DEVELOPMENT OF DURIAN PEEL ACTIVATED CARBON FOR THE REMOVAL OF COD AND COLOUR FROM SEMI-AEROBIC LANDFILL LEACHATE

by

MOHAMAD ANUAR BIN KAMARUDDIN

Thesis submitted in fulfilments of the

requirements for the degree of

Master of Science

August 2011

ACKNOWLEDGEMENT

In the name of Allah, the Most Beneficent and the Most Merciful. All praises to Allah the Almighty for giving me the strengths, guidance and patience in completing this thesis. First and foremost, I would like to express my deepest gratitude to my family for their endless love and support. My deepest appreciation goes to Dr. Mohd Suffian Yusoff for serving as a successful supervisor of this research project and for providing me with the insights and guidance. His valuable suggestion and encouragement enable me to handle this project with confidence. Furthermore, I would like to thank my co supervisor, Dr. Mohd Azmier Ahmad for his guidance and knowledge contribute to me throughout my research progress. His understanding, wide knowledge and personal guidance have provided a good basis for the present thesis.

I would like to express my grateful thanks to Mr. Zaini, Mr. Nabil, Mr. Nizam and Mrs. Shamsiah for their invaluable asisstance. Besides, special acknowledgement goes to Dr. M.J.K, Bashir for sharing his knowledge, professional advices and guidelines throughout the whole project. A special thanks goes to Rasyidah Alrozi for her guidance during experimental work and report writing. Useful discussions and suggestions from her is deeply appreciated. Last but not least, I would like to express deepest gratitude to Universiti Sains Malaysia that provides me with fellowship scheme throughout my candidature period. For those who have directly and indirectly contributed to the accomplishment of this project, thank you so much.

Mohamad Anuar Kamaruddin

August 2011

TABLE OF CONTENTS

		Page
ACKNOWLEDGEMENT		**ii**
TABLE OF CONTENTS		**iii**
LIST OF TABLES		**ix**
LIST OF FIGURES		**xiii**
LIST OF PLATES		**xviii**
LIST OF ABBREVIATIONS		**xix**
ABSTRAK		**xxi**
ABSTRACT		**xxiii**

CHAPTER ONE: INTRODUCTION

1.0	Introduction	1
1.1	Problem statement	5
1.2	Research objectives	7
1.3	Organization of the thesis	7

CHAPTER TWO: LITERATURE REVIEW

2.1	Waste disposal by landfill and its impact	10
2.2	Sanitary landfill	13
2.2.1	Anaerobic landfill	13
2.2.2	Semi-aerobic sanitary landfill	14
2.2.3	Aerobic landfill	16
2.3	Decomposition process in landfill site	17
2.3.1	Aerobic phase	19
2.3.2	Anaerobic phase	20
2.3.3	Acidic phase	21
2.3.4	Methanogenic phase	22

2.3.5 Maturation phase 24

2.4 Leachate 26

2.4.1 Factors affecting leachate quantity 28

2.4.1 (a) Precipitation 28

2.4.1.(b) Groundwater intrusion 28

2.4.1.(c) Moisture content of waste 29

2.4.1(d) Final cover 29

2.5 Leachate composition 29

2.6 Landfill eachate treatment 32

2.6.1 Adsorption 34

2.6.1.1 Activated carbon adsorption 34

2.6.1.2 Activated carbon in leachate treatment 36

2.7 Precursors for Preparation of activated carbon 39

2.7 1 Durian peel *(Durio zibethinus Murray)* peel 40

2.8 Preparation of activated carbon 41

2.8.1 Physical activation 41

2.8.2 Chemical activation 42

2.9 Optimization of operating conditions for activated carbon preparation 43

2.10 Characterization of activated carbon 45

2.10.1 Physical properties 45

2.10.1(a) Activated carbon yield 45

2.10.1(b) Surface area and pore characteristics 46

2.10.1(c) Surface morphology 48

2.10.2 Chemical properties 49

2.10.2 (a) Proximate and elemental analysis 50

2.10.2 (b) Surface chemistry 51

2.11 Adsorption performance 52

2.11.1 (a) Effect of initial pH 52
2.11.1 (b) Effect of particle size 53
2.11.1 (c) Effect of contact time 54
2.11.1 (d) Effect of adsorbent dosage 54

2.12 Adsorption isotherms 55

2.12.1 Langmuir isotherm 56

2.11.2 Freundlich isotherm 58

2.13 Adsorption kinetic 59

2.13.1 Pseudo-first-order kinetic model 59

2.12.2 Pseudo-second-order kinetic model 60

CHAPTER THREE: MATERIALS AND METHODS

3.1 Materials 62

3.2 General description of equipment 63

3.2.1 Activated carbon preparation 63

3.2.2 Batch adsorption test 68

3.2.3 Characterization system 68

3.2.3 (a) Surface area analysis 68

3.2.3 (b) Scanning electron microscopy 69

3.2.4 (c) Proximate analysis 69

3.2.4 (d) Ultimate analysis 70

3.2.4 (e) Surface chemistry 70

3.3 Experimental procedure 71

3.3.1 Precursor preparation 71

3.3.2 Activated carbon preparation 72

3.3.2 (a) Physical activation 72

3.3.2 (b) Chemical activation 73

3.3.3 Experimental design for preparation of activated carbons 74

3.3.3(a) Model fitting and statistical analysis 77

3.3.4 Adsorption performance test 78

3.3.4 (a) Effects of Initial pH 79

3.3.4 (b) Effect of particle size 79

3.3.4 (c) Effect of contact time 80

3.3.4 (d) Effect of adsorbent dosage 80

3.3.4 (e) Adsorption isotherm 80

3.3.5 Batch kinetic studies 80

3.3.6 Experimental activities 81

CHAPTER FOUR: RESULTS AND DISCUSSIONS

4.1 Experimental design 83

4.1.1 Preparation of durian peel activated carbons by physical activation using design of experiment 84

4.1.1(a) Development of regression model equation for 86 preparation of DP activated carbon by physical activation

4.1.1 (b) COD removal of DP activated carbon by physical activation 92

4.1.1 (c) Colour removal of DP activated carbon by physical activation 94

4.1.1 (d) Carbon yield of DP activated carbon by physical activation 95

4.1.2 Preparation of DP activated carbon using design of experiment by chemical activation 96

4.1.2 (a) Development of regression model equation for preparation of DP activated carbon by chemical activation 99

4.1.2(b) COD removal of DP activated carbon by chemical activation 105

4.1.2 (c) Colour removal of DP activated carbon by chemical activation 107

4.1.2 (d) Carbon yield of DP activated carbon yield by chemical activation 109

4.1.3 Optimization of operating parameters 111

4.2 Characterization of prepared activated carbons 115

4.2.1 Surface area and pore characteristics 116

4.2.2 Surface morphology 119

4.2.3 Proximate and elemental analysis 121

4.2.4 Surface chemistry 123

4.3 Batch adsorption tests of ACC and ACP on the removal of COD and colour 127

4.3.1 Effect of initial pH 127

4.3.2 Effect of particle size 129

4.3.3 Effect of contact time 131

4.3.4 Effect of adsorbent dosage 134

4.3.5 Adsorption Isotherm 136

4.3.5 (a) COD and colour adsorption isotherms 136

4.3.6 Batch kinetic studies 143

CHAPTER FIVE: CONCLUSIONS AND RECOMMENDATION

5.1 Conclusions 148

5.2 Recommendations 150

REFERENCES 152

APPENDICES 163

LIST OF TABLES

Table 1:	Totals landfills in Malaysia	4
Table 2.1:	Leachate composition during acetogenic phase	22
Table 2.1:	Leachate composition during methanogenic phase	23
Table 2.3:	Heavy metals composition during acidogenic phase and methanogenic phase. Unit: mg/L	25
Table 2.4:	Substance composition during acetogenic phase and methanogenic phase. Unit: mg/L	25
Table 2.5:	Variation of leachate composition in different countries	31
Table 2.6:	Previous studies on the adsorption of leachate parameters using activated carbon	38
Table 2.7:	Isotherm model applied in adsorption study	56
Table 3.1:	List of chemicals	62

Table 3.2:	Lists of gases	63
Table 3.3:	Independent variables and their coded levels for the central composite design for physical activation	74
Table 3.4:	Independent variables and their coded levels for the central composite design for chemical activation	74
Table 3.6:	Experimental design matrix for physical activation	75
Table 3.7:	Experimental design matrix for chemical activation	76
Table 4.1:	Experimental design matrix for preparation of durian peel activated carbon by physical activation	85
Table 4.2:	Analysis of variance (ANOVA) and lack-of-fit test for response surface quadratic model for COD removal of DP activated carbon by physical activation	88
Table 4.3:	Analysis of variance (ANOVA) and lack-of-fit test for response surface quadratic model for colour removal of DP activated carbon by physical activation	89
Table 4.4:	Analysis of variance (ANOVA) and lack-of-fit test for response surface quadratic model for DP activated carbon yield by physical activation	90

Table 4.5: Experimental design matrix for preparation of durian peel activated carbon by chemical activation 98

Table 4.6: Analysis of variance (ANOVA) and lack-of-fit test for response surface quadratic model for COD removal of durian peel activated carbon 101

Table 4.7: Analysis of variance (ANOVA) and lack-of-fit test for response surface quadratic model for colour removal of durian peel activated carbon 102

Table 4.8: Analysis of variance (ANOVA) and lack-of-fit test for response surface 2 FI model for carbon yield of durian peel activated carbon 102

Table 4.9: Model validation for activated carbon prepared via physical activation 113

Table 4.10: Model validation for activated carbon prepared via chemical activation 113

Table 4.11: Surface area and pore characteristics of the prepared activated Carbons 117

Table 4.12: Proximate and elemental contents 121

Table 4.13: Elemental analysis of carbon element in the precursor of other 122

biomass

Table 4.14: Langmuir and Freundlich isotherm model parameters and correlation coefficients for COD adsorption 141

Table 4.15: Langmuir and Freundlich isotherm model parameters and correlation coefficients for colour adsorption 141

Table 4.16: Langmuir and Freundlich equations for COD adsorption 142

Table 4.17: Langmuir and Freundlich equations for colour adsorption 142

Table 4.18: Parameter values of Pseudo-first order and Pseudo-second order for adsorption of COD and colour (ACP) 147

Table 4.19: Parameter values of Pseudo-first order and Pseudo-second order for adsorption of COD and colour (ACC) 147

LIST OF FIGURES

Figure 1:	Solid waste composition for the year 2005	2
Figure 2.1:	Landfill structures	12
Figure 2.2:	Anaerobic landfill structures	14
Figure 2.3:	Semi-aerobic sanitary landfill design	15
Figure 2.4:	Semi – aerobic sanitary landfill mechanism	15
Figure 2.5:	Different between anaerobic landfill and semi – aerobic sanitary landfill	16
Figure 2.6:	Aerobic landfill design	17
Figure 2.7:	Aerobic landfill echanism	17
Figure 2.8:	Leachate characteristic during degradation of solid waste	26
Figure 2 9:	SEM micrograph of (a) Precursor; (b) Char; (c) DSAC (magnifications 500×)	49

Figure 2.10: FTIR spectrum of (CS700) char and activated carbon (CS850A 52

Figure 3.1: Schematic diagram of the experimental setup for activated carbon 66

Figure 3.2: Vertical tubular furnace and reactor 67

Figure 3.3: Schematic flow diagrams of experimental activities 82

Figure 4.1: Predicted versus experimental COD removal of DP activated carbon by physical activation 91

Figure 4.2: Predicted versus experimental colour removal of DP activated carbon by physical activation 91

Figure 4.3: Predicted versus experimental DP activated carbon yield 92

Figure 4.4: Three-dimensional response surface plot of COD removal (Effect of activation temperature and activation time, CO_2 = 100 ml/s) of durian peel activated carbon by physical activation 93

Figure 4.5 Three-dimensional response surface plot of colour removal (Effect of activation temperature and CO_2 flow rate, t = 2 h) of DP activated carbon by physical activation 94

Figure 4.6: Three-dimensional response surface plot of carbon yield (Effect of activation temperature and CO_2 flow rate, t = 2 h) of DP activated carbon by physical activation 96

Figure 4.7: Predicted versus experimental COD removal of DP activated carbon by chemical activation 103

Figure 4.8: Predicted versus experimental colour removal of DP activated carbon by chemical activation 104

Figure 4.9: Predicted versus experimental carbon yield of DP activated carbon by chemical activation 104

Figure 4.10: Three-dimensional response surface plot of COD removal (Effect of activation temperature and IR, t = 2h) of DP activated carbon by chemical activation 106

Figure 4.11: Three-dimensional response surface plot of colour removal (Effect of activation temperature and IR, t = 2h) of DP activated carbon 109

Figure 4.12: Three-dimensional response surface plot of colour removal Effect of activation temperature and activation time, t = 2h) of durian peel activated carbon 111

Figure 4.13: FTIR spectrums of DP raw, char, ACP and ACC 124

Figure 4.14 (a): Effect of initial pH on COD removal 128
Figure 4.14 (b): Effect of initial pH on colour removal
129

Figure 4.15 (a): Effect of particle size on COD removal 131

Figure 4.15 (b): Effect of particle size on colour removal 131

Figure 4.16 (a): Effect of on contact time on COD removal 133

Figure 4.16 (b): Effect of on contact time on colour removal 133

Figure 4.17 (a): Effect of adsorbent dosage on COD removal 135

Figure 4.17 (b): Effect of adsorbent dosage on colour removal
135

Figure 4.18 (a): Plots of Langmuir isotherm of ACP on for COD adsorption 136

Figure 4.18 (b): Plots of Freundlich isotherm of ACP on for COD adsorption 137

Figure 4.18 (c): Plots of Langmuir isotherm of ACC on COD adsorption 137

Figure 4.18 (d):	Plots of Freundlich isotherm of ACC on for COD adsorption	138
Figure 4.19 (a):	Plots of Langmuir isotherm of ACP on for colour adsorption	138
Figure 4.19 (b):	Plots of Freundlich isotherm of ACP on for colour adsorption	139
Figure 4.19 (c):	Plots of Langmuir isotherm of ACC on for colour adsorption	139
Figure 4.19 (d):	Plots of Freundlich isotherm of ACC on for colour adsorption	140
Figure 4.20 (a):	Linearized plots of pseudo-first-order kinetic model for COD adsorption on ACP and ACC	144
Figure 4.20 (b):	Linearized plots of pseudo-first-order kinetic model for colour adsorption on ACP and ACC	145
Figure 4.21 (a):	Linearized plots of pseudo-second-order kinetic model for COD adsorption on ACP and ACC	145

Figure 4.21 (b): Linearized plots of pseudo-second-order kinetic model for colour adsorption on ACP and ACC 146

LIST OF PLATES

Plate 3.1:	Vertical electrical tube furnace	64
Plate 3.2:	Durian fruit with durian peel	72
Plate 4.1:	SEM micrographs (x500) of (a) Raw DP (b) Char	120
Plate 4.2:	SEM micrographs (x500) of ACP	121
Plate 4.3:	SEM micrographs (x500) of ACC	121

LIST OF ABBREVIATIONS

AC	Activated carbon
ACC	Activated carbon – Prepared by chemical activation
ACP	Activated carbon – Prepared by physical activation
ANOVA	Analysis of variance
BET	Brunauer-Emmett-Teller
CCD	Central composite design
COD	Chemical oxygen demand
DP	Durian peel
EA	Elemental analysis
FTIR	Fourier Transform Infrared
GAC	Granular activated carbon

IR	Impregnation ratio
IUPAC	International Union of Pure and Applied Chemistry
PAC	Powder activated carbon
RSM	Response surface methodology
SEM	Scanning electron microscopy
TGA	Thermogravimetric analyzer
US	United State
2FI	Two factor interaction

PENGGUNAAN KARBON TERAKTIF BERASASKAN KULIT DURIAN BAGI RAWATAN LARUT LESAPAN DI TANAH KAMBUS

ABSTRAK

Pencemaran larut lesapan adalah masalah utama yang di hadapi oleh pihak pengurusan tapak pelupusan sampah kerana pembuangan larut lesapan tanpa rawatan yang sesuai akan mengancam hidupan akuatik dan manusia. Larut lesapan mengandungi pelbagai pencemar pekat seperti ammoniakal nitrogen, keperluan oksigen kimia (KOK), warna dan logam. Terkini, pelbagai kajian yang menumpukan kepada usaha-usaha untuk menukar hasil sisa pertanian ataupun buah-buahan tropika kepada karbon teraktif sedang giat dijalankan. Di dalam kajian ini, karbon teraktif berasaskan kulit durian diaktifkan melalui kaedah fizikal dan kimia dalam sistem penjerapan berkelompok. Pengaktifan fizikal melibatkan gas karbon dioksida (CO_2) dalam penghasilan karbon teraktif. Daripada keputusan rekabentuk eksperimen, suhu pengaktifan dan masa pengaktifan telah dikenal pasti sebagai faktor penting dalam mempengaruhi penghasilan karbon teraktif, penjerapan KOK dan kecekapan penyingkiran warna. Keadaan optimum yang dicapai untuk menghasilkan karbon teraktif ini secara pengaktifan fizikal (KTF) ialah 800 ^{o}C, 3 jam, dan 150 ml/s masing-masing untuk suhu pengaktifan, masa pengaktifan suhu pengaktifan dan kadar aliran nitrogen. Keadaan optimum yang dicapai untuk menghasilkan karbon terkatif ini secara pengaktifan kimia (KTK) ialah 533 ^{o}C, 2.45 jam dan 5.45 masing-masing bagi suhu pengaktifan, masa pengaktifan dan nisbah jerap isi. Karbon teraktif yang terhasil berciri liang meso dengan purata diameter liang lebih besar daripada 2.2 nm. Analisis mikroskopi elektron imbasan membuktikan bahawa karbon teraktif ini menunjukkan jenis struktur liang yang homogen dan heterogen. Analisis infra merah pengubahan Fourier memaparkan kehadiran pelbagai kumpulan berfungsi pada permukaan karbon teraktif ini. Kesan pH awal, saiz partikel, masa sentuhan dan berat penjerapan terhadap kecekapan dinilai melalui ujian penjerapan berkelompok. Kadar penjerapan KOK dan warna meningkat apabila pH larut lesapan meningkat pada saiz 1 mm untuk KTF dan 0.425 mm untuk KTK. Penyingkiran warna yang tinggi (21.55 – 65.89 %), diperolehi pada saiz partikel 0.425 mm bagi kedua-dua jenis karbon teraktif. Keadaan optimum masa sentuh dicapai bagi penyingkiran KOK untuk KTF dan KTK masing-masing ialah 8 dan 7 jam. Masa sentuhan optimum bagi penyingkiran warna untuk KTF dan KTK masing-masing ialah 5 dan 3 jam. Model garis suhu Freundlich dikenalpasti yang terbaik bagi penjerapan KOK dan warna untuk KTF. Sebaliknya untuk kes KTK, penjerapan KOK adalah terbaik dipadankan oleh model garis sesuhu Freundlich manakala model garis suhu Langmuir dikenal pasti sesuai bagi penjerapan warna. Penjerapan KOK dan warna pada KTF dan KTK adalah terbaik dihuraikan masing-masing oleh model kinetik pseudo tertib pertama dan model kinetik pseudo tertib kedua. Penjerapan KOK dan warna adalah terbaik dihuraikan oleh model kinetik pseudo tertib kedua untuk kes KTK.

DEVELOPMENT OF DURIAN PEEL ACTIVATED CARBON FOR THE REMOVAL OF COD AND COLOUR FROM LANDFILL LEACHATE

ABSTRACT

Leachate pollution has been a major problem in landfill management since discharging of it without proper treatment could cause hazard to aquatic life and human being. Leachate consists of various concentrated pollutants such as ammoniacal nitrogen, COD, colour and iron. Recently, a lot of works focuses on converting agricultural or tropical fruit wastes to activated carbon are actively done. In this work, activated carbon derived from durian peel (DP) wastes was activated through physical and chemical methods in batch adsorption system. Physical activation involves carbon dioxide (CO_2) gasification which was used to prepare the activated carbons. The experimental design results revealed that activation temperature and activation time were important factors influencing the activated carbon yield, and adsorption of COD and colour removal efficiency. The optimum conditions obtained for preparing the activated carbon (sample ACP) were 800 °C, 3 h and 150 ml/s, respectively for activation temperature, activation time and CO_2 flow rate, respectively. For chemical activation the important factors influencing the adsorption capacity were activation temperature and impregnation ratio. The optimum conditions obtained for preparing the activated carbon by chemical activation (sample ACC) were 533 °C, 2.45 h and 5.45, respectively for activation temperature, activation time and impregnation ratio. The activated carbons prepared were mesoporous with high mesopores surface area, mesopore volumes and average pore diameter larger than 2.2 nm. Scanning electron microscopy (SEM) analyses proved the activated carbons demonstrated homogeneous and heterogeneous type pore structure as well. Fourier Transform Infrared (FTIR) spectroscopy analyses revealed the presence of various functional groups on the activated carbon surfaces. The effects of initial pH, particle size, contact time and adsorbent dosage onto adsorption performance were evaluated through batch adsorption test. The COD adsorption uptakes increased with the increased in initial pH when the particle size was 1 mm for ACP and 0.425 mm for ACC. Particle size of 0.425 mm provides high colour removal (21.55-65.80%) for ACP and ACC. The optimum contact time for COD removal for ACP and ACC were found 8 and 7 h, respectively. For colour removal, 5 and 3 h required for ACP and ACC to achieve highest removal efficiency. For ACP, adsorption of COD and colour were best fitted by the Freundlich isotherm model whereas COD adsorption was fitted by the Freundlich. For ACC, the Langmuir model was found fit to colour adsorption. Adsorptions of COD and colour on ACP were best represented by the pseudo-first-order and pseudo-second-order kinetic models, respectively. Pseudo-second-order kinetic model was found fit the data well for both COD and colour adsorption for the case of ACC.

CHAPTER ONE

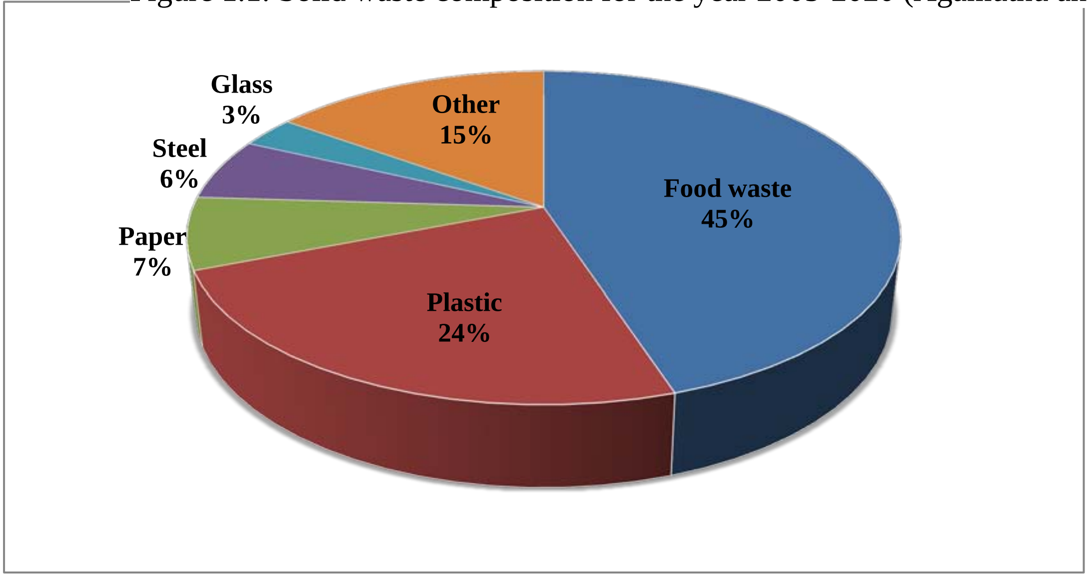
INTRODUCTION

1.0 Introduction

The solid waste generated in urban areas has been increasing year by year due to an increase in population, rapid economy growth, industrialisation and urbanization process. The modernisation process in Malaysia has created new landscape particularly in solid waste management in terms of technology applicability and management. The management of solid waste continues to be a major challenge because of the evolution of changes in solid waste generation (Manaf *et al.*, 2009). Rapid development and changing lifestyles have also changed waste composition from organic to plastics, paper, and packaging materials that are complex in nature (Idris *et al.*, 2004).

According to Department Statistical of Malaysia, the population growth in Malaysia is increasing 2.5 % every year. Malaysian waste generation has been increasing drastically where solid waste generation was estimated to increase from about 9.0 million tonnes in 2000 to about 10.9 million tonnes in 2010, to about 12.8 million tonnes in 2015 and finally to about 15.6 million tonnes in 2020. Malaysian e-waste was estimated to be about 652 909 tonnes in 2006 and was estimated to increase to about 706 000 tonnes in 2010 and finally to about 1.2 million tonnes in 2020 (Agamuthu and Victor, 2011). In fact, Malaysia solid waste contains a very high concentration of organic waste which is represented by the moisture content (Kathirvale *et al.*, 2004). Accordingly, the high density of solid waste which is represented 200 kg/m^3 proves that moisture content is high. Figure 1 shows the solid waste composition in Malaysia estimated from 2005- 2020.

Figure 1.1: Solid waste composition for the year 2005-2020 (Agamuthu and



Victor, 2011)

Solid waste management in Malaysia has been in practiced since the first act implemented under the Local Government Act 1976 which highlighted the requirement to provide systematic regulations for the waste disposal system and control by the local authorities under Section 73. Under this act, the local authority was regulated to provide directly or through contract, public cleansing services of equitable and acceptable quality to all urban and semi urban communities within its jurisdiction, and must dispose of all the waste collected in a sanitary manner (Manaf *et al.*, 2009). According to Statistical Department of Malaysia, in 2010, the number of solid waste landfill sites in operation are 176 and 114 have ceased their operations in the country.

At present, landfilling is the ultimate disposal method for municipal solid waste in Malaysia where most of the landfill sites are practicing open dumping system. With the increasing volume of solid waste generated, disposal of wastes through landfilling is becoming more difficult because existing landfill sites are filling up at very fast rate. This is followed by the current situation of land scarcity together with higher land price especially in urban areas. Therefore, local authorities have planned to provide recovery materials facilities before solid wastes being transferred to landfill sites to optimize the consumption of landfill sites where only organic materials can be dumped on the sites. However this effort has yet to be fully implemented since it needs proper planning with the integration of various agencies in order to provide the full use of recovery materials facilities. For many developing Asian cities, materials recovery and recycling are not normally carried out by the local authorities or landfill operators. However, the activities of scavengers or unauthorized waste pickers at landfill sites reduce the amount of recyclable items such as paper, plastics, glass and metals in the waste (Idris *et al.,* 2004).

The major potential environmental impacts associated with landfilling activites are leachate generation. The problems which may arise due to excessive leachate generation are pollution of groundwater and surface water. Numerous reports have been published regarding the hazard of the untreated leachate when flow into water bodies and groundwater since it contains a large amount of organic matter, heavy metals, chlorinated organic and inorganic salts, ammoniacal nitrogen and suspended solids (Wang *et al.,* 2002, Halim *et al.,* 2009a, Bashir *et al.,* 2009). Landfill leachate may be produced from precipitation, surface run-off, and infiltration or intrusion of groundwater percolating through a landfill (Wang *et al.,* 2002). It may be also excessively generated due to the overburden of tipping soil on the landfill site when daily cover has taken place.

Leachate quantity and quality dependent on several factors such as characteristics of deposited wastes, physio-chemical conditions, rainfall regime that regulates the moisture level and landfill age (Cotman and Gotvajn, 2010). The variable concentration and volume of leachate have made the treatment of leachate is a challenge to the scientist in order to meet the strict quality standard. Table 1 shows the total landfills in Malaysia

Table 1.1: Total landfills in Malaysia

State	Landfills in operation	Landfills which have ceased operation
Johor	13	21
Kedah	10	5
Kelantan	13	4
Melaka	2	5
Negeri Sembilan	8	10
Pahang	19	13
Perak	20	9
Perlis	1	1
Pulau Pinang	1	2
Sabah	21	1
Sarawak	51	12
Selangor	6	12
Terengganu	9	12
Wilayah Persekutuan Kuala Lumpur	1	7
Wilayah Persekutuan Labuan	1	0
Total	176	114

(Source: National Solid Waste Management Department, 2010)

1.1 Problem statement

Due to the high generation of leachate from landfilling activities, the possible of hazardous pollutants flow into the surface water is high and become one of the greatest problems to human being, aquatic life and surrounding. However, landfill operators are still facing difficult problem in finding suitable treatment method to overcome this problem. Although an effective advanced leachate treatment available operators seek alternatives because of their high capital costs and specialized management requirement (Tyrrel *et al.,* 2002). In Malaysia, local authorities are facing difficulty in finding the most economical and practical solution to overcome leachate pollution although some of the landfills occupied with leachate treatment facilities, the discharge of leachate still not following the minimal standard B discharge limit provided under the Department of Environment.

Activated carbon adsorption has been proven to be superior compared to other techniques in terms of its simplicity of design, high efficiency and ease of operation. It is recognized as the most efficient and promising fundamental approach in the waste water treatment processes (Daifullah *et al.*, 2004). The option of activated carbon to be utilized in water treatment is mainly due to its high adsorption capacity (Khaled *et al.*, 2009), and high surface area (Kalderis *et al.*, 2008). In recent years, many investigations have focused on activated carbon for the removal of pollutants in high strength waste water. Previous findings revealed that commercially activated carbon has successfully treated leachate for removal of several high concentrations of pollutants such as COD colour and NH_3-N. In the most cases, activated carbon adsorption is employed for removal of COD (Akta *et al.,* 2001, Kargi and Pamukoglu, 2003, Liyan *et al.*, 2009), colour (Aghamohammadi *et al.*, 2007) and NH_3-N (Aziz *et al.*, 2004a, Liyan *et al.*, 2009, Kurniawan *et al.*, 2006a).

However, little finding has been discussed regarding the production of activated carbon derived from biomass waste to be utilized in landfill leachate treatment. An economic sorbent is defined as one which is abundant in nature, or is a by-product or waste from agricultural residue, has little or no economic value and requires little processing (Tunc et *al.,* 2009). The conversion of this solid waste into activated carbon is most enviable. Agricultural residues, also called lignocellulosic biomass resources, are defined as a biomass by-product from the agricultural system. In this work, durian peel activated carbon was produced via physical and chemical activation. Durian peel is considered suitable to be converted to activated carbon due to its nature and structure demonstrated by the lignin existence which is the major contributor of activated carbon (Khedari *et al.,* 2004).

1.2 Research objectives

i) To prepare activated carbon from durian peel using physical and chemical activation using carbon dioxide (CO_2) gasification for physical activation and phosphoric acid (H_3PO_4) impregnation, respectively

ii) To study the optimum activated carbon preparation conditions for physical and chemical activation by using design of experiment.

iii) To characterize the activated carbon in terms of surface area, pore volume, pore size distribution, surface morphology, proximate content and surface chemistry.

iv) To study the effects of initial pH, particle size, contact time, and adsorbent dosage on the adsorption performance using batch adsorption test.

1.3 Organization of the thesis

The thesis consists of five chapters, where each chapter represents an important topic for general construction of the thesis.

Chapter one presents an overview of the current scenario on the solid waste generation in Malaysia. The solid waste composition that influences the amount of solid waste generation also included. Problem statement, objectives and the organization of the thesis are also highlighted.

Chapter two presents a literature review which covered the waste disposal by landfill and its impact to the environmental and health, followed by the literature review on three types of sanitary landfill. In addition, an overview of landfill decomposition process was also discussed in this chapter. Information of optimization of activated carbon preparation conditions are also discussed in detail. Adsorption performance of activated carbon in batch adsorption is included in this chapter. Next, of the adsorption isotherm and kinetic studies is also discussed in the chapter two. Lastly, concluding remarks from the literature review is given to draw a comprehensive understanding in achieving research objectives.

Chapter three presents list of materials and chemicals reagents used in the present research work. The experimental procedure consists of precursor preparation, experimental design for the activated carbon preparation, model fitting and statistical analysis, batch adsorption, adsorption isotherm and kinetics. It is followed with the schematic flow diagram showing the overall activities carried out in this research.

Chapter four presents the result from the experimental design used to prepare activated carbon, characterization and adsorption studies of the activated carbon prepared. Thus, this chapter is divided into three main sections. The first section presents the regression model equation developed, together with the optimization results based on the percentage removal for COD and colour as well as the activated carbon yield for each activated carbon prepared. Section two discusses on the characterization of the activated carbons prepared. Section three covers the batch adsorption studies of the activated carbons prepared.

Chapter five finally presents the conclusions that reflect the achievements of all the objectives which were obtained throughout the study as well as the recommendations for future research.

CHAPTER TWO

LITERATURE REVIEW

This chapter provides the background information regarding (i) waste disposal by landfill;(ii) sanitary landfilling; (iii) leachate characteristic; (iv) leachate treatment; (v) leachate treatment via activated carbon adsorption; (vi) activated carbon preparation; (vii) optimization of operating conditions for activated carbon preparation; (viii) adsorption isotherm and kinetics; (x) and concluding remarks from literature review.

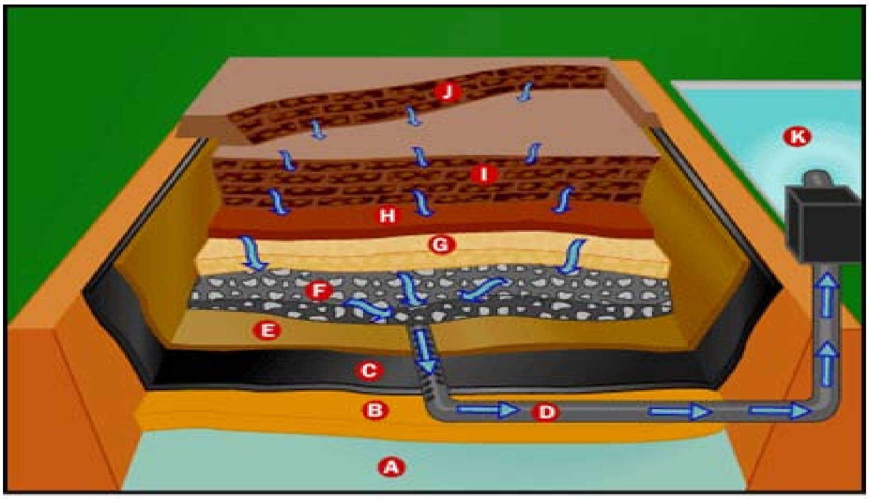
2.1 Waste Disposal by landfill and its impact

In general, landfill receives a mixture of municipal, commercial, and mixed industrial waste (Kjeldsen *et al.*, 2010). Solid waste also includes waste generated from institutional construction, and demolition processes (Ngoc and Schnitzer, 2009). The disposal of solid waste by landfilling method is the most common practice in most countries. It has received a lot of interests because of the economic advantages. Waste generation rates are affected by socioeconomic development, degree of industrialization, and climate. Generally, the greater the economic prosperity and the higher percentage of urban population, the greater the amount of solid waste produced. For example, China had an average annual population growth of 0.63% between 2000 and 2006. During this period, the average annual generation of non-industrial waste water increased by 6.4% and non-hazardous industrial solid wastes increased by 12.7% (Agamuthu *et al.*, 2009). In Thailand, the generated solid waste was approximately 40165 tons/day where 24% came from the Bangkok

Metropolitan Administration, 31% from municipalities, and 45% from rural areas (Idris *et al.,* 2004). While in Malaysia, the average municipal solid waste generated is between 0.5 – 0.8 kg/person/day and increased to 1.7 kg/person/day in major cities (Kathirvale *et al.* 2004). From 2000 – 2006, the population rate increases annually to 4.7%. The total solid was generated is equivalent to 8.33 million tonne per year. Manaf *et al.* (2009) in their study reveals that about 45% of the future waste is made up of food waste, 24% of plastic, 7% of paper, and 6% of iron and glass, with the balance made up of other materials.

All municipal solid wastes produced are disposed in landfills. There are four level of landfill available in Malaysia. There are; controlled dumping (level 1); sanitary landfill with daily cover (level 2); sanitary landfill with leachate circulation (level 3); and sanitary landfill with leachate treatment (level 4). In general, most of the landfills in Malaysia are practicing level 3. All the solid waste generated will be collected and transferred to the landfills for disposing purpose. However, some of the local municipal councils have provided transfer station service for recovering valuable materials by implemented segregation process before unwanted wastes transferred to the landfills. The purpose of landfill site is to stabilize the solid waste and make it hygienic through proper storage of waste and use of natural metabolic function. Since more municipal waste being transferred to the landfills, there are several issues and problems concerning the landfilling management system.

All landfill sites that receive solid waste for disposal have several requirements before operation takes place. Some of the specific requirements related to: location pre siting requirements (1), stability (2), and protection of soil and water through storm water control via leachate management and landfill gas management (3), and nuisances and hazards management (4). In general, the basic part of a landfill consists of bottom liner system which separates garbage and subsequent leachate from ground water; leachate collection and management system, road network, drainage system, and final capping system (Ariffin, 2006). The detail structures of a landfill is shown in the Figure 2.1 which explained by Freundrich (2000).



A	Ground water	G	Drainage layer
B	Compacted clay	H	Soil layer
C	Plastic liner	I	Old cells
D	Leachate collection pipe	J	New cells
E	Geotextile mat	K	Leachate pond
F	Gravel		

Figure 2.1: Landfill structures (Freundrich, 2000)

The major potential of hazardous environmental impacts are related to the landfilling operation. Improper tipping activities on the land fill enable water clogged creating breeding place for insects. This can bring dangerous diseases such as cholera and dengue fever to the workers and people surrounding landfill site. Besides, vectors such as rats and vermin are easily attracted to improper tipping of solid wastes. The odours emitted from landfilling activities also produce uneasy smell to the workers and people living near to the landfill site. Open burning activity on the landfill site also release several hazardous gas such as methane, sulphide and carbon monoxide that diminish air quality level surrounding the area.

2.2 Sanitary landfill

A sanitary landfill is a control method of solid waste disposal. The site must be geologically, hydrologically and environmentally suitable. In general there are 3 types of sanitary landfills that are commonly used in practicewhich are anaerobic landfill, semi-aerobic landfill and aerobic landfill.

2.2.1 Anaerobic landfill

An anaerobic landfill site is a dumping place for solid waste decomposition. This type of landfill contributes to the adverse environmental effects and health problems to human being as it produces toxic substances with high concentration of organic material. Other than that, this system produces methane gas and carbon dioxide in large quantities and cause global warming. In general, anaerobic landfill system receives waste and digged in area of plane field or valley. These wastes are then filled with water in anaerobic condition. Biodegradation occurs in the absence of oxygen (anaerobically) and produces landfill gas (Timothy, 2008). Figure 2.2 shows the structure of anaerobic landfill, anaerobic sanitary landfill and improved anaerobic sanitary landfill.

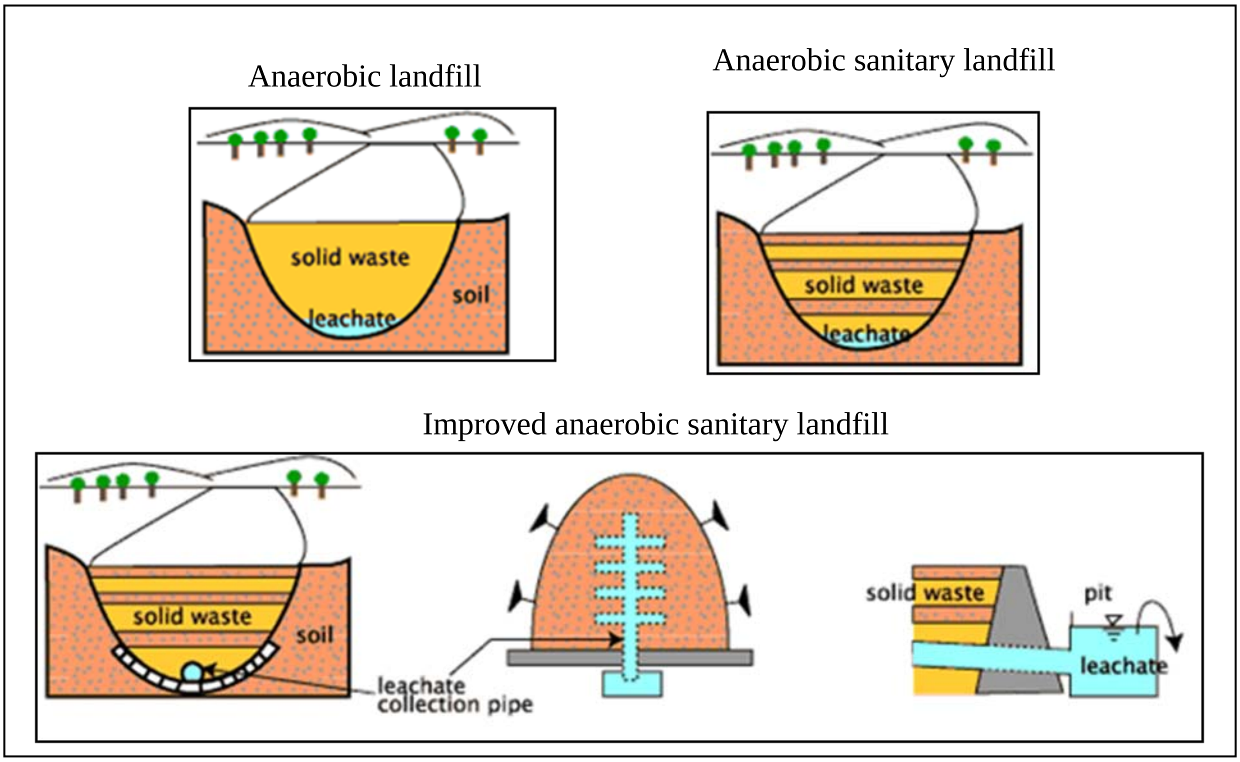


Figure 2.2: Anaerobic landfill structures (Matsufuji et al., 1993)

2.2.2 Semi-aerobic sanitary landfill

In semi-aerobic landfill system, a leachate collection pipe (perforated pipe) is provided at the bottom of the site covered with gravel. Leachate produced from landfilling will be channeled into the perforated pipe thus prevent the leachate from absorbed into the soil and remains in the layer. This also will prevent leachate from seeping into the original ground and retain leachate remaining in the solid waste layer and takes air into the solid waste layer through the collection pipe. It serves to purify leachate in the solid waste layer before collection (Shimaoka *et al.,* 2000). In addition to the perforated pipe, it also serves as the entry routes for the air from outside into the layer of solid waste in landfill sites. This also helps to enlarge aerobic parts and to make aerobic bacteria active and accelerates the rate of waste decomposition. Semi-aerobic system can be achieved through a convection process. The latter involves the decomposition of organic matter inside the landfill and will cause an increase in temperature. The difference in temperature between inside and outside of the landfill will generate a heat convection current into the landfill through the leachate pipe (Aziz *et al.*, 2004). Figures 2.3, 2.4 and 2.5 illustrate the structure of semi-aerobic sanitary landfill systems.

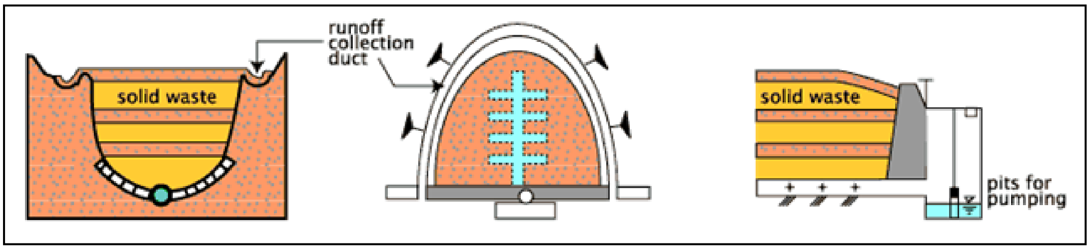


Figure 2.3: Semi-aerobic sanitary landfill structures (Matsufuji *et al.*, 1993)

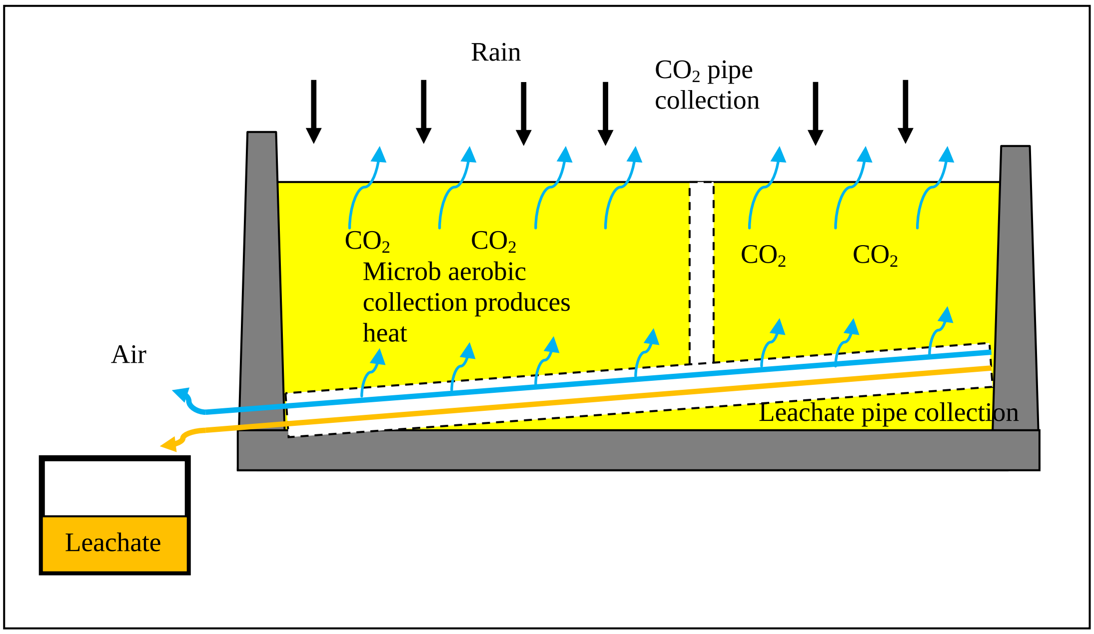


Figure 2.4: Semi-aerobic landfill system (Matsufuji *et al.*, 1993)

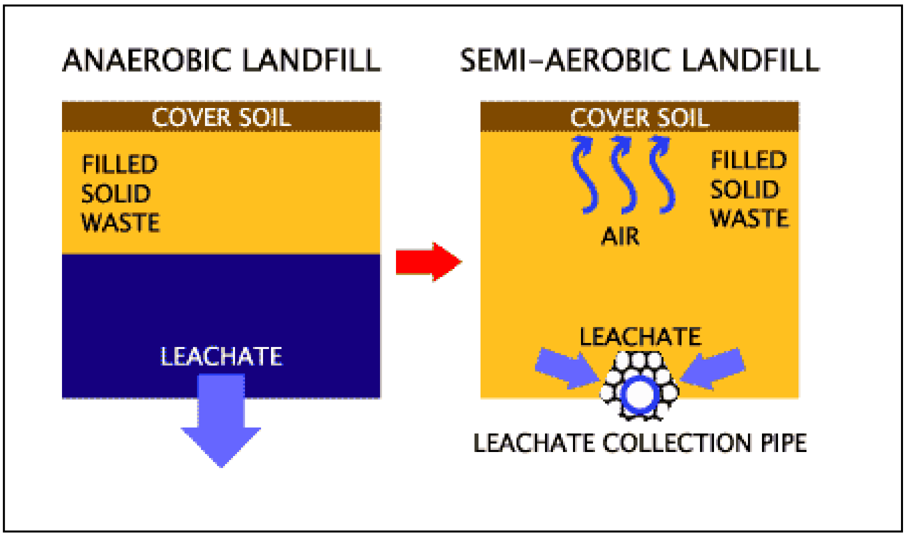


Figure 2.5: Different between anaerobic landfill and semi – aerobic sanitary landfill (Matsufuji *et al.*, 1993)

2.2.3 Aerobic Landfill

Aerobic landfill in general is equipped with perforated pipe for leachate collection at the bottom of the site. It is installed in such a way to allow the collection of leachate that produced from refuse, flowing out of the landfill site in short residence time. In addition, the aeration pipe is also installed underneath the soil bed for supplying air into the layer of solid waste. Leachate recycling is carried out in order to retain moisture and provides nutrients for the biodegradable process by microorganisms. This condition will help microorganisms to convert organic waste into biodegradable materials and humus. Leachate that produced from aerobic landfill can improve its quality, produces low methane gas and improve the stability of solid waste. Thus, the decomposition process become faster and prolongs the life of the landfill site (Shimaoka *et al.*, 1993). Figures 2.6 and 2.7 illustrate the aerobic landfill structures.

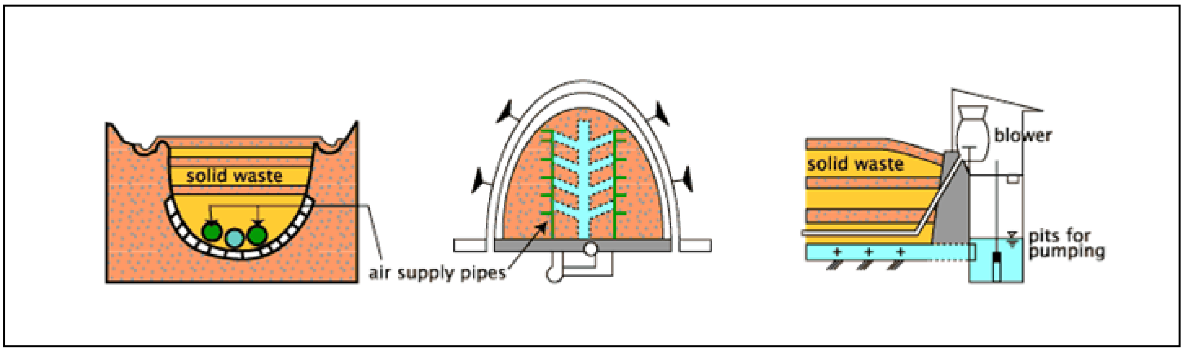


Figure 2.6: Aerobic landfill structures (Matsufuji *et al.*, 1993)

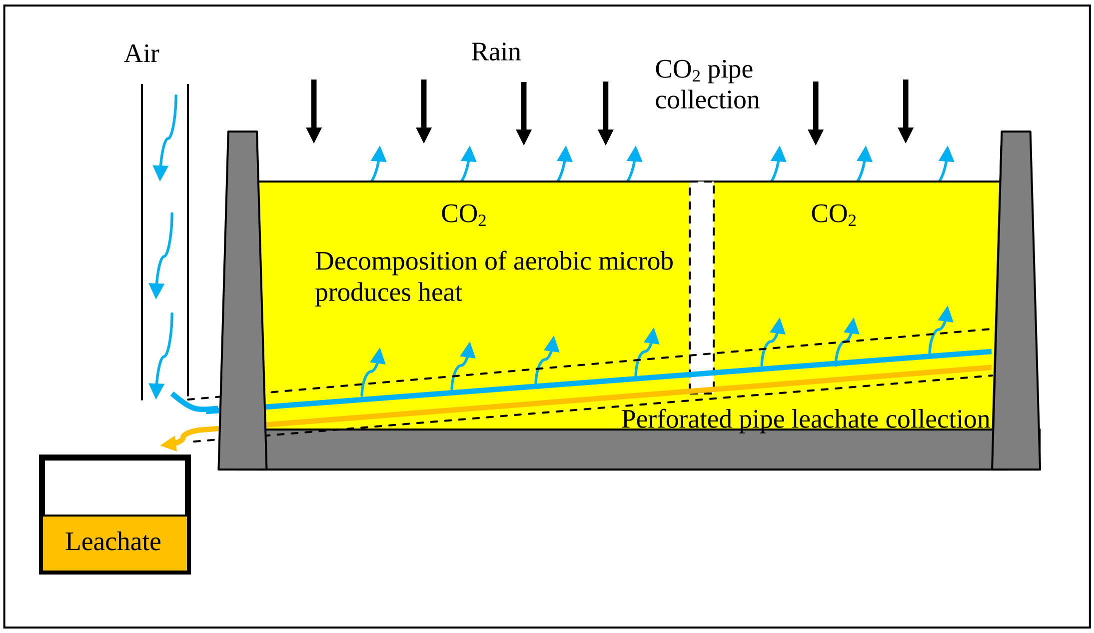


Figure 2.7: Aerobic landfill system (Matsufuji *et al.*, 1993)

2.3 Decomposition process in landfill site

Decomposition process of solid waste at the landfill site is complex and varies from one site to another. It depends on various factors such as composition of solid waste, landfill operations, weather, and hydrological conditions in the landfill site, seasonal changes, landfill site age, temperature, moisture content, and pH (Guo *et al.*, 2010, Visanthan *et al.*, 2003). Changes in the decomposition of solid waste are very important for the design, operation and control of leachate treatment plant.

When refuse is buried in a landfill, a complex series of biological and chemical reactions occurred as the refuse decomposes (Kjeldsen *et al.,* 2002). Decomposition process in landfill sites can be divided into five phases: aerobic phase, acidogenic phase, methanogenic phase and methane reduction phase. Characteristics and rates of waste generation as well as production of gas from the landfill site were different from each phase and is closely related to the microbiological response occur at each phase of the landfill site. Decomposition rates in each phase are dependent on physical factors, chemical and microbiology at the landfill site on time.

In general, once the tipping process of solid waste is completed, aerobic condition occurs where air pocket exists in the landfill decomposed the solid waste via aerobic biological processes. The second stage is transition phase. Transition occurs from aerobic to anaerobic phase where oxygen in the landfill site reduced or exhausted. Once the biodegradation of solid waste employed oxygen and no replacement of the free oxygen available, the tip becomes anaerobic (Crawford and Smith, 1985). Next, the acidogenic phase occurs where the complex organic materials in the tipped waste biodegraded into simpler organic materials which are typified by salts of acetic acid (CH_3COOH), propionic acid (C_2H_5COOH), pyruvic acid ($CH_3COCOOH$) or other simple organic acids (Crawford and Smith, 1985).

Next, fermentation or methanogenic phase occurs where methanogenic bacteria utilize the end products from the first stage of anaerobic decomposition and yield methane and carbon dioxide. It will occur under strictly anaerobic condition categorically exergonic (Deublein and Steinhauser, 2008). The final phase of solid waste is methane reduction phase where methane production rate will reach its maximum, and decrease thereafter as the pool of soluble substrate (carboxylic acids) decreases. In this phase, the rate of CH_4 production is dependent on the rate of cellulose and hemicelluloses hydrolysis (Kjeldsen *et al.*, 2002). The decomposition of solid waste in landfill site will be discussed further in the following section. Figure 2.8 shows the leachate characteristic during degradation of solid waste.

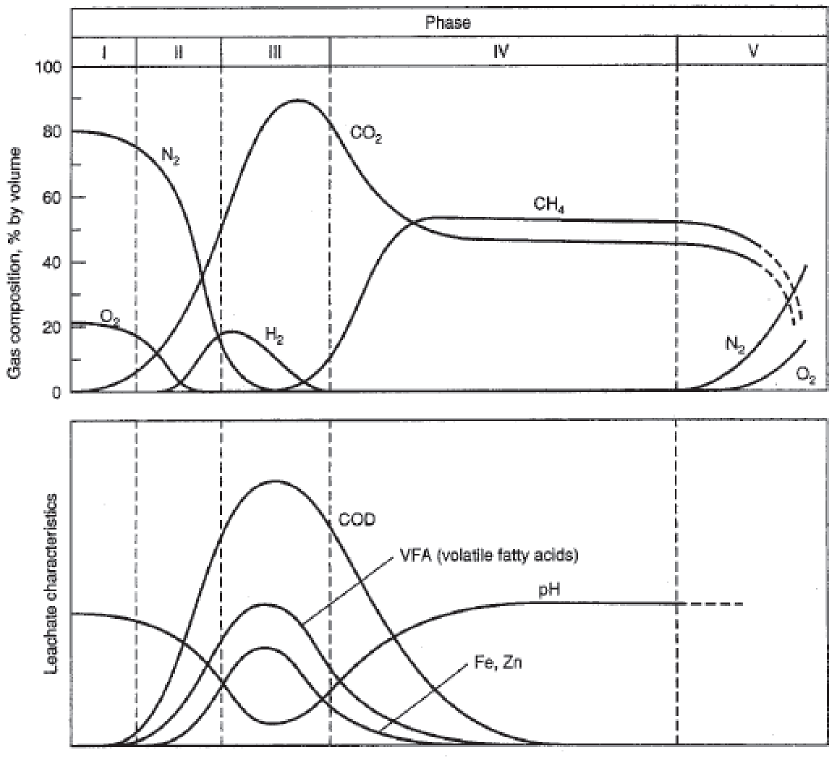


Figure 2.8: Leachate characteristic during degradation of solid waste (Daniel, 1993)

2.3.1 Aerobic phase

During the initial aerobic phase, oxygen present in the void spaces of the freshly buried refuse is rapidly consumed, resulting in the production of CO_2 and may increase in temperature (Kjeldsen *et al.*, 2002). Biodegradable organic materials react quickly with oxygen to form carbon dioxide, water, and other by-products (e.g.

bacterial cells). Carbon dioxide is produced in approximate molar equivalents to the oxygen consumed. Oxygen depletion marks the onset of anaerobic microbial processes, which persist much longer (Khoury *et al.*, 2000).

The only layer of landfill involved in aerobic metabolism is the upper layer where oxygen is trapped in fresh waste and supplied by diffusion of rainwater. Usually, the aerobic phase is quite short and no substantial leachate generation takes place (Jordening and Winter, 2005). The presence of oxygen and aerobic bacteria to decompose solid waste into soluble organic compound provide source of carbon for energy and nutrients It will facilitate the formation and propagation of new cells (Barlaz and Ham, 1993).

This stage, due to exothermicity of reactions of biological oxidation, may reach elevated temperatures if the waste is not compacted. In old landfills, when only the more refractory organic carbon remains in the landfilled wastes, a second aerobic phase will appear in the upper layer of the landfill (Chirstensen *et al.*, 1992). The heat generated from the exothermic degradation reaction can raise the temperature of the waste to up to 70 – 90 $^{\circ}$C (Hester and Harrison, 2002).

2.3.2 Anaerobic phase

Transition from aerobic to anaerobic phase takes from 6 to 18 months after the solid waste has been tipped off with top layer at the landfill site. Once oxygen supply is depleted or reduced, anaerobic phase started to develop. Biodegradation processes in anaerobic systems depend upon many variables including waste characteristics, moisture content, temperature, pH, the availability of nutrients and microbes, and the presence of inhibitors such as oxygen, metals, and sulfates (Khoury *et al.,* 2000).

At this stage, aerobic organisms in the reaction will be reduced whereas facultative bacteria and anaerobic bacteria become the primary decomposers. Anaerobic bacteria decompose the substance produced by aerobic bacteria to acetic acid, lactic acid, formic acid and alcohols such as methanol and ethanol. Most of the acid produced during this phase resulted in a decrease of pH in the leachate. At the end of this phase of the concentration of COD in the leachate will reduce from 18,000 mg/L to 480 mg / L and volatile organic acids (VOA) from 3000 mg/L to 100 mg/L. Ammonia is still being released and is not converted in the anaerobic environment (Chirstensen *et al.*, 1992).

2.3.3 Acidic phase

Bacteria do not flourish in dry condition. So the biodegradation starts only during when the landfill is moist (Crawford and Smith, 1985). Continuous process of hydrolysis solid waste, followed by microbiology changes of biodegradable organic matter can produce very high concentration of VOA, ammonia, hydrogen and CO_2 (Tchobanoglous *et al.,* 1993). In general pH continued to reduce in in this phase, resulting increase in acid concentration particularly in heavy metals such as chromium, manganese that dissolved in the leachate.

During this phase there is a wide range of bacteria and some anaerobic bacteria utilize the acids formed to preserve the stability of the environment by preventing the pH from reduced Fermenting bacteria convert the organic acids,