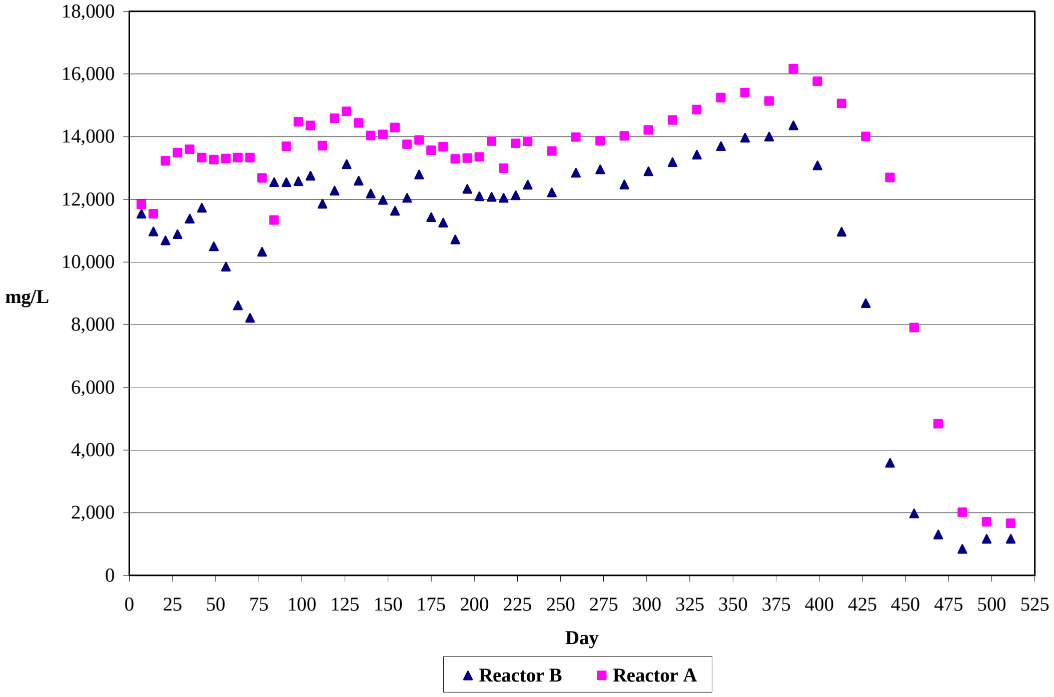


Figure 4.3 Dissolve organic carbon (DOC) of Reactor A and Reactor B

The plot between % Pb extracted from Akra mine tailing by simulated leachate and DOC values are presented in Figure 4.4. From this Figure, % Pb extracted was very low in low DOC values and increased when DOC values increased. At DOC less than 12,000 mg/L, % Pb extracted was lower than 10% while many of them showed no extraction ability. When DOC values were between 12,000 to 16,000 mg/L, extraction ability ranges from no extraction ability to nearly 70% Pb extracted. The reason for this appearance is the high % Pb extracted at high DOC leachate are representative of leachate in low pH range (initial and acidogenesis phase). While some of high DOC values leachate are representative of last part in acidogenesis phase before going to methanogenesis phase because DOC remained nearly constant for a long period of time during Day 140 to Day 385. It can be observed that the highest DOC values, 16,168 mg/L for leachate in Day 385 still showed no extraction ability for Pb.

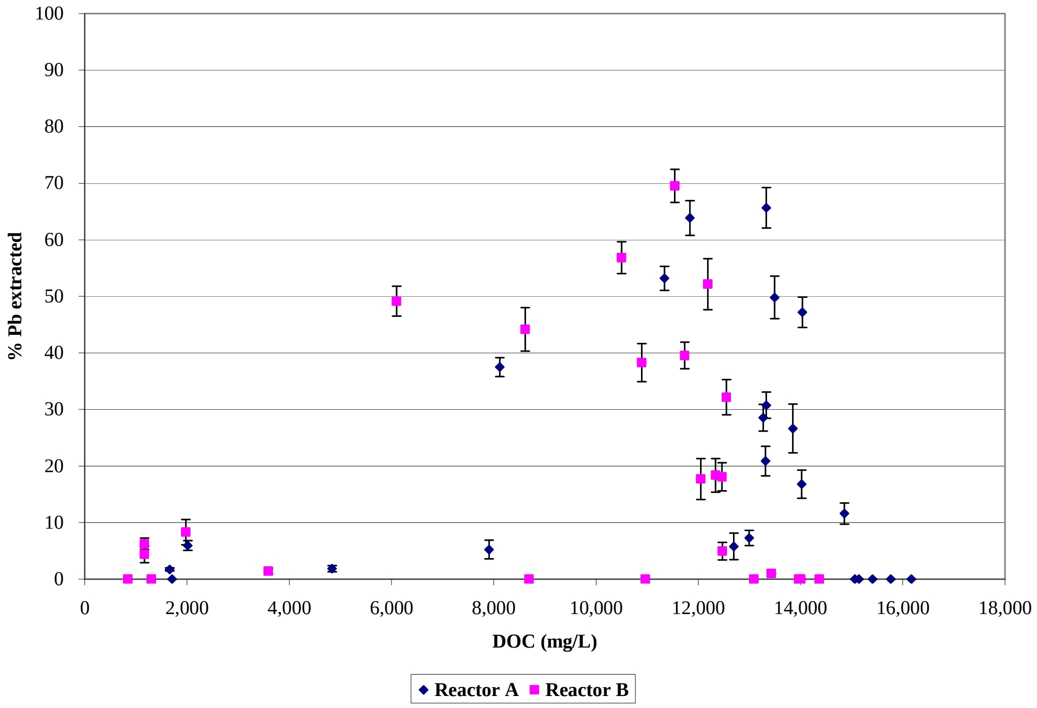


Figure 4.4 % Pb extracted by simulated leachate and their DOC

DOC values were high during initial phase and acidogenesis phase of reactor which generated low pH. Most of DOC of low pH leachate was acetic acid and also other intermediate organic acids. At pH lower than 4.5, pH have stronger effect to leachate extraction ability than DOC. When pH values range between 5 and 8, leachate showed no extraction ability to Pb though DOC values were very high (12,000-14,000 mg/L). At low DOC there was a little increase in % Pb extracted. Low DOC leachate was representative of samples from last phase of experiment of which generation of HS was observed (Chapter V). Thus it might be effect of complexation of HS that increased % Pb extraction. However, the humification process was in the beginning step resulted in small content of HS produced. Therefore, it can be concluded that for this kind of leachate, pH showed stronger effect on extraction ability of leachate on Pb. From conclusion in Chapter III, the degradation process of the system did not reach maturation phase, therefore HA that show a strong effect to complexing ability (from literature) was not generated or generated in a very small amount (Chapter V). Thus, there is no evidence of positive effect from a strong complexing agent as HA from this leachate.

Water soluble organic matter may have affected Pb movement because FA (including simple organic acids and chelating agents) are important components of water soluble organic matter (Linehan and Shephard, 1979; Sposito et al., 1982). These acids can form stronger complexes with Pb than other metals such as Zn. Lead mobility is favored by high DOC concentration (Tyler, 1978; Bergkvist, 1986). Kuiters and Mulder (1993) investigated the effects of water soluble organic matter extracted from different soils on metal movement and reported that Pb and other metals were solubilized by DOM.

Christensen et al. (1996) investigated the ability of DOC from landfill leachate polluted groundwater to form complexes with Cd, Ni and Zn. The results showed that DOC from landfill leachate polluted groundwater has the ability to form complexes with Cd, Ni and Zn and the distribution coefficient were a factor of 2-6 lower in the presence of DOC. They also concluded that the contribution of DOC to the migration of Cd, Ni and Zn in an aquifer is directly proportional to the complex formation constant and the ligand concentration but inversely proportional to the distribution coefficient to the metal ion sorbing onto the aquifer material.

4.3.4 Pb extraction ability and simulated leachate pH

The pH of simulated leachate from different time periods presented in Figure 4.5 and the leachate pH as a function of the % Pb extracted is presented in Figure 4.6. The pH values of simulated leachate from fruits and vegetables waste are very low in the beginning, between 3.5 and 3.7. The pH values were slightly increase from 3.5 within Day 7 to 4.5 in Day 40 and then reached pH 5.0 at Day 67. After that, pH was stable at around 5.0 until Day 200. From pH values, it is suggested that simulated landfill processes of both reactors were still in acid phase because pH 5.0 was not a proper value for methane fermentation phase. After buffering the system with NaOH in order to increase the buffering capability of the system, the pH started to increase gradually from pH 5.0 in Day 200 to pH 6.5 in Day 380. Finally, the system showed enough buffering capacity and pH increased more rapidly from 6.5 to 9 in the end of experiment Day 518.

During the changes of pH values in degradation process of the system, % extracted Pb values also showed changes as a function of pH change. From Figure 4.6, the leachate extraction ability of Pb was very high at pH between 3.5 and 4.5. The extraction ability were 65 - 70% at pH 3.5 and 30 – 55% at pH 4.5. When pH increased from 4 to 5, % Pb extracted decreased dramatically from 65% at pH 4 to approximately 20% at pH 5. Then the extraction ability of leachate for Pb decreased gradually from 20% at pH 5 to no extraction ability at pH 6. After that leachate showed no extraction ability until pH values reached 8. After simulated leachate had pH 8, % Pb extracted started to increase again but still had very low values, less than 10% Pb extracted.

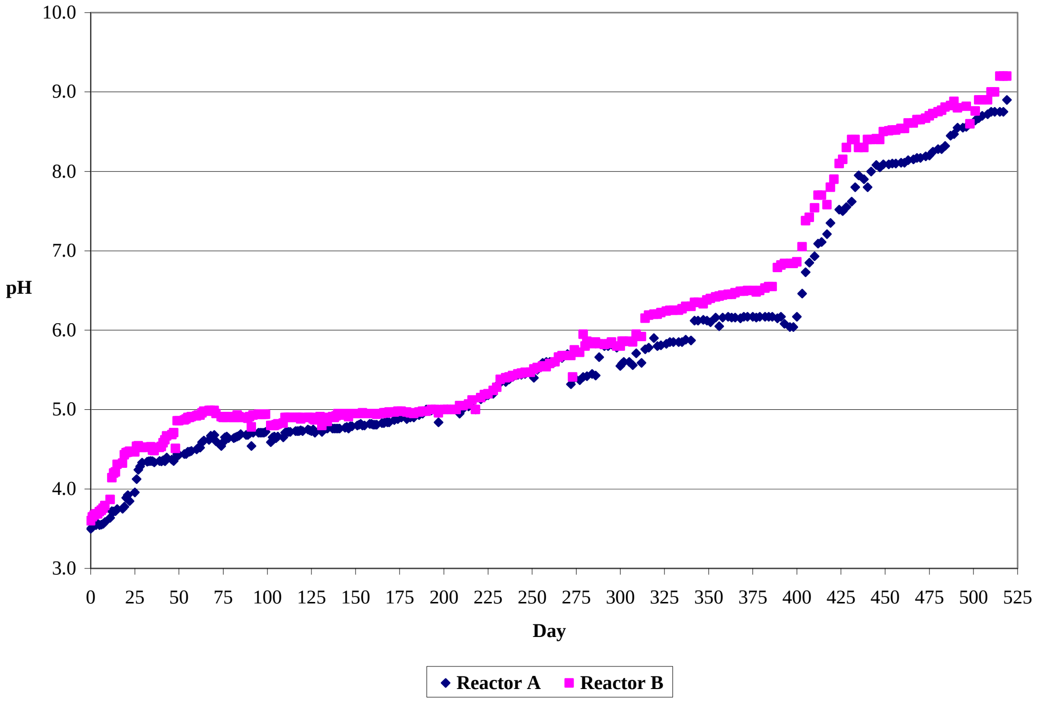


Figure 4.5 pH of Reactor A and Reactor B

It can be concluded that the Pb extraction ability for Akra mine tailing with simulated leachate is significantly effected by the pH value of the leachate. This can also be concluded that the very low pH value in the first phase of experiment which is the initial phase and acidogenesis phase leachate showed the highest Pb extraction ability. While this phase of leachate may be used as extracting agent (leachate with pH<4.5), the leachate in methanogenesis phase that has pH between 6 and 8 can not be used as extraction agent. Though extraction ability of leachate pH>8 (methanogenesis phase) increased, the extraction values were too low compared to leachate from the first phase. The results showed similar result to Impellitteri et al. (2002) because the extract equilibrium pH for Cu and Pb from their results are greatest at low (<3) and high pH (>6).

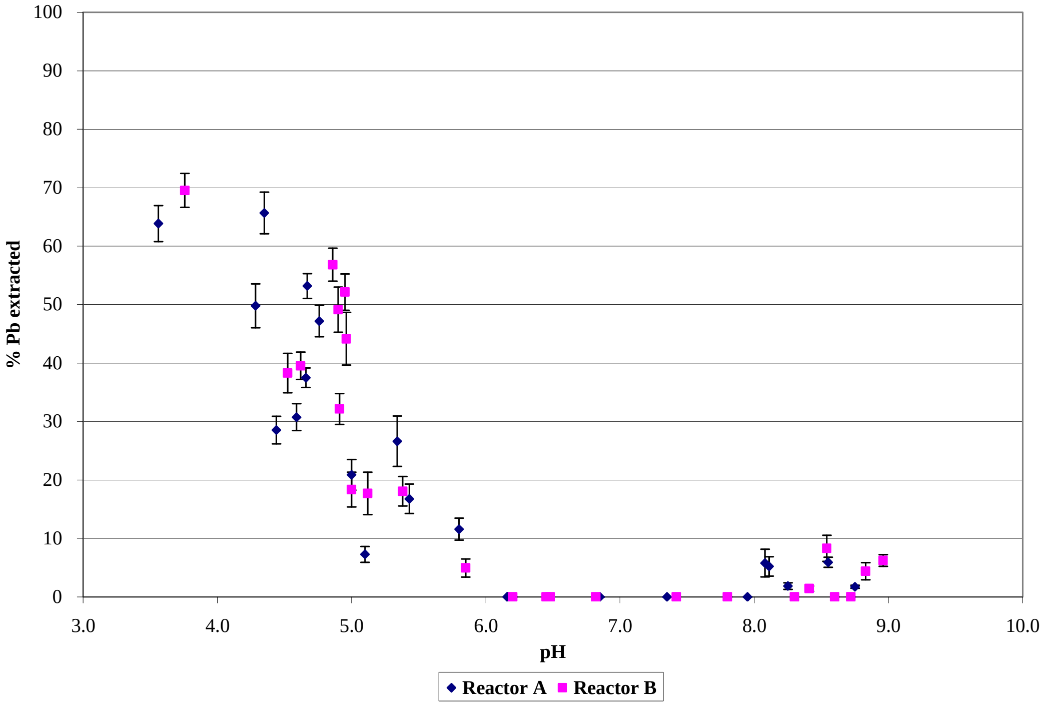


Figure 4.6 Plot between % Pb extracted and pH values of simulated leachate

Impellitteri et al. (2002) studied correlation of the partitioning of DOC fraction with the desorption of Cd, Cu, Ni, Pb and Zn from 18 Dutch soils. The results revealed that Cu and Pb concentrations in solutions a function of extract equilibrium pH are greatest at low (<3) and high pH (>6) resulting in parabolic desorption/dissolution curves. While processes such as proton competition and proton promoted dissolution can account for high solution metal concentrations at low pH, these processes cannot account for higher Cu and Pb concentration at high pH. When studied the amount of DOC with varying pH they found that DOC increases with increasing pH, concurrently with increase in Cu and Pb solution concentrations. They suggested that the effects of DOC on the mobility of Cd, Ni and Zn may only occur in systems governed by very high pH. Their results also revealed that the presence of Cu and Pb in the water extracts can be more precisely associated with the operationally defined HA fraction.

According to Impellitteri et al. (2002) experiment, they found that the percentage of each metal extracted from soil at low pH are Cd-80%, Cu-2.5%, Ni-22%, Pb-9.2%, and Zn-87%. They suggested that even at lower pH values, stronger binding with soil of Cu and Pb occurs relative to the binding of Cd, Ni, and Zn. A significant increase in extractable Cu and Pb occurs as the pH increases from 5 to 9. This increase in water extractable metal as a function of pH is much less significant for Cd, Ni and Zn. They concluded that the increase in solubility of Cu and Pb could be due to the pH –induced solubilization of organic matter. Pb leaching behavior can be divided into three stages based on the leachate pH: a high alkalinity leaching stage at pH>12, where Pb formed soluble hydroxide anion complexes and leached out; a neutral to alkaline immobilization stage in the pH range of 6-12, which was characterized by low Pb leachability caused by adsorption and precipitation; and an acid leaching stage with pH<6, where the acid neutralizing capacity was totally consumed and therefore free Pb-ion leached out (Jing et al.,2004).

4.3.5 Pb extraction ability and simulated leachate VFA

VFA of different leachate ages are presented in Figure 4.7. Due to VFA was not measured from the beginning of the experiment, the result started from Day 182, a few weeks before alkali addition. However, VFA of the system remained constant at 8,000 mg/L as CH_3COOH until Day 217. The alkali addition for this period was not enough to buffer the system. VFA started to increase from Day 224 the same Day as pH started to increase and reached the highest value 12,825 mg/L as $CaCO_3$ in Day 385. Then the system gained enough buffering capacity so VFA values dramatically drop until the end of experiment. A plot between VFA values and % Pb extracted is presented in Figure 4.8. Figure 4.8 shows a similar plot as Figure 4.4 of DOC. Though the high VFA show the higher extraction ability than low VFA, the highest VFA showed the lowest extraction ability. The highest VFA was in acidogenesis phase but pH value was getting higher.

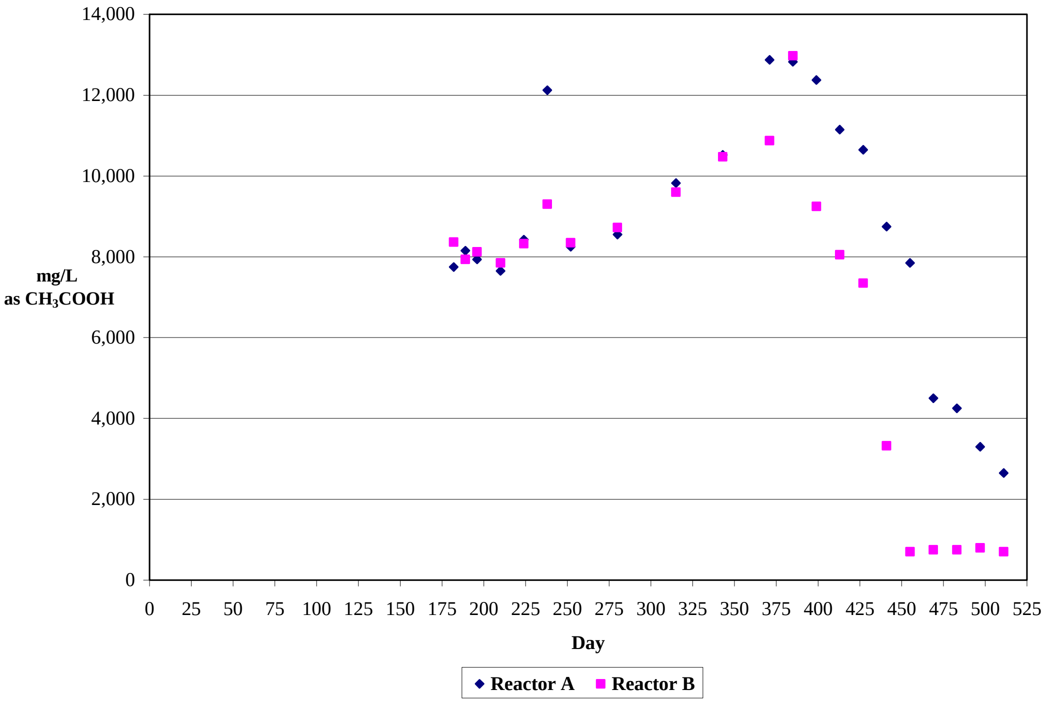


Figure 4.7 Volatile Fatty Acid (VFA) of simulated leachate

Percentage of Pb extracted was highest at high VFA concentration approximately 8,000 mg/L as CH_3COOH and low the pH (pH < 5) because of pH effect on Pb extraction. At higher concentration of VFA (>8,000 mg/L as CH_3COOH), leachate pH was also increased to a precipitation range for Pb. Moreover, VFA was in acetate form which was not able to form complex with metals. Therefore, there was no Pb extracted at this range of VFA. While at VFA lower than 4,000 mg/L as CH_3COOH, there was a generation of HS that could act as chelating agent to form complex with heavy metal (Christensen et al., 1996).

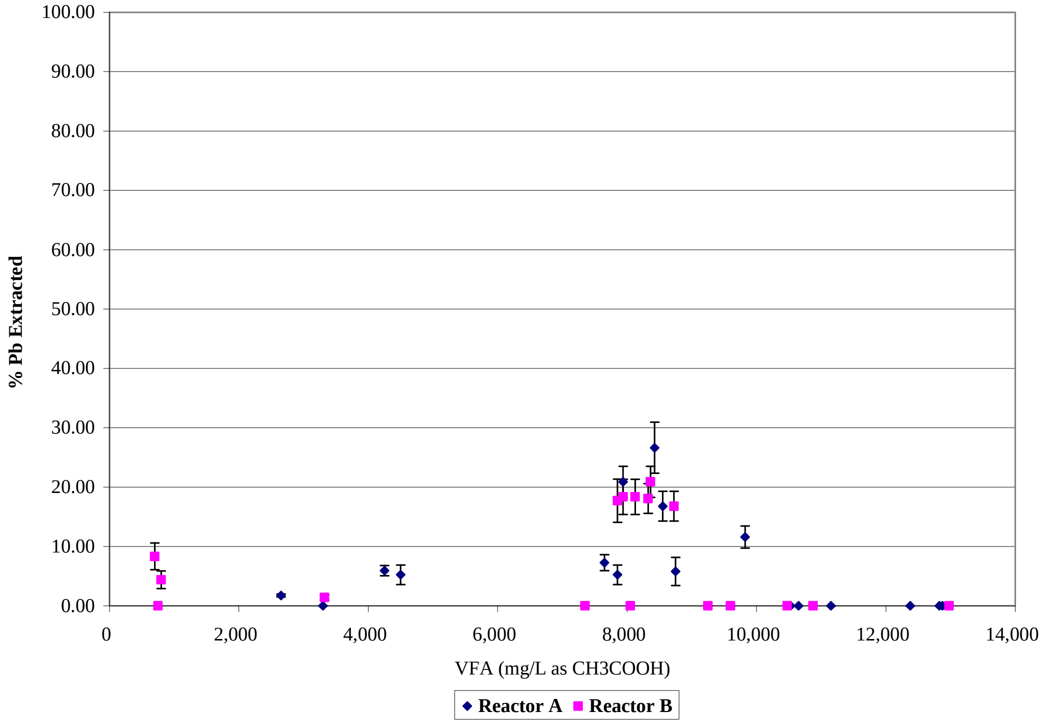


Figure 4.8 Plot between VFA and % Pb extracted

4.3.6 Pb extraction ability of EDTA and AHA

Pb extraction by EDTA solutions are presented in Table 4.2. EDTA can extract high amount of Pb from mine tailing with 36.55 ppm (61%) by 0.04 M EDTA and 45.11 ppm (75%) by 0.1M EDTA. The extraction ability of EDTA increased with increasing concentration of EDTA. Compare to simulated leachate, EDTA showed higher and more stable extraction ability while simulated leachate showed some fluctuation. However, low pH leachate in initial phase and acidogenesis phase showed high Pb extraction also.

Table 4.2 Pb extracted value and % Extracted from mine tailing by EDTA.

EDTA	Pb extracted (ppm)	% Extracted
0.04 M	36.55±2.07	61.09±3.46
0.1 M	45.11±3.26	75.4±5.45

The extraction ability of mine tailing with AHA is presented in Figure 4.9. The higher concentration (1,000 mg/L) presented the higher extraction ability than 500 mg/L concentration. The extraction ability of AHA increased with increasing pH. However, in comparison with simulated leachate, AHA showed lower extraction ability in the same pH. The resulted presented in Figure 4.10.

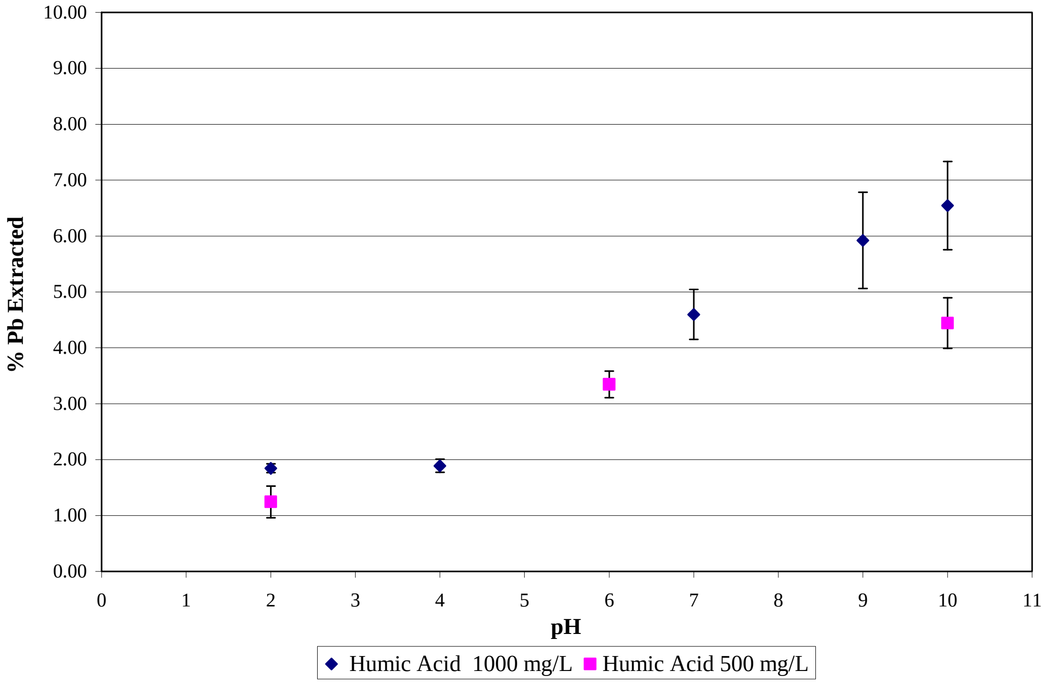


Figure 4.9 Plot between % Pb extracted and pH values of simulated leachate

The extracted heavy metals existed virtually all as the 1:1 metal-EDTA complexes (Sun et al.,2001). The agreement between total soluble Pb and Pb-EDTA complex was poorer than for other metals such as Cu, Ni or Zn. Pb was the least mobile of the four heavy metals. When the molar ratio of EDTA to total heavy metals in soil increased, the ratio of heavy metals leached to the EDTA added decreased. This means that the heavy metal extraction efficiency of EDTA decreases with increasing ratio of EDTA to total heavy metals in soil (Sun et al.,2001).

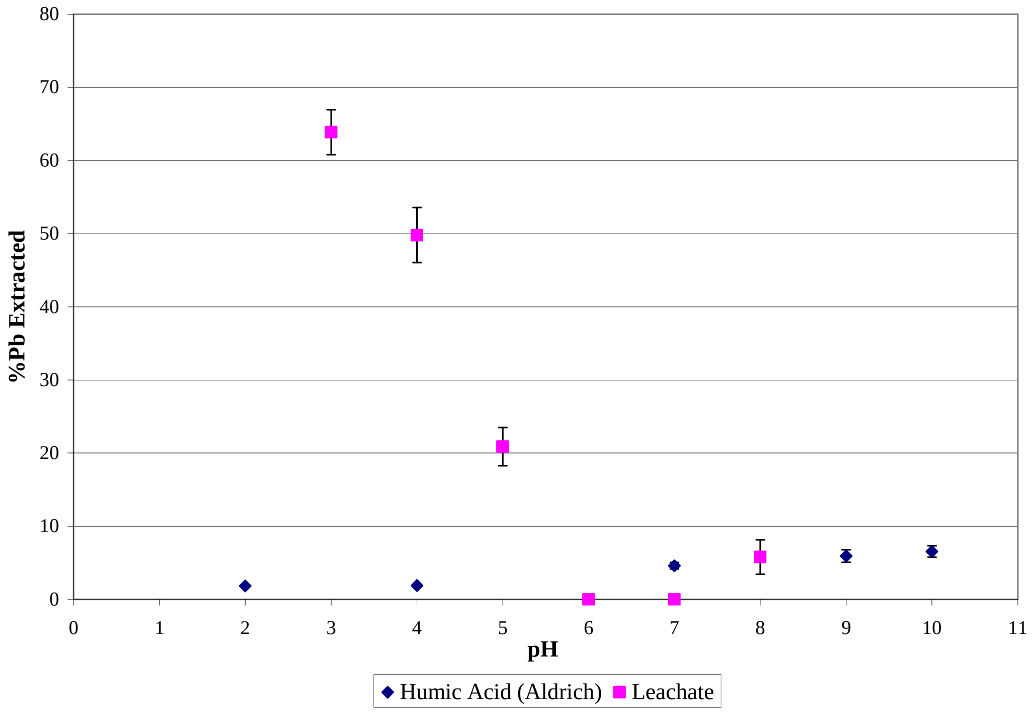


Figure 4.10 Plot between % Pb extracted and pH values of simulated leachate

EDTA was an effective extractant because of its strong chelating ability for various heavy metals (Xia et al., 2008). The average extraction efficiencies for Pb, Zn, Cu and Cd were 27.3-42.1%, 42.9-45.4%, 40.3-41.1% and 46.6-61.3% respectively. Percentage extractabilities of metal followed the sequence of Cd>Zn>Cu>Pb. The leaching of metals from granular solid wastes is a relatively quick process, in which equilibrium is attained within several hours (Janos et al., 2002). EDTA has strong complexing ability and forming well soluble metals complexes, exhibited a higher ability to leach metals in comparison with HA. Although HA and FA form also rather strong complexes with metals, their complex metal salts are usually sparingly soluble in water, which affects the leaching ability.

4.3.7 Fractions of heavy metals

The sequential extraction results of Akra mine tailing are presented in Table 4.3. The release of metals from contaminated matrix depends not only on the extraction conditions such as pH, reagent concentration etc., but also on the modes of metal retention within the soil. Consequently, metal reactivity and behavior towards the extracting solution also depend on the nature of the metal fixation on the matrix particles, which can be operationally measured by application of sequential extraction procedures. Weakly sorbed fractions such as exchangeable and carbonate could be readily extracted, but an effective extraction of strongly sorbed metals in oxide and residual fractions was not always guaranteed within different types of matrix and contamination sources.

Table 4.3 The results of sequential extraction of Akra mine tailing

Pb (mg/kg)	Fraction 1 Acid-soluble	Fraction 2 Reducible	Fraction 3 Oxidizable	Fraction 4 Residual	Total	Recovery (%)
Pb[(a)]	10.92±1.5	28.45±2.4	7.7±1.2	9.57±1.7	56.64	96
Pb (%)	19.28	50.24	13.59	16.88	100	
Pb in Soil[(b)]	0.093±0.007	21.5±1.2	1.43±0.08	14.8±1.5	37.8	97
Pb (%)	0.25	56.88	3.78	37.83	100	
Pb in Soil[(c)]	3.36 ±0.74	107±5	9.3±4.2	14.3±1.0	133.96	-
Pb (%)	2.50	79.87	6.94	10.67	100	

(a) This experiment

(b) data obtained from Cuong and Obbard (2006)

(c) data obtained from Zemberyova et al.(2006)

The predominant fraction of Pb is reducible fraction which is similar to other literatures (Cuong and Obbard, 2006; Zemberyova et al., 2006). Acid soluble and reducible fractions are more easily leaching fractions of heavy metal from matrix compared with oxidizable and residual fraction (Bacon et al., 2006). From Table 4.3, the combination of acid soluble and reducible fractions is 69.52% which is close to value of highest Pb extractable by leachate (69.54%). The residual fraction accounted for 16.88% which give significant fraction of Pb that could not easily be leached out.

Usually, the higher the proportion of the clay and silt content in soil, the lower extraction efficiency of EDTA for metal extraction, because extracted heavy metals could easily be adsorbed by iron-manganese oxides located on the surface of those soil particles (Zhuang et al., 2000). Li and Shuman (1996) also found the concentration of Zn in the Fe and Mn oxide fraction, which was not affected by EDTA, probably due to high association of Zn with the oxides. The amount of Pb that was removed correlated with the amount of Pb associated with the Fe and Mn-oxide and organic matter soil fractions (Barona and Romero (1996). Wasay et al. (1998) studied speciation of metals in polluted soils and found that most of the heavy metals were found to be bound to Fe-Mn oxides and the organic fraction (30-40%) except for Cd and Zn, which were mainly present on the exchangeable fraction (68-87%).

4.4 Conclusion

At very low pH (initial phase) simulated leachate of fruit and vegetable waste can give high Pb extraction ability. From these results pH showed the strong effect to Pb extraction ability of simulated leachate. Due to this experiment did not reach maturation phase, therefore tiny amount of HS was generated. From literature, HS has a major role for heavy metal mobility. Though, simulated leachate in initial phase of experiment showed high Pb extraction ability, it might not be appropriate for used as extracting agent because of its unstable properties. EDTA is a commonly used chemical for heavy metal remediation for contaminated matrix such as soil or mine tailing. In comparison with complexing agent as EDTA, some extraction results are higher than 0.04M EDTA and slightly lower than 0.1M EDTA. However, most of results had low extraction ability.

CHAPTER V

CHARACTERIZATION OF THE DISSOLVED ORGANIC CARBON IN SIMULATED LEACHATE FROM FRUIT AND VEGETABLE WASTES

Abstract

The purpose of this study is to characterized the composition and functional groups of fruit and vegetable waste simulated leachate. Simulated leachate was fractionated into HA, FA and HyI fraction by using DAX-8 resin. Then all fractions were characterized by CHNS/O Analyzer, UV-visible and FTIR. HA fraction can be isolated from medium-aged (Day 378) and old-aged(Day 520) simulated leachate only. Elemental analysis results indicated that HA from fruit and vegetable wastes is typical to HA from other sources such as AHA and leachate from MSW landfill. HA also showed higher carboxylic functional group than FA or HyI.

Keywords: Humic acids, Fulvic acids, Hydrophilic, DAX-8

5.1 Introduction

The leachate from a landfill deposit contains a large variety of different substances, both inorganic and organic. The composition of leachate can exhibit considerably spatial and temporal variations. He et al. (2006) found that it contained a high content of DOC. The existence of DOC is wide spread in aquatic environments and exhibits highly stable and microbial refractory properties. Many investigations have focused on characterizing the chemical structure, molecular size and formation source of DOC in aquatic environments. DOC is regarded as a continuum of organic molecules of different molecular weight and structures that could pass through 0.45 µm filtration membranes, including low molecular weight substances like amino acids, carbohydrates, organic acids and some high molecular weight substances like HS. DOC could be further fractionated into HA, FA and HyI fractions according to their hydrophilic hydrophobic interactions (Christensen et al., 1998; Wang and Zhou, 2003).

After fractionation, all these fractions can be further analyzed for its functional group and properties. Elemental analysis, spectroscopic characterization, molecular distribution and titration are commonly used to describe the properties of the fractions. Gobbels and Puttmann (1997) found that the structural characteristics of HA and FA consisted of an aromatic core surrounded by hydrolysable units of aromatic acids and phenols linked by ester and ether bonds. To date, characterizations of DOC in landfill leachate have been reported in many articles (Calace et al., 2001; Christensen et al., 1998; Kang et al., 2002; Wang et al., 2005). The great variety of leachate constituents prevents evaluation of the fate and the role played by each component in the environmental impact, so the studied of leachate characterization is proposed.

The DOC originates from the organic waste in the landfill and is a product of the anaerobic degradation processes in the landfill. Even in the old landfills with extensive methanogenesis , the leachate may after decades contain DOC at the level of thousands of milligrams per litre (Ehrig, 1983). The DOC may by itself be a groundwater contaminant, but it may also influence the behavior of many other contaminants. It has ability to form complexes with heavy metals such as Cd, Ni and

Zn (Christensen et al., 1996) and also capacity for binding hydrophobic organic contaminants (Chiou et al., 1986). The current understanding of the composition of DOC from landfill leachate is very limited. Harmesen (1983) showed that 33% of the DOC content of leachate from a methanogenic landfill was high molecular-weight compounds (MW>1000 Da) with low degradability. Artiola-Fortuny and Fuller (1982) described more than 60% of the DOC content of anaerobic leachate as humic-like material, and they suggested that FA apparently were formed before HA. Thus, as the leachte became older and more diluted, the ratio of HA/FA changed from below unity to above unity. The reports in the literature show that both HA and FA are present in old leachates, but in only very few cases both the HA and FA have been characterized and no reports exist on the fraction of the DOC that belongs neither to the HA nor to the FA. This fraction is usually called the HyI and is expected to constitute a substantial fraction of the DOC content.

The components of refractory organics are mainly HS, which are a naturally occurring mixture of organic compounds, ubiquitous in nature, which play an important role in both pollutant chemistry and the biogeochemistry of natural waters and soils. HS are formed through the breakdown of plant and animal tissues by chemical and biological processes (Kang et al., 2002). HS are refractory anionic macromolecules of moderate (1 kDa MW-FA) to high (10 kDA MW-HA) molecular weight. These HS contain both aromatic and aliphatic components with primarily carboxylic and phenolic functional groups (Trebouet et al., 2001). One of the unique characteristics of HS is its heterogeneity in terms of element composition, chemical functionality, and molecular size distribution. Because of this versatility, HS are known to significantly affect the behavior of some pollutants in natural environments, such as trace metal speciation and toxicity (Nederlof et al., 1993), solubilization and adsorption of hydrophobic pollutants (Chiou et al., 1986). These chemical features of HS make it a promising candidate for pollution remediation. Furthermore, being an all-natural substance, it is especially attractive for this use, because its own pollution potential is minimal. From heavy metals removal (Yates and Wandruszka, 1999) to solubilization of hydrophobic organic compounds (Chiou et al., 1986), and oxidative coupling or binding reactions (Dec and Bollag, 2000) comprise these kinds of research using HS or humic-metal complexes. However, the knowledge of its complexities and the structural characterization of HS have been major challenges, which in turn to understand its functioning in the environment.

Due to DOC or HS has chelating properties, Pb extraction from mine tailing in Thailand by simulated leachate from fruit and vegetable waste was studied and the results were presented in the previous chapter. However, knowledge of DOC characterization is very limited and there is no characterization information from these kinds of leachate. In this chapter, the characterization of simulated leachate of fruit and vegetable waste was performed. DOC was fractioned into three fractions as follow; HA fraction, FA fraction and HyI fraction before further analyzed by UV-visible, FTIR and Elemental Analysis. Some data was presented compare to information gained from literatures.

5.2 Material and methods

The isolation and fractination procedure was performed as described by Leenheer (1981), Marhaba et al. (2003) and Christensen et al. (1998).

5.2.1 Resin Cleanup Procedure

DAX-8 Resin

DAX-8 resin is a macroporous methylmetha crylate copolymer with an average surface area of 450 m^2/g and an average pore diameter of 250 ^oA. DAX-8 resin was prepared by slurring with 0.1 N NaOH, decanting off the fines, and storing the remainder in 0.1 N NaOH for 24 h. Organic resin contaminants were removed by sequential 24-h Soxhlet extractions with acetone and hexane. The resin slurry was stored in methanol and packed the column to be used. Methanol was pumped through the column until the effluent was free of hexane and then pump distilled water until the DOC of the effluent was 1 mg/L or less. The DAX-8 resin column was rinsed with 0.1 N NaOH, 0.1 N HC1, and distilled water just before application of the sample. Cleaned DAX-8 resin was stored in methanol.

AG-MP-50 Cation-Exchange Resin

AG-MP-50 is a strong acid, sulfonated, polystyrene macroporous resin. This resin was purified by Soxhlet extraction with methanol for 24 h. Resin was slurried with distilled water and packed the column to be used. Pump 3 N NH_4OH through the column until breakthrough of ammonia was observed. Hydrogen-saturated the resin by pumping four bed volumes of 2 N HC1 through the resin and rinse with distilled water until the specific conductance of the effluent was less than 10 mho. This resin should be stored in methanol.

5.2.2 Fractionation Procedure

The amount of DAX-8 (SUPELCO) resin was determined according to Leenheer (1981) with a capacity factor of 50 and a porosity of 0.6. DAX-8 resin refined with cleanup procedure was transferred into column (cylindrical glass column, 2.5 cm x 120 cm) in slurry of methanol. The packed resin was rinsed with two times

2.5 bed volumes of 0.1 N of NaOH first, then HCl and finished with distilled water until the conductivity and DOC of the effluents were below 10 µs/cm and 0.2 mg/L, respectively.

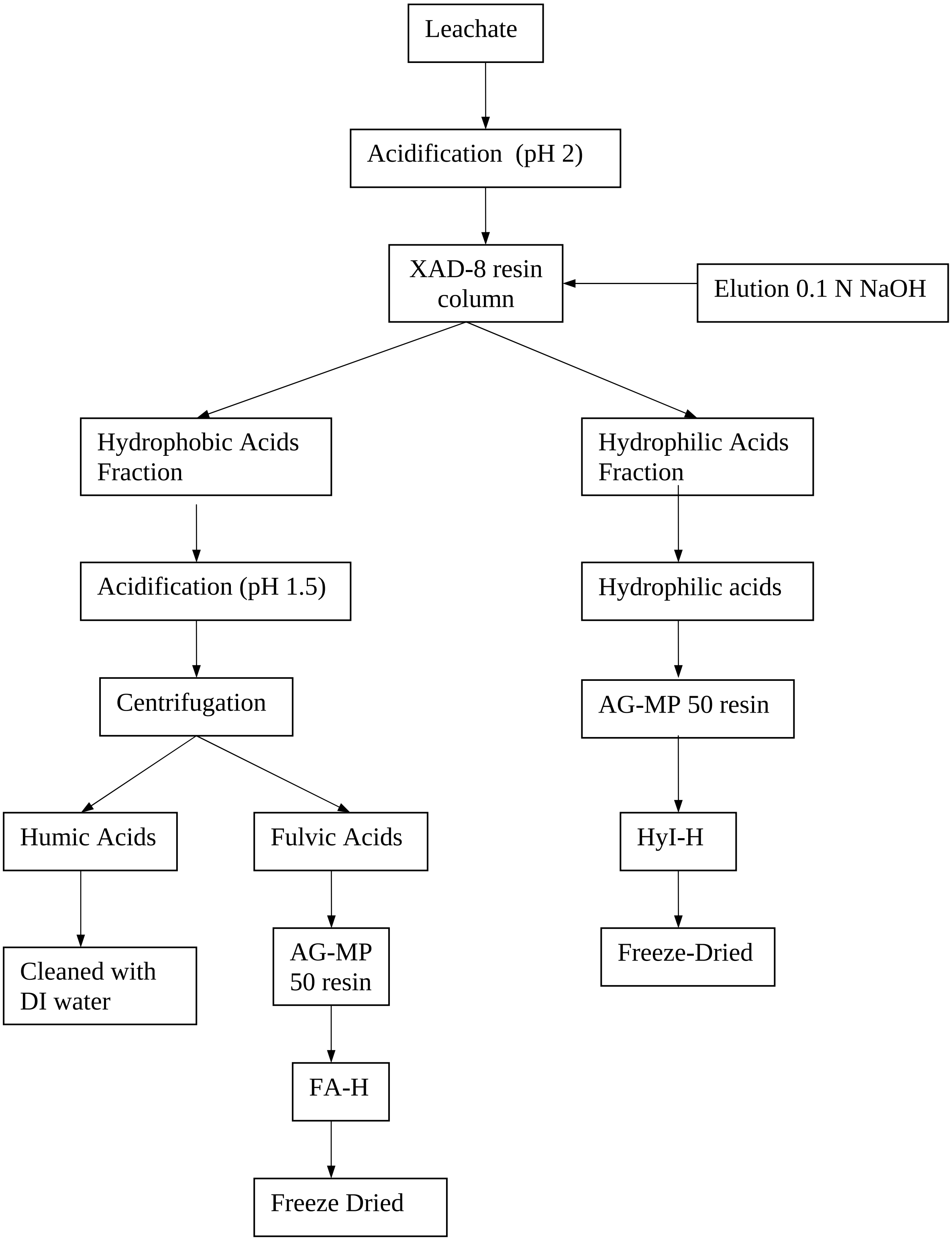


Figure 5.1 Fractionation diagram for the HA, FA and the HyI fraction from simulated landfill leachate

The fractionation procedure is presented in Figure 5.1. Simulated leachate collected from Day 115, Day 378 and Day 520 were used as representative of young-aged, medium-aged and old-aged simulated leachate, respectively. All three leachate were selected form the difference in their Pb extraction ability and also their quality as representative of different stabilization phase. All leachate was filtered through 0.45 µm membrane filter (Whatman) to clarify as DOC. Filtered leachate from the experiment (2 L) was acidified to pH 2 with concentrated HCl. There was no precipitate at this point but there was extensive bubbling of CO_2 release occurred because of acidification. Then leachate was loaded to the prepared column and filtered by gravity through DAX-8 resin column with a flow rate less than 4 mL/min. The elution was performed using 0.25 bed volumes of 0.1 N NaOH followed by 1.25 bed volumes of 0.01 N NaOH at velocity less than 3 mL/min. The effluent was hydrophobic fraction then it was acidified to pH 1.5 with concentrated HCl and left for 24 hr at 4 ^{o}C to precipitate and then solution was centrifuged at 10,000 rpm for 15 min to separate the precipitation. This procedure was repeated 3 - 4 times until the formation of a precipitation was no longer observed. HA fraction was precipitated from previous step and supernatant fraction was FA fraction. The HA fraction was washed with deionized water before being use. FA was passed through second column of DAX-8 resin to desalt and then eluted with the NaOH. After that FA was protonated by passing through AG-MP-50 (Biorad) cation exchange resin column with flow 3 mL/min. The FA was freeze-dried and stored in an exsiccator containing silica gels.

The residual DOC that was not sorbed onto the DAX-8 resin is in general terms called the HyI fraction. The HyI fraction was passed through a cation exchange resin (AG-MP-50, hydrogen saturated form) with flow 3 mL/min. The permeate from the column was freeze-dried and stored in an exsiccator containing silica gels.

5.2.3 Instrumental analyses

DOC of leachate was measured after leachate was passed through 0.45 µm membrane filter and the analysis was carried out with TOC analyzer.

UV-visible absorption spectra of all fractions were recorded on UV-vis spectrophotometer. 100mg/L of freeze-dried HA, FA and HyI fractions were prepared and pH adjusted to 6.0 (Kang et al., 2002). Spectra of the solutions were obtained over a wavelength range of 200-800 nm. Absorbance at 280, 465 and 665 nm were measured also.

FT-IR spectra were collected from potassium bromide disks (2-3 mg humic acids, fulvic acids or hydrophilic fractions and 300 mg KBr) using a FT-IR spectrophotometer.

Elemental analysis (C, H, N) was performed with a CHNS/O Analyzer (Perkin Elmer PE2400 SeriesII).

5.3 Results and discussion

5.3.1 Fractionation

The ratio of DOC to TOC concentration is as high as 96%, indicating that the DOC comprises a majority of the organic substances in the simulated leachate from fruit and vegetable wastes. The fractionation result revealed that the FA and HyI fraction of young-aged leachate account for 15.33% and 84.67% of DOC concentration, respectively while there was no HA at all. For medium-aged leachate, HA, FA and HyI fraction account for 0.48%, 22.34% and 77.18% of DOC concentration, respectively. For old-aged leachate, HA, FA and HyI fraction account for 0.92%, 29.46% and 69.62% of DOC concentration, respectively. The HS is about 15.33 – 30.38%. The HS (includes HA and FA) contents of simulated leachate is lower than the range of the reported landfill leachate samples (60-90%) and the content of HA is much lower than other aquatic DOC (Christensen et al., 1998; Kang et al., 2002). The HA fraction usually account for 30% or less, but HA from this experiment is less than 1%. It can be proven that the process in the simulated reactors was in the beginning of the humification process. It can also be proven that HA is formed after FA. HA receives a deeper humification process and has lower biodegradability than FA (Kang et al., 2002; Nanny and Ratasuk, 2002).

Zhang et al. (2007) studied DOM from landfill leachate rejected by nanofiltration. They found that HA, FA and HyI accounted for 40.86%, 34.15% and 24.99% respectively. Christensen et al. (1997) fractionated DOC from landfill leachate-polluted groundwater at Vejen Landfill, Denmark to HA, FA and HyI fractions. They found that FA fraction predominated accounting for about 60% of the total amount of DOC, the HyI fraction constituted about 30% of the total amount of DOC and the HA fraction was about 10% of the total amount of DOC.

5.3.2 Characterization

5.3.2.1 Elemental analysis

To obtain more detailed information on the HA, FA and HyI atomic ratio of H/C and O/C were calculated from the element analysis results. The elemental analysis is presented in Table 5.1. This is only results of HA of old-aged leachate that can be used. H/C ratios for HA is similar to Christensen (1989) but much lower than Kang et al. (2002). The value of H/C ratio here is closer to 1, indicating the predominance of the aromatic frame work in the compounds. The high H/C ratios in DOC in the aquatic imply that the structure contains significant portions of aliphatic functional groups. A lower H/C ratio in HA indicates that it has more condensed aromatic structure and is slightly less aliphatic than FA. Therefore, the relatively high H/C ratios in the leachate HA implied that the structures contain significant portions of aliphatic functional groups. The O/C ratio is correlated with the oxidation degree of DOC. The O/C ratios of HA simulated leachate is 0.64 which similar to Christensen (1989) but much higher than Knag et al. (2002).

In comparison with AHA (Kang et al. (2002)), HA fractionated from simulated leachate have a lower content of carbon, hydrogen and oxygen than those of AHA and the literature. Moreover, the value of H/C and O/C ratio are close to values from AHA (Kang et al., 2002). The high molecular weight fractions of old leachate are complex structures formed by condensed nuclei of carbons substituted by functional groups containing nitrogen, sulphur and oxygen atom; the low molecular weight fractions of leachate are, instead, characterized by linear chains substituted by oxygenated functional groups such as carboxyl and/or alcoholic groups (Calace et al., 2001).

Table 5.1 Elemental composition of HA, FA and HyI

	C (w/w%)	H (w/w%)	N (w/w%)	O (w/w%)	H/C	O/C
HA (from this experiment)	47.2	5.2	7.1	40.5	1.32	0.64
Literature[(a)]						
HA	50.7	4.0	2.2	42.1	0.95	0.62
FA	51.4	4.4	0.9	42.5	1.02	0.62
HyI	47.4	4.7	2.5	42.2	1.19	0.67
Literature[(b)]						
HA (young landfill)	56.2	8.8	8.3	26.7	1.54	0.39
HA (medium-aged landfill)	57.1	7.0	5.7	30.2	1.48	0.40
HA (old landfill)	56.1	7.2	7.4	29.3	1.88	0.36
FA (young landfill)	45.6	9.6	12.0	32.8	1.51	0.52
FA (medium-aged landfill)	53.6	6.7	2.5	33.8	1.49	0.47
FA (old landfill)	50.9	6.4	2.4	35.2	2.53	0.54
Aldrich HA	50.3	5.7	0.4	43.6	1.35	0.65

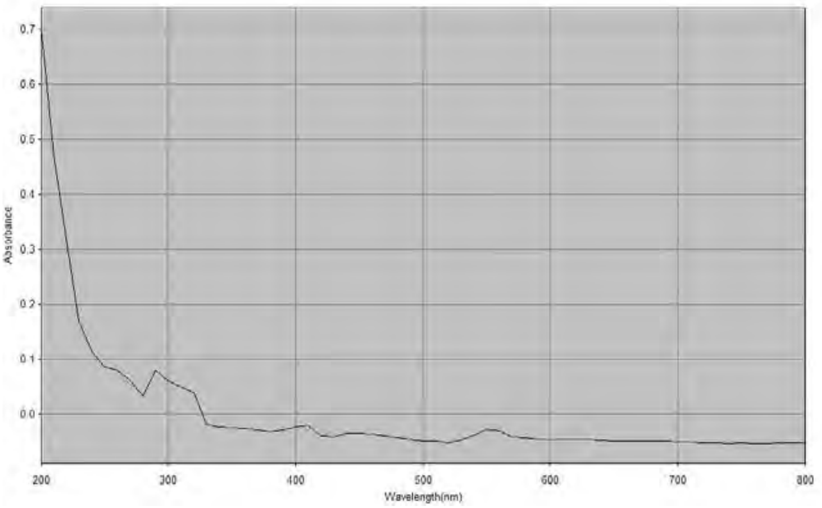
(a) Data obtained from Christensen (1998) for DOM from landfill leachate

(b) Data obtained from Kang et al. (2002) for DOM from different landfill ages leachate

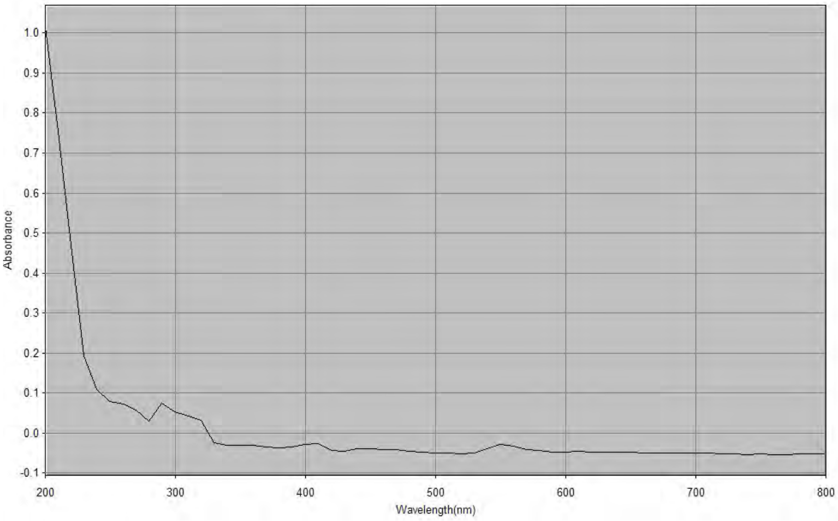
Christensen et al (1997) also calculated the O/C ratio from the elemental analyses which showed similar O/C ratios for HA, FA and the HyI fraction. The O/C ratios were relatively high HA from leachate-polluted groundwater compared to O/C ratios reported for HA from other origins. This indicates a high content of carboxylic groups, of phenolic groups or of carbohydrates in HA isolated from leachate-polluted groundwater. According to Steelink (1985), aquatic FA generally has a higher O/C ratio than HA. The H/C ratios calculated from the elemental analyses were higher for the HyI fraction than for the HA and FA, indicating a more aliphatic character of the HyI fraction (Kim et al., 1991). With similar oxygen contents for all three DOC fractions, the more aliphatic character of the HYI would imply also a lower aromaticity and, thus, a less efficient binding of hydrophobic organic contaminants (Gauthier et al., 1987)

5.3.2.2 UV-vis

The UV-vis spectra of the simulated leachate are shown in Figure 5.2. HyI fraction of medium-aged and old-aged leachate show lower absorbance than FA which is same result as Kang et al. (2002) and Zhang et al. (2007) except young-aged leachate. HA of old-aged leachate shows the highest absorbance comparing to FA and HyI fraction of all leachate. This may suggest that the aromaticity and molecular weight which are known to increase as humification process proceeds (Kang et al., 2002). However, the absorbance spectra of HA from simulated leachate gave lower absorbance than Aldrich HA.



(a)



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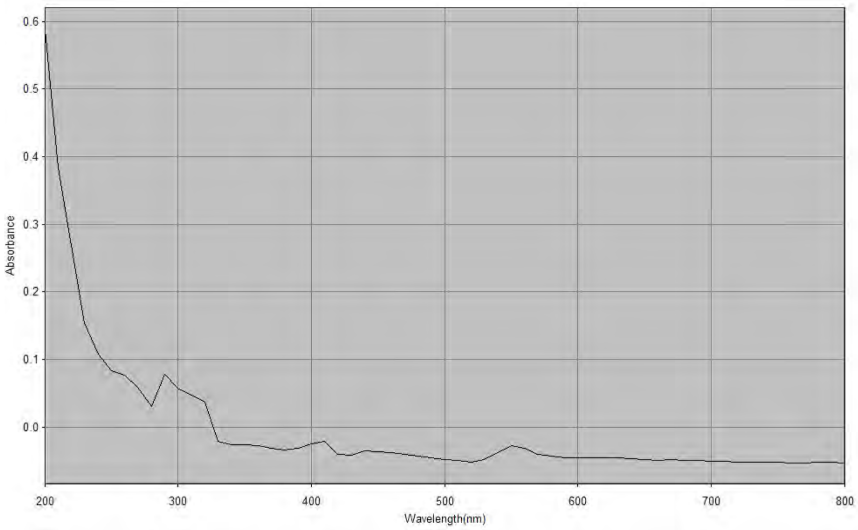

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0.2
0.1
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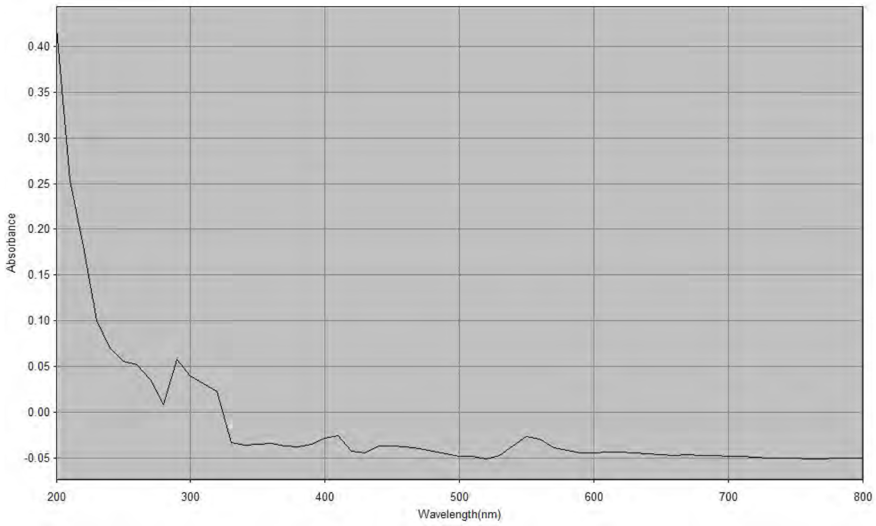
200
300
400
500
600
700
800
Wavelength(nm)

(c)



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0.20
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0.00
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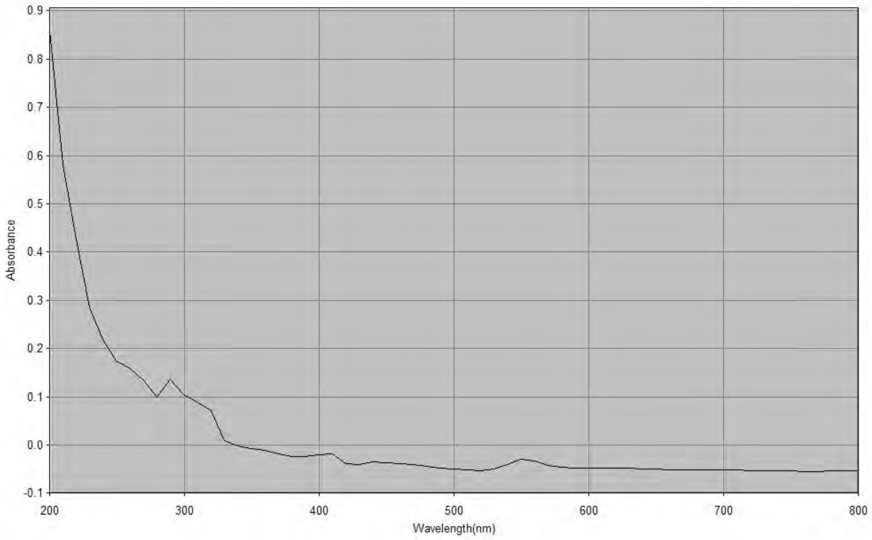
300
400
500
600
700
800
Wavelength(nm)

(d)



Absorbance
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0.7
0.6
0.5
0.4
0.3
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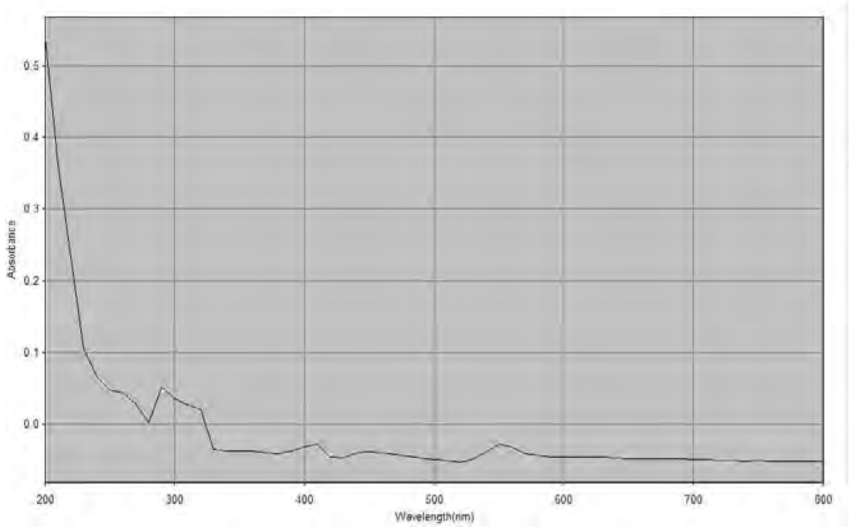
0.1
0.0
-0.1
200
300
400
500
600
700
800
Wavelength(nm)

(e)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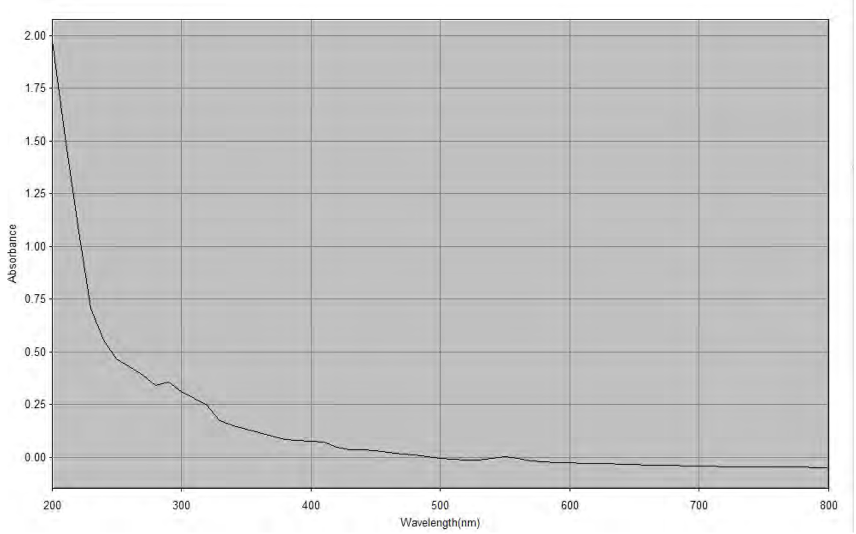
Absorbance
200
300
400
500
600
700
800
Wavelength(nm)

(f)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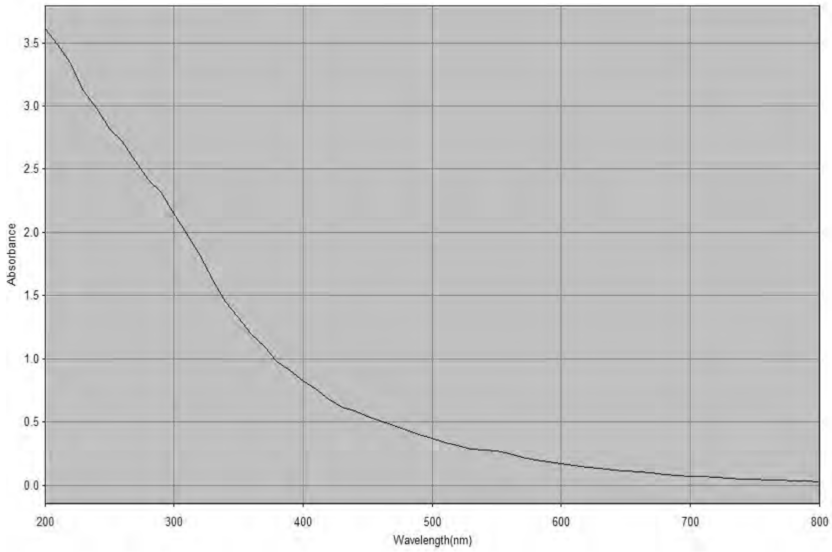
500
600
700
800
Wavelength(nm)

(g)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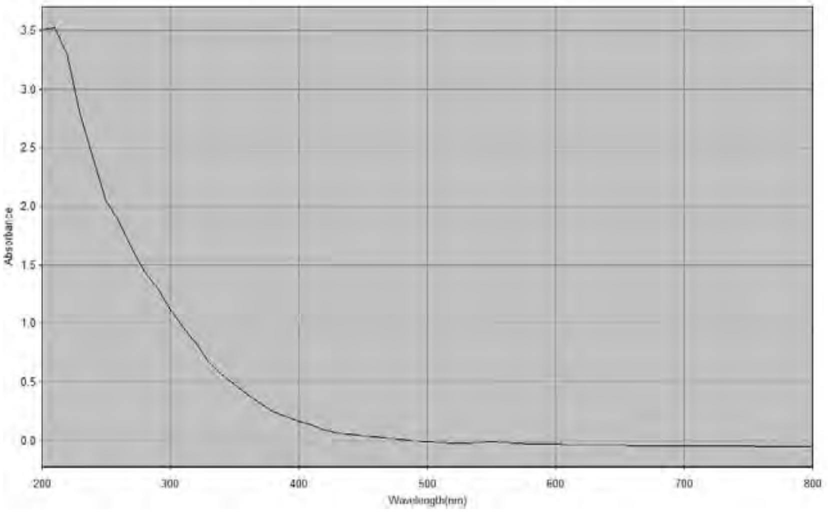
500
600
700
800
Wavelength(nm)

(h)



(i)

Figure 5.2 UV-vis spectra of (a) FA young leachate; (b) HyI young leachate; (c) FA medium-aged leachate; (d) HyI medium-aged leachate; (e) FA old leachate; (f) HyI old leachate; (g) HA old leachate; (h) Aldrich HA; (i) Suwanee River FA

Zhang et al. (2009) found that their absorbance of UV-visible spectra follows the order: Aldrich HA > HA > FA > HyI. HA shows a deeper humification process and larger molecular weight compared with the FA spectra.

To investigate more information on the characteristics, ratio of absorption coefficient at 465 and 665 nm (*e*4/*e*6) were measured and presented in Table 5.2. The values of *e*4/*e*6 are generally known to be inversely proportional to molecular weight and proportion to acidity (Kang et al., 2002). The larger *e*4/*e*6 values were associated with lower molecular weights (Christl et al., 2000). The *e*4/*e*6 ratio is inversely related to the degree of condensation of the aromatic network in HS (Senesi and Loffredo, 1999). The data of FA obtained from this experiment showed similar result to Kang et al. (2002). HA gave values of *e*4/*e*6 lower than Kang et al. (2002) but higher than AHA which means that HA from simulated leachate has lower molecular weight than AHA and higher acidity than AHA. FA gave a little higher value than HA thus HA from this experiment has higher molecular weight than FA. Zhang et al. (2009) found that the *e*4/*e*6 from their experiment follows FA > HA > HyI > AHA.

Table 5.2 Ratio of absorption coefficient of HA, FA and HyI fractions (100 mg/L at pH 6.0)

Landfill age		*e*4/*e*6
This experiment		
Young leachate	FA	5
	HyI	1.50
Medium-aged leachate	FA	3.00
	HyI	1.30
Old leachate	FA	6.00
	HyI	1.00
	HA	4.80
Aldrich	HA	3.49
Suwannee River	FA	13
Young leachate(a)	FA	6.52
	HA	5.52
Medium-aged leachate(a)	FA	6.88
	HA	6.5
Old leachate(a)	FA	5.46
	HA	5.1

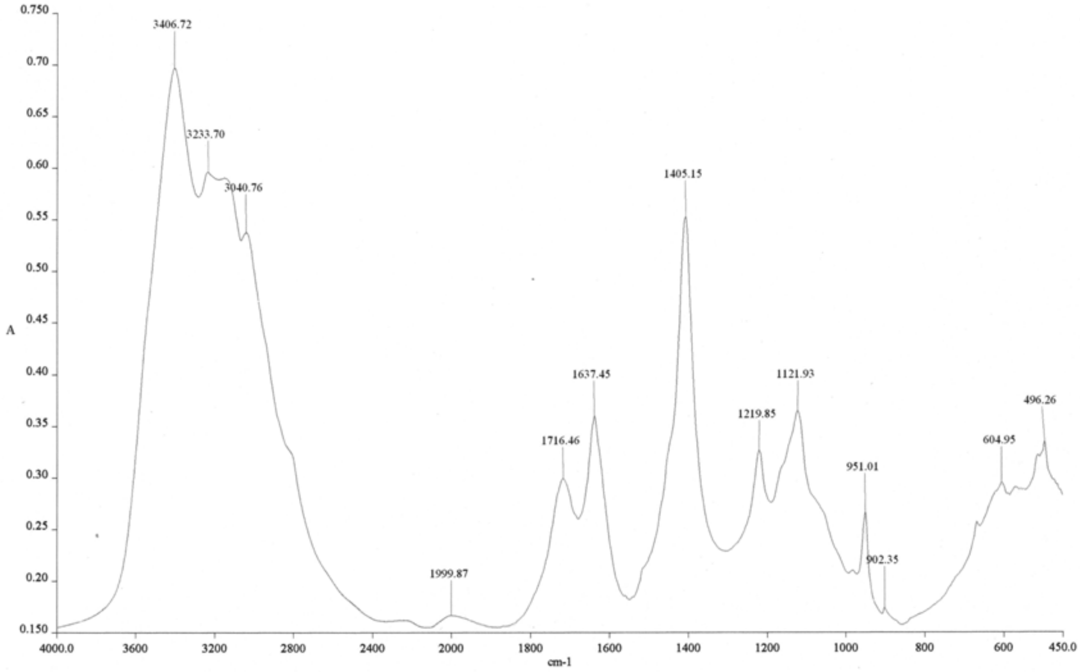
(a) Data obtained from Kang et al. (2002)

5.3.2.3 FTIR

FTIR spectra are presented in Figure 5.3 that give information about specific molecular structures and various functional groups. The results show FA and HyI spectra of all samples but it shows HA spectra from old-aged leachate only because of limited amount of fractioned HA from medium-aged leachate. The FTIR spectra were dominated by absorbance due to aromatic aliphatic, carboxylic and hydroxylic groups mainly. The typical bands of common soil and aquatic HS are 3400 cm^{-1} (H-bonded OH), 2900 cm^{-1} (aliphatic C-H stretching), 1690-1710 cm^{-1} (C=O), 1540 cm^{-1} (C=N stretching, amide II band), 1240 cm^{-1} (C-O stretching) (Kang et al, 2002).

In comparison of FA from all samples, FA from young and medium-aged leachate show similar spectra with absorption band at 1402 cm^{-1} due to bending of CH_2 adjacent to C=O oxygen (-CH_2-C=O), 1630 cm^{-1} due to C=C double bonds in benzene rings (Fan et al., 2006), 1720 cm^{-1} due to C=O stretching of COOH and ketonic C=O, and 3400 cm^{-1} due to intermolecular O-H stretching. FA spectra of old-aged leachate shows similar absorption band as FA from young-aged and medium-aged leachate except it shows high absorption band at 1571 cm^{-1} due to the first and second band of amides (stretching of C=O and C-N bonds) (Calace et al., 2001) and higher absorption band at 3400 cm^{-1}. When compare between HyI fractions, HyI from medium-agd and old-aged leachate show similar spectra. In addition it also shows similar spectra to spectra of FA from young-aged and medium-aged leachate. However, HyI shows lower absorbance at 3400 cm^{-1} than FA and HyI from medium-aged leachate hardly shows absorption at this band. HyI fraction from young-aged leachate has much different spectra. It has much higher absorbance at 3400 cm^{-1} and a little higher at 1630 cm^{-1} and 1710 cm^{-1} but lower at 1405 cm^{-1}. In can be indicated that HyI of young-aged leachate have higher intermolecular O-H stretching (3400 cm^{-1}) and lower carboxylic group (1710 cm^{-1}).

Unlike FA and HyI, HA shows much different spectra. It shows a very high absorbance at 1720 cm^{-1} which means that it has much higher carboxylic group. It also shows high absorbance at 1080 cm^{-1} which is typical of stretching C-O bonds in alcohol and ethers. FA and HA of old leachate show content of aliphatic group (2900 cm^{-1}) with similar absorbance value. From HISS, HA from aquatic DOM has a strong absorption band at 1630 cm^{-1}, which is an important distinction between aquatic FA and HA. The results presented in HA spectra shows that it has much higher absorbance at this band than FA.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A
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0.150
3406.72
3233.70
3040.76
1999.87
1716.46
1637.45
1405.15
1219.85
1121.93
951.01
902.35
604.95
496.26
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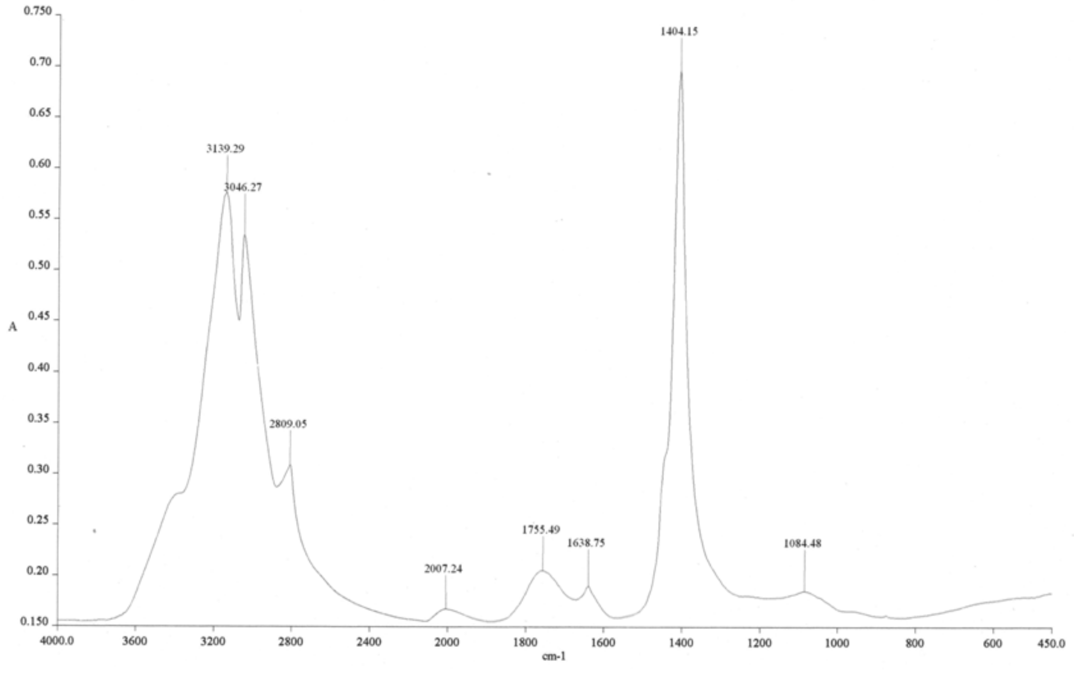
cm-1

(a)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3046.27
2809.05
2007.24
1755.49
1638.75
1404.15
1084.48
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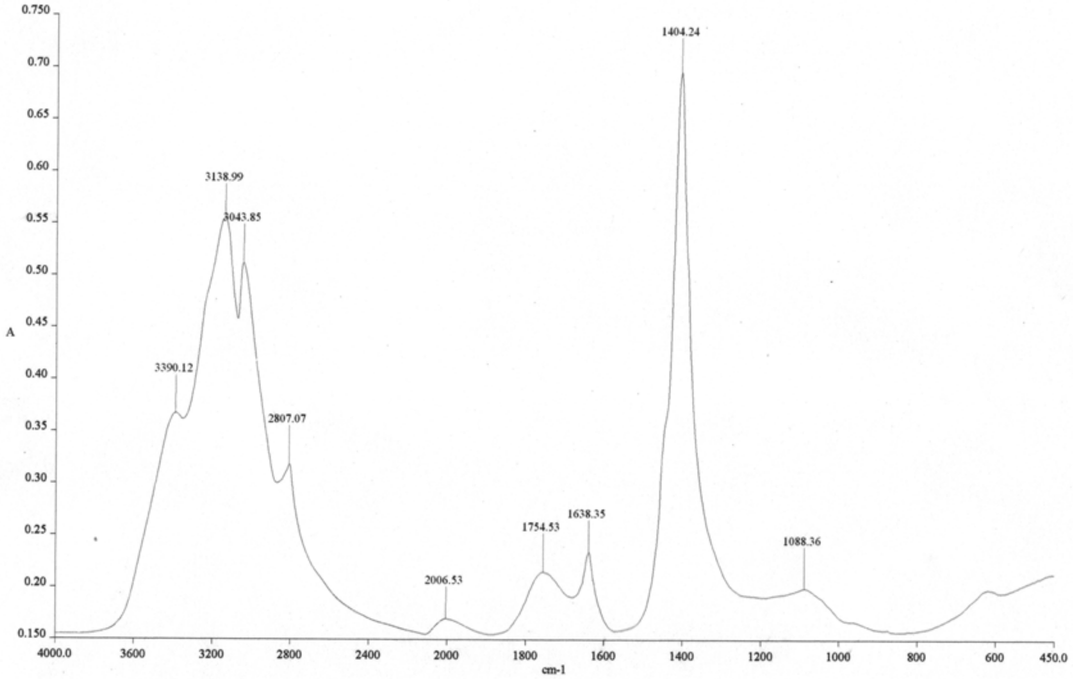
cm-1

(b)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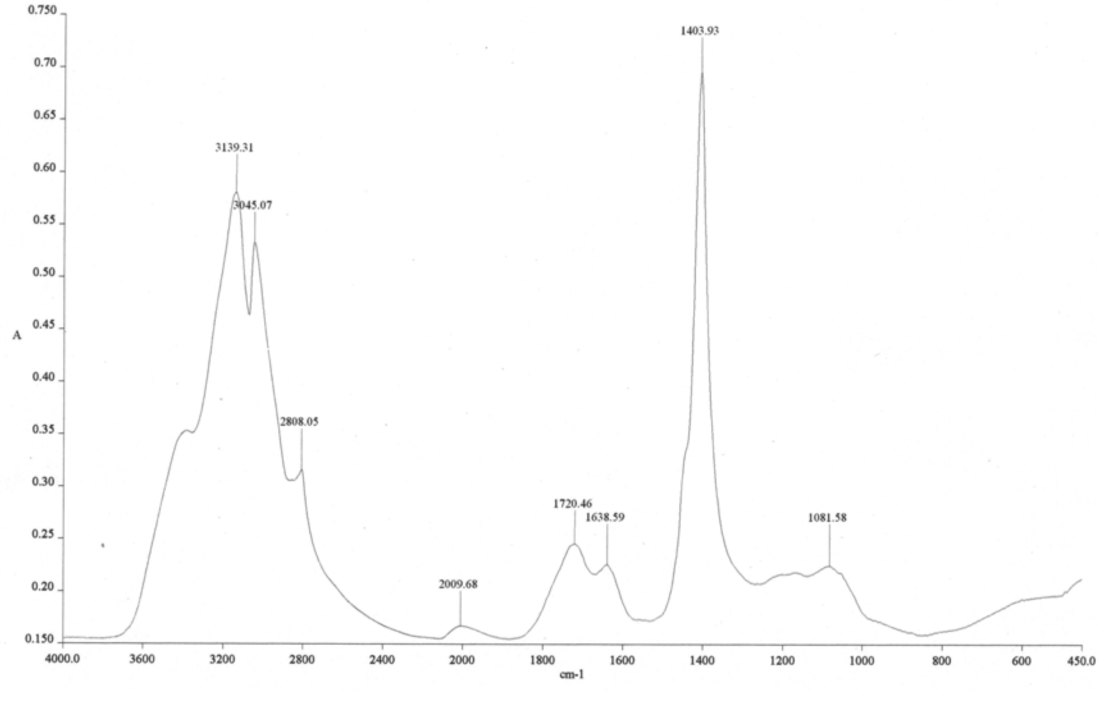
cm-1

(c)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3045.07
2808.05
1720.46
1638.59
2009.68
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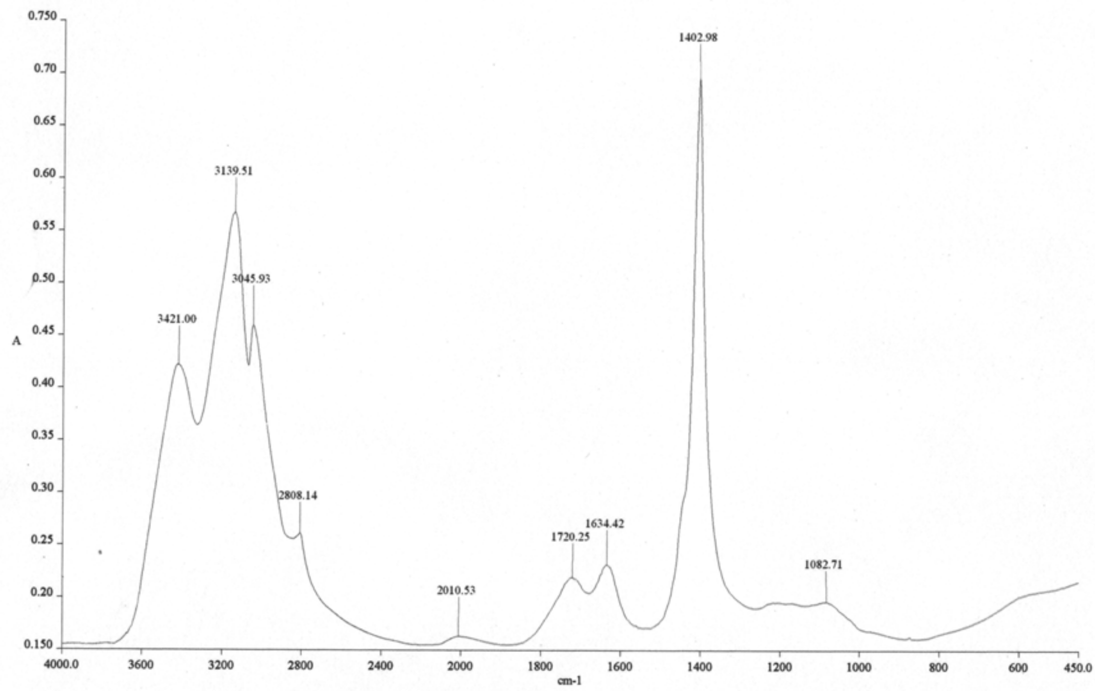
450.0
cm-1

(d)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1600
1400
1200
1000
800
600
450.0
cm-1
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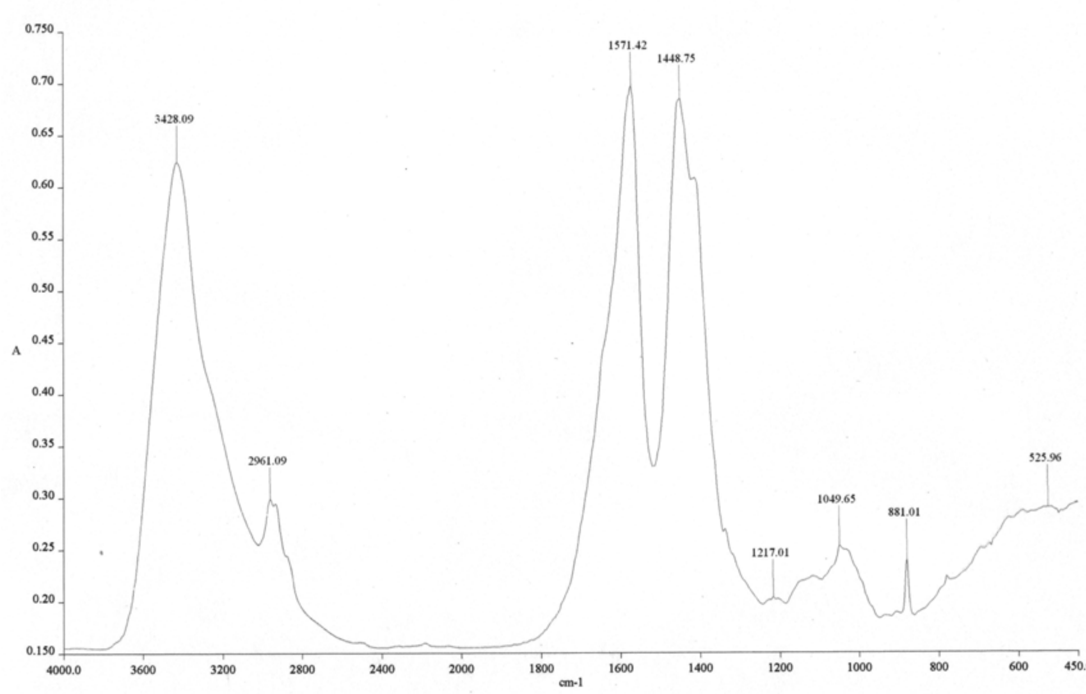
(e)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A
4000.0
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
450.0
cm-1
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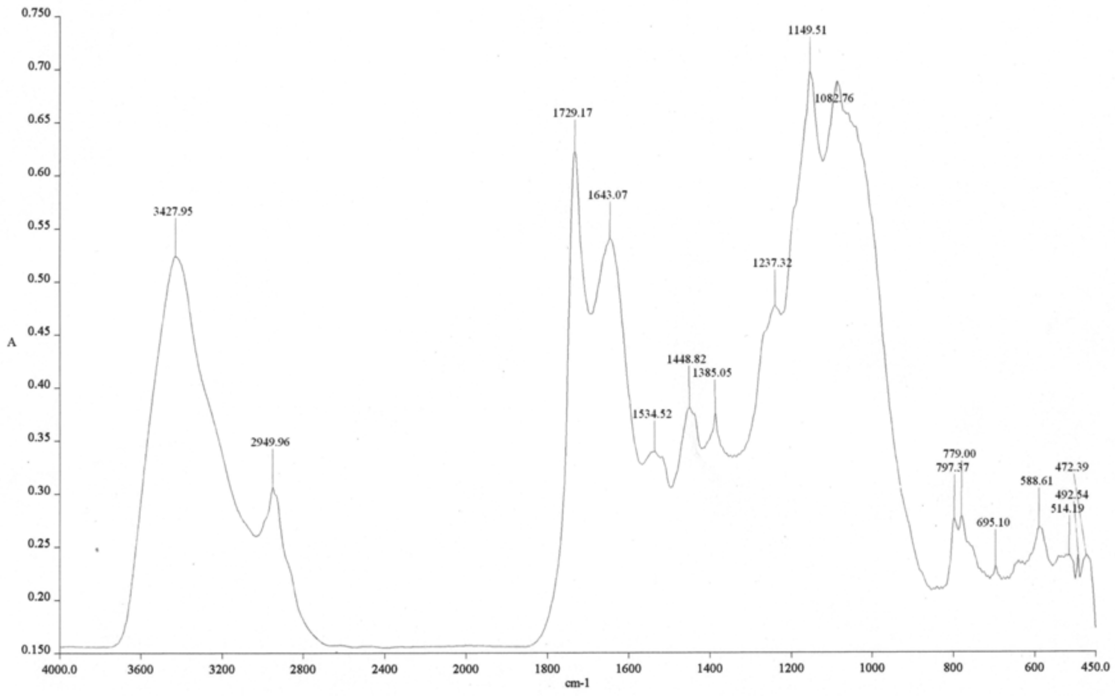
1049.65
881.01
1217.01

(f)



(g)

Figure 5.3 FTIR spectra of (a) HyI young leachate; (b) HyI medium-aged leachate; (c) HyI old leachate; (d) FA young leachate; (e) FA medium-aged leachate; (f) FA old leachate; (g) HA old leachate

Kang et al. studied characterization of HS presented in landfill leachate with different landfill ages. The elemental analysis and spectral features showed that the aromatic character in the leachate HS was relatively lower than that of AHA, and higher in the HS of older landfill leachate. Fluorescence spectra indicated that HA had a relatively higher content of condensed aromatic compounds than the FA obtained from the same sources, and the spectrum of commercial HA showed that aromatic compounds may be present in a much more condensed and complex form. They concluded that the characteristics of functional groups of both leachate HS and AHA molecules were basically similar. Their results indicated that leachate FA had higher acidity and AHA was more aromatic than leachate HS. They also concluded that the degree of humification increased as the landfill age increased.

The results from FTIR showed similar spectra to Zhang et al. (2009) at the following absorption bands: 3400-3200 cm^{-1} due to intermolecular O-H stretching, 1710-1690 cm^{-1} due to C=O stretching of COOH and ketonic C=O and 1240 due to C-

O stretching and also the C=C double bonds in benzene ring. Their results also showed that HyI fraction shows more complicated absorption bands at low wave numbers due to halogenated compounds or some other hydrophilic organic compounds. One of significant peak from HA of this experiment was 1720 cm^{-1} which related to CO stretching in carboxylic acids, aldehydes and ketone groups while Christensen et al. (1998) found this peak dominated in FA. It was indicated that HA was dominated by carboxylic acids, aldehydes and ketone groups. In addition, FTIR spectra of the HA indicate a higher proportion of carboxylic groups than FA and the hydrophilic fraction. The content of aliphatic groups (2900 cm^{-1}) appeared more pronounced in the FA and in the HyI fraction than in the HA (Christensen et al., 1998) which was different results of simulated leachate. The spectra at 2900 cm^{-1} of HA and FA from old-aged showed not much different values, indicating similar content of aliphatic groups.

5.4 Conclusion

HA, FA and HyI fraction were isolated and purified from three simulated leachate of fruit and vegetable wastes. Only HA from medium-aged and old-aged leachate that can be isolated, however it was a very tiny amount, less than 1%. This is much lower than HA fraction from literature (10 - 40%). FA fraction is about 22-29% and HyI is about 69-77%. The elemental analysis of HA of old-aged leachate was in the typical range for HS for HA from other substances. The value of H/C ratio here is closer to 1, indicating the predominance of the aromatic frame work in the compounds. An O/C ratio for HA indicates a considerable content of carboxylic groups or carbohydrates. From FTIR spectra, it indicated that HA contains higher content of carboxylic groups than FA or HyI, thus there is a potential to form complexes with heavy metals. However, the small content of HA indicated the initial process of humification in the system. Though higher content of carboxylic group of old-aged HA has higher potential to form complexes with Pb, its small quantity might not present the significant affect to extraction ability of leachate.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

Simulated leachate generated from fruit and vegetable wastes (market waste) were studied to extract Pb from mine tailings. This study consists of three parts. Firstly, bioreactor generation of leachate from fruit and vegetable wastes. Simulated leachate was collected and measured for its properties regularly. Secondly, simulated leachate collected from different period of degradation process was used to extract Pb from mine tailing (Akra Mining, Thailand). The studies of correlation between leachate extraction ability and its properties such as DOC, VFA were conducted. The investigation of others complexing agents extraction ability, for example, EDTA and AHA, were also employed. Finally, dissolved organic carbon (DOC) from simulated leachate with different ages were fractionated into HA, FA and HyI. All these fractions were characterized by UV-visible, elemental analysis and FTIR.

The bioreactor study of fruit and vegetable wastes revealed that the system had very low pH in first part of experiment which not appropriate for anaerobic bacteria and the system showed insufficient buffering capacity. The stabilization process was longer than expected. Therefore, alkalinity addition and leachate recirculation were brought to enhance the degradation process and reduce the stabilization time. Without alkali addition, the system became cease and no methane production. Since the beginning of the operation, pH tended to increase rapidly during the first 30 Days from pH 3.5 to pH 4.5. After that, pH increased gradually from 4.5 on Day 30 to 4.7-5 on Day 80. After Day 200, alkali addition phase, pH value increased gradually from 5 and reached 9 at the end of experiment. The conversion of fatty acids caused an increase in the pH levels within the alkalinity supplemented reactors. ORP values started at 150-180 mV and then -50 to -100 mV, indicating the anaerobic environmental condition occurs. After that the ORP values seem stable until alkalinity addition. Then they showed a highly drop from -389 to -420 mV for both reactors. The degradation value of ORP shows the positive effect of pH neutralization of leachate. There was no methane production before alkalinity addition, after that methane production increased to 60%-70% at the end of the experiment. Methane gas production, dramatically drop of VFA and COD were observed after alkali addition. The alkali addition showed the acceleration of fruit and vegetable wastes stabilization and also enhance gas production. However our system did not go to maturation phase as expected at the end of experiment.

The simulated leachate from previous experiment was used as extracting agent. The extraction ability results of different leachate samples showed very high extraction ability only the first few 140 days of leachate. After that the extraction ability decreased gradually until there was no extraction ability in the middle of experiment. However, after recirculation and buffering addition started from Day 200, the leachate stabilization was improved. The extraction ability of leachate started to increase from no Pb extracted to 7% - 9% extracted. DOC values remained nearly constant from the beginning of experiment at approximately 12,000 – 14,000 mg/L then decrease dramatically from 16,168 in Day 385 to 1,662 mg/l in Day 511 until the end of experiment. % Pb extracted was very low in low DOC values and increasing when DOC values increased. When DOC values are between 12,000 to 16,000 mg/L, % extraction ability ranges from no extraction ability to 70% Pb extracted. Though the leachate showed high extraction ability at high DOC value during the first 140 days of the experiment, DOC from this phase came from acetic acid and also organic acids which remained as a molecule at low pH. While the last phase of experiment (Day 455 onward), DOC showed lower values but contain higher content of HS (30.38%). The correlation between leachate extraction ability and leachate pH was similar to leachate ages because pH increase when leachate age increase. The results were similar to desorption/dissolution curves from literature that shows the desorption for Cu and Pb are greatest at low (<3) and high pH (>6). From these results, DOC from old-aged leachate might have positive effect to extraction ability of leachate however while pH has stronger effect to leachate extraction ability than DOC in pH lower than 4.5. In comparison with simulated leachate, AHA showed lower extraction ability while EDTA showed more stable and higher extraction ability.

From the extraction experiment, leachate samples with different extraction ability were fractionated into HA, FA and HyI fraction to clarify the functional group of each fraction After the fractionation of leachate DOC, the results revealed that HA was the smallest fraction which was less than 1% in DOC from medium-aged and old-aged leachate while there was no HA fraction from young-aged leachate. FA and HyI presented approximately 22-29% and 70-77% respectively. The leachate from the end of experiment was in the beginning of humification process. From elemental analysis results, HA showed similar characteristic to HA from other sources. The relatively high H/C ratios in the leachate HA imply that the structures contain significant portions of aliphatic functional groups. HA of old leachate shows the highest absorbance comparing to FA and HyI fraction of all leachate. This may suggest that the aromaticity and molecular weight which are known to increase as humification process proceeds. Results from UV-visible presented that HA from simulated leachate has lower molecular weight than AHA and higher acidity than AHA and HA higher molecular weight than FA. From FTIR spectra, it indicated that HA contained higher content of carboxylic groups, thus there was a potential to form complexes with heavy metals. Leachate from this kind of waste contain limited amount of HS so the chelating property showed less effect than pH.

According to our analysis, high extraction ability of DOC in maturation phase was seen since the stabilization process was longer than expected. This allowed for short period of time and resulting in small production of HS. Though, fruit and vegetable waste gave high yield of methane gas (nearly 70%) and large volume of leachate, limited production of HS prohibited further use of leachate as Pb extractant.

6.2 Recommendations

1. Due to the fact that HS generation from this kind of waste was lower content than other aquatic sources, the improvement of leachate properties or waste composition to increase HS production should be studied.
2. In addition, the improvement of simulated leachate properties such as more alkali addition, a temperature control, could be studied to increase biodegradation process for this kind of waste.
3. Since mine tailing contains many heavy metals that can be competed and extracted before Pb, single extraction of heavy metal from spiked matrix should be studied.

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APPENDICES

APPENDIX A

A.1 pH & ORP of simulated leachate

Day	pH		ORP (mV)	
	Reactor A	Reactor B	Reactor A	Reactor B
0	3.50	3.60	-	-
1	3.52	3.65	124.1	120.0
2	3.56	3.67	154.2	174.4
3	3.55	3.69	136.5	167.8
4	3.56	3.69	118.5	148.3
5	3.55	3.72	117.3	126.9
6	3.55	3.73	120.2	130.5
7	3.56	3.76	143.3	153.6
8	3.58	3.79	130.8	63.7
11	3.64	3.87	91.7	114.5
12	3.72	4.14	80.3	109.5
13	3.72	4.20	90.3	105.5
14	3.72	4.21	105.2	100.7
15	3.75	4.31	110.5	97.5
18	3.75	4.33	108.4	100.2
19	3.78	4.43	105.6	97.8
20	3.89	4.46	103.8	98.9
21	3.92	4.46	93.1	93.9
22	3.85	4.48	90.8	91.7
25	3.96	4.47	90.3	89.5
26	4.12	4.54	85.7	75.6
27	4.24	4.54	83.3	64.9
28	4.28	4.52	80.5	61.8
29	4.33	4.52	79.2	60.1
32	4.34	4.53	78.8	58.6
33	4.35	4.53	77.9	58.2
34	4.35	4.53	77.1	57.8
35	4.35	4.49	78.9	74.5
36	4.34	4.48	77.2	70.5
39	4.35	4.52	73.8	62.4
40	4.35	4.54	70.9	54.2
41	4.36	4.58	76.8	26.3
42	4.35	4.62	91.5	85.7
43	4.40	4.67	76.9	56.9

Day	pH		ORP (mV)	
	Reactor A	Reactor B	Reactor A	Reactor B
46	4.37	4.69	49.6	45.1
47	4.35	4.71	71.5	72.7
48	4.39	4.51	45.3	-5.0
49	4.44	4.86	58.8	55.4
50	4.43	4.86	63.4	43.3
53	4.44	4.87	60.8	38.2
54	4.44	4.88	55.4	29.0
55	4.47	4.90	68.1	17.9
56	4.47	4.90	67.3	18.4
57	4.48	4.91	20.9	25.3
60	4.50	4.92	5.2	-13.2
61	4.52	4.93	34.9	18.7
62	4.52	4.93	-43.5	-74.8
63	4.59	4.96	49.5	25.1
64	4.61	4.98	55.7	20.3
67	4.62	4.99	80.3	22.1
68	4.67	4.99	-26.1	-54.8
69	4.65	4.98	-20.5	-48.2
70	4.68	4.99	10.8	-33.7
71	4.60	4.95	23.7	28.4
74	4.54	4.91	36.7	16.9
75	4.59	4.90	57.0	13.7
76	4.65	4.91	-34.7	-57.2
77	4.66	4.90	-12.4	-42.0
78	4.64	4.91	19.1	-20.8
81	4.64	4.90	44.2	21.7
82	4.65	4.90	-20.3	-40.7
83	4.66	4.93	-8.0	-37.6
84	4.67	4.91	-14.7	-33.2
85	4.69	4.90	-43.2	-75.0
88	4.68	4.90	-60.5	-89.7
89	4.68	4.89	-77.4	-112.0
90	4.70	4.91	-67.7	-93.1
91	4.54	4.78	-54.6	-82.2
92	4.71	4.93	-17.7	-83.9

Day	pH		ORP (mV)	
	Reactor A	Reactor B	Reactor A	Reactor B
95	4.71	4.94	2.3	-76.4
96	4.71	4.94	5.7	-56.6
97	4.71	4.94	-7.8	-54.3
98	4.71	4.94	-8.2	-40.8
99	4.72	4.94	-3.0	-20.8
102	4.59	4.80	-52.0	-78.2
103	4.65	4.80	-44.4	-83.3
104	4.66	4.80	-30.6	-54.9
105	4.64	4.81	-28.6	-49.3
106	4.66	4.82	-11.0	-42.1
109	4.65	4.83	-4.7	-67.5
110	4.71	4.90	-10.4	-32.8
111	4.72	4.90	-14.0	-35.2
112	4.72	4.90	-39.8	-47.1
113	4.72	4.90	-51.1	-66.8
116	4.73	4.90	-44.2	-63.3
117	4.73	4.90	-18.3	-37.3
118	4.73	4.90	-14.2	-35.0
119	4.74	4.88	-21.6	-5.5
120	4.73	4.90	-75.0	-90.3
123	4.75	4.90	-64.6	-87.3
124	4.74	4.90	-58.3	-48.4
125	4.73	4.90	-49.2	-44.9
126	4.75	4.88	-12.7	-20.9
127	4.71	4.87	-21.0	-34.0
130	4.75	4.91	-36.9	-45.3
131	4.72	4.80	-48.3	-52.3
132	4.76	4.90	-67.3	-59.7
133	4.76	4.88	-54.3	-63.4
134	4.76	4.85	-50.0	-75.0
137	4.76	4.91	-38.4	-57.1
138	4.76	4.90	12.5	-49.3
139	4.76	4.92	-74.4	-73.0
140	4.76	4.95	-75.3	-69.4
141	4.76	4.93	-83.6	-77.3

Day	pH		ORP (mV)	
	Reactor A	Reactor B	Reactor A	Reactor B
144	4.77	4.95	-76.7	-53.5
145	4.78	4.93	-37.5	-39.9
146	4.76	4.91	-27.8	-43.6
147	4.79	4.95	-20.7	-57.7
148	4.79	4.95	-19.7	-53.5
151	4.80	4.95	-21.8	-57.3
152	4.81	4.95	-11.3	-63.4
153	4.82	4.95	-17.4	-61.4
154	4.80	4.96	-19.9	-58.9
155	4.80	4.95	-20.7	-59.9
158	4.82	4.95	-27.3	-55.9
159	4.82	4.95	-21.3	-52.0
160	4.81	4.95	-27.2	-62.1
161	4.81	4.95	-29.4	-50.5
162	4.81	4.94	-28.1	-50.9
165	4.83	4.95	-18.4	-45.3
166	4.83	4.96	-30.3	-50.6
167	4.85	4.96	-17.5	-56.3
168	4.84	4.96	-22.8	-49.7
169	4.84	4.97	-28.0	-45.0
172	4.87	4.97	0.8	-39.8
174	4.88	4.98	1.4	-35.5
176	4.90	4.98	-25.0	-40.1
179	4.88	4.97	-29.8	-42.0
181	4.90	4.96	-38.4	-50.3
183	4.90	4.95	-35.9	-48.8
186	4.93	4.97	-38.7	-50.2
188	4.95	4.98	-43.1	-52.3
190	5.00	4.98	-46.3	-50.8
193	4.99	5.00	-50.9	-56.3
195	5.00	5.00	-49.2	-55.4
197	4.84	4.96	-40.3	-52.0
200	5.00	5.00	-50.1	-54.0
202	5.00	5.00	-52.1	-54.9
204	5.00	5.00	-53.5	-60.9
207	5.00	5.00	-41.7	-67.0
209	4.95	5.05	-45.7	-69.2
211	5.01	5.05	-48.6	-66.5

Day	pH		ORP (mV)	
	Reactor A	Reactor B	Reactor A	Reactor B
214	5.04	5.07	-45.6	-58.9
216	5.10	5.12	-40.8	-48.3
218	5.00	5.00	-32.6	-39.1
221	5.13	5.15	-33.0	-45.7
223	5.16	5.19	-35.2	-48.9
225	5.18	5.20	-25.5	-47.9
228	5.20	5.24	-38.2	-49.3
230	5.30	5.28	-48.3	-50.7
232	5.34	5.38	-55.6	-54.2
235	5.35	5.40	-57.4	-55.8
237	5.38	5.41	-58.9	-58.5
239	5.41	5.43	-78.0	-62.0
242	5.44	5.45	-87.9	-64.1
244	5.44	5.46	-88.7	-71.1
246	5.45	5.47	-90.5	-72.3
249	5.46	5.47	-96.3	-76.5
251	5.40	5.51	-101.8	-81.0
253	5.50	5.53	-105.0	-88.0
256	5.59	5.55	-106.6	-90.4
258	5.60	5.54	-110.0	-92.3
260	5.60	5.58	-100.8	-95.9
263	5.60	5.60	-111.0	-97.8
265	5.65	5.66	-117.2	-90.0
267	5.65	5.68	-115.2	-94.2
270	5.70	5.68	-110.0	-80.0
272	5.32	5.68	-112.0	-80.3
274	5.40	5.75	-110.0	-88.9
277	5.37	5.72	-119.0	-98.7
279	5.41	5.95	-112.2	-99.6
281	5.42	5.86	-109.8	-106.4
284	5.45	5.83	-105.6	-113.7
286	5.43	5.85	-103.0	-120.9
288	5.66	5.83	-108.0	-126.3
291	5.80	5.82	-110.0	-135.0
293	5.80	5.83	-104.9	-148.0
295	5.82	5.85	-115.0	-153.8
298	5.78	5.80	-112.9	-157.3
300	5.55	5.80	-110.0	-155.5

Day	pH		ORP (mV)	
	Reactor A	Reactor B	Reactor A	Reactor B
302	5.60	5.86	-115.6	-157.3
305	5.60	5.86	-117.9	-148.5
307	5.56	5.85	-105.0	-155.9
309	5.71	5.95	-109.4	-128.9
312	5.59	5.92	-112.0	-163.2
314	5.76	6.15	-116.3	-165.2
316	5.78	6.19	-110.0	-159.1
319	5.90	6.20	-115.3	-168.4
321	5.80	6.20	-116.4	-171.4
323	5.81	6.22	-118.0	-167.8
326	5.83	6.24	-116.9	-154.5
328	5.85	6.25	-120.0	-166.2
330	5.85	6.25	-120.5	-175.7
333	5.85	6.25	-126.9	-180.2
335	5.85	6.27	-122.0	-179.9
337	5.88	6.30	-120.7	-172.7
340	5.87	6.30	-130.0	-165.3
342	6.12	6.35	-125.5	-155.3
344	6.12	6.35	-120.4	-159.3
347	6.13	6.33	-116.7	-167.8
349	6.12	6.38	-123.4	-169.0
351	6.10	6.40	-118.3	-172.2
354	6.16	6.42	-118.9	-173.2
356	6.05	6.43	-110.9	-158.9
358	6.16	6.44	-111.4	-150.0
361	6.17	6.45	-125.0	-155.0
363	6.16	6.45	-118.3	-164.9
365	6.16	6.47	-101.9	-165.9
368	6.15	6.49	-115.0	-188.3
370	6.17	6.49	-107.6	-168.5
372	6.17	6.50	-129.1	-160.3
375	6.17	6.50	-121.4	-154.8
377	6.16	6.48	-120.8	-164.2
379	6.17	6.50	-115.1	-170.8
382	6.17	6.53	-132.1	-195.2
384	6.17	6.55	-128.7	-190.5
386	6.17	6.55	-125.4	-183.7
389	6.15	6.79	-120.3	-197.2

Day	pH		ORP (mV)	
	Reactor A	Reactor B	Reactor A	Reactor B
391	6.17	6.82	-122.0	-200.0
393	6.08	6.84	-130.8	-243.0
396	6.04	6.84	-140.6	-265.8
398	6.04	6.84	-135.9	-300.6
400	6.17	6.86	-138.3	-339.4
403	6.46	7.05	-133.0	-368.0
405	6.73	7.38	-165.6	-356.3
407	6.85	7.42	-189.1	-360.8
410	6.93	7.54	-238.4	-375.5
412	7.09	7.70	-245.3	-387.3
414	7.11	7.70	-255.6	-377.6
417	7.21	7.58	-285.4	-380.0
419	7.35	7.80	-287.2	-376.4
421	0.35	7.90	-296.0	-376.5
424	7.52	8.10	-310.0	-380.2
426	7.50	8.15	-312.4	-388.5
428	7.55	8.30	-306.4	-395.1
431	7.62	8.40	-312.6	-387.5
433	7.80	8.40	-328.3	-399.2
435	7.95	8.30	-320.9	-397.5
438	7.90	8.30	-330.2	-410.2
440	7.80	8.40	-345.3	-386.5
442	8.00	8.40	-349.0	-399.7
445	8.08	8.41	-350.5	-406.9
447	8.05	8.40	-352.3	-408.7
449	8.09	8.50	-327.1	-412.0
452	8.09	8.51	-330.3	-398.9
454	8.10	8.52	-345.8	-387.6
456	8.10	8.52	-350.6	-396.9
459	8.11	8.54	-354.5	-387.9
466	8.15	8.61	-317.4	-387.5
468	8.17	8.65	-330.7	-395.3
470	8.17	8.65	-316.4	-403.6
473	8.19	8.67	-338.5	-412.2
475	8.20	8.70	-358.5	-422.4
477	8.25	8.73	-349.6	-415.4
480	8.28	8.75	-354.5	-428.6
482	8.28	8.77	-357.9	-428.6

Day	pH		ORP (mV)	
	Reactor A	Reactor B	Reactor A	Reactor B
484	8.32	8.81	-362.6	-417.5
487	8.45	8.83	-377.6	-427.8
489	8.47	8.88	-387.6	-435.1
491	8.55	8.80	-388.0	-437.7
494	8.55	8.00	-385.5	-427.5
496	8.56	8.82	-377.4	-444.1
498	8.60	8.60	-375.9	-432.8
501	8.64	8.76	-333.5	-435.7
503	8.67	8.90	-365.5	-420.7
505	8.70	8.90	-374.5	-415.6
508	8.72	8.90	-388.6	-438.0
510	8.75	9.00	-356.9	-428.4
512	8.75	9.00	-342.8	-456.1
515	8.75	9.20	-363.7	-429.7
517	8.75	9.20	-376.5	-453.3
519	8.90	9.20	-389.5	-420.5

A.2 Gas production of simulated leachate

Day	Gas production (mL)		Accumulated Gas (mL)	
	Reactor A	Reactor B	Reactor A	Reactor B
0	0	0	0	0
1	54	36	54	36
2	34	14	88	50
3	80	60	168	110
4	80	80	248	190
5	80	110	328	300
6	200	250	528	550
7	556	633	1,084	1,183
8	816	768	1,900	1,951
9	820	770	2,720	2,721
10	820	800	3,540	3,521
11	870	798	4,410	4,319
12	900	876	5,310	5,195
13	950	954	6,260	6,149
14	960	984	7,220	7,133
15	952	1,000	8,172	8,133
16	988	950	9,160	9,083
17	975	900	10,135	9,983
18	980	970	11,115	10,953
19	1,000	900	12,115	11,853
20	1,050	850	13,165	12,703
21	1,044	864	14,209	13,567
22	1,000	850	15,209	14,417
23	1,000	900	16,209	15,317
24	1,100	800	17,309	16,117
25	1,050	800	18,359	16,917
26	1,050	780	19,409	17,697
27	1,000	760	20,409	18,457
28	1,104	720	21,513	19,177
29	780	672	22,293	19,849
30	700	620	22,993	20,469
31	750	600	23,743	21,069
32	600	550	24,343	21,619
33	580	540	24,923	22,159
34	450	460	25,373	22,619
35	405	405	25,778	23,024

Day	Gas production (mL)		Accumulated Gas (mL)	
	Reactor A	Reactor B	Reactor A	Reactor B
36	600	600	26,378	23,624
37	700	850	27,078	24,474
38	750	900	27,828	25,374
39	820	1,040	28,648	26,414
40	800	1,120	29,448	27,534
41	840	1,200	30,288	28,734
42	672	1,248	30,960	29,982
43	700	1,200	31,660	31,182
44	650	1,100	32,310	32,282
45	650	1,200	32,960	33,482
46	700	900	33,660	34,382
47	672	960	34,332	35,342
48	300	700	34,632	36,042
49	200	480	34,832	36,522
50	34	120	34,866	36,642
51	35	120	34,901	36,762
52	35	80	34,936	36,842
53	35	70	34,971	36,912
54	35	45	35,006	36,957
55	29	37	35,035	36,994
56	40	35	35,075	37,029
57	50	55	35,125	37,084
58	55	34	35,180	37,118
59	35	35	35,215	37,153
60	29	56	35,244	37,209
61	70	63	35,314	37,272
62	80	77	35,394	37,349
63	70	58	35,464	37,407
64	102	78	35,566	37,485
65	89	70	35,655	37,555
66	80	60	35,735	37,615
67	60	45	35,795	37,660
68	40	40	35,835	37,700
69	50	48	35,885	37,748
70	45	45	35,930	37,793
71	35	40	35,965	37,833
72	50	34	36,015	37,867
73	45	45	36,060	37,912

Day	Gas production (mL)		Accumulated Gas (mL)	
	Reactor A	Reactor B	Reactor A	Reactor B
74	60	47	36,120	37,959
75	30	23	36,150	37,982
76	32	14	36,182	37,996
77	15	12	36,197	38,008
78	35	34	36,232	38,042
79	25	0	36,257	38,042
80	28	20	36,285	38,062
81	35	11	36,320	38,073
82	16	13	36,336	38,086
83	13	35	36,349	38,121
84	34	44	36,383	38,165
85	55	32	36,438	38,197
86	49	33	36,487	38,230
87	24	37	36,511	38,267
88	36	25	36,547	38,292
89	44	23	36,591	38,315
90	28	34	36,619	38,349
91	54	45	36,673	38,394
92	40	23	36,713	38,417
93	22	18	36,735	38,435
94	0	19	36,735	38,454
95	30	0	36,765	38,454
96	29	0	36,794	38,454
97	26	32	36,820	38,486
98	55	45	36,875	38,531
99	32	22	36,907	38,553
100	35	36	36,942	38,589
101	38	43	36,980	38,632
102	17	55	36,997	38,687
103	24	32	37,021	38,719
104	20	32	37,041	38,751
105	26	18	37,067	38,769
106	35	15	37,102	38,784
107	19	0	37,121	38,784
108	29	23	37,150	38,807
109	37	0	37,187	38,807
110	22	21	37,209	38,828
111	37	0	37,246	38,828

Day	Gas production (mL)		Accumulated Gas (mL)	
	Reactor A	Reactor B	Reactor A	Reactor B
112	40	15	37,286	38,843
113	48	34	37,334	38,877
114	47	52	37,381	38,929
115	29	55	37,410	38,984
116	20	47	37,430	39,031
117	17	56	37,447	39,087
118	10	37	37,457	39,124
119	39	38	37,496	39,162
120	0	33	37,496	39,195
121	35	0	37,531	39,195
122	43	23	37,574	39,218
123	50	0	37,624	39,218
124	0	16	37,624	39,234
125	0	19	37,624	39,253
126	32	25	37,656	39,278
127	37	29	37,693	39,307
128	34	28	37,727	39,335
129	26	35	37,753	39,370
130	21	16	37,774	39,386
131	18	17	37,792	39,403
132	0	26	37,792	39,429
133	21	46	37,813	39,475
134	20	53	37,833	39,528
135	36	54	37,869	39,582
136	38	27	37,907	39,609
137	47	23	37,954	39,632
138	49	21	38,003	39,653
139	27	0	38,030	39,653
140	22	34	38,052	39,687
141	0	37	38,052	39,724
142	0	43	38,052	39,767
143	0	40	38,052	39,807
144	15	45	38,067	39,852
145	17	36	38,084	39,888
146	34	17	38,118	39,905
147	26	15	38,144	39,920
148	22	35	38,166	39,955
149	0	32	38,166	39,987

Day	Gas production (mL)		Accumulated Gas (mL)	
	Reactor A	Reactor B	Reactor A	Reactor B
150	32	43	38,198	40,030
151	21	54	38,219	40,084
152	20	0	38,239	40,084
153	15	12	38,254	40,096
154	37	16	38,291	40,112
155	28	32	38,319	40,144
156	19	22	38,338	40,166
157	0	15	38,338	40,181
158	0	16	38,338	40,197
159	0	0	38,338	40,197
160	19	25	38,357	40,222
161	23	0	38,380	40,222
162	33	34	38,413	40,256
163	45	33	38,458	40,289
164	17	28	38,475	40,317
165	19	0	38,494	40,317
166	32	10	38,526	40,327
167	21	5	38,547	40,332
168	50	8	38,597	40,340
169	56	15	38,653	40,355
170	49	17	38,702	40,372
171	36	0	38,738	40,372
172	44	32	38,782	40,404
173	48	39	38,830	40,443
174	50	40	38,880	40,483
175	23	45	38,903	40,528
176	25	32	38,928	40,560
177	43	21	38,971	40,581
178	32	10	39,003	40,591
179	33	9	39,036	40,600
180	0	7	39,036	40,607
181	0	17	39,036	40,624
182	14	37	39,050	40,661
183	18	28	39,068	40,689
184	32	43	39,100	40,732
185	33	44	39,133	40,776
186	23	48	39,156	40,824
187	15	26	39,171	40,850

Day	Gas production (mL)		Accumulated Gas (mL)	
	Reactor A	Reactor B	Reactor A	Reactor B
188	17	22	39,188	40,872
189	0	43	39,188	40,915
190	43	47	39,231	40,962
191	54	54	39,285	41,016
192	59	32	39,344	41,048
193	65	0	39,409	41,048
194	70	16	39,479	41,064
195	70	6	39,549	41,070
196	80	3	39,629	41,073
197	35	18	39,629	41,091
198	80	19	39,709	41,110
199	90	20	39,799	41,130
200	65	22	39,864	41,152
201	88	43	39,952	41,195
202	67	27	40,019	41,222
203	59	25	40,078	41,247
204	64	20	40,142	41,267
205	89	18	40,231	41,285
206	96	12	40,327	41,297
207	100	11	40,427	41,308
208	110	43	40,537	41,351
209	112	0	40,649	41,351
210	124	23	40,773	41,374
211	143	0	40,916	41,374
212	98	44	41,014	41,418
213	99	45	41,113	41,418
214	86	56	41,199	41,474
215	110	78	41,309	41,552
216	124	85	41,433	41,637
217	122	78	41,555	41,715
218	121	45	41,676	41,760
219	115	98	41,791	41,858
220	117	110	41,908	41,968
221	109	126	42,017	42,094
222	105	117	42,122	42,211
223	112	118	42,234	42,329
224	120	112	42,354	42,441
225	98	159	42,452	42,600

Day	Gas production (mL)		Accumulated Gas (mL)	
	Reactor A	Reactor B	Reactor A	Reactor B
226	78	98	42,530	42,698
227	88	123	42,618	42,821
228	98	110	42,716	42,931
229	99	105	42,815	43,036
230	78	103	42,893	43,139
231	89	129	42,982	43,268
232	74	98	43,056	43,366
233	89	67	43,145	43,433
234	80	87	43,225	43,520
235	82	67	43,307	43,587
236	78	57	43,385	43,644
237	99	98	43,484	43,742
238	90	99	43,574	43,841
239	80	100	43,654	43,941
240	85	120	43,739	44,061
241	95	132	43,834	44,193
242	102	154	43,936	44,347
243	100	145	44,036	44,492
244	101	123	44,137	44,615
245	123	165	44,260	44,780
246	120	178	44,380	44,958
247	131	234	44,511	45,192
248	105	276	44,616	45,468
249	98	243	44,714	45,711
250	77	197	44,791	45,908
251	79	176	44,870	46,084
252	65	145	44,935	46,229
253	50	165	44,985	46,394
254	135	231	45,120	46,625
255	147	256	45,267	46,881
256	109	108	45,376	46,989
257	105	134	45,481	47,123
258	89	167	45,570	47,290
259	90	134	45,660	47,424
260	98	197	45,758	47,621
261	79	134	45,837	47,755
262	134	216	45,971	47,971
263	138	222	46,109	48,193

Day	Gas production (mL)		Accumulated Gas (mL)	
	Reactor A	Reactor B	Reactor A	Reactor B
264	126	145	46,235	48,338
265	125	167	46,360	48,505
266	122	184	46,482	48,689
267	110	234	46,592	48,923
268	143	165	46,735	49,088
269	128	185	46,863	49,273
270	137	146	47,000	49,419
271	135	187	47,135	49,606
272	144	165	47,279	49,771
273	104	98	47,279	49,869
274	56	68	47,335	49,937
275	76	89	47,411	50,026
276	77	67	47,488	50,093
277	80	240	47,568	50,333
278	99	345	47,667	50,678
279	150	134	47,817	50,812
280	145	155	47,962	50,967
281	148	123	48,110	51,090
282	162	145	48,272	51,235
283	143	154	48,415	51,389
284	90	143	48,505	51,532
285	87	124	48,592	51,656
286	88	156	48,680	51,812
287	87	54	48,767	51,866
288	90	78	48,857	51,944
289	80	145	48,937	52,089
290	86	98	49,023	52,187
291	85	99	49,108	52,286
292	120	104	49,228	52,390
293	132	107	49,360	52,497
294	135	156	49,495	52,653
295	156	108	49,651	52,761
296	134	190	49,785	52,951
297	96	100	49,881	53,051
298	75	245	49,956	53,296
299	43	145	49,999	53,441
300	68	187	50,067	53,628
301	97	145	50,164	53,773

Day	Gas production (mL)		Accumulated Gas (mL)	
	Reactor A	Reactor B	Reactor A	Reactor B
302	78	123	50,242	53,896
303	90	143	50,332	54,039
304	65	143	50,397	54,182
305	140	174	50,537	54,356
306	127	144	50,664	54,500
307	154	176	50,818	54,676
308	160	145	50,978	54,821
309	143	187	51,121	55,008
310	125	134	51,246	55,142
311	137	116	51,383	55,258
312	146	134	51,529	55,392
313	179	154	51,708	55,546
314	190	155	51,898	55,701
315	200	233	52,098	55,934
316	221	243	52,319	56,177
317	243	145	52,562	56,322
318	235	98	52,797	56,420
319	189	97	52,986	56,517
320	160	145	53,146	56,662
321	176	157	53,322	56,819
322	154	157	53,476	56,976
323	132	245	53,608	57,221
324	148	198	53,756	57,419
325	129	134	53,885	57,553
326	133	167	54,018	57,720
327	187	188	54,205	57,908
328	176	186	54,381	58,094
329	167	168	54,548	58,262
330	198	199	54,746	58,461
331	199	202	54,945	58,663
332	221	234	55,166	58,897
333	243	187	55,409	59,084
334	178	145	55,587	59,229
335	198	134	55,785	59,363
336	165	78	55,950	59,441
337	154	97	56,104	59,538
338	134	101	56,238	59,639
339	178	105	56,416	59,744

Day	Gas production (mL)		Accumulated Gas (mL)	
	Reactor A	Reactor B	Reactor A	Reactor B
340	137	99	56,553	59,843
341	178	100	56,731	59,943
342	176	67	56,907	60,010
343	157	98	57,064	60,108
344	155	145	57,219	60,253
345	178	189	57,397	60,442
346	126	190	57,523	60,632
347	157	134	57,680	60,766
348	197	123	57,877	60,889
349	187	153	58,064	61,042
350	156	144	58,220	61,186
351	163	167	58,383	61,353
352	155	123	58,538	61,476
353	157	143	58,695	61,619
354	150	87	58,845	61,706
355	155	123	59,000	61,829
356	142	100	59,142	61,929
357	140	154	59,282	62,083
358	135	109	59,417	62,192
359	168	87	59,585	62,279
360	156	98	59,741	62,377
361	165	122	59,906	62,499
362	188	98	60,094	62,597
363	176	99	60,270	62,696
364	145	105	60,415	62,801
365	78	103	60,493	62,904
366	95	112	60,588	63,016
367	146	144	60,734	63,160
368	155	134	60,889	63,294
369	143	143	61,032	63,437
370	147	107	61,179	63,544
371	132	109	61,311	63,653
372	187	254	61,498	63,907
373	123	243	61,621	64,150
374	145	177	61,766	64,327
375	156	154	61,922	64,481
376	198	98	62,120	64,579
377	199	78	62,319	64,657

Day	Gas production (mL)		Accumulated Gas (mL)	
	Reactor A	Reactor B	Reactor A	Reactor B
378	245	87	62,564	64,744
379	254	134	62,818	64,878
380	167	156	62,985	65,034
381	195	143	63,180	65,177
382	157	122	63,337	65,299
383	144	144	63,481	65,443
384	255	156	63,736	65,599
385	143	198	63,879	65,797
386	86	167	63,965	65,964
387	75	145	64,040	66,109
388	68	109	64,108	66,218
389	97	101	64,205	66,319
390	96	99	64,301	66,418
391	120	98	64,421	66,516
392	132	128	64,553	66,644
393	140	132	64,693	66,776
394	157	133	64,850	66,909
395	160	143	65,010	67,052
396	157	149	65,167	67,201
397	155	156	65,322	67,357
398	162	168	65,484	67,525
399	175	176	65,659	67,701
400	180	178	65,839	67,879
401	190	188	66,029	68,067
402	195	200	66,224	68,267
403	198	200	66,422	68,467
404	210	215	66,632	68,682
405	230	225	66,862	68,907
406	237	239	67,099	69,146
407	240	245	67,339	69,391
408	254	259	67,593	69,650
409	265	263	67,858	69,913
410	274	286	68,132	70,199
411	275	287	68,407	70,486
412	230	225	68,637	70,711
413	237	239	68,874	70,950
414	240	245	69,114	71,195
415	254	259	69,368	71,454

Day	Gas production (mL)		Accumulated Gas (mL)	
	Reactor A	Reactor B	Reactor A	Reactor B
416	265	263	69,633	71,717
417	274	286	69,907	72,003
418	275	287	70,182	72,290
419	287	296	70,469	72,586
420	350	334	70,819	72,920
421	357	357	71,176	73,277
422	376	380	71,552	73,657
423	376	379	71,928	74,036
424	380	376	72,308	74,412
425	390	365	72,698	74,777
426	421	388	73,119	75,165
427	432	365	73,551	75,530
428	476	397	74,027	75,927
429	487	387	74,514	76,314
430	450	376	74,964	76,690
431	498	375	75,462	77,065
432	457	355	75,919	77,420
433	426	378	76,345	77,798
434	400	386	76,745	78,184
435	423	398	77,168	78,582
436	399	378	77,567	78,960
437	425	387	77,992	79,347
438	399	376	78,391	79,723
439	387	354	78,778	80,077
440	356	387	79,134	80,464
441	398	354	79,532	80,818
442	420	334	79,952	81,152
443	445	360	80,397	81,512
444	478	345	80,875	81,857
445	487	329	81,362	82,186
446	532	387	81,894	82,573
447	522	398	82,416	82,971
448	501	376	82,917	83,347
449	450	357	83,367	83,704
450	427	300	83,794	84,004
451	412	270	84,206	84,274
452	432	328	84,638	84,602
453	422	345	85,060	84,947

Day	Gas production (mL)		Accumulated Gas (mL)	
	Reactor A	Reactor B	Reactor A	Reactor B
454	476	287	85,536	85,234
455	487	329	86,023	85,563
456	459	366	86,482	85,929
457	438	387	86,920	86,316
458	445	398	87,365	86,714
459	397	334	87,762	87,048
460	376	276	88,138	87,324
461	465	334	88,603	87,658
462	420	276	89,023	87,934
463	430	298	89,453	88,232
464	387	265	89,840	88,497
465	389	314	90,229	88,811
466	428	350	90,657	89,161
467	475	287	91,132	89,448
468	520	298	91,652	89,746
469	549	265	92,201	90,011
470	544	276	92,745	90,287
471	465	259	93,210	90,546
472	430	263	93,640	90,809
473	460	286	94,100	91,095
474	522	287	94,622	91,382
475	450	225	95,072	91,607
476	476	239	95,548	91,846
477	456	309	96,004	92,155
478	427	306	96,431	92,461
479	396	263	96,827	92,724
480	376	286	97,203	93,010
481	382	287	97,585	93,297
482	453	345	98,038	93,642
483	498	339	98,536	93,981
484	443	333	98,979	94,314
485	398	289	99,377	94,603
486	434	263	99,811	94,866
487	467	286	100,278	95,152
488	540	287	100,818	95,439
489	589	354	101,407	95,793
490	629	239	102,036	96,032
491	430	287	102,466	96,319

Day	Gas production (mL)		Accumulated Gas (mL)	
	Reactor A	Reactor B	Reactor A	Reactor B
492	389	327	102,855	96,646
493	444	345	103,299	96,991
494	487	387	103,786	97,378
495	539	365	104,325	97,743
496	565	354	104,890	98,097
497	488	387	105,378	98,484
498	432	324	105,810	98,808
499	445	412	106,255	99,220
500	387	453	106,642	99,673
501	390	445	107,032	100,118
502	376	465	107,408	100,583
503	356	487	107,764	101,070
504	343	387	108,107	101,457
505	300	332	108,407	101,789
506	321	276	108,728	102,065
507	365	250	109,093	102,315
508	354	276	109,447	102,591
509	365	287	109,812	102,878
510	329	312	110,141	103,190
511	297	324	110,438	103,514
512	324	312	110,762	103,826
513	333	345	111,095	104,171
514	321	288	111,416	104,459
515	254	267	111,670	104,726
516	286	255	111,956	104,981
517	271	276	112,227	105,257
518	325	290	112,552	105,547
519	336	312	112,888	105,859

A.3 % CO_2 & % CH_4 of simulated leachate

Day	Week	% CO_2		% CH_4	
		Reactor A	Reactor B	Reactor A	Reactor B
67	10	81.85	74.23	-	-
74	11	84.92	80.96	-	-
83	12	76.95	75.27	-	-
89	13	85.46	80.02	-	-
96	14	73.46	61.25	-	-
102	15	72.99	65.86	-	-
109	16	81.57	-	-	-
161	23	79.34	74.72	-	-
179	26	41.40	-	-	-
190	28	76.05	68.74	-	-
243	35	67.41	62.13	-	-
251	36	69.59	68.18	-	-
396	57	54.64	52.32	18.62	20.44
404	58	56.48	50.80	25.09	32.50
412	59	50.77	46.09	29.24	39.83
426	61	45.76	32.91	41.44	59.46
447	64	35.35	25.46	59.09	69.03

A.4 COD of simulated leachate

Day	Reactor A (mg/L)	Reactor B (mg/L)
12	35,886	32,000
15	39,771	32,000
21	39,771	32,000
27	34,286	30,400
34	31,314	28,114
41	32,143	31,500
48	33,643	33,643
55	33,076	29,647
62	37,286	33,643
68	37,286	33,643
76	49,714	44,571
83	38,521	39,933
90	39,328	36,504
99	39,933	33,076
111	39,933	39,933
118	39,933	39,933
125	39,933	41,950
132	41,345	38,521
139	43,361	38,521
146	43,361	38,521
153	37,916	33,076
161	39,048	34,476
168	39,048	34,476
175	39,048	35,810
182	39,619	35,810
190	39,619	35,810
197	39,048	34,476
204	38,797	33,925
210	35,729	30,857
216	33,925	29,594
223	35,143	32,743
237	36,857	33,943
251	35,688	30,857
287	34,629	36,343
316	35,627	35,627
370	29,079	38,984
385	40,731	38,400

Day	Reactor A (mg/L)	Reactor B (mg/L)
399	46,286	39,000
413	38,242	32,308
442	35,143	24,000
453	25,200	4,800
468	15,600	3,200
482	12,800	3,200
496	9,600	1,600
510	6,400	1,600

A.5 VFA & Alkalinity of Simulated leachate

Day	Week	Alkalinity		VFA	
		Reactor A (mg/L)	Reactor B (mg/L)	Reactor A (mg/L)	Reactor B (mg/L)
182	26	3,640	4,225	7,750	8,362
190	27	2,550	3,475	8,150	7,937
197	28	2,875	3,550	7,937	8,125
210	30	3,500	4,150	7,650	7,850
223	32	4,625	4,725	8,425	8,325
237	34	6,085	5,950	12,125	9,300
251	36	6,425	6,350	8,250	8,350
316	45	10,475	10,000	9,825	9,600
370	53	10,000	10,500	12,875	10,875
385	55	12,100	11,325	12,825	12,975
399	57	11,575	10,725	12,375	9,250
413	59	12,200	10,600	11,150	8,050
427	61	12,200	10,850	10,650	7,350
442	63	12,300	11,000	8,750	3,325
453	65	11,500	11,000	7,850	700
468	67	13,500	11,000	4,500	750
496	71	14,000	11,750	600	450
509	73	14,500	11,500	290	160

APPENDIX B

B.1 DOC of simulated leachate

Week	Day	Reactor A (mg/L)	Reactor B (mg/L)
1	7	11,838	11,540
2	14	11,534	10,978
3	21	13,230	10,694
4	28	13,493	10,894
5	35	13,594	11,391
6	42	13,330	11,734
7	49	13,270	10,500
8	56	13,300	9,858
9	63	13,330	8,615
10	70	13,330	8,220
11	77	12,685	10,328
12	84	11,338	12,550
13	91	13,693	12,550
14	98	14,475	12,580
15	105	14,356	12,751
16	112	13,712	11,860
17	119	14,587	12,279
18	126	14,805	13,125
19	133	14,441	12,598
20	140	14,035	12,188
21	147	14,076	11,984
22	154	14,290	11,635
23	161	13,760	12,054
24	168	13,893	12,793
25	175	13,566	11,432
26	182	13,675	11,259
27	189	13,295	10,722
28	196	13,315	12,339
29	203	13,356	12,099
30	210	13,858	12,082
31	217	12,995	12,051
33	224	13,849	12,465
35	245	13,541	12,225
37	259	13,984	12,854

Week	Day	Reactor A (mg/L)	Reactor B (mg/L)
39	273	13,872	12,955
41	287	14,023	12,471
43	301	14,215	12,895
45	315	14,532	13,184
47	329	14,859	13,428
49	343	15,244	13,703
51	357	15,410	13,966
53	371	15,143	14,006
55	385	16,168	14,366
57	399	15,767	13,088
59	413	15,062	10,968
61	427	14,008	8,690
63	441	12,695	3,590
65	455	7,906	1,976
67	469	4,838	1,304
69	483	2,015	845
71	497	1,705	1,166
73	511	1,662	1,166

B.2 % Extracted of Pb with simulated leachate

Day	% Pb extracted			
	Reactor A		Reactor B	
	Average	SD	Average	SD
7	63.86	3.07	69.54	2.91
28	49.8	3.76	38.29	3.35
42	65.67	3.57	39.53	2.35
49	28.55	2.37	56.83	2.81
63	30.75	2.32	44.16	3.85
77	37.49	1.66	49.13	2.64
84	53.18	2.12	32.16	3.11
140	47.18	2.68	52.15	4.52
196	20.88	2.62	18.36	2.96
217	7.27	1.34	17.71	3.63
224	26.63	4.31	18.08	2.50
287	16.78	2.50	4.95	1.54
322	11.59	1.87	0.98	0.05
364	0	0	0	0
378	0	0	0	0
392	0	0	0	0
406	0	0	0	0
420	0	0	0	0
434	0	0	0	0
448	5.78	2.36	1.42	0.46
462	5.23	1.66	8.32	2.24
476	1.86	0.55	0	0
490	5.93	0.86	0	0
504	0	0	4.39	1.47
518	1.73	0.27	6.22	1.01

B.3 % Extracted of Zn with simulated leachate

Day	% Zn extracted			
	Reactor A		Reactor B	
	Average	SD	Average	SD
7	33.09	2.32	36.23	2.58
28	28.88	1.66	18.94	2.91
42	28.88	1.88	23.19	2.63
49	29.57	3.02	16.53	1.86
63	26.35	2.20	12.63	1.77
77	18.85	2.30	6.01	1.19
84	14.86	1.16	12.45	2.00
105	26.52	2.62	16.8	1.97
126	19.15	1.42	7.48	1.03
140	28.54	2.19	6.78	1.69
196	-	-	9.22	2.03
224	14.32	1.93	9.52	1.22
238	15.80	1.60	6.24	1.06
287	8.41	1.32	2.61	0.78
322	3.96	0.56	1.84	0.46
364	-	-	-	-
378	-	-	-	-
392	-	-	-	-
406	-	-	-	-
420	-	-	-	-
434	-	-	-	-
448	0.64	0.12	2.18	0.22
462	0.96	0.14	1.17	0.14
476	1.88	0.25	3.61	0.29
490	0.64	0.21	2.18	0.19
504	0.96	0.17	1.17	0.06
518	1.88	0.18	3.61	0.32

B.4 % Pb extracted and DOC

	Reactor A			Reactor B	
DOC (mg/L)	% Pb extracted (average)	SD	DOC (mg/L)	% Pb extracted (average)	SD
1,662	1.73	0.27	845	-	-
1,705	-	-	1,166	4.39	1.47
2,015	5.93	0.86	1,166	6.22	1.01
4,838	1.86	0.55	1,304	0.00	0.00
7,906	5.23	1.66	1,976	8.32	2.24
8,115	37.49	1.66	3,590	1.42	0.46
11,338	53.18	2.12	6,097	49.13	2.64
11,838	63.86	3.07	8,615	44.16	3.85
12,695	5.78	2.36	8,690	0.00	0.00
12,995	7.27	1.34	10,500	56.83	2.81
13,270	28.55	2.37	10,894	38.29	3.35
13,315	20.88	2.62	10,968	0.00	0.00
13,330	30.75	2.32	11,540	69.54	2.91
13,330	65.67	3.57	11,734	39.53	2.35
13,493	49.8	3.76	12,051	17.71	3.63
13,849	26.63	4.31	12,188	52.15	4.52
14,008	0.00	0.00	12,339	18.36	2.96
14,023	16.78	2.50	12,465	18.08	2.50
14,035	47.18	2.68	12,471	4.95	1.54
14,859	11.59	1.87	12,550	32.16	3.11
15,062	0.00	0.00	13,088	0.00	0.00
15,143	0.00	0.00	13,428	0.98	0.05
15,410	0.00	0.00	13,966	0.00	0.00
15,767	0.00	0.00	14,006	0.00	0.00
16,168	0.00	0.00	14,366	0.00	0.00
1,662	1.73	0.27	845	-	-
1,705	-	-	1,166	4.39	1.47

B.5 %Pb extracted and pH

pH	Reactor A % Pb extracted (average)	SD	pH	Reactor B % Pb extracted (average)	SD
3.56	63.86	3.07	3.758	69.54	2.91
4.28	49.80	3.76	4.524	38.29	3.35
4.35	65.67	3.57	4.62	39.53	2.35
4.44	28.55	2.37	4.86	56.83	2.81
4.59	30.75	2.32	4.9	49.13	2.64
4.66	37.49	1.66	4.91	32.16	3.11
4.67	53.18	2.12	4.95	52.15	4.52
4.76	47.18	2.68	4.96	44.16	3.85
5.00	20.88	2.62	5	18.36	2.96
5.10	7.27	1.34	5.12	17.71	3.63
5.34	26.63	4.31	5.38	18.08	2.50
5.43	16.78	2.50	5.85	4.95	1.54
5.80	11.59	1.87	6.2	0.98	0.05
6.16	0.00	0.00	6.45	0.00	0.00
6.16	0.00	0.00	6.48	0.00	0.00
6.17	0.00	0.00	6.82	0.00	0.00
6.85	0.00	0.00	7.42	0.00	0.00
7.35	0.00	0.00	7.8	0.00	0.00
7.95	0.00	0.00	8.3	0.00	0.00
8.08	5.78	2.36	8.41	1.42	0.46
8.11	5.23	1.66	8.54	8.32	2.24
8.25	1.86	0.55	8.6	-	-
8.55	5.93	0.86	8.72	-	-
8.67	-	-	8.83	4.39	1.47
8.75	1.73	0.27	8.96	6.22	1.01

B.6 % Pb extracted with Humic Acid (Aldrich)

pH	AHA (1000 mg/L)		AHA (500 mg/L)	
	Average	SD	Average	SD
2	1.85	0.08	1.24	0.28
4	1.89	0.12	-	-
6	-	-	3.35	0.24
7	4.60	0.45	-	-
9	5.92	0.86	-	-
10	6.54	0.79	4.44	0.45

BIOGRAPHY

Miss Sirinda Lapcharoen, was born on April 16, 1972 in Bangkok, Thailand. She received Bachelor Degree from Chemical Engineering Department, Chulalongkorn University in 1994 and Master Degree from Chemical Engineering Department, Imperial College, University of London in 1996. Afterwards, she worked as an engineer for couple of companies before working for Pollution Control Department, Ministry of Natural Resources and Environment as Environmental Officer since 1998. She started her Ph.D. Degree in International Programs In Environmental Management, Chulalongkorn University and completed the program in May 2009.