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นางสาว นันทิชาพร อุคมศรี

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POTENTIAL OF LEACHATE TO LEACH CADMIUM
FROM CONTAMINATED SOIL



Miss Nanchaphorn Udomsri

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย
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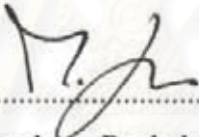
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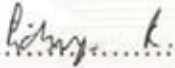
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Fulfillment of the Requirements for the Master's Degree

.....Dean of the Graduate School
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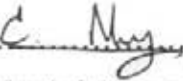
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.....Thesis Advisor
(Pichaya Rachdawong, Ph.D.)

.....Member
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.....Member
(Assistant Professor Khemarath Osathaphan, Ph.D.)

.....Member
(Chackrit Nuengjamnong, D.Tech. Sc.)

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งานวิจัยนี้จัดทำขึ้น โดยมีวัตถุประสงค์เพื่อศึกษาศักยภาพการชะโลหะหนักออกจากดินปนเปื้อนโลหะหนัก โดยใช้น้ำชะขยะแบบต่างๆ ในการศึกษาได้จัดสร้างถังหมักขยะในสภาพไร้อากาศในระดับห้องปฏิบัติการ เพื่อศึกษาลักษณะของน้ำชะขยะในช่วงเวลาต่างๆ ของกระบวนการย่อยสลายโดยแบ่งเป็น 3 ช่วง ได้แก่ ช่วงการสร้างกรด ช่วงการสร้างแก๊สมีเทน และช่วงสุดท้ายของการฝังกลบ ในศึกษานี้ได้เปรียบเทียบขยะ 2 ชนิด ได้แก่ ขยะผักและผลไม้ และหญ้า น้ำชะขยะที่ได้จาก 3 ระยะของการย่อยสลายนำไปศึกษาความสามารถในการชะโลหะหนักออกมาจากดินปนเปื้อนโดยสกัดด้วยวิธีของ TCLP นอกจากนี้ยังเปรียบเทียบความสามารถในการชะโลหะหนักกับสารสกัดต่างๆ ได้แก่ HNO_3 0.04 M EDTA 1 M CaCl_2 และ 0.05 M $\text{Ca}(\text{NO}_3)_2$ ผลการทดลองที่ได้สามารถสรุปได้ว่าน้ำชะขยะที่ได้จากการหมักผักและผลไม้สามารถสกัดแคดเมียมจากดินตัวอย่างที่เก็บจากจุดที่ 2 ได้ 2.27 3.82 และ 4.32 mg/kg และตัวอย่างดินที่เก็บจากจุดที่ 3 ได้ 2.39 4.28 และ 4.98 mg/kg สำหรับน้ำชะขยะจากช่วงเวลาต่างๆ ตามลำดับ อย่างไรก็ตามปฏิกิริยาที่เกิดขึ้นในถังหมักผักและผลไม้ไม่สามารถเกิดปฏิกิริยาย่อยสลายได้สมบูรณ์ เนื่องจากมีปริมาณของสารอินทรีย์ที่ย่อยได้ในน้ำชะขยะที่สูงและไม่ได้ทำการเวียนน้ำชะขยะกลับมาใหม่ ทำให้ปฏิกิริยาการย่อยสลายเกิดขึ้นถึงระยะการสร้างมีเทนเท่านั้น ในทางตรงกันข้ามถังหมักหญ้าเกิดปฏิกิริยาสมบูรณ์และการย่อยสลายเกิดขึ้นถึงระยะสุดท้ายของกระบวนการย่อยสลาย จากการทดลองความสามารถชะแคะแคดเมียมของน้ำชะขยะจากหญ้าลดลงเมื่อเวลาเพิ่มขึ้น พบว่าความเข้มข้นของแคดเมียมที่สกัดออกมาโดยน้ำชะขยะจากช่วงสร้างกรด ช่วงการสร้างมีเทน และช่วงสุดท้ายของการฝังกลบจากดินตัวอย่างจุดที่ 2 เป็น 2.56 1.03 และ 1.35 mg/kg และสำหรับดินตัวอย่างจากจุดที่ 3 เป็น 3.01 1.44 และ 1.55 mg/kg จากผลที่ได้รับ น้ำชะขยะจากหญ้าขยะมีศักยภาพน้อยกว่าขยะจากผักและผลไม้ จากความเข้มข้นของแคดเมียมที่สกัดได้บ่งชี้ว่าน้ำชะขยะสามารถชะแคะแคดเมียมจากส่วน non-labile ของดินตัวอย่าง อย่างไรก็ตามความสามารถในการชะแคะแคดเมียมของน้ำชะขยะยังมีค่าต่ำกว่าความสามารถในการสกัดของ EDTA

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KEY WORD: LEACHATE / LANDFILL / CADMIUM / CONTAMINATED SOIL / DEGRADATION / DOC

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A propose of this research was to study leaching potential of leachate to leach cadmium from contaminated soil. It was accomplished by operating three simulated landfill reactors representing the three phases of degradation, acid formation phase, methanogenic phase, and final maturation phase. As a comparison, two types of waste were used in this investigation which were reactor A (fruit and vegetable) and reactor B (Para grass). Leachate from three stages of degradation was collected and the ability to leach cadmium from contaminated soil was determined by leaching test. Moreover, this ability of leachate was compared with the ability of water (H₂O) as control, extraction fluid#1 (TCLP), HNO₃, 0.04 M EDTA, 1 M CaCl₂, and 0.05 M Ca(NO₃)₂. For reactor A (fruit and vegetable), the Cd concentrations determined from soil samples collected from site 2 were 2.27, 3.82 and 4.32 mg/kg. For site 3, the Cd concentrations were 2.39, 4.28 and 4.98 mg/kg for the three phases respectively. However, the biological and chemical processes occurred in reactor A3 was not completely anaerobic. Reactor A3 might have to high organics in leachate and caused on incomplete attainment of the final maturation in the degradation process. In conclusion, the phases of stabilization of reactor A2 and A3 were at the initial methane formation. In contrast, the Para grass had the complete reaction and reached the final maturation phase. The leaching potential of grass leachate decreased with time. The Cd concentrations were 2.56, 1.03 and 1.35 mg/kg of Cd for soil samples collected from site 2 and 3.01, 1.44 and 1.55 mg/kg of Cd for soil samples collected from site 3 for the three phases, respectively. Leachate from grass waste had lower potential than that of fruit and vegetable waste. This indicated that leachate has an ability to leach some of non-labile fractions of Cd from soil samples. Nevertheless, the results demonstrated that the leaching ability from both leachate sources was lower than that of EDTA.

Field of Study Environmental Management Student's signature.... Nanchaphorn.V.....

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LIST OF ABBREVIATIONS

MSW	=	Municipal Solid Waste
MNRE	=	Ministry of Natural Resources and Environment
DOC	=	Dissolved Organic Carbon
BMA	=	Bangkok Metropolitan Area
SAOs	=	Sub-district Administrative Organizations
ISW	=	Industrial Solid Waste
BOD	=	Biochemical Oxygen Demand
COD	=	Chemical Oxygen Demand
TOC	=	Total Organic Carbon
HS	=	Humic Substance
MSWI	=	Municipal Solid Waste Incinerator
MSOR	=	Mechanically Separated Organic Waste
BTCs	=	Breakthrough Curves
EDTA	=	Ethylenediaminetetraacetic Acid
ICP-MS	=	Inductively Coupled Plasma-mass spectrometry
FAAS	=	Flame Atomic Absorption Spectrometry
TCLP	=	Toxicity Characteristic Leaching Procedure
ORP	=	Oxidation-Reduction Potential
VFA	=	Volatile Fatty Acids

CHAPTER I

INTRODUCTION

1.1 Statement of problem

Landfill is the main method of waste disposal for many kinds of solid waste that cannot be recycled. It is also the most popular long-term handling of solid waste that is available. In 2005, the amount of municipal solid waste generated in Thailand was approximately 40,000 tons/day or 14 million tons per year, of which 21.2% 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 (MNRE). Some typical solid wastes found in Thailand are: food waste, paper, plastics, textiles, rubber, and wood with organic waste accounting for a major portion of MSW.

Municipal landfill consists of a mixture of household waste, industrial waste and other wastes. Many problems accompany the use of landfill, such as leachate containing heavy metals, gas emission, odors, etc. Inappropriate management of landfill may cause the migration of leachate and later the contamination of groundwater. This is the predominant problem associated with landfills.

Among many other constituents, landfill leachate might contain heavy metals in considerable concentration (Baun et al., 2003). It has also been suggested that the leachate itself may have the capacity to leach extract heavy metals. Leachate can be acidic and often contains a high concentration of dissolved organic carbon (DOC). The organic material present 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). As solid waste in landfill ages, it is expected that the ability of leachate to extract and solubilize heavy metals will change.

This ability of leachate should be considered in order to understand the transport of heavy metals through the landfill and into underlying groundwater. Artificial leachate was produced in this study to determine the ability of landfill leachate to extract heavy metals from solid metrics. Finally, if leachate has a significant capacity to extract heavy metals, producing artificial leachate with high

extraction capacity could be an application to extract or remediate metals from metal ores or contaminated soils.

1.2 Objectives of the study

The objectives of this research were:

- 1) To determine the ability of landfill fermentation of organic waste leachate to extract and solubilize metal ions and to understand how this ability changes with the age of degradation.
- 2) To compare the ability of landfill fermentation of organic waste leachate to extract metals based on different types of waste.

1.3 Scopes of the study

- 1) Construction and operation of reactors with organic waste will be capable of running landfill fermentation of organic waste stabilization experiment with leachate recycle scheme.
- 2) The ability of leachate to extract and solubilize heavy metals (Cd) from solid metrics will be measured with standard leaching test including DOC fractions.
- 3) The leachate will be measured for 3 stages, therefore the initial, the intermediate, and the final stage during stabilization phase, 3 times from 5 stages

CHAPTER II

LITERATURE REVIEWS

2.1 Backgrounds

Growing urbanization and industrialization have led to the generation of large quantities of wastes, which can be broadly classified as MSW (municipal solid waste) and ISW (industrial solid waste). In the last year (2005), Thailand municipal solid waste production was up to approximately 40,000 tons/day or 14 million tons per year. The amount of total MSW were generated from Bangkok Metropolitan Area (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)	18,295‡	46.6
Total	39,270	100.0

Note: # Included 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 municipality

areas, and 0.4-0.6 kg/capita/day in Sub-district Administrative Organizations (SAOs) areas. The composition of MSW was shown in Table 2.2. It was apparently characterized that organic waste (garbage) took a large portion of MSW in year 2004.

In rural areas, collection services are not widely covered and open dumping and burning are typical disposal techniques for MSW.

Table 2.2 Average physical compositions of MSW at disposal facilities in urban area*

Composition	% of Total
Organic waste (garbage)	63.6
Plastics	16.8
Papers	8.2
Metals	2.1
Clothes	1.4
Wood	0.7
Para grasses	3.5
Rubbers/Leathers	0.5
Misc.	3.2
Total	100.0

Source * Pollution Control Department (2004), Surveying and Evaluation of Physical Compositions of MSW.

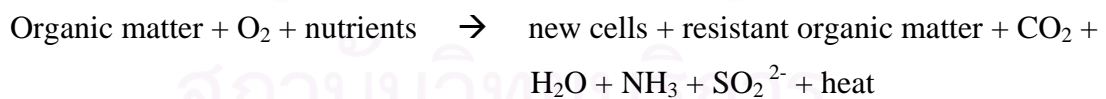
Major portion of MSW is dumped in landfill sites. The uncollected waste usually finds its way in sewers. Some of it is eaten by cattle. Some is left to rot in the open. And some is burnt on roadsides. Dumping of ISW on public land or making it a part of MSW is quite common. All these practices lead to air and water pollution. As a result of emissions of a wide variety of organic compounds such as xylene, cresol, and esters results in serious health problems. Moreover landfill sites require large areas of land (nearly 150 hectares/year, in cities such as Bombay; MNES 1995). Also the waste decomposition is very slow. All this has led to the development of various alternative technologies such as incineration, pelletization, composting, and biomethanation.

2.2 Phases of landfill stabilization

Municipal solid waste disposed of in landfill produces decompositions a combination of chemical, physical and biological processes. These processes are present in landfills and produce solid waste, biomass, leachate, heat and gases as by-products. Most landfills are influenced by different climatological conditions, landfill operation, management options and control factors operative in the landfill environment (Pohland et al., 1983). 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.

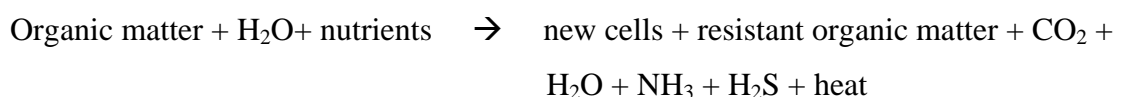
Phase I: Initial adjustment

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 water treatment plants and the recirculation of leachate. Organic fractions of MSW can be converted to a stable organic residue known as compost and represented by the following equation.



Phase II: Transition

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.



This anaerobic condition can be monitored by measuring the oxidation/reduction potential 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.

Phase III: Acid formation

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. Carbon dioxide and hydrogen gas increase as a result of the anaerobic process. The presence of organic acids and also CO₂ drop the pH of landfill. During the acid phase, biochemical oxygen demand (BOD), chemical oxygen demand (COD), and the conductivity of the leachate will increase significantly due to the dissolution of organic acids. Also due to the decreasing pH, inorganic constituents and heavy metals will solubilize in the leachate.

Phase IV: Methane fermentation

Methane and carbon dioxide are generated from the conversion of organic acids and hydrogen gas. The pH of leachate increases to neutral, in the range of 6.8 to 8 with the decreasing amount of organic acids. Chemical oxygen demand (COD), biochemical oxygen demand (BOD), and total organic carbon (TOC), in leachate all decrease as the result of organic acids consumption. In the methanogenic phase, oxidation-reduction potentials are highly negative and indicative of highly reducing conditions (Stratakis, 1991). Heavy metal release from solid waste by precipitation and complexation with sulfide and carbonate anions proceed and appear in leachate. The highest volume of methane is produced during this phase.

Phase V: Final maturation

The biological process present in this phase is low including the removing of nutrients with the leachate. The oxidation-reduction potential will rise slowly and the more resistant organics will slowly degrade and influence mobility of other species. The predominant gases evolving in this phase are CH₄ and CO₂ and small amounts of nitrogen and oxygen may also be found. During maturation phase, the leachate will

often contain humic and fulvic acids, which are difficult to process further biologically.

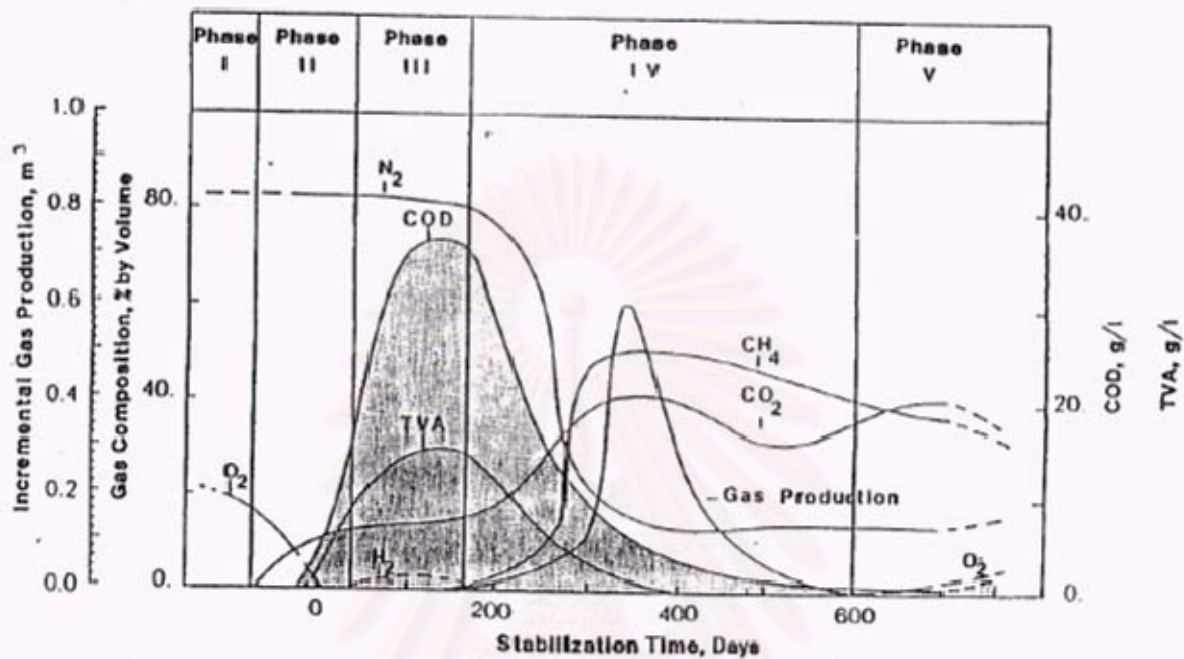


Figure 3. Changes in selected indicator parameters during the phases of landfill stabilization. Pohland and Harper (1985).

Figure 2.1 Changes in selected indicator parameters during the phases of landfill stabilization (Pohland and Harper,1985)

2.3 Leachate generation

Leachate in most landfill is generated from external water such as surface drainage, rainfall, groundwater, water from underground sources including the liquid produced from waste. The produced liquid has percolated through the solid waste and has extracted dissolved or suspended materials during degradation process (Tchobanoglous et al., 1993).

The characteristics of leachate are highly variable depending on phase of degradation, the composition of the waste, rate of water infiltration, refuse moisture content, landfill operation and age. Organic containment of leachate is primarily

soluble refuse components or decomposition products of biodegradable fractions of waste.

Organic compounds in landfill included 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 humic acids, fulvic acids and the hydrophilic fraction which are called 'humic substances' can be isolated and purified from landfill leachate. These fractions play an important role to form complexes with heavy metals present in leachate. The molecules of humic substances consist of hydrophilic and hydrophobic groups, charge sites and counter ions, the identity and proportion of which vary from molecule to molecule (Swift, 1996).

2.4 Dissolved organic carbon (DOC)

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 tannic substances also often have natural acids associated with them (which can influence pH levels).

Dissolved Organic Carbon (DOC) is generated from organic waste in landfill and is a product of the anaerobic degradation processes. DOC was defined as the fraction of Total Organic Carbon (TOC) that passes through a 0.45- μm -pore-diam filter. Christensen et al. (1999), Christensen and Christensen (1999), and Christensen et al. (1996) 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 behavior. 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.

2.5 Leachate: vary by 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 humic substances 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 the Humic Substances increased with increasing 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 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 ($< 0.45 \mu\text{m}$ or $< 0.001 \mu\text{m}$), the results indicate 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).

The existing literature was reviewed based on the uncertainty of the understanding of the heavy metal complexation by DOC in landfill leachate. For this study, the ability to extract metals will be measured for the DOC from simulated bioreactor landfill.

2.6 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 contaminated soil, including ex-situ washing with physical-chemical methods (Anderson, 1993) 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 soils, 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 batch 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 (Blaylock et al., 1997; 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, inducing toxic effects in the new crop and contributing to the dispersion of metals in soil profile.

Alternatively, the humic substances, main constituent of organic matter, are an association of organic molecules and macromolecules and are distinguished in three categories: humin, humic acids and fulvic acids. The humic substances have an important role in the interaction phenomena (absorption/desorption, transport, diffusion, etc.) of organic and inorganic pollutants. The study of opportune natural chelate substances, like humic and fulvic acids, can be an important alternative to apply in the assisted phytoextraction, with reduced risks for the environment (Tassi).

As the ability to form complex with metals of DOC, it can be another technique apply to enhance bioavailability of heavy metals uptake by plants.

2.7 Related studies

Effect of dissolved organic carbon on the mobility of Cadmium, Nickel and Zinc in leachate polluted groundwater

Christensen (1996) studied the ability of dissolved organic carbon (DOC) from landfill leachate 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 and were studied in the original matrix with a minimum of manipulation. The experiments were performed as batch sorption experiments and the metal distribution between the aquifer material and the solution (K_d) was determined in the leachate polluted groundwater samples and in reference solutions of synthetic inorganic leachate. The difference in distribution coefficients was a direct indication of complex formation between DOC and heavy metals. The results showed, that DOC from landfill leachate polluted groundwater has the ability to form complexes with Cd, Ni and Zn, and the distribution coefficients were a factor of 2-6 lower in the presence of DOC. Based on the distribution coefficients, the relative migration velocities of the heavy metals were estimated. The migration velocity of the metals was increased by the presence of DOC but did not exceed 1.2% of the water migration velocity, indicating that the effect of DOC on the mobility of Cd, Ni and Zn may have only minor environmental importance. Conditional complex formation constants were estimated from the K_d -values. The constants for 1 : 1 complexes increased slightly in the following order $Zn < Cd < Ni$. However, increasing the metal concentration into the mg level decreased the constants by about one order of magnitude, showing the importance of determining the constants at environmentally relevant metal concentrations.

The effect of pH on the complexation of Cd, Ni and Zn by dissolved organic carbon from leachate-polluted groundwater

Complexation of cadmium (Cd), nickel (Ni) and zinc (Zn) by dissolved organic carbon (DOC) in leachate-polluted groundwater was measured using a resin equilibrium method. Metal-DOC complexation was measured at different DOC concentrations over a range of pH values. The results were compared to simulations made by two speciation models (WHAM and MINTEQA2). Of these models, WHAM came closest to simulating the experimental observations although it systematically overestimated the pH dependence of metal-DOC complexation. Accepting a variation in the free metal ion activity of a factor of 3.4 the WHAM model provided useful predictions of the complexation of Cd and Zn by DOC in the pH range 5.8, and of Ni in the pH range 5.7. At pH 8, however, the model overestimates the extent of Ni-DOC complexation to an unacceptable degree. The

MINTEQA2 model predicts virtually no pH dependence for DOC complexation of Cd, Ni and Zn and is thus in very poor agreement with the experimental results. As an alternative approach, relations between the conditional complex formation constant ($\log K_c$) and pH were estimated for each metal. Using these relations for estimating the complexation of Cd, Ni and Zn by DOC, a deviation in the free metal ion activity up to a factor of 2 can be expected.

Characterization of humic substances present in landfill leachates with different landfill ages and its implications

Kang et al. (2002) studied the characteristic of extracted humic substance (HS) from several landfills with different landfill ages using elemental analysis and various spectroscopic methods. Molecular size distribution of the humic substances (HS) was also determined using the batch ultrafiltration technique and permeation coefficient model.

The element analysis and spectral features obtained from UV/visible, IR, and ^1H and ^{13}C NMR showed that leachate HS has an aromatic character lower than that of commercial humic acid (Aldrich Co.), and higher than in the HS of older landfill leachate. Fluorescence spectra indicated that humic acids had a relatively higher content of condensed aromatic compounds than the fulvic acids obtained from the same sources, and the spectrum of commercial humic acid showed that aromatic compounds may be present in a much more condensed and complex form. Molecular size distribution data revealed that the leachate humic acids contained a higher percentage of smaller molecules of 10,000 D, it was compared with that of the commercial humic acid (45%~49% vs. 33%), and molecular size of the leachate HS had a tendency to increase as landfill age increased. These results indicate that the HS from landfill leachates were in an early stage of humification, and the degree of humification increased as the landfill age increased, which implies important information on various related researches, such as interactions of HA with pollutants in terrestrial environments, and optimization of leachate treatment processes with respect to landfill age.

Similarities in the long term leaching behavior of predominantly inorganic waste, MSWI bottom ash, degraded MSW and bioreactor residues.

Van der Sloot et al. (2001) studied a comparison of four types of landfill waste, a combination of laboratory leaching test, a lysimeter study, and field scale. Measurements were carried out in various related studies. These were a predominantly inorganic waste, a partially degraded municipal solid waste, municipal solid waste incinerator (MSWI) bottom ash and the product of degradation of mechanically separated organic waste (MSOR) in a bioreactor. The goal of these studies was to elucidate the reactions taking place within the landfill and to understand controlling factors determining leachate quality. For the different nature of wastes taken to landfills, a better understanding of the waste-waste interactions in landfills is needed to identify which wastes impropotionally affect the leachate quality of an entire landfill.

For the result, it could be concluded that the leaching behavior in all of these “mixed” materials proves to be dominated for many constituents as measured by dissolved organic carbon (DOC) similar to topsoil’s. At neutral pH, DOC measured can be used as the degradability standard of waste by comparing the DOC release levels to a data set. In addition, the DOC levels as observed for top soils can be used as a reference for final storage quality.

Transport of humic and fulvic acids in relation to metal mobility in a copper-contaminated acid sandy soil

Weng et al. (2002) studied the transport behavior of Humic Acids (HA) and Fulvic Acids (FA) in an acid sandy soil and their response to the changes in the Ca concentration in the bulk solution. Researchers focused on the major factors that are involved in the HA and FA transport by using the breakthrough curves (BTCs) and speciation model calculations. The data showed that the transport behavior of HA was different from that of FA. On the basis of their model calculation, the characterization of HA transport could be explained by the coagulation of HA largely upon the binding of Al. The increase of Ca concentration resulted in further coagulation of HA because of increased Ca adsorption. For FA, the adsorption to the soil matrix was more likely the process that controls its solubility and mobility. The mobility of Al and Cu in the soil column was closely related to the solubility and transport of the dissolved organic matter (DOM) in soil solution. The concentration of Ca in the effluent was lower than in the influent because Ca was retained in the soil due to the retardation of HA and

FA and due to the compensation of the other cations released from the soil to the solution.

Leaching of heavy metal from contaminated soils using EDTA

From Sun et al. (2000), ethylenediaminetetraacetic acid (EDTA) extraction of Zn, Cd, Cu, and Pb from four contaminated soils was studied using batch and column leaching experiments. In the batch experiment, the heavy metals extracted were virtually all as 1:1 metal EDTA complexes. The ratio of Zn, Cd, Cu and Pb of the extracted were similar to these in the soils, suggestion 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. Sequential fractionations of leached and un-leached soils showed that heavy metals in various operationally defined fractions contributed to the removal by EDTA. Considerable mobilization of Fe occurred in two of the four soil during EDTA leaching. Decrease in the Fe and Mn oxide fraction of heavy metals after EDTA leaching occurred in both soils, as well as in the third soil that showed little Fe mobilization. The results suggest that the lability of metals in soil, the kinetics of metal desorption/dissolution and the mode of EDTA addition were the main factors controlling the behavior of metal leaching with EDTA.

The determination of labile cadmium in some biosolids-amended soils by isotope dilution plasma mass spectrometry

Gray et al. studied an isotope dilution inductively coupled plasma-mass spectrometry (ICP-MS) technique, using an enriched stable Cd isotope, was applied to determine the labile fraction of Cd in 20 biosolids-amended soils. The measured labile Cd fraction was compared with the amounts of Cd solubilised or extracted by HNO₃, EDTA, CaCl₂, and Ca(NO₃)₂. Labile Cd, as a proportion of total soil Cd (%labile), ranged between 33% and 84% with a mean of 50% indicating that a significant proportion of the Cd added to these soils from biosolids is in non-labile forms. EDTA was found to release Cd from non-labile sites, solubilising on average of 30% more Cd than labile forms as measured by isotope dilution. In contrast, the proportion of Ca(NO₃)₂-extractable Cd was significantly less than the measured labile fraction and probably represents Cd in soil solution. Extraction of soil with 1 M CaCl₂, however,

was found to provide a very good estimate of labile Cd in these biosolids-amended soils. Isotope dilution ICP-MS using an enriched stable Cd isotope and ICP-MS appears to be an analytical technique which has the potential to measure labile Cd in soils without the problems associated with the use of radioisotopes.

2.8 Leaching experiment

From the previous work, the ability of DOC to form complex with Cd was adapted in this study by varying of DOC content in leachate (Christensen et al, 1996).

Basic extractants such as HNO_3 , 0.04 M EDTA, 1 M CaCl_2 , and 0.05 M $\text{Ca}(\text{NO}_3)_2$, were used in this study to provide comparison of the extraction ability with leachate of different ages and sources. Method for conducting the extraction experiment was adapted mostly from those obtained in Gray et al. (2003). Leaching experiment to determine leaching ability of leachate various by phase of degradation was done by TCLP method and compared with the extraction fluid #1. Furthermore, water was used as control.

CHAPTER III

METHODOLOGY

3.1 Materials and methods

3.1.1 Configuration of the simulated landfill fermentation of organic waste reactors

The six simulated landfill fermentation of organic waste reactors were constructed using 20 L plastic tanks. The reactors were assembled with two 1.2 cm outer diameter PVC pipes to provide support for bottom lids. A coating of Silicone was applied to the interior and exterior of the flanged joints to ensure that the junctions would be water and gas tight. The design and operation features of the simulated landfill fermentation of organic waste reactor with recycling are shown in Figure 3.1

The reactors were equipped with three ports, the bottom port was used for leachate drainage and sampling while the other two inlet/outlet ports were placed at the top lid to collect gas samples and to add liquid.

The gas production from the reactor was collected and measured by an inverted glass cylinder method as shown in Figure 3.1. By using one 250-ml glass cylinder placed invert in one 1,000 L glass cylinder which was filled with confining solution (20% Na_2SO_4 in 5% H_2SO_4). The inner cylinder was lifted until the level of the confining solution in both cylinders equilibrated, and the amount of gas produced in a certain period was indicated by the volume occupied by gas in the inner cylinder.



Figure 3.1 Configuration of the simulated landfill fermentation of organic waste reactors

3.1.2 The simulated landfill fermentation of organic waste reactors loading

Solid waste typically found in Thailand included organic waste such as vegetable, paper, plant and etc. The solid waste in this experiment was Para grass and the mixture of fruit and vegetable waste. The components of solid waste were divided into 2 type reactors depending on the type of refuse. Each type was divided into 3 reactors represented to 3 phases of degradation that were acid formation,

methanogenic and final maturation phase. Therefore, 6 reactors were used in this experiment which is explained in Table 3.2. There are 2 reasons for divide 3 reactors in each type of waste. First, the size of the simulated bioreactor may be too big if was constructed and run to produce enough leachate for the 3 phases of degradation. Second, there was another 2 reactors kept in reserve if any of the bioreactor was failed. For example the unexpected duration time of each phase may cause the overestimate time for leachate collected.

Reactor A; the simulated solid waste was the mixture of fruits and vegetables waste representing typical solid waste composition of Sri-Mum-Muang Market. The mixture of waste consisted of 80% vegetables and 20% fruits by weight as shown in Table 3.1. This reactor was loaded with 10 kg of waste for each reactor.

Table 3.1 Solid waste composition of Sri-Mum-Muang Market (Chewha, 2003)

Type	Total weight (wet) (kg)	Percent (by weight)
Chinese white cabbage	3.75	12.5
Morning glory	3.45	11.5
Eggplant	9.45	31.5
Kale	3.00	10.0
Cow pea	3.75	12.5
Water mimosa	0.90	3.00
Cabbage	0.90	3.00
Chinese cabbage	0.60	2.00
Bitter cucumber	0.75	2.50
Banana	1.50	5.00
Orange	1.95	6.50
Total	30.0	100.0

Reactor B; the solid waste was 4.5 kg of Para grass (*Brachairia mutica*) for each reactor.

The solid wastes were prepared, shredded and mixed with 0.5 L of anaerobic digested sludge obtained from an aerobic digester at the Utility Business Alliance Co., Ltd. to initiate and enhance the rate of solid waste degradation and stabilization with

methane production in each reactor system. The characteristics of sludge are presented in Table 3.3. After that, the solid waste were divided and loaded into 3 reactors representing to 3 phases of degradation.

Table 3.2 Phase of collected sample in each reactor

No	Reactor	Phase of collected sample
A1	Fruit and vegetable	Acid phase
A2	Fruit and vegetable	Methanogenic phase
A3	Fruit and vegetable	Maturation phase
B1	Para grass	Acid phase
B2	Para grass	Methanogenic phase
B3	Para grass	Maturation phase

Table 3.3 Analysis of the digested sludge added to all six simulated landfill fermentation of organic waste reactors.

Parameter	Analysis
Total solids (mg/L)	46,449
Total volatile solids (mg/L)	120
pH	6.84

3.1.3 The simulated landfill fermentation of organic waste reactors operation

In preliminary operations of the reactors, both types of refuse were analyzed for moisture content. Deionized water was added into reactor B to make up water equal to that of reactor A. The liquid collected at the bottom of each reactor on the next day was recycled to the top of reactor. This water application procedure was repeated until the amount of liquid introduced each day, would equal to the amount of liquid collected on the next day. This date was then defined as Day 0, or when

indicated field capacity was reached and leachate production began. A sample of leachate from each cell was collected at that time and analyzed for all indicator parameters.

For this experiment, the simulated landfill fermentation of organic waste reactors did not use leachate recirculation to accelerate biological processes. There was no water addition to all recycle reactors since the leachate production began.

3.1.3.1 Reactor A operation

Reactor A (fruit and vegetable) consisted of 3 reactors as presented in Table 3.2. Each reactor was not started at the same time but for all reactors Day 0 was defined as the field capacity was reached and later 'Day 1' was started counting. Reactor A3 which representing to final maturation phase was firstly operated for preliminary investigated the acid formation and methanogenic phase. In other hand, the biological and chemical process occurred since the initial stage until the process transferred from acid formation phase through methane formation by monitoring the gas production and leachate characterization. In addition, reaching to final maturation phase of degradation could unexpected and may take long time. The preliminary investigated information could indicate the duration of acid formation and methanogenic phase occurred. During methanogenic phase of reactor A3, reactor A2 was loaded and operated. Therefore, the characterize leachate information and gas production that changes in parameters indicative of methane formation could be determine to identify the sequential phases of fruit and vegetable waste degradation. Later, reactor A1 was loaded and operated.

3.1.3.2 Reactor B operation

Reactor B (Para grass) was consisted of 3 reactors as presented in Table 3.2. The operation for reactor B remained the same as reactor A. Reactor B3 was started to operate first followed by reactor B2 and B1.

3.1.4 Sampling and analyses

The collected leachate and gas was monitored in each reactor for checking the same reactions for the same solid waste. Leachate samples were collected from the bottom of the recycle reactors, and were analyzed for dissolved organic carbon

(DOC), pH, oxidation-reduction potential (ORP), volatile-fatty acids (VFAs), and Alkalinity, if any. The daily gas production rate and gas composition were also observed as percent by volume and determine for methane. The frequency and method of analyses are listed in Table 3.4

Table 3.4 Frequency and method of analyses for simulated landfill fermentation of organic waste reactor parameters.

Measurement	Procedure	Frequency
pH	pH meter	Every day
ORP	ORP meter	Every week
DOC	TOC-Vcph	Every week
VFA	Standard methods for water and waste water Examination	Every week
Alkalinity	Standard methods for water and waste water Examination # 4500-P(Titration method)	Every week
Gas production	Inverted glass Cylinder Method	Every day
% CH ₄	Gas Chromatography (TCD)	Every week

3.1.4.1 Gas analysis

The gas produced by the simulated landfill fermentation of organic waste reactors was collected and analyzed for methane. The amount of gas was measured using inverted glass cylinder method. The gas composition was analyzed by Gas Chromatograph (GC) 19091P-MS4 equipped with a Thermal Conductivity Detector (TCD). The glass packed column used to separate neon, argon, oxygen, nitrogen, methane, carbon monoxide was 30m × 0.32 mm ID. The typical operating conditions for the GC were.

Column: HP-PLOT Agilent Technologies 30m × 0.32 mm ID ,
12 μm
P/N: 19091P-MS4

GC:	6890
Carrier:	Helium, 2 mL/min
Sample:	250 μ L, split (75:1)
Detector	TCD (Agilent Technology 6890 N Network GC system)

3.1.4.2 Leachate analysis

The leachate parameters analyses and method were shown in Table 3.4 according to Standard Methods (Standard methods for Examination of water and waste water 1980). Dissolved organic carbon (DOC) is the fraction of TOC that pass through a 0.45- μ m-pore-diam filter. After filter, the sample was taken to determine the amount of organic carbon by TOC-Vcph. The typical operating conditions for the TOC analyzer were shown as below.

TOC:	Vcph
Carrier:	Oxygen, Air zero
Temperature:	680 $^{\circ}$ C

3.1.5 Leachate collection

The quantity and quality of leachate varied as different phases of stabilization occurred. Therefore, monitoring for changes in parameters indicative of landfill fermentation of organic waste stabilization was done to identify the sequential phases of solid waste degradation. The characteristics of the leachate are highly variable depending on the composition of the waste, rate of water infiltration, refuse moisture content, landfill fermentation of organic waste design and operation, and age. These variations are demonstrated in Table 3.5, where ranges in concentration of significant leachate components are presented as a function of stabilization phase. Leachate will be collected in each phase according to these corresponding values as presented in Table 3.5.

Table 3.5 Ranges in landfill leachate stabilization parameters (Chewha, 2003)

Parameter	Phase II	Phase III	Phase IV	Phase V
	Transition	Acid formation	Methanogenic	Final maturation
BOD, mg/L	100-10,000	1,000-57,000	600-3,400	4-120
COD, mg/L	480-18,000	1,500-71,000	580-9,760	31-900
TVA, mg/L as CH ₃ COOH	100-3,000	3,000-18,000	250-4,000	0
BOD/COD	0.23-0.87	0.4-0.8	0.17-0.64	0.02-0.13
NH ₃ -N	120-125	2-1,030	6-430	6-430
pH	6.7	4.7-7.7	6.3-8.8	7.1-8.8
Conductivity, μ mhos/cm	2,450-3,310	1,600-17,100	2,900-7,700	1,400-4,500

3.1.6 Soil samples

The Cd contaminated soil was characterized and selected for the leaching test. Cadmium was chosen because it is the most mobile heavy metal in soil and groundwater. The 4 contaminated soil samples were collected from Mae Sot, Tak province. The soil types were Nakornpanom (Nn), Hangchat (Hc), and Rachburee (Rb-h) soil series. The soil samples were air-dried and passed through a stainless steel to obtain the < 2-mm fraction before analysis. Soil pH was measured in a water suspension using a soil to solution ratio of 1:1. The leaching efficiency depends on many factors such as the lability of heavy metals in soil, the strength of extracted solution, pH and soil matrix. Therefore, two samples (site 2 and 3) were selected from 4 soil samples by the difference of pH and the highest amount of Total Cd. The value of Total Cd in soil samples were analyzed by Flame Atomic Absorption Spectrometry (FAAS) as shown in Table 3.6

Table 3.6 Value of pH (1:1), organic carbon (%), Total Cd (ppm) and texture of soil samples

Site	pH	%OC	Total Cd (ppm)	%sand	%Silt	%Clay	Texture
1	6.55	1.21	2.05	40.4	31.3	28.3	Clay loam
2*	7.45	1.78	10.52	39.7	42.5	17.8	Loam
3*	5.85	1.56	7.02	41.9	38.6	19.5	Loam
4	6.45	1.77	0.60	35.5	29.9	34.6	Clay loam

* The selected site used in this study

3.2 Leaching test (U.S. EPA Standard Method 1311)

The ability of this leachate to leach metals from solid metrics was measured with a leaching test. Leaching test for determine the solubilize and extracted Cd from contaminated soil was Toxicity Characteristic Leaching Procedures (TCLP) test which is the way to determine if a particular waste is considered hazardous. The solid phase is extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase. For this study, extraction fluid #1 was used because it is recommended for extract of the solid, and whether inorganics, semivolatile organics, pesticides, and herbicides. The extraction fluid #1, consisting of 5.7 mL of glacial acetic acid, 64.3 mL of 1.0 N NaOH, and 930 mL of distilled water with a final pH of approximately 4.98, was employed as an extraction medium. Samples were taken to the agitator apparatus and were rotated for a period of 18 hours at 30 rpm. In this experiment, the leaching test was conducted to evaluate the potential of leachate to solubilize and extracted Cadmium from contaminated soil.

Leachate from both refuses (reactor A: fruit and vegetable and reactor B: Para grass) were collected at acid formation, methanogenic and final maturation phases of degradation. In addition, the DOC fractions from the leachate were isolated and examined. Six leachate samples were filter through a 0.45 μm Whatman filter to separate DOC.

Two grams of soil was extracted by 20 mL of leachate samples and shake for 18 h. After extraction the suspension was centrifuge at 10,000 rpm for 10 min and filtered through a Whatman 42 filter paper before analysis of Cd by Flame Atomic Absorption Spectrometry.

Moreover, this ability of leachate will be compared with the ability of water (H_2O) for the control, extraction fluid #1, including HNO_3 , 0.04 M EDTA, 1 M CaCl_2 , and 0.05 M $\text{Ca}(\text{NO}_3)_2$ followed by the methodology of previous research by Gray et al. (2003). Gray et al. (2003), studied of labile cadmium in some biosolids-amended soils by isotope dilution plasma mass spectrometry, it was found that EDTA was found to release Cd from non-labile sites. In contrast, $\text{Ca}(\text{NO}_3)_2$ -extractable Cd was significantly lower than labile fraction and probably presents of Cd in soil solution. For CaCl_2 , it was found to provide a very good estimate of labile Cd in biosolid-amended soils.

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 soils, 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). Therefore, the ability of EDTA complexing with heavy metals was compared to leachate produced from the bioreactors.

Calcium nitrate extraction

Three grams of soil was extracted with 30 mL of 0.05 M $\text{Ca}(\text{NO}_3)_2$ for 18 h on a shaker. After extraction the suspension was centrifuge at 10,000 rpm for 10 min and filtered through a Whatman 42 filter paper before analysis of Cd by Flame Atomic Absorption Spectrometry.

Calcium chloride extraction

Three grams of soil was extracted with 30 mL of 1 M CaCl_2 for 18 h on a shaker. After extraction the suspension was centrifuge at 10,000 rpm for 10 min and filtered through a Whatman 42 filter paper before analysis of Cd by Flame Atomic Absorption Spectrometry.

Ethylene diamine tetraacetic acid (EDTA) extraction

Three grams of soil was extracted with 30 mL of 0.04 M Na-EDTA for 18 h on a shaker. After extraction the suspension was centrifuge at 10,000 rpm for 10 min and filtered through a Whatman 42 filter paper before analysis of Cd by Flame Atomic Absorption Spectrometry.

Total soil Cd

One gram of soil was digested with nitric acid and perchloric acid in a block digester. (Sparks et al, 1996)

To examine factors effecting leaching potential, the two soil to solution ratios were used. There were 1:10 as recommended by Gray et al. (2003) and 1:20 according to TCLP method. All leaching tests were done using 3 replications and the variation of the results by standard deviation was given accordingly (Table C-1 and C-2 in Appendix C).



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CHAPTER IV

RESULTS AND DISCUSSIONS

4.1 Reactor experiment

Graphical representations of the results of analyses performed on leachate and gas samples collected from six simulated bioreactor landfill fermentation of organic waste during the degradation phase are presented in this section and tabulated in Appendices A and B.

Table 4.1 indicated the characteristics of leachate samples collected before these samples were taken to determine the ability to leach cadmium from contaminated soil by leaching test.

Table 4.1 Characteristic of leachate samples collected from simulated landfill fermentation of organic waste bioreactor at date of sample collection

Analyses	Reactor					
	A1	A2	A3	B1	B2	B3
Day of collection	15	56	98	11	70	116
pH	5.30	5.33	6.25	5.60	8.14	8.37
DOC (mg/L)	10,525	15,865	17,155	4,378	1,314	1,484
Alkalinity (mg/L as CaCO ₃)	1,684	2,594	2,623	1,635	1,811	1,698
VFA (mg/L as CH ₃ COOH)	8,502	19,465	19,913	8,293	1,309	1,018
% CH ₄	-	70.02	32.22	-	58.62	-
Background level of Cd in leachate (mg/L)	0.07	0.11	0.12	0.08	0.07	0.06

4.1.1 Reactor A operation

Reactor A1 was operated for acid formation phase of stabilization. The fruit and vegetable waste was loaded and the liquid collected at the bottom of this reactor on the next day was approximately 450 mL. The collected liquid was recycled to the top of reactor. This water application procedure was repeated until the third day, the

amount of liquid introduced from the third day (approximately 600 mL), would be higher than the amount of liquid collected on the second day (approximately 360 mL), indicating that the field capacity was reached. This date was then defined as Day 0. The initial pH and ORP value were 5.93 and -141.7 mV (Tables A-1 and A-2 in Appendix A). Leachate from acid formation was collected at Day 15 and then stored at 4°C.

For reactor A2 that represents methanogenic phase, the initial liquid was produced approximately 440 mL. The collected liquid was recycled to the top of reactor and repeat everyday until the field capacity was reached. For reactor B2, the percentage of methane was determined since Day 15 to check the end of acid formation phase. The leachate and gas production were continually monitored since the methane was produced from the bioreactor and pH value gradually increased. The methane percentage could be detected since Day 35 as presented in Table 4.2. The highest methane production was 70 % and the leachate was collected at Day 56. Nevertheless, it could not be concluded that the phase of degradation of reactor A2 was completely reached the methanogenic phase due to the high concentration of VFAs and TOC. In addition, pH value increased but was never higher than neutral. The process occurred in reactor A2 was the initial methanogenic phase due to the presence of high VFAs (19,465 mg/L as CH₃COOH).

Reactor A3 was operated for 98 days. The pH value was constant lower than neutral. The DOC, VFAs and alkalinity concentrations were gradually increased. Furthermore, methane percentage continually produced. Characterization of leachate for all parameters could not indicate the final maturation phase of stabilization. As mentioned in Table 3.5 in Chapter III, the VFAs concentration should decreased when the reaction was transferred into methanogenic phase and was disappeared at final maturation phase. Moreover, pH value should increase by the depletion of VFAs. In contrast, the analyses of leachate did not correspond to those reported above. There were the constantly higher DOC (17,155 mg/L), alkalinity (2,623 mg/L as CaCO₃) and VFAs concentration (19,913 mg/L as CH₃COOH) presence in leachate and the low pH which was never higher than neutral until the end of the study. In addition, the gas production of reactor A3 was greatly smaller than that of reactor B3 as shown in Figure 4.9. The reactor may leak at a coating of Silicone that was applied to the interior and exterior of the flanged joints. Otherwise, the degradation process was

taken long residence time because of leachate recirculation and neutralized with base was not applied to the entire reactors in this study. In conclusion, the phase of stabilization of reactor A2 and A3 were at the initial methane formation at the times of sampling.

4.1.2 Reactor B operation

Reactor B1 was loaded with Para grass and represented acid formation phase. The initial liquid collected from the bottom of reactor was 580 mL. The liquid was recycled at the top of reactor until the field capacity was reached at the fifth day. At this day was defined as Day 0. The pH value and ORP concentration of Day 1 were 5.68 and -168.3 mV respectively (Table A-1 and A-2 in Appendix A). Acid formation phase was taken 11 days and then leachate was collected and stored at 4°C.

For reactor B2, the reactor was monitored for methane formation phase after Day 11. The methane percentage could be detected since Day 35 and the results were presented in Table 4.2 as followed. The highest methane production was approximately 59 % as a result of the conversion of organic acids and hydrogen gas to generate methane and carbon dioxide. The concentration of TOC, VFAs and Alkalinity gradually decreased as presented in Table 4.1 indicated that degradation process of reactor A2 was in the methane formation stage. The leachate sample of methanogenic phase was collected at Day 70.

Finally, the degradation process occurred in reactor B3 was from acid formation to produce methane gas and continued to maturity as indicated by the depletion of methane gas and the increasing of pH level to higher than 8 even though the leachate recirculation was not applied and neutralized with base. Moreover, DOC, VFAs and Alkalinity concentrations decreased corresponded to that presented in Table 3.5 in Chapter III. Leachate sample was drained from the simulated landfill fermentation of organic waste bioreactor B3 at Day 116 and were used to represent the maturation phase of stabilization. In conclusion, reactor B had completely biological and chemical processes and leachate samples were perfectly represented the acid formation, methanogenic and final maturation phases of degradation.

4.2 Leachate analyses

4.2.1 pH

For reactor A (fruit and vegetable), the initial pH for reactor A1, A2 and A3 were 4.64, 4.65 and 4.94 respectively. The low initial pH values in all reactors were caused by high amount of moisture content from vegetable and fruit waste that can be produced high amount of acid formation during degradation process in all reactors. For reactor A1, the pH was below 5 until Day 1 which pH increased to 5.93. After that, pH of the leachate fluctuated and decreased to 5.31. The low pH represented the acid formation phase. Therefore, the sample of reactor A1 was collected at Day 15. The pH level continued to increase during the methanogenic phase and remained constant below than 6.0 for the other two reactors. At the end of the study, sample from reactor A3 was collected at pH 6.25 which was closed to neutral. The changes in leachate pH are shown in Figure 4.1 (Table A-1 in Appendix A).

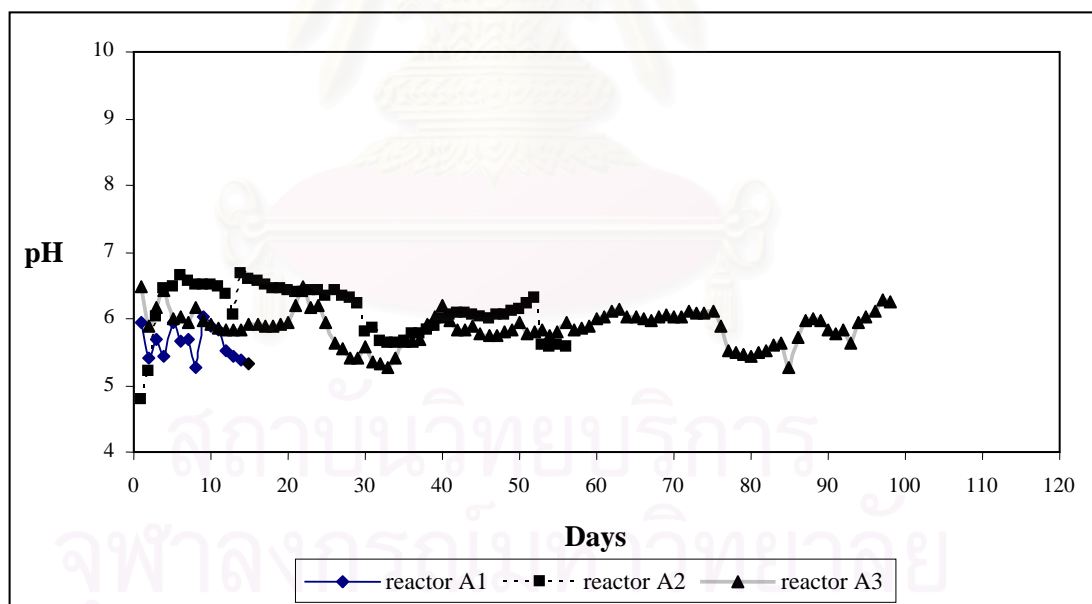


Figure 4.1 pH of leachate from the simulated landfill fermentation of organic waste reactor A

For reactor B (Para grass), the initial pH for reactor B1, B2 and B3 were 5.68, 5.69 and 5.38 respectively (Day 1). The pH of these reactors increased slowly since the process transferred to produce methane. For reactor B1, pH continued constant

from Day1 through Day 10 before collected. After that, pH level of reactor B2 and B3 increased to 7.0 on Day 12 and remain fluctuated in the range 8.0-9.0. The increase of pH was higher than neutral which indicated that the reaction was introduced to methane phase. The pH of reactor B3 was rise up to 9.23 at the end of the study. The changes in leachate pH for reactor B were shown in Figure 4.2 (Table A-1 in Appendix A).

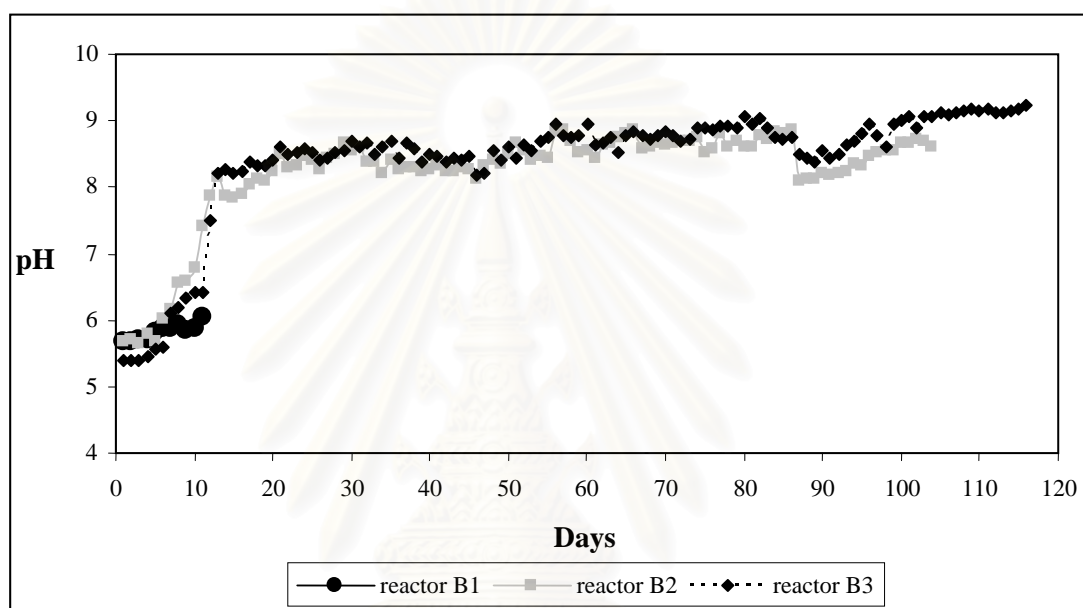


Figure 4.2 pH of leachate from the simulated landfill fermentation of organic waste reactor B

4.2.2 Oxidation-reduction potential (ORP)

Oxidation-Reduction Potential was measured in this study to indicate state of landfill degradation. ORP is a measure of the oxidation state of the system. Since oxygen in the simulated reactors depleted, the ORP was decreased to negative values. Figure 4.3 and 4.4 (Table A-2 in Appendix A) shown the ORP value of the simulated reactor A and B respectively.

For reactor A (fruit and vegetable), the initial ORP value of reactor A1, A2 and A3 at Day 1 were -141.7 mV, -34.6 mV and -163.0 mV respectively. The negative ORP values represent the reducing condition of all reactors. Gradually decreasing of ORP value continued to occur at the initial stage of degradation process. On Day 12 the ORP value increase significantly until the end of the study. That may

caused by the leakages occurred at the joints of reactor and the outer oxygen was introduced into the reactor. Therefore, the ORP value gradually increased as shown in Figure 4.3.

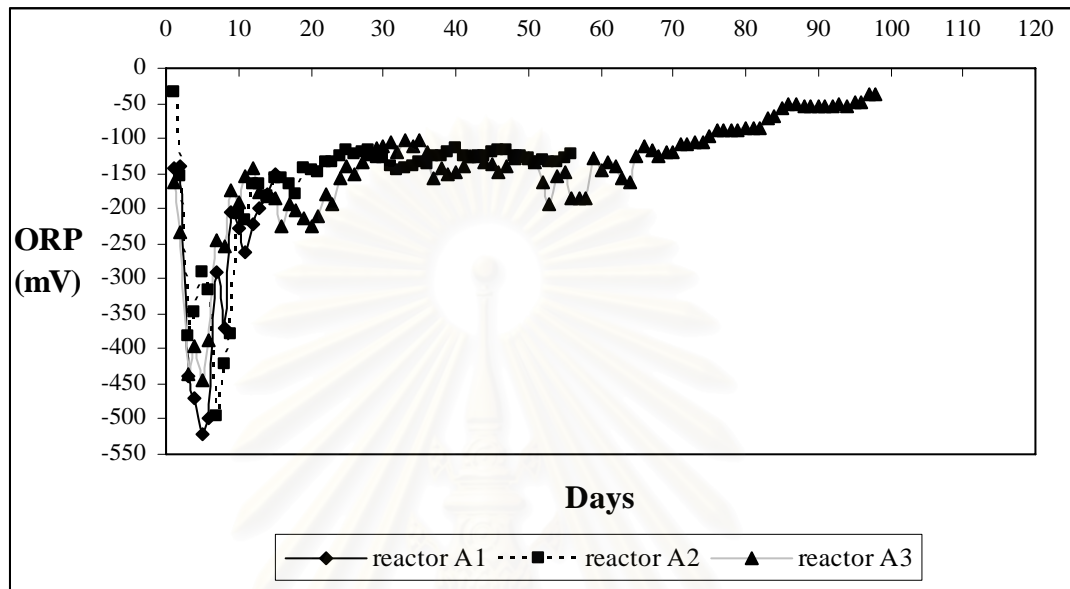


Figure 4.3 ORP of leachate from the simulated landfill fermentation of organic waste reactor A

For reactor B (Para grass), the initial ORP value at Day 1 for reactor B1, B2 and B3 were -168.3 mV, -99.6 mV and -132.9 mV respectively. The ORP value of reactor B was fluctuated at Day 1 to Day 70 which decreased to lower than -350 mV for reactor B3. At Day 71, the ORP value increased gradually then became constant at the last period. For reactor B3, the degradation process transfer to maturation phase which the ORP value was between -100 to -150 mV as shown in Figure 4.4.

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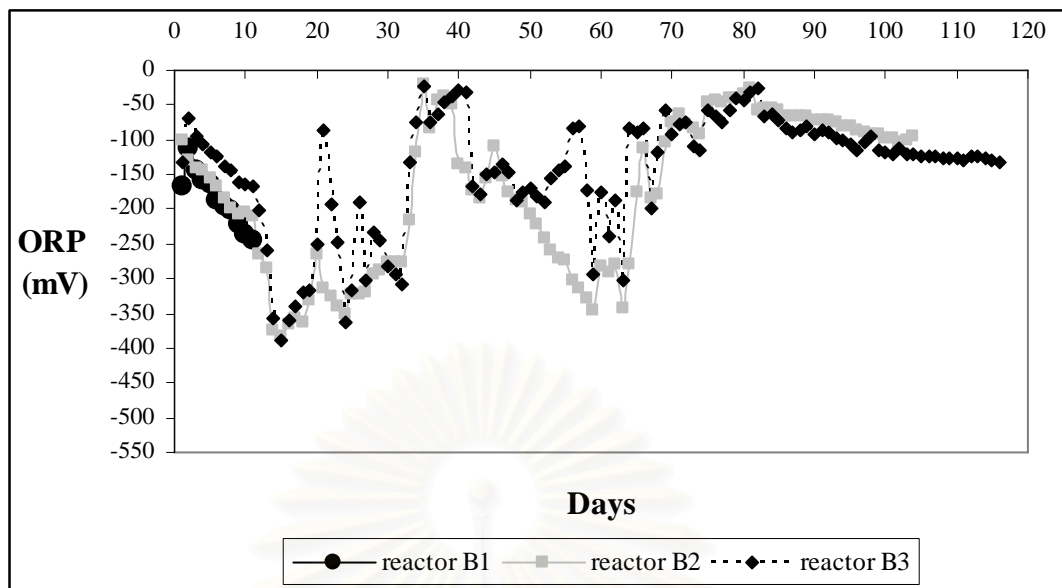


Figure 4.4 ORP of leachate from the simulated landfill fermentation of organic waste reactor B

4.2.3 Alkalinity

Alkalinity reflects the relative presence of acid formation and bases such as H_2CO_3 , HCO_3^- , CO_3^{2-} , total volatile acid formations, phosphorus and ammonia. The total alkalinity of leachate during the acid formation phase is dominated by the volatile organic acid formations and the associated buffer system due to the high concentrations present and the fact that they are stronger acid formations than those constituting the bicarbonate buffer system. The total alkalinity concentrations of reactor A and B are presented in Figure 4.5 (Table A-3 in Appendix A).

The initial alkalinity values for reactor A1, A2 and A3 were 2,447 mg/L as CaCO_3 , 2,814 mg/L as CaCO_3 and 2,508 mg/L as CaCO_3 respectively. The alkalinity values of all three reactors were increase by time. At the end of the experiment the alkalinity values rise up to 3,548 mg/L as CaCO_3 for reactor A3.

For reactor B, total alkalinity values were less than reactor A. There are 1,407 mg/L as CaCO_3 , 1,285 mg/L as CaCO_3 and 1.224 mg/L as CaCO_3 for reactor B1, B2 and B3 respectively. However, the alkalinity values in reactor B were not steady but they tended to be increase as shown in Figure 4.5

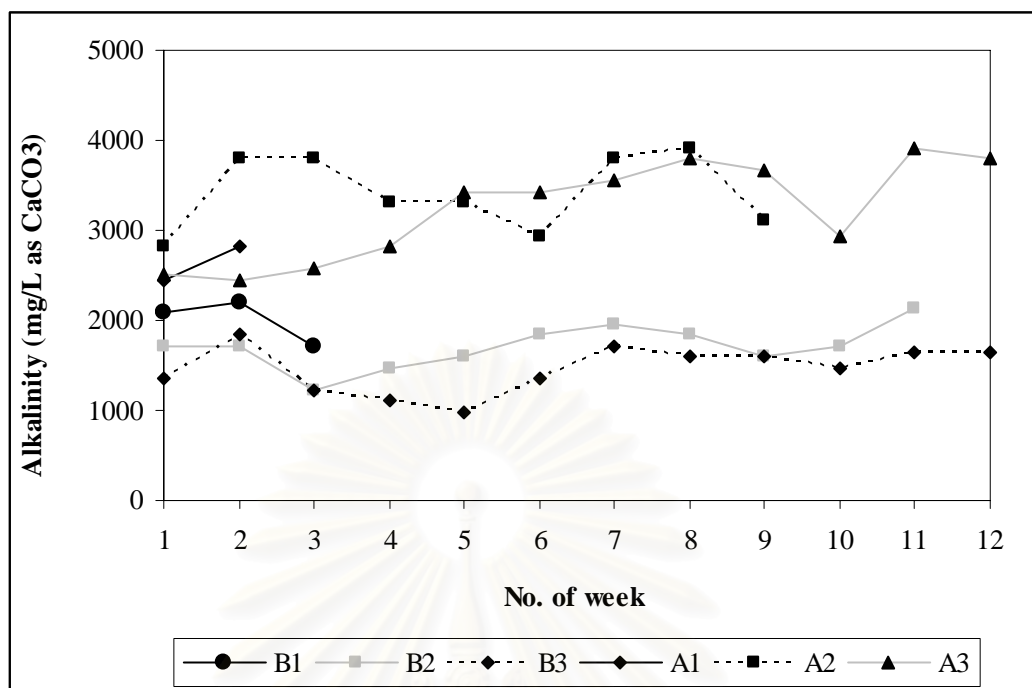


Figure 4.5 Alkalinity of leachate from the simulated landfill fermentation of organic waste reactor A and B

4.2.4 Volatile fatty acids

Volatile fatty acids (VFAs) represented the major organic constituent of landfill fermentation of organic waste leachate and provide the greatest potential for leachate indeed organic contamination of groundwater (e.g. as represented by an increase in the concentration of dissolved organic carbon and chemical oxygen demand). The results of VFAs were presented in Table 4.1 and Figure 4.6. As mentioned earlier, reactor A was not reached final maturation phase due to the high concentration of VFAs and it continually increased. The VFAs concentration of reactor B decreased as it was transferred into methanogenic and final maturation phase. The results corresponded to those reported in Figure 2.1 in Chapter 2 and Table 3.5 in Chapter 3. VFAs concentration should be decreased by the conversion to generate methane and carbon dioxide. There were 8,502 mg/L as CH_3COOH for reactor A1, 19,465 mg/L as CH_3COOH for reactor A2 and 19,913 mg/L as CH_3COOH for reactor A3, respectively. In addition, VFAs concentration found in reactor A were higher than those found in reactor B and were continually produced until the end of the study. For reactor B, VFAs concentrations were 8,293 mg/L as

CH_3COOH for acid formation, 1,309 mg/L as CH_3COOH for methanogenic and 1,018 mg/L as CH_3COOH for final maturation phase.

As noted earlier, the alkalinity dominated by the volatile organic acid formations and the associated buffer system due to the high concentrations present. The volatile fatty acid and total alkalinity for both reactors remained the same.

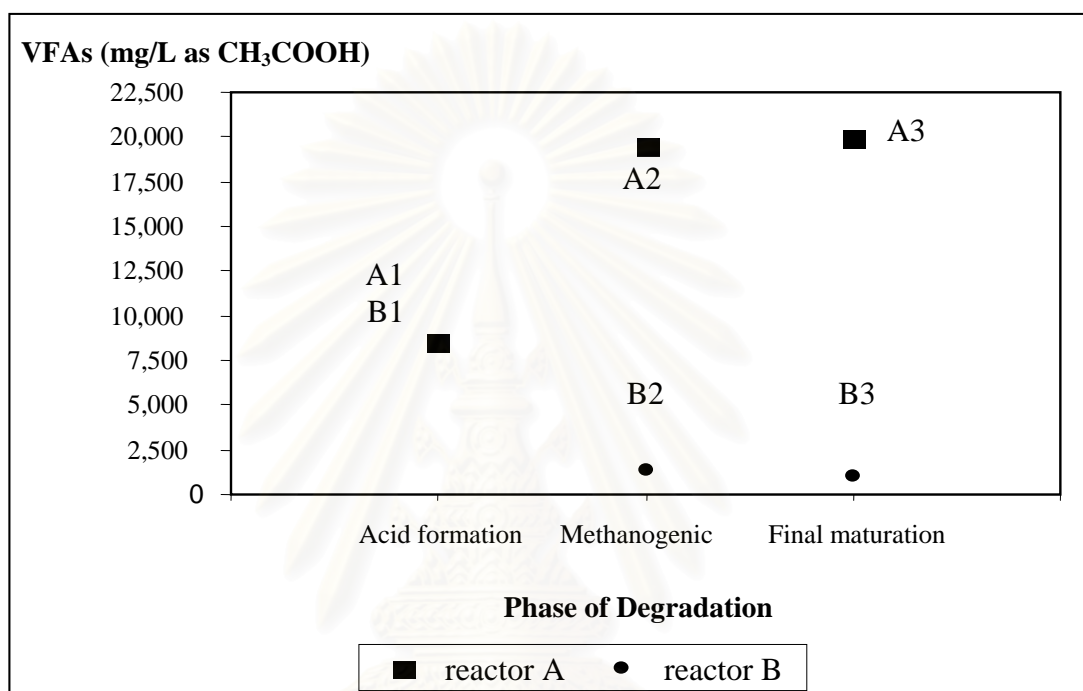


Figure 4.6 VFAs (mg/L as CH_3COOH) of leachate from the simulated landfill fermentation of organic waste reactor A and B

4.2.5 Dissolved organic carbon

DOC is measurement of dissolved organic content in sample which is independent of the oxidation state of the organic matter and does not measure other organically bound element and inorganic. The DOC concentration of all reactors was shown in Figure 4.7 and 4.8 (Table A-4 in Appendix A).

For reactor A, the DOC concentration at Day 1 for reactor A1, A2 and A3 were 9,390 mg/L, 15,832 mg/L and 9,684 mg/L respectively. The DOC concentration was quite fluctuated in between 10,000 to 15,000 mg/L for all reactors.

The concentration of DOC in reactor B was lower than reactor A and was in the range between 1,000-4,000 mg/L. This result may occur by the different type of

waste. The initial DOC concentration for reactor B1, B2 and B3 were 4,414 mg/L, 5,170 mg/L and 3,387 mg/L respectively. After Day 16, the concentration for all reactors was decreased and steady until the end of the study.

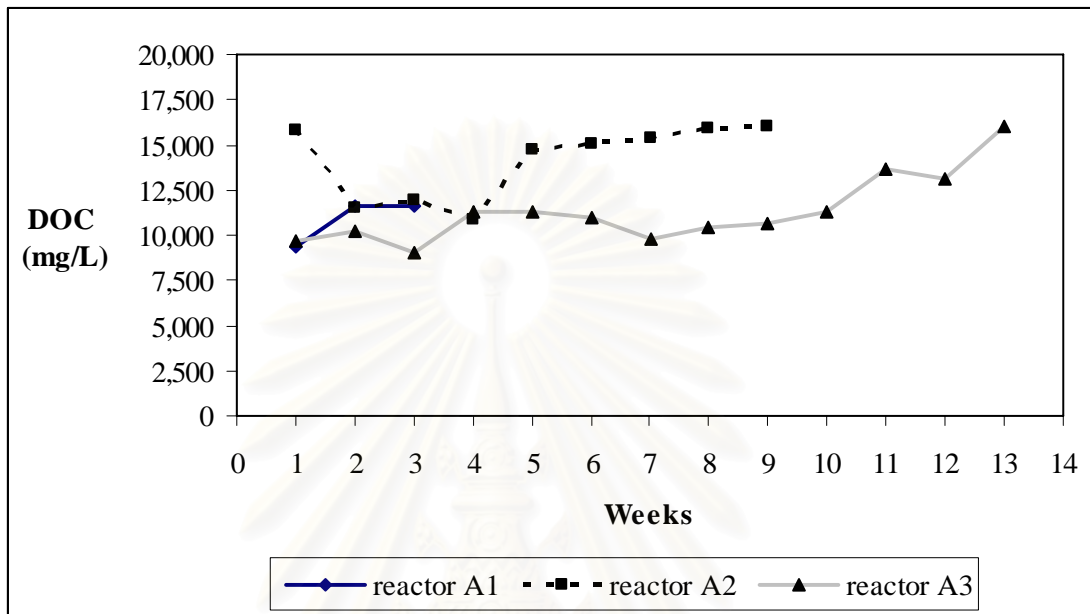


Figure 4.7 DOC of leachate from the simulated landfill fermentation of organic waste reactor A

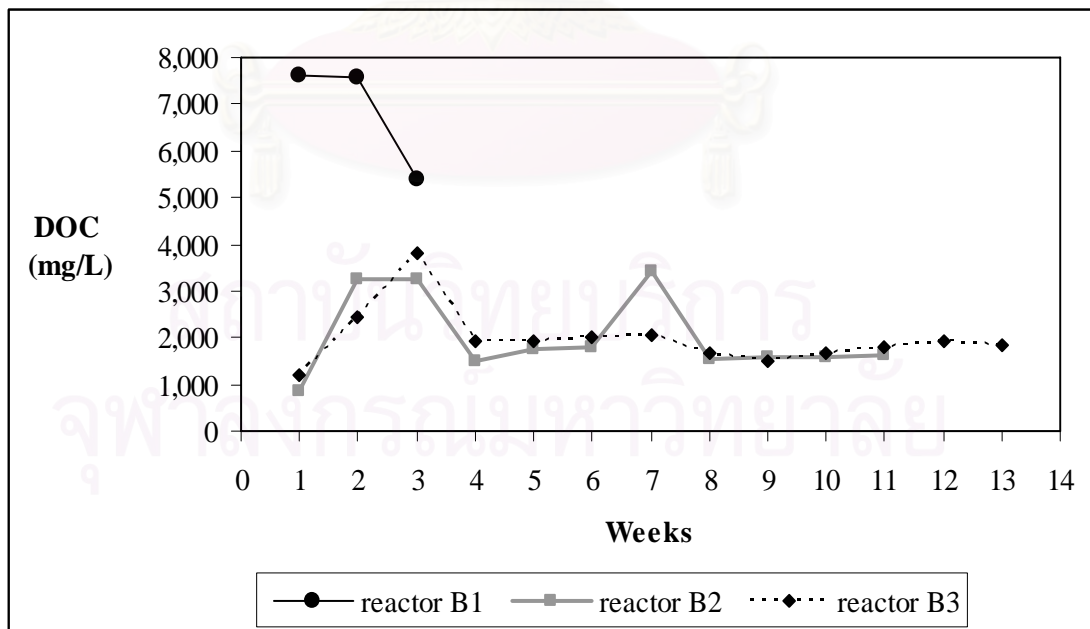


Figure 4.8 DOC of leachate from the simulated landfill fermentation of organic waste reactor B

4.3 Gas analysis

Gas volume and gas composition from three simulated landfill fermentation of organic waste reactors were monitored as the main indicators of the progression of solid waste stabilization processes and as an indicator of the rate of biological activity and organic material conversion within the landfill environment.

4.3.1 Gas production

Cumulative gas volumes produced from both reactors was shown in Figure 4.9 (Table A-5 in Appendix A). The initial gas production rate in reactor A1, A2 and A3 were 350, 327 and 350 cm³ respectively. The daily gas volumes were continuously decreased on Day 62 (reactor A3). The initial gas production rate in reactor B remained the same as reactor A but the volume of gas was higher.

This is because the biological and chemical processes of reactor A3 were not completely anaerobic and may be leak at a coating of silicone that was applied to the interior and exterior of the flanged joints. Moreover, there was less conversion of organic acids and hydrogen gas to generate methane and carbon dioxide.

The daily gas production parameter and cumulative gas production was not obvious indicator for ability of leachate to leach heavy metal from soil sample. In addition, the daily gas produced in different rate for the different duration of time could be the affected from temperature.

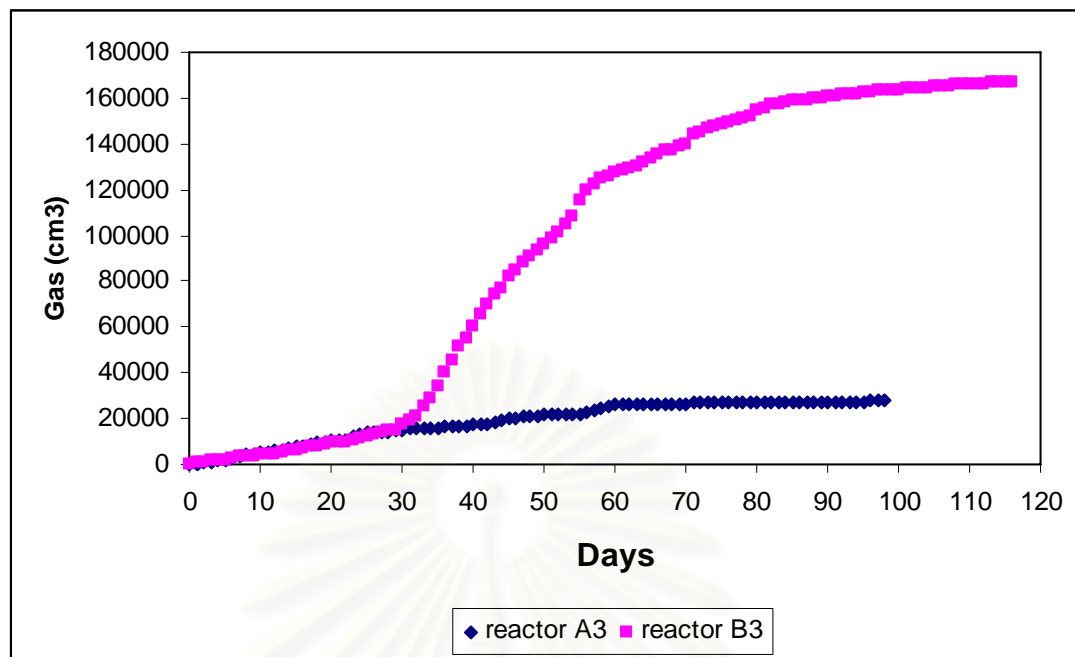


Figure 4.9 Cumulative gas productions from the simulated landfill fermentation of organic waste reactor A3 and reactor B3 (representing the reactors in group A and B respectively)

4.3.2 Methane production

The change of methane percentage for this experiment was studied as the indicator for changing of degradation process of simulated landfill fermentation of organic waste reactor into methanogenic phase. As methanogenic phase, methane was typically produced significantly in the range 50-55 % at beginning, and then remains constant for several years. The percentage of methane in the study was presented in Table 4.2

Table 4.2 Percentage of methane from reactors A2, A3, B2 and B3

Week	A2	A3	B2	B3
5	12.01	-	8.20	5.62
6	14.44	-	14.10	13.51
7	33.48	39.68	25.73	22.58
8	70.02	13.52	42.02	46.57
9	-	26.38	58.62	8.30
10	-	32.22	27.60	3.23

The data of methane production were available for reactor A2, A3, B2 and B3 since week 5. The data of methane production for reactor A1 and B1 did not exist because these two reactors operation were stopped since acid formation phase. As noted earlier, the final matured phase of reactor A was not reached and the methanogenic was also not completed due to the fact that high amount of organic acids still presented. Percentage of methane from reactor A2 and A3 were continually generated, thus indicated the methanogenic phase until the end of the study. In contrast, methane gas of reactor B3 depleted as presented in Table 4.2. The leachate was collected when the methane percentage was 70.02 % and 58.62 % for reactor A2 and B2 respectively.

4.4 Leaching test

Leachate collected in each reactor was determined for background level of Cd concentration and the results present in Table 4.1. As the leaching test, the results were subtracted with background correction and presented in Table 4.3 in unit mg Cd/kg of soil, and Figure 4.10 and 4.11 in unit % of total Cd.

Table 4.3 indicate the average concentration of Cd in soil samples as extracted by HNO_3 , 0.04 M EDTA, 1 M CaCl_2 , 0.05 M $\text{Ca}(\text{NO}_3)_2$ and also Extraction fluid #1 and were compared with the amount of Cd leaching by leachate from six simulated landfill fermentation of organic waste reactors. For all samples, the magnitude of the Cd fractions decreased in the order: $\text{HNO}_3 > \text{EDTA} > \text{leachate} > \text{extraction fluid} > \text{CaCl}_2 > \text{Ca}(\text{NO}_3)_2$. Leaching Cd by water as control could not be detected.

In a more recent study, Gray et al. (2003) studied of labile cadmium in some biosolids-amended soils by isotope dilution plasma mass spectrometry. The labile fraction was defined as that portion of an element in a soil that rapidly exchanges with the changes of soil system. HNO_3 was used to extract total Cd fractions occur in soil samples. EDTA was found to release Cd from soil including 'non-labile' sites. For CaCl_2 , it was found to provide a very good estimate of labile Cd in biosolid-amended soils which presence in soluble form of precipitate and exchangeable fractions. In contrast, $\text{Ca}(\text{NO}_3)_2$ -extractable Cd was significantly lower than 'labile' fraction and probably presented the Cd in soil solution.

Table 4.3 soil pH, total carbon, and total EDTA, CaCl₂, Ca(NO₃)₂ and leachate Cd in soil samples (unit: mg Cd/kg of soil)

site	pH	% OC*	Total Cd (mg/kg)	EDTA Cd (mg/kg)	CaCl ₂ Cd (mg/kg)	Ca(NO ₃) ₂ Cd (mg/kg)	Extraction fluid-Cd (mg/kg)	Cd in H ₂ O**	Cd in Leachate (mg/kg)					
									A1	A2	A3	B1	B2	B3
2	7.45	1.78	10.52	7.35	0.63	0.11	1.70	-	2.27	3.82	4.32	2.56	1.03	1.35
3	5.85	1.56	7.02	3.72	2.63	0.54	0.65	-	2.39	4.28	4.98	3.01	1.44	1.55

Note : solid: solution ratio of soil to leachate samples were 1:20

*percent of organic carbon in soil samples

** Cd concentration could not be detected

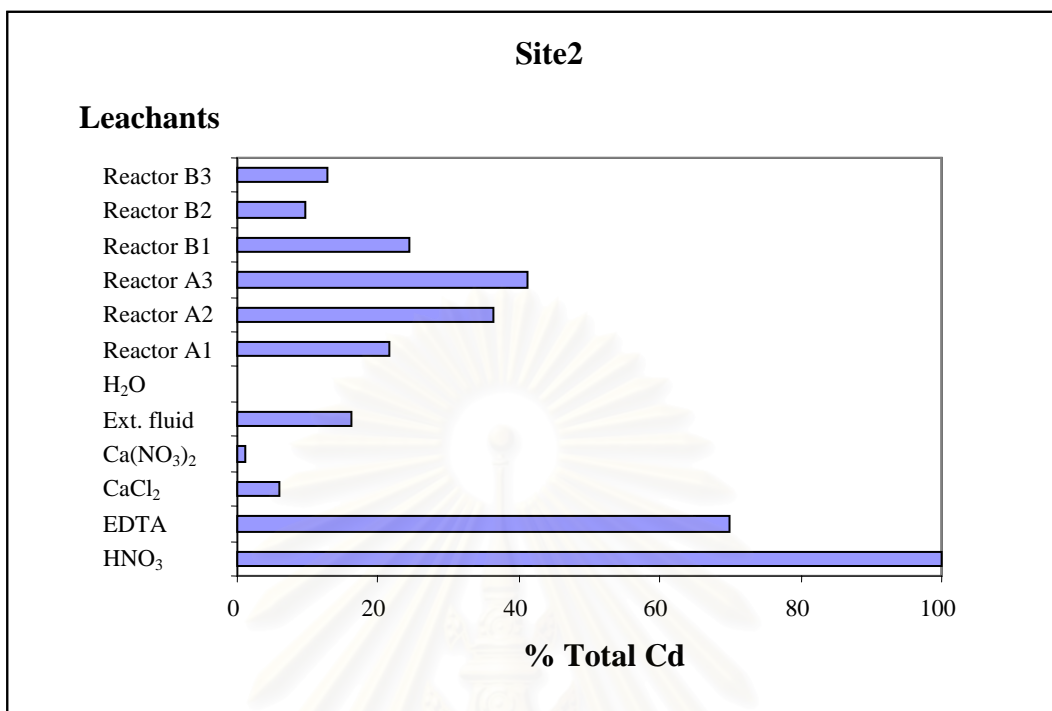


Figure 4.10 HNO₃, EDTA, CaCl₂, Ca(NO₃)₂ and leachate Cd in soil samples site 2 (unit:% of Tatal Cd)

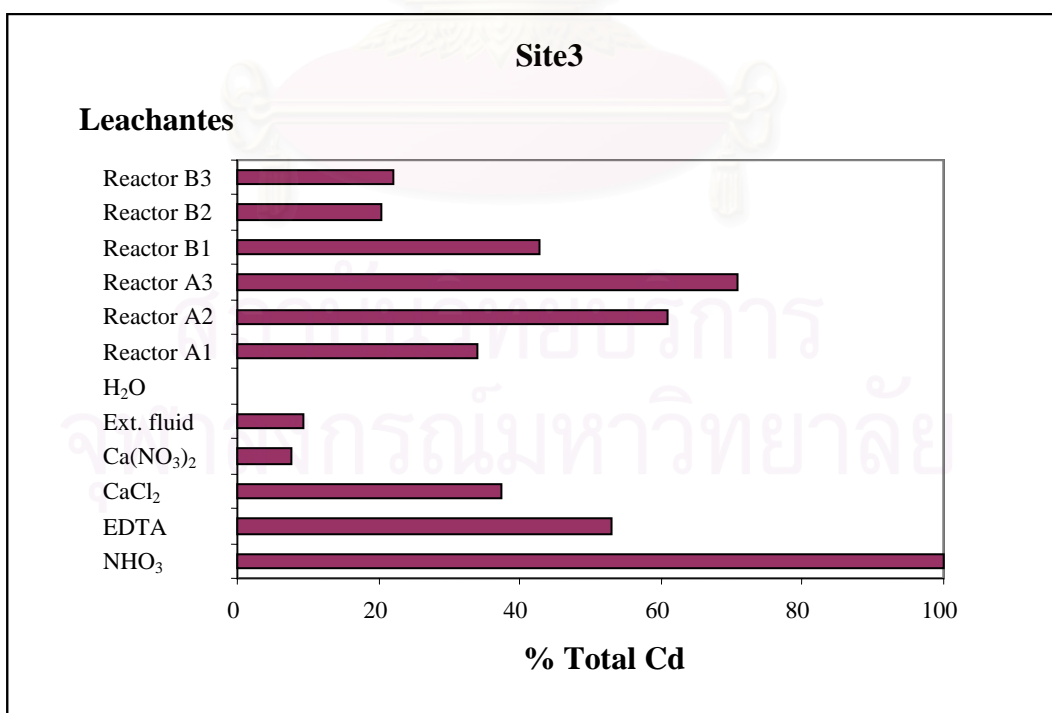


Figure 4.11 HNO₃, EDTA, CaCl₂, Ca(NO₃)₂ and leachate Cd in soil samples site 3 (unit:% of Tatal Cd)

As the result presented, it could be concluded that labile Cd from contaminated soil samples were 5.99 % and 37.5 % of total Cd fraction (Figure 4.10 and 4.11, Table C-3 in Appendix C). The non-labile fraction that extracted by EDTA were 69.9 and 60.0 % of total Cd because its strongly chelating agent and is thought to act by chelating surface-bound and solubilizing moderately soluble metal ions from soil solid phase (Gray et al., 2003).

For reactor A (fruit and vegetable), the Cd concentration determined from both sites was increased from reactor A1 to A3. From Table 4.3 the Cd concentration for site 2 was 2.27, 3.82 and 4.32 mg/kg. For site 3, the Cd concentration was 2.39, 4.28 and 4.98 mg/kg respectively. As a proportion of total soil Cd, cadmium leachate by leachate was higher than CaCl_2 or labile fraction. The result in this study indicated that leachate from fruit and vegetable waste has an ability to leach some part of non-labile fraction from soil samples. The highest cadmium concentration was leached by leachate collected from reactor A3. In comparison between site 2 and 3, the trend remained the same as presented in Figure 4.12.

In contrast, the Cd concentration presented in reactor B (Para grass) was decreased from acid formation, methanogenic and final maturation phase. Therefore, the Cd concentration was 2.56, 1.03 and 1.35 mg/kg for soil samples collected from site 2 and 3.01, 1.44 and 1.55 mg/kg for soil samples collected from site 3 respectively. The concentration of cadmium leached by leachate from reactor B1 (acid formation phase) was highest and slightly higher than Cd concentration from labile phase (site 3). Leachate from Para grass reactor (B) has lower ability than reactor A and weakly leached labile-Cd from soil samples due to the lower Cd concentration leached than that of extracted from CaCl_2 and the results remained the same for both sites as presented in Figure 4.13. Nevertheless, the results demonstrated that the ability of both leachates was lower than that of EDTA.

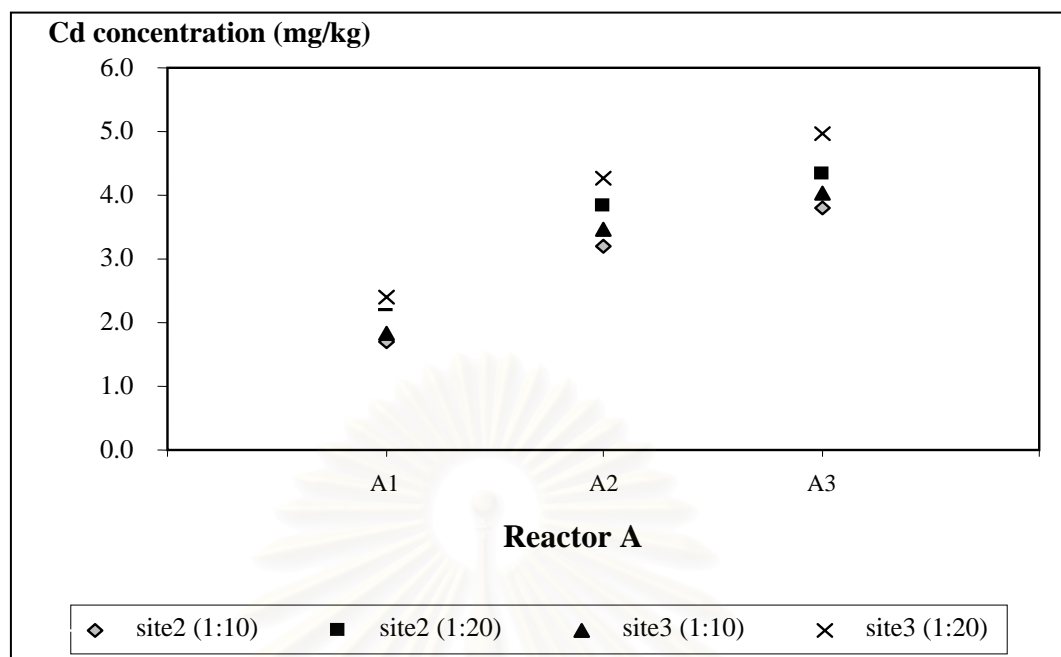


Figure 4.12 Cadmium concentration leached from soil sample site 2; comparison of solid to solution ratio between 1:10 and 1:20

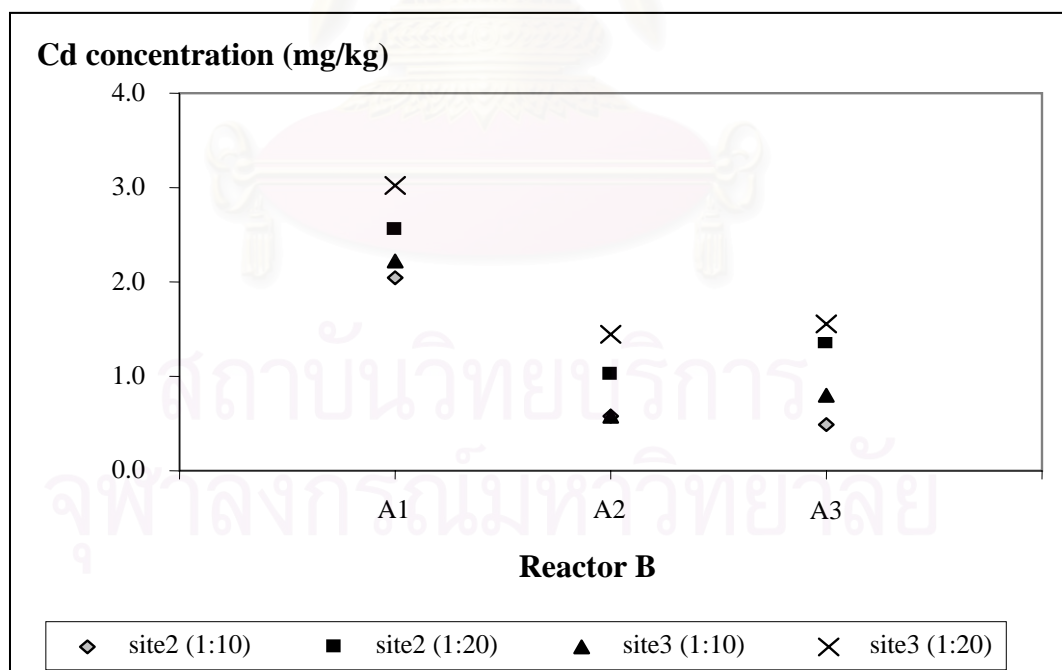


Figure 4.13 Cadmium concentration leached from soil sample site 3; comparison of solid to solution ratio between 1:10 and 1:20

4.4.1 Dissolved organic carbon

From Table 4.1, DOC concentration was considered in this study by its ability to form complexes with heavy metals. It reduces metal adsorption onto soil surfaces by both competing more effectively for the free metal ion and forming soluble organo-metallic complexes or being preferentially adsorbed onto the surfaces instead of the metals it is competing with (Antoniadis, 2002). The results indicated that the released Cd concentration into leachate increased with increasing DOC concentrations. The results are similar to those reported by Christensen et al, 1996; the DOC from landfill leachate polluted groundwater has high ability to form complexes with Cd, Ni and Zn, and that the presences of DOC decrease the distribution coefficients were a factor of 2-6 by varying concentrations of DOC (40%, 60%, 80%, of the leachate polluted groundwater samples). The presence of DOC in two leachate samples (reactor A and B) seems to have about the same leaching ability indicating that that DOC was the important factor to form complex with cadmium.

As noted in the methodology section, the solid to extracted solution (0.04 M EDTA, 1 M CaCl₂, or 0.05 M Ca(NO₃)₂) ratio was 1:10. For comparison the leaching potential between extracted solution and leachate samples, the leaching test was done by using 2 ratios. Therefore, the solid to solution (leachate) were 1:10 and 1:20 (this ratio followed by TCLP method). The leaching results for both ratios presented in Figure 4.14 for reactor A and Figure 4.15 for reactor B (Table C-4 in Appendix C). It was found to release Cd significantly the same for both ratio for each soil sample. Those two Figure 4.14 and Figure 4.15 indicate to point out the same trend.

The cadmium leached by leachate from reactor B also decrease with the decreasing of DOC. As the result presented, leachate collected from acid formation phase was dominated leaching ability.

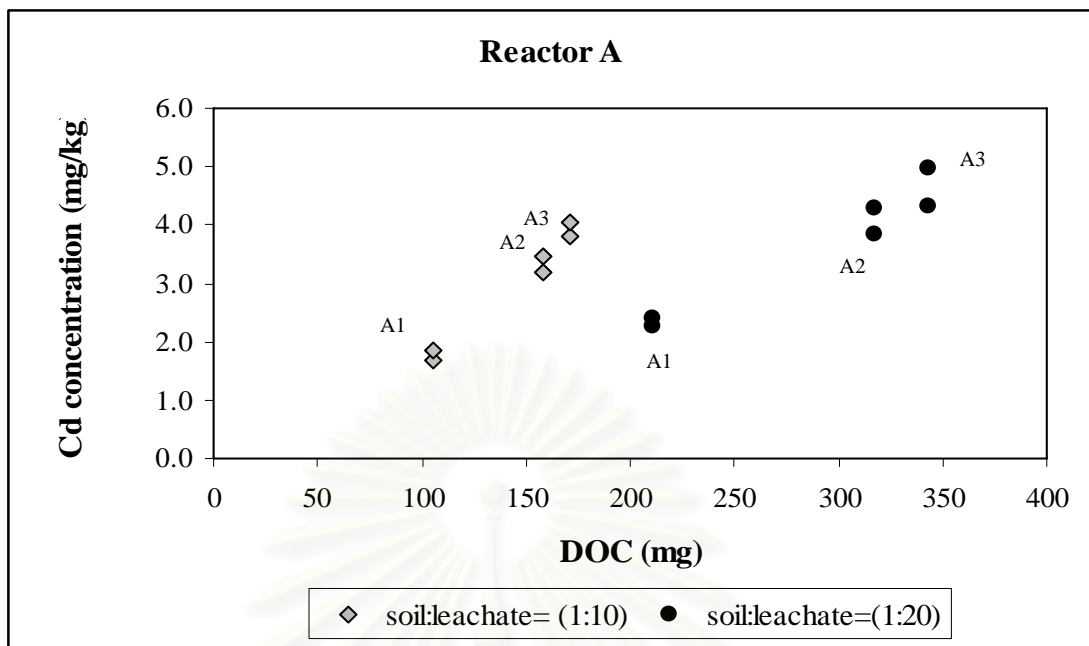


Figure 4.14 Reactor A: Cd concentration leached from soil sample site 2 and 3 and the amount of DOC content in leachate at two different ratio (1:10 and 1:20)

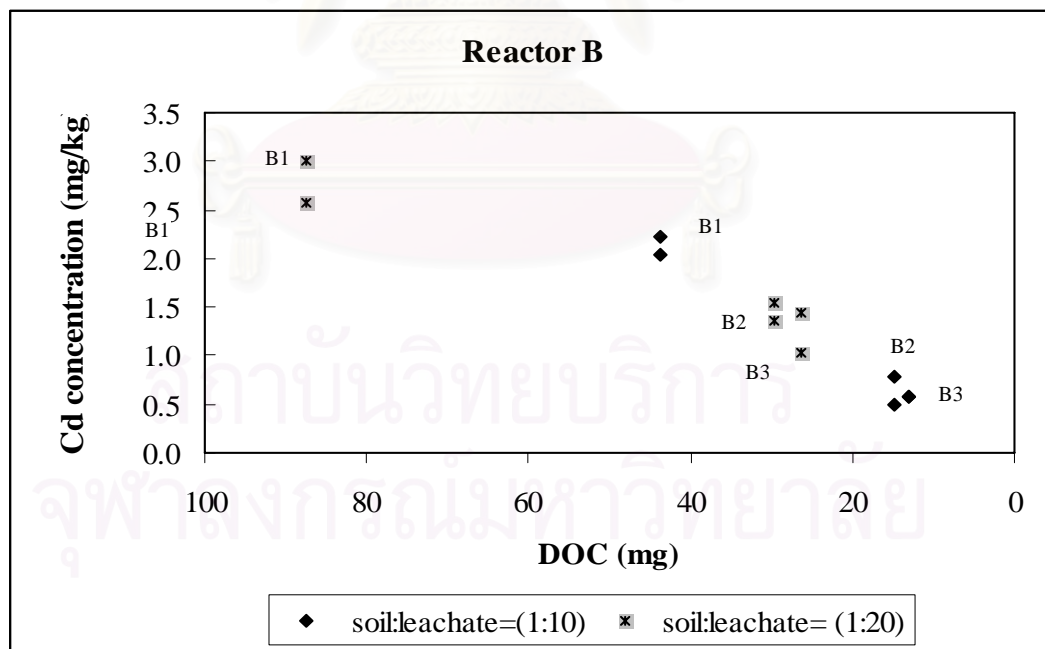


Figure 4.15 Reactor B: Cd concentration leached from soil sample site 2 and 3 and the amount of DOC content in leachate at two different ratio (1:10 and 1:20)

4.4.2 Volatile fatty acids

Another factor should be considered was the high content of volatile fatty acids (VFAs) presence in acid formation phase. VFAs was found that were the dissolved simple organic compound. First, the carboxylic group acts as an acid, and these simple compound can significantly affect pH. Second, carboxylate can complex metal ions and will thus effect the concentration and activity of metal cations in solution (White, 1998). Acetic acid was the representative of VFAs and its functional group, carboxylic group that are primarily responsible for cadmium complexation of leachate from acid formation phase due to the high concentration of Cd extracted. According to the decreasing of VFAs, the cadmium concentration detected from leachate in methanogenic and maturation phase of reactors B2 and B3 also decreased. The leaching ability of these two phases was similar and the trend remained the same for both soil samples as presented in Table 4.4.

Table 4.4 Cadmium concentration leached from soil samples compare with the amount of VFAs (mg/L as CH₃COOH) presence in leachate

Sample	VFA (mg/L as CH ₃ COOH)	Cd concentration (mg/kg)	
		Ratio 1:10	Ratio1:20
A1-site2	8,502	1.69	2.27
A2-site2	19,465	3.19	3.82
A3-site2	19,913	3.79	4.32
A1-site3	8,502	1.84	2.39
A2-site3	19,465	3.46	4.28
A3-site3	19,913	4.05	4.98
B1-site2	8,293	2.04	2.56
B2-site2	1,309	0.57	1.03
B3-site2	1,018	0.49	1.35
B1-site3	8,293	2.22	3.01
B2-site3	1,309	0.58	1.44
B3-site3	1,018	0.79	1.55

VFAs were found in high concentration for reactor A (fruit and vegetable). Table 4.5 showed the relation of VFAs concentration and Cd that was leached from both soil samples. VFAs remained in reactor A in high concentrations which were

8,502 mg/L as CH₃COOH for reactor A1, 19,465 mg/L as CH₃COOH for reactor A2 and 19,913 mg/L as CH₃COOH for reactor A3 respectively.

4.4.3 Effect of pH

Metal-organic complexation is strongly pH dependent (White, 1998). The results indicated that at low pH (reactor A1, A2, A3, and B1) the Cd could be leached more. For example in comparison for reactor B, reactor B1 represented to acid formation phase demonstrated the highest Cd extraction. It could be concluded that pH level also being the major factor controlling the leaching ability. From Table 4.1, pH of the simulated landfill fermentation of organic waste bioreactor increased to neutral when the degradation process became stable. The fraction of cadmium leached decreased significantly corresponding to the decreasing of VFAs concentration present in methanogenic (reactor B2) and maturation (reactor B3) phase. As noted earlier, pH levels of reactor B rose up to 8.14 and 8.37 for methanogenic and maturation phase and indicated that cadmium solubility slowly decreased. The decreasing solubility could be explained further as in Figure 4.16. For acid formation phase, pH level of reactor B1 probably acidic (pH= 5.60) corresponded to high VFAs concentration and dramatically leached more Cd than that of reactor B2 and B3. The solubility of cadmium-ion depends on pH-value. At pH level above neutral, Cd²⁺ will precipitate that reduced Cd in solution. Rothe et al., 1988 studied the pH-dependent solubility of heavy metals from sewage sludge of different compositions. Their conclusion was that the concentrations of soluble Cd in anaerobically digested sludge only increased at pH values lower than pH 4.

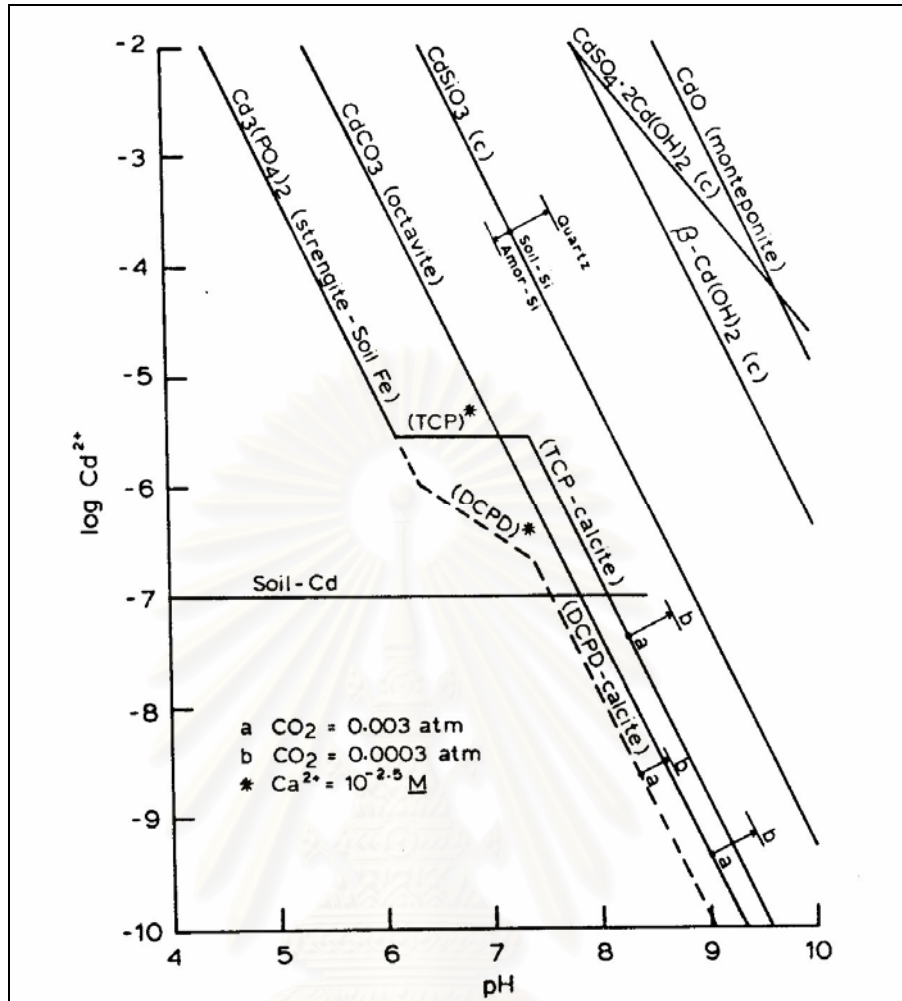


Figure 4.16 Solubility of several cadmium minerals at various pH and at 10^{-3}M concentration

In conclusion, reactor A (fruit and vegetable) had higher leaching potential than that of reactor B (Para grass) due to the high DOC and VFAs concentration. A DOC content presence in leachate plays an important role to form complexes with cadmium and to release cadmium from soil surfaces including some of non-labile site. The DOC concentration of leachate was high corresponded to VFA concentration presence in acid formation phase which represented the major organic constituent of leachate and also affected to lower pH level. The simulated landfill fermentation of organic waste leachate demonstrated a significant capacity for leaching Cd from contaminated soil and this ability varies with the type of organic waste and maturation time. Unfortunately, the leached cadmium by leachate was lower than those extracted by EDTA.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The objectives of this study were to determine the ability of landfill fermentation of organic waste leachate to leach metal ions and to understand how this ability changes with the age of degradation including comparing the ability based on different types of waste. Based on the results of this research study, the following conclusion may be drawn:

1. Reactor A (fruit and vegetable) had higher leaching potential than that of reactor B (Para grass) due to higher concentration of DOC and VFAs. For example, Cd was leached by leachate from reactor A3 (DOC = 17,155 mg/L and VFAs = 19,913 mg/L as CH₃COOH) was 4.98 mg/kg higher than reactor B1 (DOC = 4,378 mg/L and VFAs = 8,293 mg/L as CH₃COOH) which Cd concentration was 3.01 mg/kg.
2. Leachate has an ability to leach some part of non-labile cadmium from contaminated soil especially leachate generated from organic waste (fruit and vegetable). Even though, the potential of leaching was not as high as those extracted by EDTA.
3. The leaching potential of different type of refuse did not remain the same. The ability may be significantly affected by the high concentration of dissolved organic carbon (DOC). In particular in leachate from fruit and vegetable waste, the concentration of DOC can be high and remain constant and significant complexation has been demonstrated in reactor A3. The DOC concentration for reactor A1, A2 and A3 was 10,525 mg/L, 15,865 mg/L, and 17,155 mg/L respectively. In addition, the complexing ability of DOC is primarily related to VFAs concentration (8,502 19,465 and 19,913 mg/L as CH₃COOH) and pH of the system (5.30, 5.33 and 6.25 respectively).

4. In contrast, the ability for leachate from Para grass waste has been demonstrated in leachate from acid phase and this ability decrease depending on the depletion of DOC and VFAs content. The DOC and VFAs concentration for reactor B1, B2 and B3 were 4,378 1,314 and 1,484 mg/L for DOC and 8,293 1,309 and 1,018 mg/L as CH₃COOH for VFAs respectively. In old leachate, neutral pH in the system plays an important role for the complexing ability.
5. DOC content presences in leachate play an important role to form complexes with cadmium and to release some of cadmium from non-labile site (labile Cd was indicated by fraction that leached by CaCl₂ as leachant). Not only the DOC affect the leaching ability but also VFAs and pH level associated with the complexation of cadmium and released from soil surfaces.

5.2 Recommendations for future work

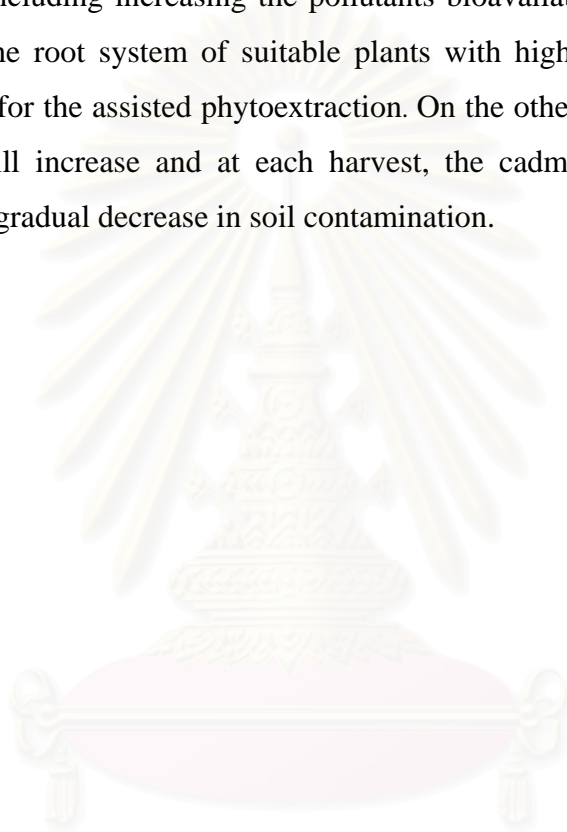
Some analysis and characterization of the DOC would be good for future study. Two simple analyses should be determine, infra-red spectroscopy and elemental analyses (H, C, O). Infra-read spectroscopy will identify oxygenated functional groups that have the ability to complex metals; for example: carboxylic acids and phenolic groups. Changes in these functional groups with time and with metal leaching ability could help to explain why the leaching capacity of DOC changes with aging in the landfill. Elemental ratios, O/C and H/C, provide an indication of the extent of oxidation or reduction of the DOC. For example, an increase in O/C could indicate that the organic matter is being oxidized and carboxylic acid functional groups are forming.

5.3 Management

Simulated landfill fermentation of organic waste leachate demonstrates a significant capacity for leaching heavy metals. Therefore, producing artificial leachate with high extraction capacities could be a viable strategy to leach metals from metal ores or remediate heavy metals from contaminated soils. Moreover, leachate could be produced only few months but contain high capacity to form complex with heavy metals as comparison to the leachate from the 'real world' landfill fermentation of

organic waste. This study tried to point out differences, advantage and short-coming of leachate to be able to induce in phytoremediation for further study.

The ability of leachate could be applied to induce to accumulate metals by the complexation and added to the soil for phytoremediation. The leaching potential may be chosen to increase of cadmium contaminant leached from exchangeable form, precipitate, and some part of non-labile fractions of solid phase towards the liquid phase of soil, including increasing the pollutants bioavailabilities and inducing their absorption in the root system of suitable plants with high biomass production and short life cycle for the assisted phytoextraction. On the other hand, the bioavailability of cadmium will increase and at each harvest, the cadmium was concentrated in biomass with a gradual decrease in soil contamination.



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APPENDICES

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APPENDIX A

Leachate analysis data from
the simulated landfill fermentation of organic waste reactors

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Table A-1 pH of leachate from the simulated landfill reactor A (fruit and vegetable) and reactor B (Para grass)

DAY	Reactor A1	Reactor A2	Reactor A3	Reactor B1	Reactor B2	Reactor B3
1	5.93	4.80	6.48	5.68	5.69	5.38
2	5.40	5.22	5.89	5.69	5.72	5.39
3	5.70	6.03	6.17	5.71	5.66	5.40
4	5.45	6.44	6.42	5.70	5.78	5.44
5	5.93	6.48	6.01	5.83	5.68	5.55
6	5.65	6.65	6.03	5.88	6.02	5.58
7	5.68	6.57	5.93	5.89	6.15	6.10
8	5.28	6.51	6.17	5.94	6.55	6.20
9	6.03	6.51	5.98	5.86	6.60	6.33
10	5.88	6.52	5.92	5.88	6.78	6.41
11	5.83	6.47	5.86	6.04	7.41	6.41
12	5.53	6.37	5.84		7.86	7.51
13	5.43	6.06	5.83		8.16	8.21
14	5.37	6.69	5.84		7.88	8.26
15	5.31	6.59	5.92		7.83	8.21
16		6.57	5.92		7.90	8.25
17		6.52	5.88		8.04	8.39
18		6.46	5.89		8.12	8.32
19		6.45	5.92		8.10	8.32
20		6.41	5.94		8.23	8.42
21		6.39	6.20		8.48	8.60
22		6.40	6.47		8.29	8.49
23		6.41	6.17		8.33	8.52
24		6.43	6.21		8.46	8.59
25		6.35	5.93		8.4	8.53
26		6.43	5.63		8.27	8.42
27		6.33	5.54		8.45	8.43
28		6.31	5.42		8.50	8.53
29		6.23	5.40		8.65	8.55
30		5.81	5.58		8.55	8.69
31		5.86	5.36		8.61	8.60
32		5.67	5.31		8.37	8.66
33		5.64	5.28		8.38	8.50
34		5.64	5.41		8.22	8.62
35		5.66	5.67		8.40	8.68
36		5.78	5.66		8.26	8.43
37		5.77	5.68		8.28	8.66
38		5.82	5.92		8.30	8.57
39		5.88	6.04		8.25	8.38
40		6.01	6.21		8.26	8.49
41		6.05	5.98		8.31	8.47
42		6.08	5.84		8.25	8.38
43		6.09	5.83		8.25	8.45
44		6.07	5.88		8.30	8.42
45		6.02	5.78		8.27	8.46
46		6.01	5.75		8.11	8.17

Table A-1 pH of leachate from the simulated landfill reactor A (fruit and vegetable) and reactor B (Para grass) (Cont.)

DAY	Reactor A1	Reactor A2	Reactor A3	Reactor B1	Reactor B2	Reactor B3
47		6.07	5.74		8.32	8.22
48		6.05	5.80		8.40	8.56
49		6.11	5.82		8.35	8.42
50		6.15	5.95		8.50	8.60
51		6.23	5.78		8.66	8.44
52		6.31	5.80		8.54	8.64
53		5.61	5.82		8.40	8.55
54		5.59	5.76		8.46	8.70
55		5.61	5.81		8.45	8.76
56		5.59	5.94		8.83	8.94
57			5.84		8.87	8.78
58			5.87		8.70	8.75
59			5.90		8.51	8.79
60			6.00		8.55	8.95
61			6.02		8.45	8.64
62			6.11		8.63	8.66
63			6.14		8.66	8.74
64			6.02		8.76	8.51
65			6.03		8.80	8.78
66			6.00		8.85	8.84
67			5.97		8.59	8.78
68			6.02		8.62	8.71
69			6.07		8.65	8.79
70			6.03		8.64	8.82
71			6.02		8.66	8.77
72			6.10		8.68	8.70
73			6.08		8.70	8.73
74			6.09		8.76	8.88
75			6.11		8.53	8.9
76			5.89		8.57	8.87
77			5.53		8.80	8.91
78			5.48		8.60	8.92
79			5.47		8.70	8.88
80			5.43		8.6	9.06
81			5.50		8.62	8.96
82			5.52		8.77	9.03
83			5.61		8.73	8.89
84			5.64		8.82	8.75
85			5.28		8.8	8.71
86			5.72		8.87	8.75
87			5.97		8.10	8.49
88			6.01		8.12	8.43
89			5.96		8.12	8.37
90			5.84		8.22	8.56
91			5.77		8.18	8.44
92			5.82		8.20	8.49

Table A-1 pH of leachate from the simulated landfill reactor A (fruit and vegetable) and reactor B (Para grass) (Cont.)

DAY	Reactor A1	Reactor A2	Reactor A3	Reactor B1	Reactor B2	Reactor B3
93			5.63		8.25	8.64
94			5.95		8.34	8.68
95			6.04		8.33	8.8
96			6.12		8.46	8.95
97			6.28		8.52	8.77
98			6.25		8.54	8.61
99					8.54	8.95
100					8.65	9.01
101					8.67	9.05
102					8.73	8.90
103					8.70	9.07
104					8.61	9.05
105						9.12
106						9.10
107						9.11
108						9.16
109						9.17
110						9.15
111						9.18
112						9.12
113						9.11
114						9.14
115						9.18
116						9.23

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Table A-2 ORP of leachate from the simulated landfill reactor A (fruit and vegetable) and reactor B (Para grass)

DAY	Reactor A1	Reactor A2	Reactor A3	Reactor B1	Reactor B2	Reactor B3
1	-141.7	-34.6	-163.0	-168.3	-99.6	-132.9
2	-138.3	-154.2	-234.0	-113.5	-130.3	-69.9
3	-439.0	-382.2	-436.0	-143.5	-142.5	-95.0
4	-470.5	-348.0	-394.9	-158.4	-144.8	-107.7
5	-522.6	-289.6	-443.9	-164.3	-154.6	-118.9
6	-497.3	-316.4	-387.3	-187.0	-166.7	-124.0
7	-291.5	-496.8	-246.4	-196.4	-184.6	-137.5
8	-369.2	-421.7	-252.6	-201.8	-198.1	-144.6
9	-206.2	-380.3	-174.7	-220.3	-207.8	-160.9
10	-227.2	-207.8	-190.7	-236.7	-205.8	-164.3
11	-263.1	-216.1	-152.7	-245.5	-210.4	-166.4
12	-221.2	-165.1	-143.1		-265.0	-201.4
13	-198.1	-164.7	-177.4		-284.0	-258.1
14	-180.9	-181.8	-181.8		-374.4	-358.1
15	-151.4	-157.3	-185.4		-383.1	-388.8
16		-156.4	-225.9		-364.8	-358.7
17		-164.78	-193.6		-356.6	-341.2
18		-178.7	-201.5		-361.6	-319.5
19		-142.2	-212.4		-331.4	-317.2
20		-144.8	-225.1		-263.8	-250.9
21		-149.6	-211.2		-313.4	-85.7
22		-132.8	-180.7		-324.5	-191.6
23		-133.5	-194.0		-338.9	-247.2
24		-126.8	-157.9		-352.3	-363.3
25		-117.8	-139.4		-322.7	-317.2
26		-122.2	-150.9		-323.3	-191.3
27		-118.9	-133.4		-321.0	-301.8
28		-116.8	-123.0		-292.5	-233.0
29		-127.4	-114.8		-287.5	-245.6
30		-128.8	-112.4		-277.6	-281.3
31		-140.4	-104.7		-275.8	-294.6
32		-144.9	-119.5		-276.1	-307.5
33		-143.8	-101.5		-216.7	-133.1
34		-138.4	-112.3		-118.5	-75.8
35		-133.6	-103.5		-20.9	-22.6
36		-136.5	-121.1		-83.1	-75.9
37		-125.6	-156.3		-42.3	-64.3
38		-124.8	-142.3		-38.2	-44.7
39		-118.6	-151.2		-48.7	-38.5
40		-114.7	-147.6		-136.0	-28.6
41		-124.5	-139.5		-142.0	-32.5
42		-128.1	-124.1		-173.5	-168.1
43		-124.3	-125.6		-185.5	-179.5
44		-126.0	-134.2		-154.2	-150.3
45		-119.3	-138.2		-110.8	-147.8
46		-118.2	-147.2		-151.2	-134.1

Table A-2 ORP of leachate from the simulated landfill reactor A (fruit and vegetable) and reactor B (Para grass) (Cont.)

DAY	Reactor A1	Reactor A2	Reactor A3	Reactor B1	Reactor B2	Reactor B3
47		-117.2	-139.6		-176.2	-147.9
48		-125.6	-128.4		-186.5	-187.3
49		-124.6	-125.6		-191.2	-175.3
50		-129.1	-128.1		-206.8	-168.8
51		-132.6	-133.8		-221.6	-180.6
52		-130.9	-162.3		-241.3	-190.3
53		-133.3	-194.6		-258.3	-154.3
54		-134.0	-152.5		-270.9	-144.7
55		-128.5	-148.5		-273.4	-138.4
56		-122.3	-184.3		-302.5	-82.4
57			-185.6		-314.8	-81.5
58			-185.4		-329.6	-172.6
59			-128.4		-344.9	-292.9
60			-144.8		-281.9	-175.1
61			-134.0		-291.5	-238.3
62			-139.8		-280.0	-188.4
63			-155.6		-341.6	-301.0
64			-162.6		-280.0	-82.3
65			-125.2		-175.5	-88.3
66			-112.3		-113.1	-84.4
67			-117.2		-184.5	-197.3
68			-124.3		-178.5	-118.4
69			-121.0		-104.5	-57.0
70			-119.1		-75.0	-92.4
71			-107.0		-64.1	-77.8
72			-109.3		-77.4	-73.6
73			-104.9		-84.3	-108.5
74			-104.6		-92.6	-116.5
75			-98.3		-46.0	-58.2
76			-88.6		-42.8	-66.8
77			-88.1		-46.7	-74.6
78			-89.5		-40.6	-58.3
79			-88.3		-41.3	-41.4
80			-86.5		-35.4	-41.8
81			-86.1		-26.3	-30.9
82			-86.3		-58.6	-26.8
83			-71.0		-55.9	-66.4
84			-69.3		-55.1	-63.5
85			-55.8		-58.4	-72.4
86			-52.1		-66.3	-84.6
87			-50.2		-67.2	-88.2
88			-54.8		-67.1	-85.1
89			-53.3		-67.1	-81.6
90			-54.2		-72.9	-92.6
91			-55.4		-70.6	-85.6
92			-53.8		-71.7	-88.5

Table A-2 ORP of leachate from the simulated landfill reactor A (fruit and vegetable) and reactor B (Para grass) (Cont.)

DAY	Reactor A1	Reactor A2	Reactor A3	Reactor B1	Reactor B2	Reactor B3
93			-52.0		-74.6	-97.2
94			-55.5		-79.8	-99.5
95			-49.0		-79.3	-106.5
96			-49.2		-86.8	-115.2
97			-38.2		-90.3	-104.7
98			-38.1		-91.4	-95.5
99					-91.4	-115.2
100					-97.8	-118.6
101					-98.9	-120.9
102					-102.4	-112.3
103					-100.7	-122.1
104					-95.5	-120.9
105						-125.0
106						-123.8
107						-124.4
108						-127.3
109						-127.9
110						-126.7
111						-128.5
112						-125.0
113						-124.4
114						-126.2
115						-128.5
116						-131.4

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Table A-3 Alkalinity of leachate from the simulated landfill reactor A and B

week	Reactor A1	Reactor A2	Reactor A3	Reactor B1	Reactor B2	Reactor B3
1	2,447	2,814	2,508	2,079	1,713	1,346
2	2,814	3,793	2,447	2,202	1,713	1,835
3		3,793	2,569	1,713	1,224	1,224
4		3,303	2,814		1,468	1,101
5		3,303	3,426		1,591	979
6		2,936	3,426		1,835	1,346
7		3,792	3,548		1,958	1,713
8		3,915	3,792		1,835	1,591
9		3,119	3,670		1,590	1,591
10			2,936		1,713	1,468
11			3,915		2,141	1,652
12			3,792			1,652

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Table A-4 DOC of leachate from the simulated landfill reactor A and B

week	Reactor A1	Reactor A2	Reactor A3	Reactor B1	Reactor B2	Reactor B3
1	9,390	15,832	9,684	7,614	852.3	1,177
2	11,620	11,491	10,252	7,561	3,235	2,425
3	11,571	11,966	9,049	5,410	3,252	3,827
4		10,813	11,258		1,496	1,919
5		14,683	11,301		1,738	1,925
6		15,028	10,994		1,796	2,025
7		15,391	9,784		3,427	2,058
8		15,905	10,398		1,544	1,684
9		16,047	10,647		1,593	1,502
10			11,279		1,602	1,651
11			13,624		1,624	1,812
12			13,079			1,904
13			16,060			1,834

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APPENDIX B

Gas production data from
the simulated landfill fermentation of organic waste reactors

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Table B-1 Gas production volume from the simulated landfill reactor A (fruit and vegetable) and reactor B (Para grass)

DAY	Reactor A1	Reactor A2	Reactor A3	Reactor B1	Reactor B2	Reactor B3
1	350	327	350	664	782	546
2	400	345	386	350	350	416
3	500	300	380	401	426	426
4	350	757	310	425	236	540
5	542	379	584	410	241	214
6	660	216	684	358	350	356
7	800	1280	800	264	246	694
8	650	1634	650	352	354	256
9	500	1246	500	301	310	334
10	500	785	500	286	270	280
11	350	793	350	350	350	350
12	350	379	350		320	332
13	410	576	461		400	440
14	690	738	700		426	500
15	460	2448	580		320	550
16		2100	630		290	591
17		1850	620		450	800
18		1050	586		450	650
19		1408	591		450	550
20		980	264		500	510
21		872	220		350	350
22		740	387		350	350
23		1280	1152		426	458
24		1920	871		660	800
25		508	640		560	650
26		587	373		670	1000
27		415	210		670	750
28		610	141		654	840
29		540	389		658	621
30		554	287		864	2016
31		670	346		641	1842
32		350	97		553	1958
33		640	120		5616	4032
34		660	198		2810	3950
35		424	334		1546	4800
36		652	144		1173	6720
37		384	210		1100	5100
38		310	246		4720	5760
39		284	169		856	4114
40		210	281		851	5120
41		360	320		720	5040
42		180	364		292	4608
43		246	648		640	3640
44		350	682		871	3256
45		384	1001		1272	4800
46		270	349		864	2880

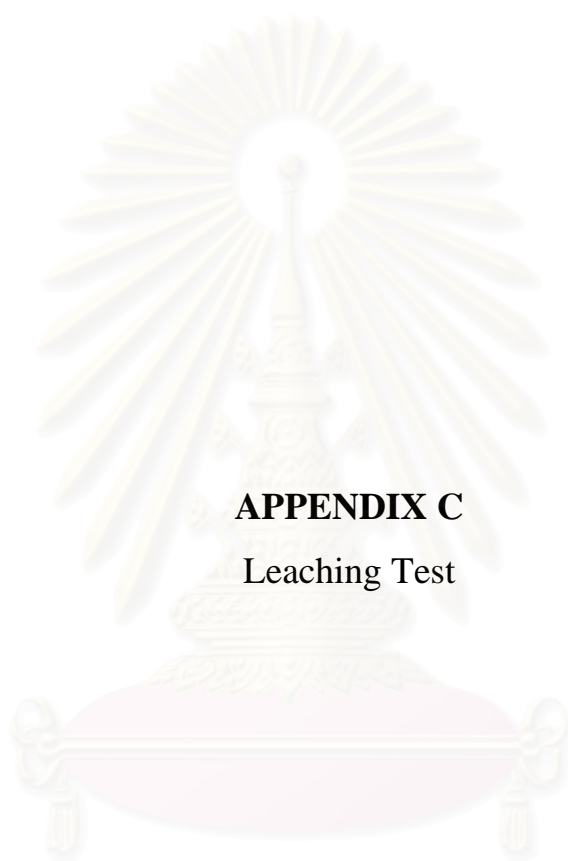
Table B-1 Gas production from the simulated landfill reactor A (fruit and vegetable) and reactor B (Para grass) (cont.)

DAY	Reactor A1	Reactor A2	Reactor A3	Reactor B1	Reactor B2	Reactor B3
47		362	450		1010	3510
48		342	250		1446	2410
49		302	104		861	2600
50		280	162		1052	3110
51		360	162		2180	2540
52		408	57		3450	2450
53		390	134		2160	3200
54		346	152		2270	3640
55		284	198		5760	7200
56		220	411		2181	4320
57			1175		1860	2500
58			949		1420	2320
59			960		1320	1320
60			738		1667	1364
61			-		1440	947
62			25		1224	972
63			64		1480	1200
64			-		1751	1556
65			-		1432	1640
66			12		2057	2244
67			28		1293	940
68			35		854	791
69			16		1152	1190
70			50		1181	1476
71			110		2400	3840
72			-		1587	1403
73			-		410	1218
74			24		847	1228
75			46		704	768
76			34		620	956
77			28		410	845
78			70		510	670
79			40		620	880
80			22		1920	2880
81			-		609	813
82			30		705	1116
83			18		475	712
84			26		634	650
85			50		496	510
86			64		290	245
87			45		324	356
88			38		410	440
89			60		490	520
90			24		340	320
91			-		286	260
92			-		510	482

Table B-1 Gas production from the simulated landfill reactor A (fruit and vegetable) and reactor B (Para grass) (cont.)

DAY	Reactor A1	Reactor A2	Reactor A3	Reactor B1	Reactor B2	Reactor B3
93			56		246	360
94			60		290	380
95			72		302	250
96			84		320	296
97			60		340	380
98			44		390	410
99					180	210
100					226	160
101					350	220
102					380	218
103					214	186
104					210	146
105						224
106						340
107						250
108						230
109						186
110						140
111						168
112						130
113						240
114						216
115						202
116						182

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APPENDIX C

Leaching Test

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Table C-1 Leaching test data for soil sample site 2

Sample	Ratio (solid:solution)	pH	Cd in soil (mg/kg)			Average conc.	S.D.
			Rep 1	Rep 2	Rep 3		
H ₂ O*	1:10	7.04	-	-	-	-	-
Extraction fluid #1	1:20	5.06	1.63	1.71	1.77	1.70	0.07
Ca(NO ₃) ₂	1:10	6.62	0.13	0.12	0.09	0.11	0.02
CaCl ₂	1:10	7.21	0.67	0.63	0.60	0.63	0.04
Na-EDTA	1:10	4.64	7.29	7.63	7.14	7.35	0.25
A1	1:10	5.74	1.72	1.68	1.67	1.69	0.03
A2	1:10	5.42	3.16	3.18	3.22	3.19	0.03
A3	1:10	5.35	3.84	3.81	3.73	3.79	0.05
B1	1:10	5.75	2.06	2.04	2.01	2.04	0.03
B2	1:10	8.79	0.57	0.57	0.56	0.57	0.01
B3	1:10	8.76	0.45	0.48	0.55	0.49	0.05
A1**	1:20	5.69	2.23	2.30	2.27	2.27	0.04
A2**	1:20	5.38	3.64	3.68	4.16	3.82	0.29
A3**	1:20	5.32	4.27	4.39	4.31	4.32	0.07
B1**	1:20	5.68	2.63	2.50	2.56	2.56	0.07
B2**	1:20	8.72	1.00	1.01	1.06	1.03	0.03
B3**	1:20	8.8	1.47	1.19	1.41	1.35	0.15

* Undetected

**soil to solution ratio = 1:20

Table C-2 Leaching test data for soil sample site 3

Sample	Ratio (solid:solution)	pH	Cd in soil (mg/kg)			Average conc.	S.D.
			Rep 1	Rep 2	Rep 3		
H ₂ O*	1:10	6.34	-	-	-	-	-
Extraction fluid #1	1:20	4.94	0.66	0.63	0.67	0.65	0.02
Ca(NO ₃) ₂	1:10	5.76	0.48	0.55	0.59	0.54	0.05
CaCl ₂	1:10	7.07	2.64	2.57	2.69	2.63	0.06
Na-EDTA	1:10	4.52	3.60	3.74	3.83	3.72	0.12
A1	1:10	5.61	1.82	1.88	1.82	1.84	0.04
A2	1:10	5.37	3.40	3.43	3.54	3.46	0.08
A3	1:10	5.27	3.94	3.99	4.22	4.05	0.15
B1	1:10	5.59	2.25	2.21	2.19	2.22	0.03
B2	1:10	8.69	0.56	0.64	0.56	0.58	0.05
B3	1:10	8.79	0.84	0.92	0.62	0.79	0.16
A1**	1:20	5.60	2.30	2.47	2.41	2.39	0.09
A2**	1:20	5.34	4.32	4.30	4.21	4.28	0.06
A3**	1:20	5.24	4.78	5.00	5.14	4.98	0.18
B1**	1:20	5.60	3.16	2.94	2.94	3.01	0.12
B2**	1:20	8.69	1.49	1.40	1.42	1.44	0.04
B3**	1:20	8.74	1.65	1.59	1.40	1.55	0.13

* Undetected

**soil to solution ratio = 1:20

Table C-3 soil pH, total carbon, and total EDTA, CaCl₂, Ca(NO₃)₂ and leachate Cd in soil samples (unit: % of total Cd)

site	pH	% OC	Total Cd (mg/kg)	EDTA Cd (% T)	CaCl ₂ Cd (% T)	Ca(NO ₃) ₂ Cd (% T)	Extraction fluid-Cd (% T)	Cd in H ₂ O	Cd in Leachate (% T)					
									A1	A2	A3	B1	B2	B3
2	7.45	1.78	10.52	69.9	5.99	1.05	16.2	-	21.6	36.4	41.1	24.4	9.80	12.9
3	5.85	1.56	7.02	53.0	37.5	7.70	9.26	-	34.1	60.9	70.9	42.9	20.5	22.0

Note : solid: solution ratio of soil to leachate samples were 1:20

*percent of organic carbon in soil samples

** Cd concentration could not be detected

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Table C-4 Cadmium concentration extracted from soil samples compare with the amount of DOC presence in leachate

Sample	DOC (mg/L)	Ratio 1:10		Ratio1:20	
		amount of DOC (mg)	Cd concentration (mg/Kg)	amount of DOC (mg)	Cd concentration (mg/kg)
A1-site2	10,525	105.25	1.69	210.5	2.27
A2-site2	15,865	158.65	3.19	317.3	3.82
A3-site2	17,155	171.55	3.79	343.1	4.32
A1-site3	10,525	105.25	1.84	210.5	2.39
A2-site3	15,865	158.65	3.46	317.3	4.28
A3-site3	17,155	171.55	4.05	343.1	4.98
B1-site2	4,378	43.78	2.04	87.56	2.56
B2-site2	1,314	13.14	0.57	26.28	1.03
B3-site2	1,484	14.84	0.49	29.68	1.35
B1-site3	4,378	43.78	2.22	87.56	3.01
B2-site3	1,314	13.14	0.58	26.28	1.44
B3-site3	1,484	14.84	0.79	29.68	1.55

*Calculation the amount of DOC contain in leachate sample

$$\text{DOC (mg)} = V_{\text{leachate}} \times C_{\text{DOC}}$$

Where; V_{leachate} = volume of leachate (mL)

C_{DOC} = DOC concentration of leachate of each reactor (mg/1000 mL)

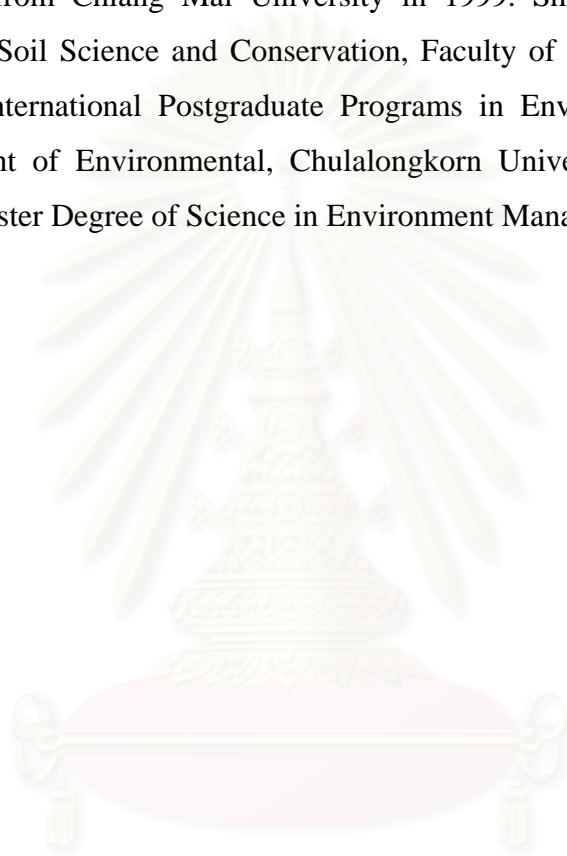
For example; For soil sample site 2, DOC concentration of reactor A1=10,525 mg/1000 mL , at soil: solution ratio= 1:10 the amount of DOC was

$$\begin{aligned} \text{DOC (mg)} &= V_{\text{leachate}} \times C_{\text{DOC}} \\ &= \frac{10 \text{ mL} \times 10,525 \text{ mg}}{1000 \text{ mL}} \end{aligned}$$

Therefore; DOC (mg) = 105.25 mg

BIOGRAPHY

Miss Nanchaphorn Udomsri was born on June 26, 1978 in Chiang Mai province, Thailand. She graduated Bachelor's degree in Science (Soil Science and Conservation) from Chiang Mai University in 1999. She work as a scientist in Department of Soil Science and Conservation, Faculty of Agriculture, CMU before apply in the International Postgraduate Programs in Environmental Management, Inter-Department of Environmental, Chulalongkorn University in May 2004. She finished her Master Degree of Science in Environment Management in May 2006.



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