

**PHYSICAL-CHEMICAL TREATMENT OF STABILIZED LEACHATE USING  
LIMESTONE, ACTIVATED CARBON AND ZEOLITE**

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**By**

**AHMED EL-ARABI MOHAMMED ABU FOUL**

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بسم الله الرحمن الرحيم

"قل إن صلاتي ونسكي ومحياي ومماتي لله رب العالمين لا شريك له

وبذلك أمرت وأنا أول المسلمين"

صدق الله العظيم

الأنعام (162-163)

## Dedication

*This thesis is dedicated to my family and my wife Ansam. This work is also dedicated to my lovely children, Mohammed, Asmaa, Omar, Hamza, Moamin and Sama, particularly my lovely daughter Sama that was born during the period of this research. May Allah grant them long life, health, knowledge and bright their future AMIN.*

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## LIST OF ABBREVIATION

Ac	Activated carbon
ANOVA	Analysis of variance
BDST	Design based on bed service time
BET	Brunauer-Emmett-Teller
BOD	Biological oxygen demand
COD	Chemical oxygen demand
Ls	Limestone
MAP	Magnesium ammonia phosphate precipitation
MSW	Municipality Solid Wastes
NF	Nanofiltration
RO	Reverse osmosis
TOC	Total Organic Carbon
UASB	Upflow anaerobic sludge blanket
UF	Ultrafiltration
XRF	X-Ray Fluorescence
Ze	Zeolite

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Aziz, H. A., Foul, A. A., Isa, M. H., (2007) Primary treatment of anaerobic landfill leachate using activated carbon and limestone: Batch and column studies. International Journal of Environment and Waste and Management (IJEWM), accepted. (In Press)

## **OLAHAN KIMIA-FIZIK LARUT LESAPAN TERSTABIL MENGGUNAKAN BATU KAPUR, KARBON TERAKTIF DAN ZEOLIT**

### **ABSTRAK**

Pencirian larutlesapan dari tapak kambus tanah Larut Matang Taiping telah dijalankan. Warna, COD, ferum dan nitrogen ammonia hadir pada kepekatan yang tinggi di tapak ini. Potensi kegunaan batu kapur, karbon teraktif, zeolit dan kemungkinan campuran di antaranya sebagai penyerap, dikaji dalam penyelidikan ini. Pengaruh kelajuan aruhan dan telah dikaji. Penjerapan isoterma dan pemalar kinetik ditentukan. Ujikaji kelompok menunjukkan bahawa campuran karbon teraktif bersama zeolit pada nisbah 15:25 (mengikut isipadu) dan campuran karbon teraktif bersama batu kapur dan zeolit pada nisbah 15:10:15 (mengikut isipadu) memberikan keputusan terbaik dengan kecekapan penyingkiran melebihi 90% untuk warna dan ferum, 85% untuk COD dan 80% untuk nitrogen ammonia, pada kelajuan aruhan 350 psm dan masa sentuhan 4 jam. Kedua-dua isoterma Langmuir dan Freundlich adalah berpadanan dengan data ujikaji dengan nilai pemalar korelasi melebihi 93%. Kedua-dua campuran memberikan nilai kapasiti penyerapan (dalam mg/g) masing-masing sebanyak 522.19, 232.56, 52.63, 21.01 and 500, 200, 50, 20.20 untuk warna, COD, ferum dan nitrogen ammonia. Keputusan kinetik menunjukkan bahawa data adalah sepadan dengan persamaan pseudo tertib kedua dengan korelasi menghampiri uniti bagi semua parameter dalam ujikaji. Ini menunjukkan kemungkinan langkah kawalan kadar adalah penyerapan kimia. Ujikaji regenerasi media menunjukkan bahawa 0.2 M  $\text{HNO}_3$  sesuai untuk regenerasi karbon teraktif manakala campuran 0.2 M HCl dan

NaCl sesuai untuk regenerasi zeolit, dengan kadar regenerasi melebihi 80% dalam kebanyakan kes. Keputusan ujikaji aliran berterusan bagi kedua-dua campuran menunjukkan bahawa penyingkiran warna boleh mencapai 50-90%, 70-90% COD, 85-90% ferum dan 50-90% nitrogen ammonia pada 10 hari pertama ujikaji. Keputusan juga menunjukkan bahawa susunan lapisan media penjerap dalam turus adalah tidak signifikan. Sebanyak 800 m<sup>3</sup> larutan berupaya diolah dalam 35 hari menggunakan 4 turas bersiri, setiap satu dengan keluasan 6.25 m<sup>2</sup>, ketinggian 3m dan kadar alir 15.92 L/min, sebelum nisbah C/C<sub>0</sub> melampaui 0.1. Dapat dirumuskan dari penyelidikan ini bahawa campuran karbon teraktif-batu kapur-zeolit dan campuran karbon teraktif-zeolit memberikan keputusan yang lebih baik dalam menyingkirkan kesemua parameter berbanding penggunaan media secara individu.

## **PHYSICAL-CHEMICAL TREATMENT OF STABLIZED LEACHATE USING LIMESTONE, ACTIVATED CARBON AND ZEOLITE**

### **ABSTRACT**

Leachate generated from Larut Matang landfill in Taiping was characterized. Colour, COD, iron and ammoniacal nitrogen were found to be high. The potential use of activated carbon, limestone and zeolite and their possible mixtures as an adsorbent was investigated in this research. Influence of shaking speed and contact time was studied. The adsorption isotherms and the kinetics constants were determined. The batch experiments demonstrated that both combine mixtures of activated carbon with zeolite at 15:25 (by volume) and activated carbon with limestone and zeolite at 15:10:15 (by volume) gave the best results with removal efficiencies more than 90% for colour and iron, 85% for COD, 80% for ammoniacal nitrogen at shaking speed of 350 rpm and contact time of 4 hours. Both Langmuir and Freundlich isotherms fitted well to the experimental data with correlation coefficient more than 93%. The mixtures yielded adsorption capacity of 522.19, 232.56, 52.63, 21.01 (mg/g) and 500, 200, 50, 20.20 (mg/g) for colour, COD, iron and ammoniacal nitrogen, respectively. The kinetic results showed that the data fitted well with the pseudo second order equation with correlation approaching unity for all parameters in all experiments implying that the rate limiting step may be chemisorption. The regeneration experiments showed that 0.2 M  $\text{HNO}_3$  can be used to regenerate activate carbon and 0.2 M HCl and NaCl mixture and regenerate zeolite, with regeneration more than 80% in most cases. Results of the continuous flow experiments for both mixtures indicated that removal can reach up to 50-90% of



colour, 70-90% of COD, 85-90% of iron and 50-90% of ammoniacal nitrogen in the first 10 days of the experiments. The results indicated that the arrangement of layers of adsorption media inside the column is not significant. The results also showed that it was possible to treat about 800 m<sup>3</sup> of leachate at flow rate of 15.92 L/min for 35 days, before the ratio  $C/C_0$  exceeded 0.1, by using four filters connected in series each with an area of 6.25 m<sup>2</sup>, and a height of 3 m. It can be concluded from the research that the activated carbon-limestone-zeolite and activated carbon-zeolite mixtures media exhibited better results for all parameters as compared with the use of individual media.

# CHAPTER 1

## INTRODUCTION

### 1.0 Background of study

Solid waste comprises all types of wastes arising from human and animal activities that are normally solid and that are discarded as useless or unwanted such as food wastes, yard wastes, paper, tin and bottles (Tchobanoglous *et al.*, 1993).

Most wastes generated in Malaysia are municipal solid waste that consists of paper, plastics, food wastes, glasses, metals and woods. Fauziah & Agamuthu (2006) estimated that the generation rate of solid waste may be increased about 3% per year due to the increase in population and the economic development in the country. Another problem is that there is not only an increase in the generation of solid wastes, but their characteristics today are more complicated than a few years ago.

Solid waste management involves the overall management related to solid waste activities such as generation, storage, collection, transfer, separation, transformation, reuse, recycling and disposal (Hamer, 2003). In the year 2000, the Malaysian government has targeted 22% of waste to be recycled by the year of 2020 (Chenayah & Takeda, 2005). Fauziah & Agamuthu (2006) reported that a total of 40% of the daily waste received by the landfills consists of recyclable components including 14% paper, 15% plastic, 3% metal and 3% glass. However, only about 1% of the total is actually separated and recycled in

Malaysia (UNEP, 2005, Agamuthu, 2001). To manage the huge amount of remaining solid wastes a suitable disposal technique is required.

Several technologies can be used for waste disposal such as incineration, composting and landfilling.

The use of incineration technique in Malaysia is limited (Stegmann et al., 2007). This may be due to its high capital cost and the environmental problems that appear due to incinerator emissions. Composting of MSW is also not widely practiced in big scale due to various limitations. It is normally used as the main treatment solution for agricultural products such as rice seed, rice straw, leaves and stems, rice husk and palm oil bunches.

Landfilling is one of the primary technologies used to dispose off solid waste. It is the most economical and environmentally acceptable method used in the disposal of solid waste (Rodrigues et al., 2004). In Malaysia, there are about 230 landfills recognized officially and about three times of illegal dumps (Chenayah and Takeda, 2005; Agamuthu, 2001). Most of these landfills can not be classified as sanitary landfills because there are no facilities to treat leachate or infrastructure to exploit landfill gas (Chenayah and Takeda, 2005; Agamuthu, 2001). Aziz *et al.*, (2004a & 2004b) reported that there are only three semi-aerobic landfills in Malaysia.

Although landfills offer some benefits, however they have some problems as well. These problems are associated with landfill operation even after its

closure. The main problem is leachate that seeps through the bottom of unlined landfills or through the lining of lined landfills is the main problem (Miller, 1997, Aziz et al., 2004a, Tatsi et al., 2003). Nasir, & Chong, (1999) reported that 71.4% of municipal councils have serious ground water pollution problems and 57.2% experience serious leachate problems.

### **1.1 Problem statement**

Leachate pollution is one of the big issues in environmental conservation. Leachate is produced when water percolates through the waste in landfill, carrying several types of contaminants, such as heavy metals, ammoniacal nitrogen, biological oxygen demand (BOD), chemical oxygen demand (COD), colour and suspended solids. Leachate generation continues in a cyclic pattern in operating and closed landfill sites where precipitation or groundwater may enter the landfill cell, and will correspond directly to the net infiltration rates, modified by runoff and evapotranspiration patterns (Oweis & Khera, 1998).

Waste composition, site hydrology, landfill type, landfill operation and its age are the main factors affecting leachate quality (Muzaini, et al., 1995; Aziz, et al., 2004a, Bagchi, 1994; El-Fadel et al., 2002, Farquhar, 1989). Generally high concentrations of heavy metals, BOD, suspended solids, COD and ammoniacal nitrogen are present in leachate (Jokela, *et al.*, 2002; Tyrell *et al.*, 2002). Numerous cases of leachate-contaminated ground and surface water have been documented (Murray & Beck, 1990, MacFarlane, *et al.*, 1983, Nasir, & Chong, 1999).

Contamination of water bodies and natural streams by leachate causes serious problems to humans, animals and plants. Colour can cause hazards to the environment due to the presence of a large number of contaminants such as acids, bases, inorganic contaminants and toxic organic residues (Isa *et al.*, 2006). High concentration of heavy metals such as iron, zinc, lead, copper, cadmium and chromium can cause serious water pollution and threaten the environment (Aziz *et al.*, 2004a). Ammoniacal nitrogen decreases the dissolved oxygen required for aquatic organisms. So to prevent these problems it is a necessity to remove these contaminants from leachate (Kapoor *et al.*, 1999; Kadirvelu *et al.*, 2001; Celik *et al.*, 2001).

Leachate treatment is very complicated, expensive and generally requires multiple processes (Ozturk and Bektas, 2004). Many factors need to be considered when designing a leachate treatment system. These include leachate flows, landfill age and leachate characteristics. The leachate requires treatment during the active years of the landfill and for many additional years after landfill is closed.

Leachate treatment options include, recirculation, biological, chemical, physical and their combinations.

Biological treatment is effective in removing organic matters in the early stages when the BOD/COD ratio greater than 0.4 (McBean *et al.*, 1995, Rodriguez, *et al.*, 2004). However, biological treatment has several limitations such as, the narrow range of the biodegradable waste inside the landfill, 5-20% of landfill

components only are biodegradable (Peters, 1998a), the presence of toxic substance for microorganism (Li et al., 1999), The limitation presence of microorganism nutrition (Amokrane et al., 1997) and the limited efficiency of biological treatment of old leachate (Li et al., 1999, Amokrane et al., 1997).

The common chemical treatment processes of leachate include chemical precipitation, chemical oxidation and coagulation and flocculation. The main disadvantages of chemical treatment methods include, generally effective only for single metal ions (Lee et al., 2002, Matthew & Chan, 2001), very expensive due to use of chemical reagents (Cheremisinoff, 1995) and some times produce toxicity materials (Santos et al, 2004, Gonze et. al., 2003, Silva et al., 2004, Marttinen et al., 2002).

The common physical treatment processes of leachate include evaporation, air stripping, membrane processes and adsorption. Adsorption is one of the most widely employed techniques, for the removal of recalcitrant organic compounds from landfill leachate. It is comparatively more economical and useful for pollutant removal from aqueous solutions (Fettig, 1999, Aziz *et al.*, 2004a and 2004b, Kurniawan, 2002, Ugurlu and Salman, 1998, Bable and Kurniawan, 2003 and 2004, Heavey, 2003, Kargi and Pamukoglu, 2004, Rodriguez *et al.*, 2004, Isa *et al.*, 2006, Hussain *et al.*, 2007).

A very wide variety of materials have been studied as adsorbents. Some of these materials include activated carbon, zeolite, organic polymers, palm ash, sand and activated carbon, commercial activated carbon, clay mineral,

sepiolite, Indian rosewood, sulphur and limestone, chitosan, activated carbon prepared from agricultural waste and fungus *Aspergillus's niger*.

Usually, a combination of two physical-chemical treatment or physico-chemical and biological treatment is required for optimum treatment of stabilized leachate (Kurniawan et al., 2006, Kargi and Pamukoglu, 2003, Tatsi et al., 2003). The use of limestone, activated carbon and zeolite in leachate treatment is not well established.

This research focused on the leachate generated from Larut Matang landfill site which is located at 4.49'.20.08" N and 100.40'.44.08" E in Taiping, Perak, Malaysia beside the North-South highway. The total area of the landfill is 12.0 hectares and it is equipped with a leachate collection pond. The landfill receives about 300 ton of solid waste daily (Site Record, 2006). Larut Matang landfill is classified as an improved anaerobic sanitary landfill. The landfill is more than 10 years old (Taiping Landfill Council, 2006). Larut Matang landfill leachate is considered as biologically stable with BOD/COD ratio of 0.06 (less than 0.1 for stabilized leachate) (Muzaini et al., 1995) therefore biological treatments alone is not effective.

The main purpose of this study was to investigate the suitability of using activated carbon, zeolite and limestone and their mixtures as filtering media, for removing COD, ammoniacal nitrogen, colour and iron which are among the significant pollutants present in the Larut Matang landfill leachate. Batch and

column studies were studied in this research to reduce the total cost of treatment by using limestone as low cost material to cut overall cost.

## **1.2 Objectives of Research**

The research focused on the removal of colour, COD, ammoniacal nitrogen and iron from leachate using limestone, activated carbon and zeolite.

The specific objectives of this study are as follows:

1. To establish the adsorption capacity (if any) using the best fit isotherm model i.e., Freundlich and Langmuir isotherm models.
2. To determine the adsorption kinetics using Pseudo first order kinetic, Pseudo second order kinetic, and intra-particle diffusion.
3. To investigate the best filter arrangement which give optimum removals of all parameters in column study and to determine the basic design parameters of filter column.
4. To investigate possibility of regenerating the used media by different regeneration solvents.



### **1.3 Scope of Study**

The scope of this study is as follows:

1. Characterization of leachate from the detention pond of Larut Matang landfill, Taiping, Perak, Malaysia (classified as stabilized leachate) was carried out for a period of 22 months, from 1<sup>st</sup> October 2004 to 1<sup>st</sup> August 2006, including dry and wet days.
2. Three media, limestone, activated carbon and zeolite, with a particle size of 2.0 – 3.35 mm were used as the filtering media to investigate their ability to remove colour, COD, iron and ammoniacal nitrogen from the leachate.
3. Parameters studied were colour, COD, iron and ammoniacal nitrogen that presented in significant quantities with maximum concentration of approximately 5000 Pt-Co, 1850 mg/L, 8.0 mg/L and 1100 mg/L, respectively.
4. The experiments were divided in two phases. The first one was batch experiments which include preliminary experiments to determine the optimum shaking speed and shaking time, optimum mixture ratio, effect of pH, adsorption isotherm studies (Freundlich and Langmuir), and adsorption kinetics and desorption studies. The second phase was continuous flow experiments, carried out to study the potential use of the media – their removal efficiencies and the breakthrough capacity, effect

of media layer arrangement in the column, to assist in the actual system workability and in the regeneration study.

5. Regeneration experiments involved determination of suitable chemical for the regeneration of the activated carbon and zeolite used and to determine the removal capacity of the regenerated media.
6. Only the following solvents were examined in the regeneration study, i.e., sulfuric acid ( $\text{H}_2\text{SO}_4$ ), hydrochloric acid ( $\text{HCl}$ ), nitric acid ( $\text{HNO}_3$ ), sodium chloride ( $\text{NaCl}$ ), toluene ( $\text{C}_6\text{H}_5\text{CH}_3$ ), O-xylene ( $\text{C}_6\text{H}_4(\text{CH}_3)_2$ ).

#### **1.4 Structure of Thesis**

This research is presented in six chapters including this introductory Chapter.

- **Chapter 1. Introduction:** introduces the background of this study, presents the problem statement, lists the objectives and scope of this research.
- **Chapter 2. Literature Review:** contains the following sections: definitions, sources, types, composition, and management aspects of solid waste. The incineration, composting and landfill disposal methods. Leachate and its associated control. Leachate problems and treatment alternatives. These methods include biological, chemical, physical and their combinations. Information on regeneration criteria and its importance is also provided.

- **Chapter 3. Material and Methods:** presents the experimental program and the procedures of both batch and column studies in addition to the site condition, location, samples preparation and the main methods used to determine leachate properties and the characteristics of adsorbent media used in the study.
- **Chapter 4. Results and Discussion:** includes analysis of the results obtained from the experimental work. The characterization of leachate and adsorbents. The removal efficiency of colour, COD, iron and ammoniacal nitrogen from leachate in both batch and column experiments using activated carbon, limestone, zeolite and their mixtures. Freundlich and Langmuir isotherms, adsorption kinetics results. Analysis of regeneration results obtained from the experiments and analysis of the effect of pH on the removal efficiency.
- **Chapter 5. Conclusion and Recommendations:** summarizes the finding of the research and makes recommendations based on it.

## **CHAPTER 2**

### **LITERATURE REVIEW**

#### **2.0 Introduction**

This chapter presents general information about solid waste management, leachate problem and leachate treatment alternatives. The chapter is divided into six sections. The first section discusses the definition, sources, types, composition and management aspects of solid waste. The second section details about landfill. The third section presents leachate and its associated control. The fourth section discusses the problem caused by leachate pollution. The fifth section presents the various leachate treatment methods including biological, chemical, physical and their combination and the last section presents the regeneration aspects of media used in leachate treatment.

#### **2.1 Solid Waste**

Solid wastes comprises of all types of wastes arising from human and animal activities that are normally solid and that are discarded as useless or unwanted such as food wastes, yard wastes, paper, tin and bottles (Tchobanoglous *et al.*, 1993).

Generation of solid waste increases rapidly due to the urbanization and industrialization activities. Urban lifestyle influences the solid waste characteristics and industrialization also creates communities with the "throw away" attitude. Many products are designed to be used only once (Henry & Heinke 1996). As the industries become more and more sophisticated, the

solid wastes produced require specialized techniques for their treatment and disposal (Agamuthu, 2001).

Agamuthu (2001) investigated that most wastes generated in Malaysia are municipal solid waste that consists of paper, plastics, food wastes, glasses, metals and woods. He estimated the generation rate of solid waste may be increased at about 3% per year due to the increase in population and the economic development of the country. Another problem is that there is not only an increase in the generation of solid wastes, but their characteristics today are more complicated than they were a few years ago. So to handle these problems an efficient disposal method is needed.

### **2.1.1 Types of Solid Wastes**

There are many types of solid wastes. The grouping can also vary. Tchobanoglous *et al.*, (1993) divided the solid wastes into the following types:

- Residential and commercial solid wastes consist of the organic solid waste (food waste, paper, cardboard, plastics, textiles, rubber, leather, wood and yard waste) and inorganic solid waste (glass, tin cans, aluminum, and ferrous metals) from both residential and commercial areas.
- Hazardous waste, defined as the waste that pose a substantial present or potential hazard to human health or living organisms.
- Construction and demolition wastes that are produced from construction, remodeling and repairing of structures.

- Municipal services wastes, resulting from the operation and maintenance of municipal facilities such as street sweepings, road side litter and landscape wastes.
- Treatment plant wastes and other residues which are produced from water, wastewater and industrial treatment plants.
- Agricultural wastes, resulting from diverse agricultural activities.

### **2.1.2 Quantity of Solid Waste**

It is necessary to estimate the quantities of solid waste that will be generated, by waste category, within a community. Estimates of municipality solid waste quantities are usually based on the amount of waste generated per person per day. Ministry of Housing and Local Government of Malaysia revealed that Malaysians discard about 17000 tones of solid waste daily with an average of 0.80 to 1.0 kg/person/day, this percentage increase in Kuala Lumpur city to 1.85 kg/person/day (Ministry of Housing and Local Government, 2003).

A new study reported that solid waste regeneration in Malaysia has increased to 18000 ton/day and the generation is expected to increase by 3% yearly due to increase in population and economic growth in Malaysia (Fauziah & Agamuthu, 2006).

### **2.1.3 Composition of Solid Waste**

The composition of solid wastes generated in Malaysia in 1995, 2001 and 2004 is shown in Table 2.1. The data shows that more than 70% of the wastes are in the form of compostable waste (organic waste, paper,

textile/leather and wood). The percentage of plastics is considered high (over 12.5%) and it is considered typical for a fast developing nation (Agamuthu, 2001).

Table 2.1 Malaysian Solid Waste Composition (% by weight)

Waste composition	Percentage (%)		
	1995	2001	2004
Organic/food waste	32.0	29.5	35.72
Paper	29.5	26.8	16.61
Textile/leather	3.4	3.9	5.1
Waste Yard and wood	7.0	13.6	13.85
Plastics	16.0	12.5	22.19
Rubber	2.0	1.9	0.89
Glass	4.5	2.7	3.2
Metals	4.3	1.9	2.44
Others	1.3	5.3	0.0
Total	100	100	100
Total compostable waste	71.9	73.8	71.28

Sources: Ridhuan (1995), Dini *et al.*, (2001), Syed (2004).

Kathirvale *et al.*, (2003) determined the composition of solid waste which was collected from different sources (high, medium, and low-income residential households, institutional and commercial) of the area of Kuala Lumpur. The result indicated that there is an obvious difference between the amount of organic wastes generated by the residential premises as compared with generation by the institutional and commercial sectors.

Fauziah & Agamuthu, (2006) reported their study on waste composition, carried out in urban, rural and sub-urban landfills in Malaysia, where wastes from randomly selected garbage truck were separated into 28 groups. Their results are shown in Figure 2.1. The results indicated that food waste constitutes 41% of the total wastes followed by 8% of plastic film and 6% rigid plastic.

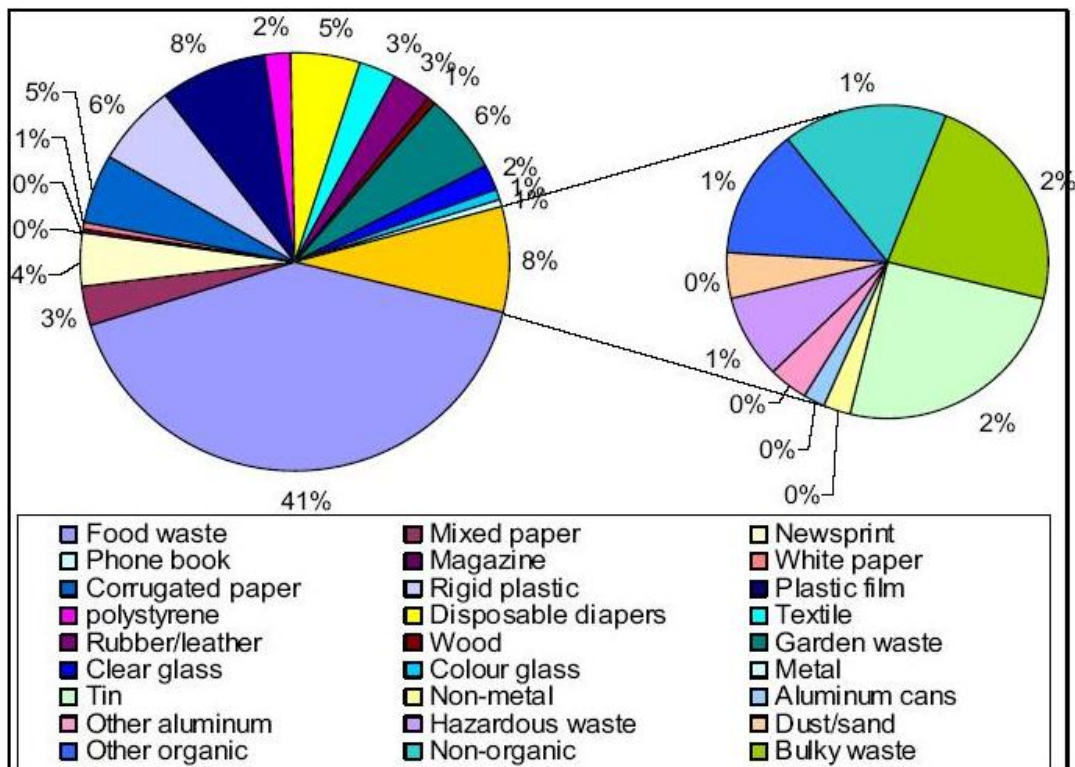


Figure 2.1: Average composition of waste received by landfill in Malaysia in 2006 (Fauziah & Agamuthu, 2006)

#### 2.1.4 Solid Waste Management

Solid waste management is required to manage the huge daily generation of solid waste. There are many objectives of solid waste management. The first one is to remove discarded materials from inhabited places in timely manner to prevent the spread of diseases; the second objective is to minimize the likelihood of fires, the third one is to reduce aesthetic insults arising and disposes of the discarded material in an environmentally acceptable way (Davis & Cornwell, 1998). Solid waste management involves the overall management related of solid waste activities such as generation, storage, collection, transfer, separation, transformation, recycling and disposal (Hamer, 2003). Landfilling is still widely used as the most common method for waste disposal in developing countries, including Malaysia.



## **2.2 Disposal Technology**

The main parameters considered in the choice of disposal methods are: type of waste, composition of waste, infrastructure facilities, availability of land, labour, economic aspects, recycling, public awareness, calorific value of waste, availability of energy and environmental impact. Generally the disposal methods should meet several conditions. The method must be environmental friendly, no effect on the workers or public health, the economic factor, availability of maximum recycling options and it should not be labour intensive. Several methods have been used for waste disposal, the main are discussed in the following sections.

### **2.2.1 Open dumping**

The waste in this method is disposed on land without covering material at the top of waste. This is also not a satisfactory method but it is common in developing countries. It is unsightly and encourages proliferation of flies and other animals scavenging on the exposed waste. In Malaysia there are about 177 disposal sites. In most cases, open dumping is being practiced and takes place at about 50% of the total landfill (Malaysia Country Report, 2001). Chenayah & Takeda, (2005) reported that there are 230 official dumping sites in Malaysia. The majority of them have no leachate or gas management facilities, (only 10% providing leachate treatment ponds and gas ventilation system) and no daily earth covering, and most of them without control mechanism or supervision, hence leaching chemicals enter the groundwater, poisoning the air with toxic gases and generally being health hazardous. Now, steps are being taken to upgrade the landfill, and this includes installation of

fence, weighbridge and site office wheel washing troughs, and gas disposal pipes.

### **2.2.2 Landfill**

Landfilling is one of the primary technologies used to dispose off solid waste. It is defined as the physical facilities used for the disposal of residue solid waste (Tchobanoglous, et al. 1993). It is the most economical and environmentally acceptable method used in the disposal of solid waste (Rodrigues *et al.*, 2004). In the landfill, disposed solid wastes undergo many physical, chemical and biological changes such as anaerobic biodegradation of high molecular weight compound of organic matters to simple compound typically methane and organic acids (Morawe, *et al.*, 1995).

#### **2.2.2.1 Sanitary Landfill**

According to Trivedi & Raj (2002), sanitary landfilling is a method of disposing of refuse on land without creating nuisances or hazards to public health or safety, by utilizing the principles of engineering to confine the refuse to the smallest particle size, to reduce it to smallest practical volume, and to cover it with a layer of soil at the end of each operation days or at frequent intervals as may necessary. Figure 2.2 and 2.3 show typical modern sanitary landfill cross section and the main facilities must be available in the sanitary landfill.

In Malaysia, there are about 230 landfills recognized officially and about three times of illegal dumps (Agamuthu, 2001). Most of these landfills can not be classified as sanitary landfill because there are no facilities to treat leachate or

infrastructure to exploit landfill gas (Chenayah and Takeda, 2005, Agamuthu, 2001). Zaman, (1992) reported that only 10% of Malaysian landfills having leachate treatment ponds and gas ventilation system while 90% of them having no control mechanism or supervision. In the seventh Malaysia plan (1995-2000), the federal government had spent RM 20.9 million to build 9 sanitary landfills and upgrade 27 existing landfills in 34 local authorities (Malaysia Country Report, 2001). Aziz *et al.*, (2004a & 2004b) reported that there only three semi-aerobic landfill in Malaysia. Agamuthu (2001) suggested that sanitary landfills can be divided into four levels. The first one is sanitary landfills with controlled tipping. The second level is sanitary landfills with daily soil cover, while the third one is sanitary landfills with leachate recirculation and the last level is sanitary landfills with complete leachate treatment facilities.

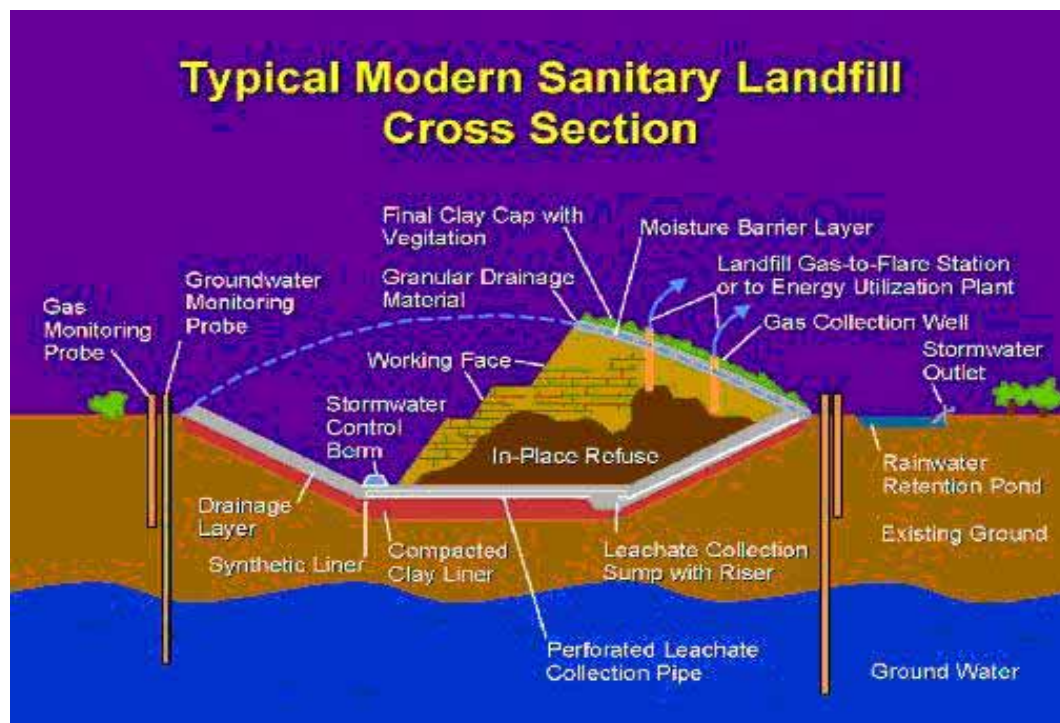


Figure 2.2 Cross section in sanitary landfill ([www.google.com/image](http://www.google.com/image) 20/7/2007)

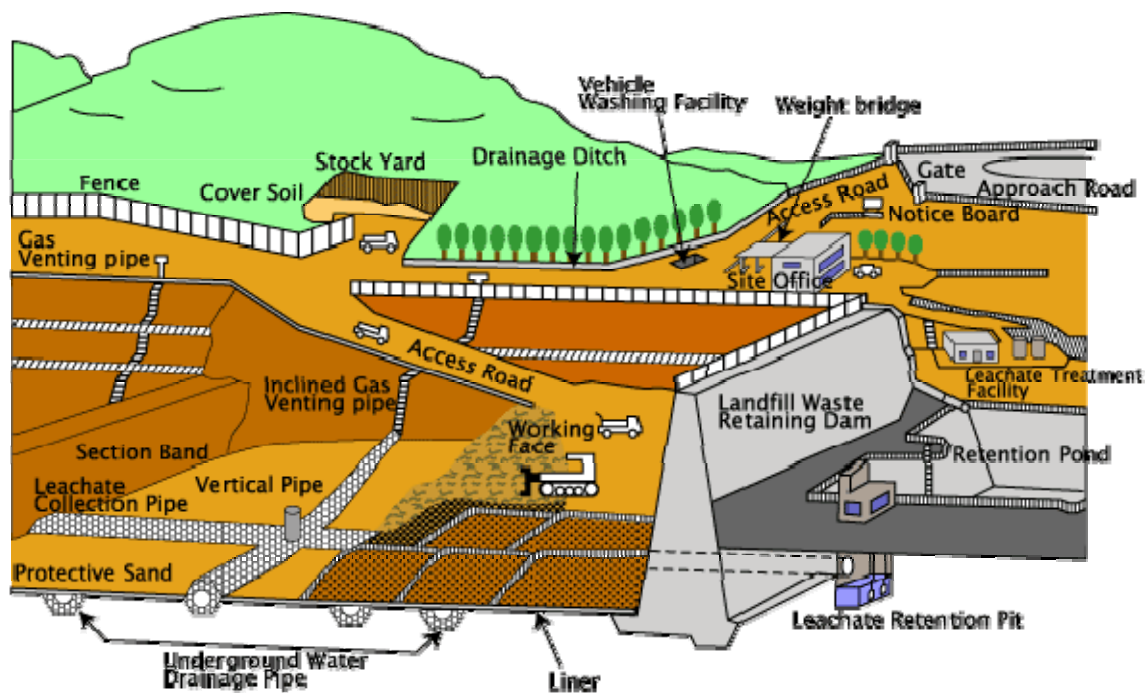


Figure 2.3 Facilities needed in sanitary landfill ([www.google.com/image](http://www.google.com/image) 20/7/2007)

#### 2.2.2.2 Landfill Types

Matsufuji (1990) reported that there are three major types of landfills.

These types are aerobic, anaerobic and semi-aerobic landfills.

##### Aerobic Landfills

The aerobic landfill system uses air addition and leachate recirculation to maintain the humidity of the air and to provide nutrients to microorganisms. In this method, several advantages can be achieved such as an increase in the quality of leachate, a reduction in methane generation and an increase in the stabilization of solid waste. In addition, the life of landfill can be increased due to increase in waste decomposition, waste sedimentation and stabilization of solid waste. However, aerobic landfills require high maintenance costs for the piping system that provides oxygen to the waste. Figure 2.4 shows a schematic design of aerobic landfill.

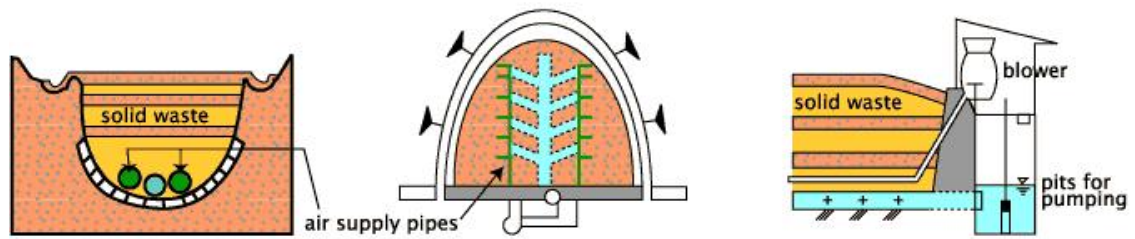


Figure 2.4 Schematic design of aerobic landfill (Matsufuji, 1990)

### Anaerobic Landfills

Anaerobic landfill system is a common system to degrade and decompose solid waste (Matsufuji, 1990). However, the system may have potential negative impacts to the environment and create health problems because it produces toxic matters and organic matters such as pathogens. It also produces high generation of methane and carbon dioxide as by-products from the anaerobic process. Generally, anaerobic landfill can be divided into normal anaerobic landfill which seems to be as open dump, an anaerobic sanitary landfill having cover layer over wastes and an improved anaerobic sanitary landfill which has additional cover layer collection system for leachate, as practiced at Larut Matang landfill. Figure 2.5 shows a schematic design of an anaerobic landfill.

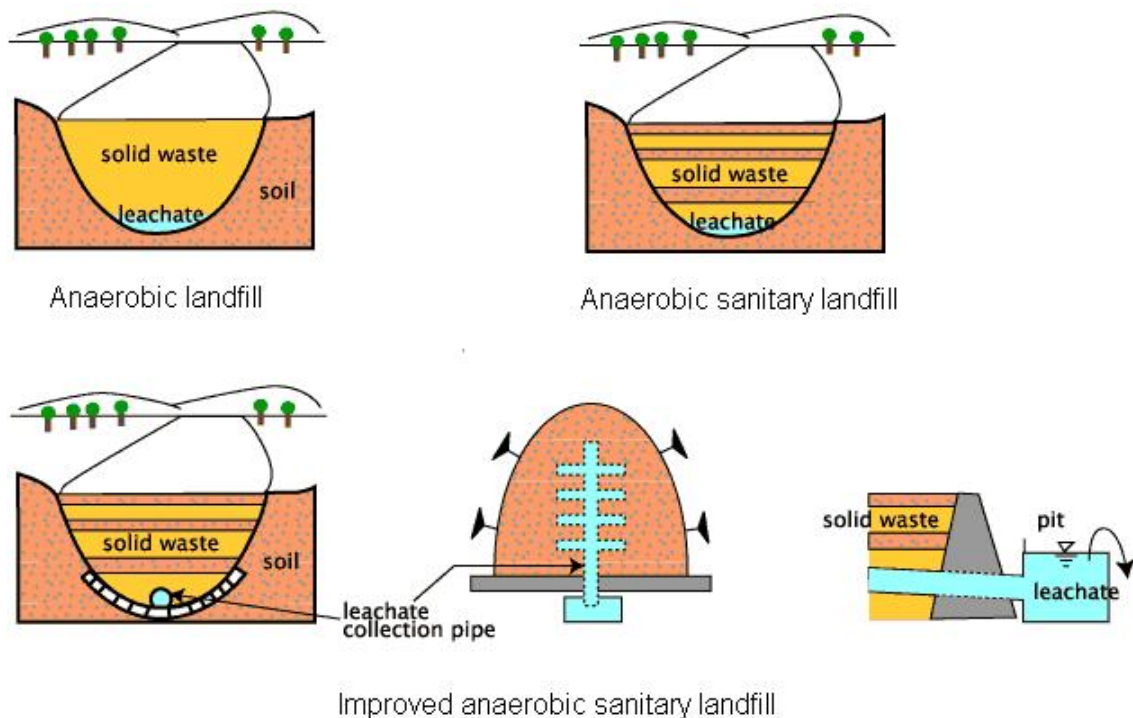


Figure 2.5 Schematic design of anaerobic landfill (Matsufuji, 1990).

### Semi- Aerobic Landfills

Semi-aerobic landfill is generally designed with a piping system underneath the landfill. The function of leachate collection pipes is to allow the air to flow inside and outside the solid waste. The main purpose of this is to enlarge the aerobic zone inside the landfill, to make active aerobic consortia, and to increase the rate of waste decomposition.

Decomposition of organic matter inside the landfill will cause an increase in temperature. The difference in temperature between inside and out side of the landfill will generate a heat convection current into the landfill through the leachate pipes (Aziz *et al.*, 2004a). These actions improve the quality of leachate and reducing the generation of hazardous gases. Aziz, *et al.*, (2004a & 2004b) reported that only three sites in Malaysia considered as semi-aerobic

landfill, one of them is Pulau Burung Landfill. Figure 2.6 shows a schematic design of semi-aerobic landfill.

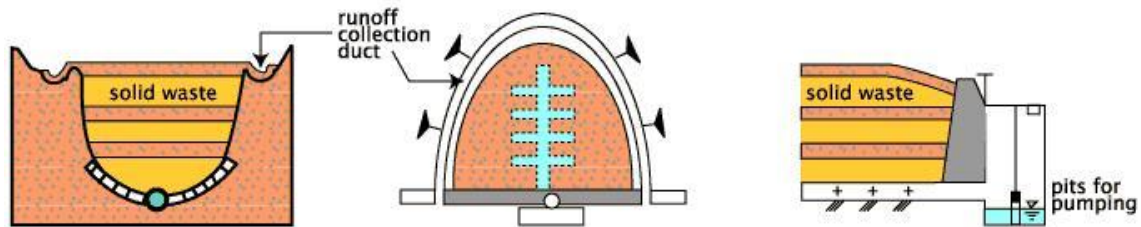


Figure 2.6 Schematic design of semi-aerobic landfill (Matsufuji, 1990).

### 2.2.2.3 Decomposition in Landfill

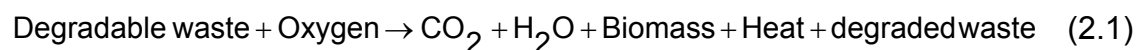
Solid waste at a sanitary landfill will undergo physical, chemical and biological degradation processes just after it is covered with landfill cover. These processes start directly after the solid waste is placed in landfill and continues until the end of the landfill's life. The period of decomposition of solid waste depends on its waste characteristics. Warith, (2002) investigated the effect of size factor of solid waste, leachate recirculation and nutrient balance on the rate of MSW biodegradation. The result indicated that the smaller the size of the MSW the faster the biodegradation rate of the waste. The results showed that the addition of supplemental materials such as sludge to the leachate during recirculation was found to have positive effect on the rate of biodegradation of MSW where a significant volume reduction in relatively short duration was achieved.

Benson *et al.*, (2007) reported that leachate recirculation will accelerate the degradation of waste. The decomposition of solid waste produces solid, liquid, and gaseous byproducts, all of which may be of concern in the overall

management of a landfill. Throughout these processes, the flow rate and characteristics of the leachate in the landfill vary from time to time.

### **Aerobic and Anaerobic Degradation**

In the aerobic degradation, organic matters are converted to carbon dioxide, water, energy and biomass by aerobic bacteria. Generally aerobic degradation stops after a short time (upon depletion of oxygen). In other words, the aerobic biodegradation might only happen in the uppermost layer of the landfill since the oxygen exists by means of diffusion and rainwater infiltration. Equation 2.1 shows the relation of aerobic decomposition of waste in landfill.



Basically, anaerobic biodegradation will be the predominant reaction subsequently after the initial short aerobic degradation. The anaerobic bacteria will consume the organic matter and convert it into carbon dioxide and methane. Anaerobic degradation is mediated by a variety of microorganism operating in series, i.e. product of one bio-reaction is used as substance in the next bio-reaction (Secka, 2002). Generally the anaerobic conversion of organic compounds involves three stages. The first stage involves the enzyme-mediated transformation of high molecular weight compounds into suitable compounds to use as source of energy. The second stage is associated with the bacterial conversion of the compounds resulting from the previous phase into identifiable lower molecular weight intermediate compounds. The last stage involves the bacterial conversion of the intermediate compounds into simpler



end products such as carbon dioxide (CO<sub>2</sub>) and methane (CH<sub>4</sub>) (Peavy *et al.*, 1985). In other words, the anaerobic decomposition in landfill involves two main phases: acid-phase and methanogenic phase. In the acid-phase, acid fermentation prevails, with characteristic end products being high level of carbon dioxide, partially degraded organics (especially organic acids), and some heat, as described by equation 2.2.



As the biodegradation of the refuse progresses, the oxygen becomes depleted and the methanogenic bacteria become dominant. These organisms produce carbon dioxide, methane, and water, along with some heat.

### **Phases of Waste Stabilization**

Leachate composition is primarily a function of the age of the landfill and the degree of waste stabilization. Stabilization of waste in landfill proceeds in five sequential and distinct phases (Pohland & Harper, 1985). The rate and characteristics of waste produced and biogas generated from a landfill vary from one phase to another and reflect the microbially mediated processes taking place inside the landfill. The rate of progress through these stages is dependent on the physical, chemical, and microbiological conditions developed within the landfill with time (Pohland *et al.*, 1985). Figure 2.7 illustrates the five sequential phases of landfill stabilization at a particular time (Tchobanoglous *et al.*, 1993). Since landfills have various sections or cells, a landfill is not