Conversion of landfill composite to activated carbon as an approach to sustainable landfill management

AbdulGaniyu Omobolaji Adelopo

A thesis submitted in partial fulfillment of the requirements
for the degree of Doctor of Philosophy

2017

Faculty of Health and Life Sciences
De Montfort University
Leicester

DEDICATION

This work is dedicated to the Glory of Almighty Allah (SWT) and all environmentally friendly entities all over the globe who are striving to ensure a safer and greener environment.

ABSTRACT

Landfilling of municipal solid waste is a major waste disposal method, especially in developing countries despite its pressing environmental challenges. Reuse of the landfill composite has been suggested as a sustainable management option that could limit its negative effect. This research evaluated the compositional trend and characteristics of landfill composites with depth in order to assess its suitability as a precursor for activated carbon. A bulk system classification was used during analysis of the composite parameters ('more degraded' and 'less degraded' components). Both landfills had similar waste constituents, but varied in relation to moisture, TOC, and heavy metals contents. The elemental and chemical constituents of an active and a closed landfill were compared using Fourier transform - infrared (FTIR) spectroscopy, scanning electron microscope/energy-dispersive X-ray (SEM/EDX) spectroscopy, and proximate analysis. The two landfills had similar major elemental constituents representing 96.5 % and 98.4 % of elemental composition for the closed ($O > C > Si > Fe > Ca > Al$) and active($C > O > Si > Al > Ca > Fe$) landfill samples respectively. A single step chemical activation process of precursor was applied involving irradiation with microwave energy and KOH as the activation agent. The average percentage yield of activated carbon (AC) from active landfill precursor was higher than that from closed landfill for all three depths of sampling (upper, 23.8 and 19.3 %; mid, 52.4 and 34.7 %; lower 35.7 and 27.0 %). Methylene blue adsorption capacity and BET surface analysis indicated adsorption capacity and surface area of AC from degraded precursor increased with depth. All AC conformed to a multilayer adsorption model and a pseudo second order kinetic. Carbonyl and hydroxyl groups were the major functional group on the surface of activated carbon. The AC properties indicated that precursors from both landfills are potentially suitable for generation of adsorbent suitable for removal of cationic dyes and pollutants.

ACKNOWLEDGEMENT

Firstly, I am grateful to Almighty Allah who kept His mercy on me throughout the sojourn of my PhD programme. This programme had been made successful despite all challenges, but for the support and warm advice of my ever ready and diligent supervisors who will stop at nothing in ensuring my success by providing constructive criticism and enabling environment for my research work. Profs Jenkins, Haris, Huddersman and Alo I am grateful for your professional impact in my life, you are one in a million supervisors.

I am also grateful to all staff in the Faculty of Health and Life science for their warm reception and assistant through the course of my research, especially: Dr T. George: EDX team, Rachel and Liz; my colleagues whom we shared a lot of research taught together, Pushpal, Emmanuel, Agogo; and my core environmental group, Mukthar, Shabbur and others.

My special gratitude to my mentors in the Chemistry Department, University of Lagos, for their encouragement and opportunity to facilities during this research work: Associate professor Lukman Adams, Dr Khalid , Dr Shuaib, Dr Olasupo and Mr Adelakun to mention a few. My research colleague: Ahmad, Kafayah . Also, my Head of Department, Dr E. A. Adeniran and my unit head Engr Nubi.

A special acknowledgement goes to my late parents: Alhaja and Alhaji I.A. Adelopo who strengthened me during the programme but could not witness its completion.

A special gratitude also goes to the entire family of Adelopo for their support and encouragement: Uncle Biodun, Owolabi, Taibah, Azeezah had rendered valuable support. My big brothers: Sulaimon and AbdulAzeez, my mentor and a pillar of support throughout my programme: Prof., Ismail Adelopo, our unique flower: Mrs Oyebanjo, my artificial twin: Abdulfatah.

I am grateful also to all my brothers and mentors who had impacted in this course positively, you are all wonderful but permit me to mention: Dr Kamil Omotoso and the UK team, Engrs. Faheed Olajide and Kamil kalejaiye, AbdulSabur, Al-Amin and Jamiu Salaudeen, all provided a wonderful support. Mr Sulaimon, Sanu and Istijaba provided positive counsel.

Lastly, a special thanks goes to my wife for the unwavering patience, endurance, understanding and editorial efforts during this research work, Mrs Nimot Adelopo, our daughters: Sumayyah, Maryam, Aasiyah, Fatimah,Asma and little prince Yusuf for their accommodation and sacrifice. I love you all and look forward to you taking up from here.

DECLARATION

I hereby declare that the work presented in this thesis is original work undertaken by me for the Doctor of Philosophy degree, at the School of Allied Health Science, Faculty of Health and Life Sciences, De Montfort University, Leicester, United Kingdom. All other material resources from other works are duly acknowledged.

Abdul Ganiyu Omobolaji Adelopo

PUBLICATIONS

Conference presentation

Adelopo, A.O., Haris, P.I., Alo, B., Huddersman, K. and Jenkins, R.O. (2016). Microwave acid digestion efficiency of landfill composites determined by ICP-MS analysis. 11th Annual Research Conference: Diversification in a Developing Economy. Lagos, Nigeria. November 2016

Adelopo A.O., Haris, P.I., Alo, B., Huddersman, K. and Jenkins, R.O. (2016). Comparative characterisation of closed and active landfill composites using spectroscopic and proximate techniques. 1st International Conference: Bioresource Technology for Bioenergy, Bioproducts & Environmental Sustainability. Sitges, Spain. October 2016, No.0610

Adelopo, A.O., Haris, P.I., Alo, B., Huddersman, K. and Jenkins, R.O. (2015). Seasonal variations in landfill moisture content with depth: active and closed landfills in Lagos, Nigeria. 3rd International Conference on Sustainable Solid Waste Management, TINOS Island, Greece. July 2015.

Published Paper

Adelopo,A.O., Haris, P.I., Alo, B., Huddersman, K. and Jenkins, R.O. (2017). Comparative Characterisation of Closed and Active Landfill Composites Using EDX, FTIR and Proximate Techniques. *Waste & Biomass Valorization*. 8:1313- 1323

Adelopo,A.O., Haris, P.I., Alo, B., Huddersman, K. and Jenkins, R.O. (2017). Seasonal variations in moisture content and the distribution of total organic carbon in landfill composites: case of active and closed landfills in Lagos, Nigeria. International Journal of Environment and Waste Management. (in press).

Table of Content

Dedication ii

Abstract iii

Acknowledgements iv

Declaration vi

Publications vii

Table of Contents viii

List of Tables xiv

List of Figures xvi

Abbreviations xviii

Chapter One Introduction and Literature Review 1

1.1 Municipal Solid Waste Generation 1

1.2 Solid Waste Classification 3

1.2.1 Approach to Waste Classification 3

1.3 Municipal Solid Waste (MSW) 4

1.3.1 MSW Composition 6

1.4 MSW Management Strategy 6

1.4.1 Management Hierarchy 6

1.4.2 Landfill Management 9

1.4.3 Type of Landfill 9

1.4.3.1 Dumpsite/Uncontrolled Landfill 11

1.4.3.2 Sanitary Landfill 11

1.5 Challenges of Landfill Management 12

1.5.1 Landfill Water Pollution 13
1.5.2 Air Pollution 14

1.6 Landfill Environmental Sustainability 16

1.7 Activated Carbon Precursor and Properties 18
1.7.1 Activation carbon chemistry 18
1.7.2 Surface chemistry 19
1.7.2.1 Structure of activated carbon 20
1.7.2.2 Porosity 21
1.7.2.3 Adsorption Isothermal of porous solid 22

1.7.3 Activation Process 25
1.7.3.1 Carbonization of carbonaceous raw material 25
1.7.3.2 Chemical activation 25
1.7.3.3 Physical activation 27
1.7.4 Raw material/precursor 27
1.7.5 Choice of activation heating system 28
1.7.6 Uses 29

1.8 Scope of the present study 30
1.8.1 Significance of Study 30
1.8.2 Research questions 31
1.8.3 Thesis layout 32

Chapter 2 General Features of the Sampling Area 34

2.1 Geological location of sampling area 34

2.2 Climatic condition 34

2.3 Population 35

2.4 Lagos State population and economy 36

2.5 Current MSW management practice in Lagos 37

2.6 Sampling location 39

2.6.1 Active landfill 39

2.6.2 Closed landfill 40

2.6.3 Anthropogenic activities around dumpsites 41

Chapter 3 Research Methodology 42

3.1 Introduction 42

3.2 Pre-sampling plan 43

3.2.1 Development of the project Data Quality Objectives(DQO) 43

3.2.2 Developing Standard Operating Procedure for Sampling 53

3.2.3 Pre Sampling Visit 53

3.3 Analytical Instrument 55

3.3.1 Inductively coupled plasma - mass spectrometry (ICPMS) 55

3.3.2 Microwave Digestion 57

3.3.3 Fourier transform-infrared (FTIR) spectroscopy 58

3.3.4 Scanning Electron Microscope/Energy Dispersive X-Ray Spectroscopy (SEM/EDX) 60

3.3.5 Ultraviolet /Visible Spectrophotometer 61

3.3.6 An Eltra CS800 Carbon Sulphur Determinator 62

3.3.7 BET surface area analyser 63

3.4 Sampling procedure 65

3.5 Summary 65

Chapter 4 Precursor characterization 66

4.1 Introduction 66

4.1.1 Compositional and Physical Characterization 66

4.1.2 Proximate analysis and Total Organic Carbon (TOC) 68

4.1.3 Heavy metals Concentration of precursors 68

4.1.4 Elemental content and surface morphology of precursor 69

4.1.5 Functionalities of the precursor 70

4.2 Methods 70

4.2.1 pH and temperature 70

4.2.2 Moisture content determination 70

4.2.3 Compositional characterization 71

4.2.4 Proximate Analysis 72

4.2.5 Total Organic Carbon (TOC) 73

4.2.5.1 Dry method 73

4.2.5.2 Walkley Blacky method 74

4.2.6 Heavy metals concentration in precursor 74

4.2.6.1 Precursor acid digestion 74

4.2.6.2 Determination of heavy metals content in digested samples using ICPMS 75

4.2.7 Elemental content and surface morphology of precursor 76

4.2.8 Functionalities of the precursors 77

4.2.9 Quality Control 77

4.2.9.1 pH 77

4.2.9.2 Heavy metal determination 78

4.2.9.2.1 Power calibration 78

4.2.9.2.2 Quality control samples 80

4.2.9.2.3 Spiked sample procedure 80

4.3 Result and discussion 80

4.3.1 pH values 80

4.3.2 Temperature 81

4.3.3 Moisture content 83

4.3.4 Composition 84

4.3.5 Total organic carbon (TOC) 84

4.3.6 Proximate analysis 90

4.3.7 Heavy metal concentrations 92
4.3.7.1 Quality control sample 92
4.3.7.2 Acid extraction effect 95
4.3.7.3 Availability of heavy metals 100
4.3.8 Elemental characterization 102
4.3.8.1 Cluster analysis for elemental constituents 106
4.3.9 Functionalities of the precursor 110
4.3.9.1 FTIR peaks common to both landfills 112
4.3.9.2 Differential FTIR peaks 113

4.4 Conclusions 114
4.4.1 Compositional and physical characterization 114
4.4.2 Proximate analysis and TOC 115
4.4.3 Heavy metals concentrations 115
4.4.4 Elemental composition 116
4.4.5 Functionalities of Precursors 116
4.5 Overall chapter conclusions 117

Chapter 5 Activation Process of Precursor 119

5.1 Introduction 119

5.2 Material and Method 125

5.2.1 Activation instrumentation 125
5.2.1.1 Conventional heating system 125
5.2.1.2 Instrumentation component 125

5.2.2 Microwave instrumentation 127
5.2.2.1 Microwave cavity design 127
5.2.2.2 Temperature measure device and gas flow design 131

5.3 Activation parameters 132
5.3.1 Conventional activation 132

5.3.2 Development of activation parameters for the microwave activation 135

5.4 Activation process 135
5.4.1 Conventional activation 137
5.4.2 Microwave activation 138
5.4.3 Comparing the activation processes 139
5.5 Result and discussion 139
5.5.1 Microwave activation 139
5.5.1.1 Activation conditions, % yield 139
5.5.1.2 Effect of irradiation power 141
5.5.1.3 Effect of activation reagent ratio 143
5.5.2 Conventional activation 144
5.6 Conclusion 146

Chapter 6 Activated Carbon Characterization 148

6.1 Introduction 148

6.2 Methods 148
6.2.1 Surface morphology 148
6.2.2 Adsorption studies 148
6.2.3 Surface area characterization 150
6.2.4 Functionalities of AC 151

6.3 Result and Discussion 151
6.3.1 Scanning electron microscopy (SEM) 151
6.3.2 Adsorption studies 153
6.3.2.1 Effect of adsorbent quantity 153
6.3.2.2 Adsorption capacity with depth of sampling 154
6.3.2.3 Temperature effect on adsorption 157
6.3.2.4 pH effect on adsorption 159
6.3.2.5 Adsorption equilibrium isotherms 161

6.3.2.6 Adsorption dynamics 166
6.3.3 BET surface analysis 170
6.3.4 Functionalities of AC 174
6.4 Conclusion 177

Chapter 7 Conclusion and Recommendation 178

7.1 Conclusions 178

7.2 Contribution to Knowledge 183

7.3 Limitation of research 184

7.4 Recommendations for future research 184

List of Table

Table 1.1 Municipal waste definition by international organization 5

Table 1.2 Categorization of landfill based available sustainable technology 10

Table 1.3 Pore Sizes of Activated Carbon 21

Table 3.1 Heavy metals and regulatory limits as set by the USEPA 47

Table 4.1 Power calibration of the Microwave digester 79

Table 4.2 Comparison of measured parameters for active and closed landfills 82

Table 4.3 Regression analysis of waste parameters for both landfills 84

Table 4.4 Composition (%) of samples with depth for both landfills 86

Table 4.5 Comparing the average proximate composition of samples from both landfills 91

Table 4.6 Detection limit using Aqua regia and HNO_3 92

Table 4.7 Duplicate studies of samples using Aqua regia and HNO_3 93

Table 4.8 Recovery studies of samples 94

Table 4.9 Certified reference sample 94

Table 4.10 Toxic metals concentrations of closed landfill samples using aqua regia 96

Table 4.11 Toxic metals concentrations of closed landfill using HNO_3 acid 97

Table 4.12 Toxic metals concentrations (mg/l) of active landfill samples using Aqua regia 98

Table 4.13 Toxic metals concentrations of active landfill using HNO_3 acid 99

Table 4.14 Comparison of the average concentrations (mg/l) of toxic metals of Samples from Active and Closed landfills to the Flemish Regulations Limit and the USPEA Toxic Metal Standards 101

Table 4.15 Descriptive analysis of the elemental constituents of closed landfill samples in each layer (w/w %) 104
Table 4.16 Descriptive analysis of the elemental constituents of active landfill samples in each layer (w/w %) 105
Table 4.17 Discrimination capacities of elemental components in the detected clusters of closed and active landfills samples 110
Table 5:1 Literature review of some activation optimum conditions 120
Table 5.2 The activations methods and the choice of precursor 122
Table 5.3 Preliminary run of samples and inference made in respect to activation parameters 128
Table 5.4 The activated carbon reproducibility with depth 140
Table 5.5 Percentage yield of AC with variations in irradiation power and impregnation ratio 142
Table 5.6 Percentage yield of AC and activation condition for the conventional Activation 145
Table 6.1 Comparison of the maximum adsorption capacities of MB onto different biogenic waste adsorbents 156
Table 6.2: ANOVAs analysis of adsorption capacity at different temperatures 159
Table 6.3 Comparing the Langmuir and Freundlich model parameters of AC 164
Table 6.4 Comparing the first and second order parameters 168
Table 6.5 BET Surface area and pore surface area 170

List of Figures

Figure 1.1 Per capita waste generation of some cities 2

Figure 1.2 Hierarchically Waste Management System 7

Figure 1.3 Municipal Solid Waste treatment report of EU states 8

Figure 1.4 Effects of uncontrolled landfill on man 16

Figure 1.5 The structure of activated carbon showing the functional group & the pH effect 20

Figure 1.6 The crystalline structure of graphitizable and non graphitizable carbon 20

Figure 1.7 Types of Adsorption Isothermal by IUPAC 23

Figure 1.8 Types of Hysteresis loop by IUPAC 24

Figure 2.1 Nigeria Map showing the location of Lagos State 36

Figure 2.2 Compactor truck used for waste disposal in Lagos state 38

Figure 2.3 Locations of active and closed landfills within Lagos State 39

Figure 2.4 Show Olushosun landfill with relation to landmarks 41

Figure 3.1 Area having sorted recyclable waste on the active landfill 54

Figure 3.2 Fresh organic waste in the closed landfill 55

Figure 3.3 Inductively coupled plasma spectrometer 57

Figures 3.4: CEM, microwave digestion MARX press USA 58

Figure 3.5 Alpha Fourier transform-infrared (FTIR) spectrometer 59

Figure 3.6: Carl Zeiss EVO HD 18 SEM and Oxford EDX 60

Figure 3.7: G120845 Thermo Electron Helios Gamma Spectrophotometer 62

Figure 3.8 Eltra CS800 Carbon Sulphur Determinator 63

Figure 3.9 Micromeritics Gemini 2365 64

Figure 4.1 Chart showing sample classification into components 72

Figure 4.2 Average distribution of types waste in the closed and active landfills samples 84

Figure 4.3 Correlation studies between moisture content and TOC 89

Figure 4.4 Dendrogram showing similarity in the closed landfill samples based on elemental composition data 108

Figure 4.5 Dendrogram showing similarity in the active landfill samples based on elemental composition data 109

Figure 4.6 Typical infrared spectra of (a) active landfill, (b) fresh municipal waste, and (c) closed landfill samples 111

Figure 5.1 Flow chart of the activation process 121

Figure 5.2 Schematic diagram of the convectional activation instrumentation 125

Figures 5.3 Showing major instrument using in conventional activation process 126

Figure 5.4 Reactor cavity design 129

Figure 5.5 Generation of hot spot using different sample holder. 130

Figure 5.6 Microwave instrumental set up 132

Figure 6.1 SEM image of precursors and of activated carbon 152

Figure 6.2 Effect of concentration of adsorbent on methylene blue and adsorption capacity of absorbent 154

Figure 6.3 Effect of temperature on the uptake of MB (methylene blue) 158

Figure 6.4: Effect of pH on the adsorption capacity of AC 160

Figure 6.5: Langmuir plots for the adsorption of methylene blue onto the activated carbons 163

Figure 6.6: Freundlich plots for the adsorption of methylene blue onto the activated carbons 165

Figures 6.7: Shows the AC adsorption effect at equilibrium 166

Figure 6.8: second order kinetic for the adsorption of methylene blue onto ACs 169

Figure 6.9: Pore size distributions of the activated carbon. 171

Figure 6.10: Nitrogen isotherms adsorption of the AC 173

Figure 6.11: Typical spectra of AC and precursor 176

ABBREVIATIONS

AC	Activated carbon
ASTM	American Society for Testing and materials
BET model	Brunauer, Emmet and Teller model
BJH model	Barrett, Joyner and Halenda model
DEFRA	Department of Environment, Food and Rural Affairs
DQO	Data Quality Objectives
EAP	Eastern Partner Countries
EDX	Energy Dispersive X ray spectroscope
EPA	Environmental protection Agency
FTIR	Fourier Transform - Infrared spectroscope
GHG	Green House Gas
GPS	Global Positioning System
ICP-MS	Inductively Coupled Plasma – Mass Spectrometry
ICP-OES	Inductive Coupled Plasma Optical Emission Spectrometry
IEA	International Energy Agency

IPCC	Intergovernmental Panel on Climate Change
IUPAC	International Union of Pure and Applied Chemistry
LAWMA	Lagos Waste Management Authority
LD	Less Degraded
LFG	Landfill Gas
MB	Methylene Blue
MD	More Degraded
MSW	Municipal Solid Waste
OECD	Organization of Economic Co-operation and Development countries
PAHO	Pan American Health Organization
RCRA	Resource Conversation and Recovery Act
SEM	Scanning Electron Microscope
STP	Standard Temperature and Pressure
TCLP	Toxicity Characteristic Leaching Procedure
TOC	Total Organic Carbon
USEPA	United State Environmental Protection Agency
WHO	World Health Organization

CHAPTER ONE

INTRODUCTION AND LITERATURE REVIEW

1.1 Municipal Solid Waste Generation

Solid Waste generation is an inevitable part of man's activities as a result of his interaction with the biotic and abiotic factors within the environment. Municipal Solid Waste (MSW) generation continues to grow both in per capita and overall terms. This increase is due largely to accelerated industrialization, urbanization, population growth and affluent life styles (Renou *et al.,* 2008).

An estimated global growth rate of 7 % in MSW generation was reported between 2003 and 2006. The current global MSW generation level of approximately 1.3 billion tons per year is expected to double by 2025 (Hoornweg and Bhada-Tata, 2012, UNEP, 2009). Per capita waste generation were significantly higher in regions and countries with dense population and increased industrialization (Hoornweg and Bhada-Tata, 2012, Kawai and Tasaki, 2016). The Organization for Economic Co-operation and Development countries (OECD) and Eastern Partner countries (EAP) constitute more than 60 % of the waste generated globally, with average per capita waste generation of 2.2 kg/capita/day. Urban waste generation was found to have influenced this growth rate trend. Urban collected MSW quantities are estimated at 1200 million tons in 2013 and it is expected to reach 2,650 million tons in 2050. This represents a 97 % increase in urban MSW generated by 2050 (IEA, 2016).

Major city centers of the world have a huge waste generation burden due to increasing economic activities attracting the residence of affluent members of the society. Beijing, Tokyo, New Delhi, Rio de Janeiro contributed large proportions of their countries per capita waste generation. Figure 1.1 present the per capita generation of some cities

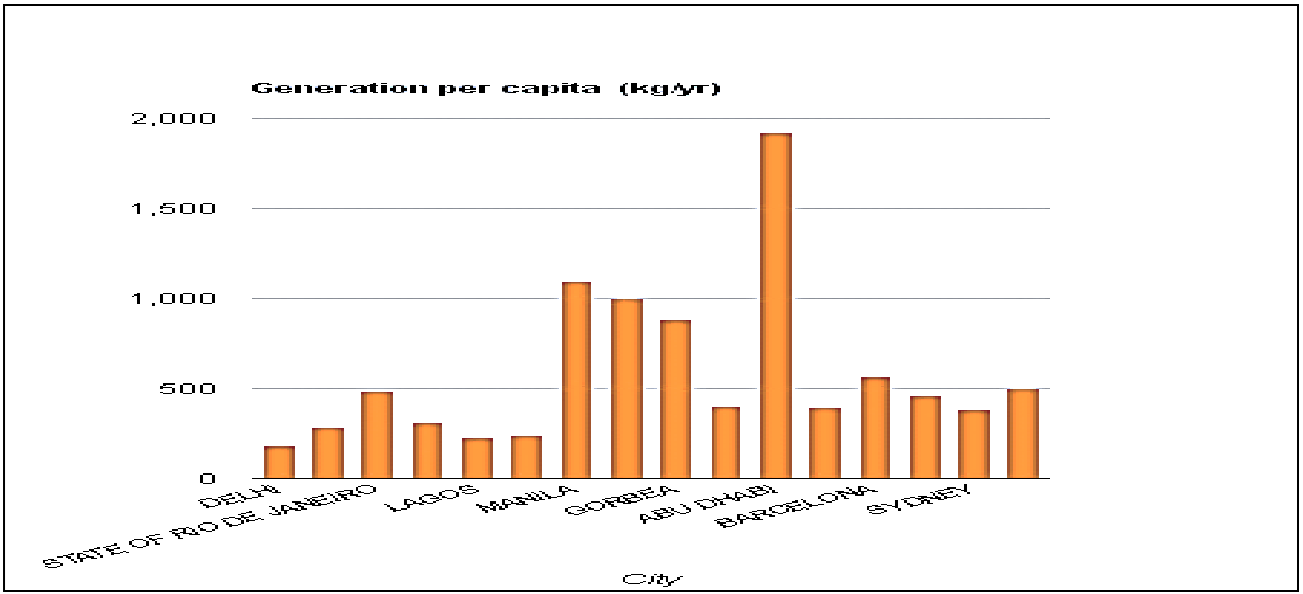


Figure 1.1: 2015 per capita waste generation of some cities (source from International Environmental Agency data base)

Irwan et al. (2011) reported that large population households in Malaysia generated less waste compared to small population households of higher economic standing. In 1997, waste generation in Rio de Janeiro, Brazil was 8042 tons/day compared to 6200 tons /day in 1994, despite the fact that population growth during that period was practically zero (Renou *et al.*, 2008). Urban residents produce about twice as much waste as their rural counterparts (Hoornweg and Bhada-Tata, 2012). Municipal waste generation is influenced by multivariance factors depending on prevailing conditions within an area (Medina, 1999).

Municipal solid waste identification and classification are tools to understanding the underlining generation factors.

1.2 Solid waste classification

1.2.1 Approach to waste classification

Waste classification is influenced by the origin, nature, properties and activities generating waste. Waste has been classified based on the United Nations Organization indexes for all economic activities; the international standard industrial classification (ISIC) (UN, 1971). The ISIC is based on the rationale of classifying economic activities beginning from the general and, from here, narrowing down to higher levels of specific. Waste generation has been investigated based on this classification in developing a model to predict waste reduction target for economic class (Sjöström and Östblom, 2010)

Classification of waste by origin of generation may generally address a heterogeneous stream of waste. Municipal waste, agricultural, mining waste, construction and demolition are waste classifications focused on the area where waste is generated. Most often, waste composition may vary widely based on peculiarity of the origin of waste. For example, agricultural waste will include heterogeneous stream of materials like raw and processed foods, manure and fertilizers, machineries and tools, pesticide other materials used in the agricultural process.

Wastes are also grouped based on different intrinsic properties of the waste. Waste can be grouped based on: toxicity, hazardous and non- hazardous; degradability, degradable/ non degradable; and moisture content, dry or wet.

1.3 Municipal Solid Waste (MSW)

Municipal solid waste (MSW) is a complex solid waste stream, consisting of different classes of waste generated from diverse activities. (Hoornweg and Bhada-Tata, 2012). Municipal wastes are solid waste collected by municipalities or local authorities with properties of a household waste (EU 1999).

Municipal wastes have been defined based on the strategic policy and goals of agencies and governmental institutions, although most definitions underline the similarity in the waste generation source: municipal and household waste (see Table 1.1). The MSW waste generation patterns depends on the distribution of activities within the area (Sjöström and Östblom, 2010). A hierarchical source classification of MSW has established connection between the source of waste and the type of waste generated in the municipal (Buenrostro *et al.*, 2001). An IPCC report in 2006 highlighted three main sources of municipal waste: household waste; garden (yard) and park waste; and commercial/institutional waste. The MSW waste generation patterns and composition will depend on the distribution and volume of activities within the area.

Definition of MSW
EU Directive (1999): “waste from household, as well as other waste which, because of its nature or composition, similar to waste from household"
IPCC (2006): “waste collected by municipalities or other local authorities, include household waste. garden yard and park waste, and commercial Institutional waste"
Gol (2008): "waste from household and household-like waste derives from commercial area, industrial areas, special areas, social facilities. public facilities, and/or other facilities"
PAHO (2010): “solid or semi-solid waste produced through the general activities of a population center_ includes waste from households. Commercial businesses, services, and institutions, as well as common (non-hazardous) hospital waste, waste from industrial offices, waste collected through street sweeping. and the trimmings of plants and trees along streets and in plazas and public green spaces"
OECD (2013): 'materials that are not prime products that is, products produced for the market) for which the generator has no further use in terms of his/her own purposes of production, transformation or consumption, and of which he/she wants to dispose"

Table 1.1: Municipal waste definition by international organization (source: Munawar, 2014)

1.3.1 MSW composition

The MSW waste composition mainly reflects the climatic condition, culture norm, economic development, lifestyle, geographic, and local legislation within the generation locality (Irwan et al.2011; AbdAlqader and Hamad, 2012; Hoornweg and Bhada-Tata, 2012). Classification of the MSW composition is often influenced by the management strategy intended for the waste. For example, the UK Environmental Agency has classified MSW into 44 categories in evaluating collection and management procedures (EA, 2015), while the inter-governmental committee on climate change (IPCC 2006) has identified 11 classes of MSW in evaluating the green gas generation potentials. Amijo de vega et al. (2008) identified MSW characterization as the first step to any successful waste management strategy, in order to: estimate material recovery potential; determine sources and component of generated waste; identify processing machineries; determine physico-chemical and thermal properties of the wastes; and to maintain compliance with regulations.

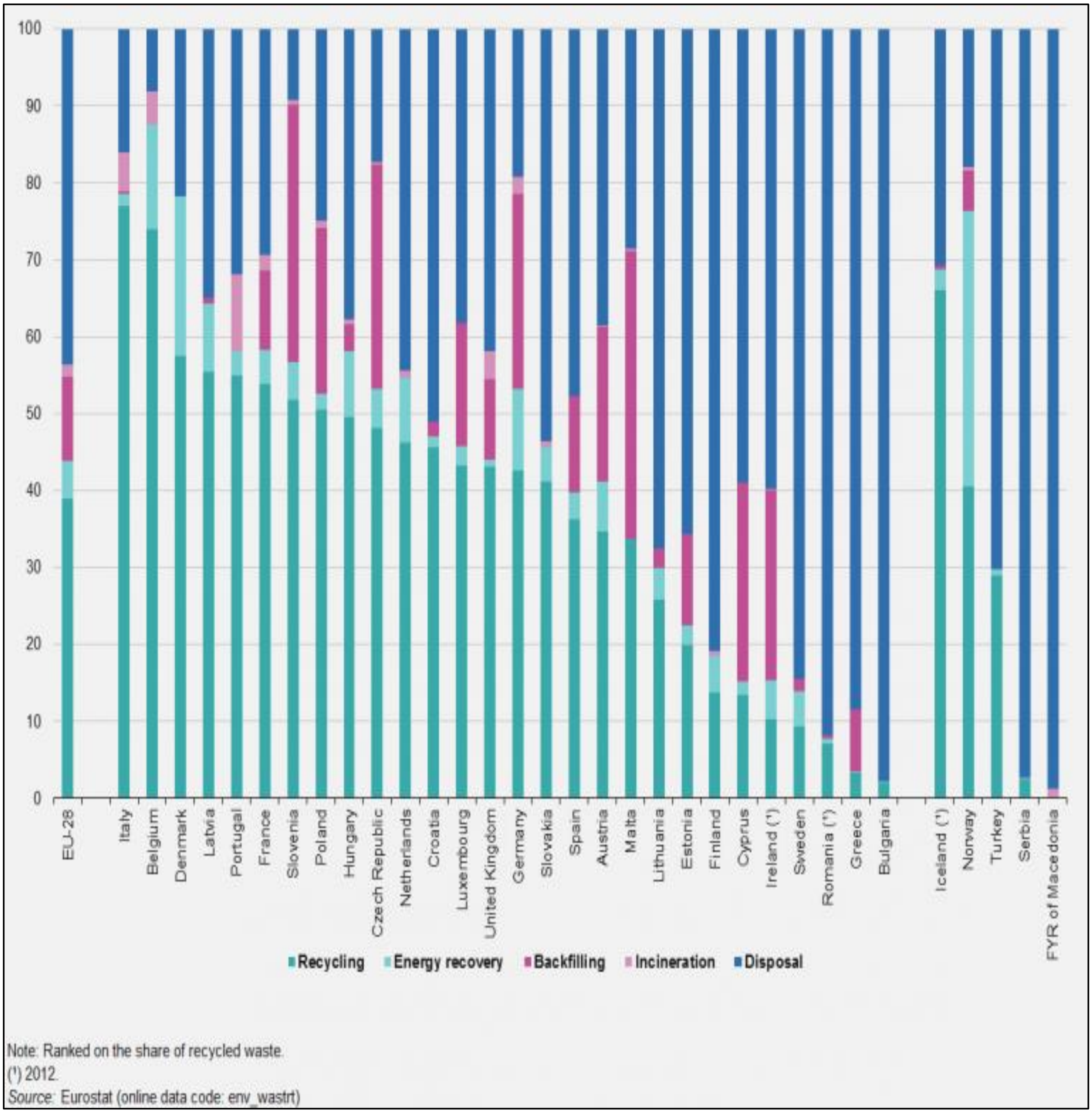
1.4 MSW management strategy

1.4.1 Management hierarchy

The integrated solid waste management principle has identified five distinct steps for effective MSW management. The waste management pyramid presented in Figures 1.2 shows management options in order of preference and environmental friendliness.

Figure 1.2: Hierarchically Waste Management System

In reality, there is no single treatment system which is generally appropriate to solving the ever-growing MSW disposal problems. A combination of all the methods is required to have balance waste management strategy which can effectively management all classes of MSW composition (Menikpura *et al.,* 2013). This is referred as the integrated Solid Waste Management System (ISWM). The EU's Waste Framework Directive (EU, 2008) and Landfill Directive (EU, 1999) set binding targets aimed at increasing waste prevention, recycling and discouraging landfilling for members countries based on its hierarchical solid waste management system. The cross-country report on the EU's Waste Framework Directive (EU, 2008), which analyzed the municipal solid waste management in 32 European countries, showed that recycling grew with over 0.9 billion of tons of recycled waste but about half of the total waste (2.5 billion tons) still been landfilled for twenty-one member countries between 2001- 2012. Figures 1.3 present the performance of each waste management system.



Note: Ranked on the share of recycled waste.
(¹) 2012.
Source: Eurostat (online data code: env_wastrt)

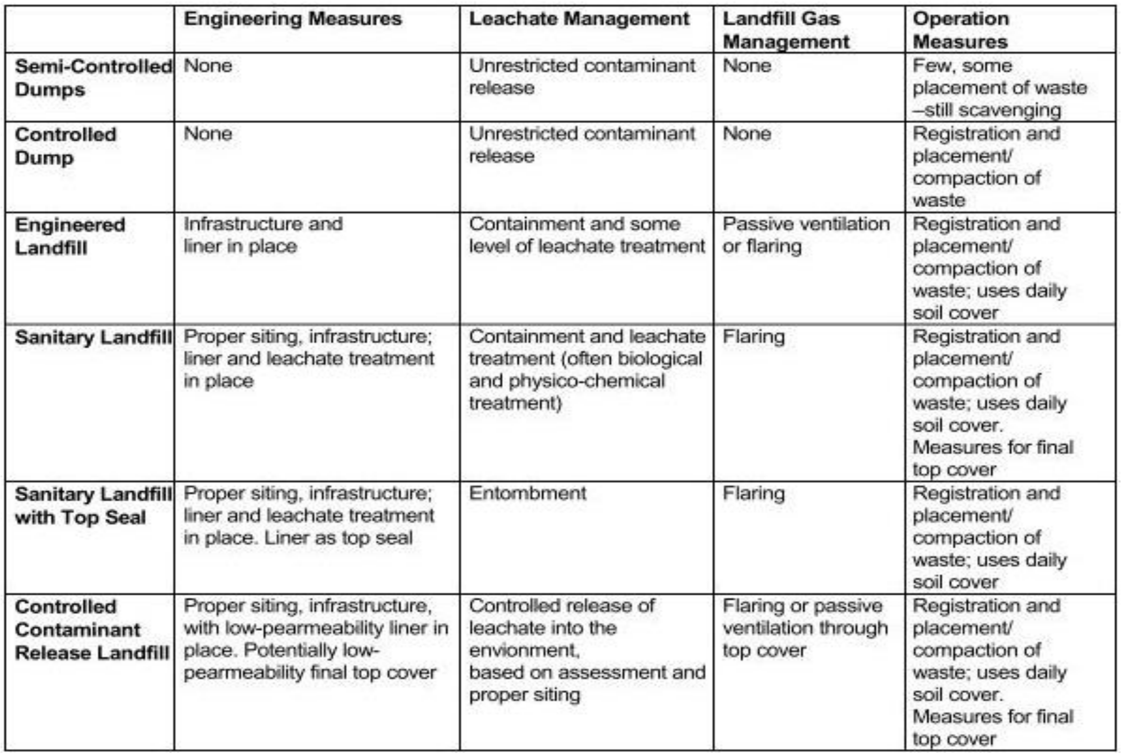
Figure 1.3: Municipal Solid Waste treatment report of EU states (Eurostat), Disposal: landfilled waste.

1.4.2 Landfill management

Landfill is the final waste disposal site, where MSW is disposed into or onto the land (DEFRA, 2010). A municipal solid waste landfill (MSWLF) is a discrete area of land or excavation site that receives household waste or other types of non-hazardous wastes such as commercial solid waste. It acts as a final sink, a long-term geological deposit which closes the material loop (Cossu, 2012). Landfill is one of the most widely employed methods for the disposal of municipal solid waste (Yang *et al.*, 2013). There are hundreds of thousands of active, closed, and abandoned landfills worldwide, with nearly 100,000 in the U.S. and more than 150,000 in Europe (Jain *et al.*, 2014, Friedrich and Trois, 2013). In Ireland, landfill accepts over two million tons of waste per year from household, commercial and industrial wastes (EA, 2015). Landfill represents the major means of waste management in sub-Sahara Africa. Most countries in Africa practiced open dumping for final disposal of solid waste (Johannessen and Boyer, 1997). The main reasons for wide used of landfill practice are due to the low cost and simplicity in handling the MSW, particularly in less developed countries (Munawar, 2014).

1.4.3 Type of landfill

Landfill is classified based on the management practice on the landfill or types of waste disposed on the landfill. For example, the EU waste directive frame work 1999/31/EC classified landfill based on the nature of waste disposed in the landfill (EU, 1999): i) hazardous landfill (for disposal of reactive, corrosive, toxic, waste); ii) non-hazardous landfill, (for disposal of MSW, non-corrosive bottom ash, and industrial waste); iii) and inert landfill (for disposal of inert construction & demolition material, soil and other inert material). Landfill can be broadly classified into controlled and uncontrolled, based on the management system employed in the day to day running of the landfill (Themelis and Priscilla, 2007). WHO’s evaluation of landfill practice had grouped landfill based on availability of pollution control management facilities. This includes the incorporation of technology to ensure collection and control of landfill gas, leachate collection and treatment, application of a daily soil cover on waste, and implementation of plans for closure and after closure care. Table1.2 present types of landfill based on these criteria.



	Engineering Measures	Leachate Management	Landfill Gas Management	Operation Measures
Semi-Controlled Dumps	None	Unrestricted contaminant release	None	Few, some placement of waste –still scavenging
Controlled Dump	None	Unrestricted contaminant release	None	Registration and placement/ compaction of waste
Engineered Landfill	Infrastructure and liner in place	Containment and some level of leachate treatment	Passive ventilation or flaring	Registration and placement/ compaction of waste; uses daily soil cover
Sanitary Landfill	Proper siting, infrastructure; liner and leachate treatment in place	Containment and leachate treatment (often biological and physico-chemical treatment)	Flaring	Registration and placement/ compaction of waste; uses daily soil cover. Measures for final top cover
Sanitary Landfill with Top Seal	Proper siting, infrastructure; liner and leachate treatment in place. Liner as top seal	Entombment	Flaring	Registration and placement/ compaction of waste; uses daily soil cover
Controlled Contaminant Release Landfill	Proper siting, infrastructure, with low-pearmeability liner in place. Potentially low-pearmeability final top cover	Controlled release of leachate into the envionment, based on assessment and proper siting	Flaring or passive ventilation through top cover	Registration and placement/ compaction of waste; uses daily soil cover. Measures for final top cover

Table 1.2: Categorization of landfill based on availability of sustainable technology (source: Johannessen and Boyer, 1997)

1.4.3.1 Dumpsite/uncontrolled landfill

The open dumping of solid waste is the primitive stage of waste management which still remains the predominant waste disposal option in most of the developing countries. Open dumps involves indiscriminate disposal of solid waste in an area with no measures to control operations, including those related to the environmental effects of the dumpsite. MSW is deposited until it reaches a height considered undesirable based on esthetic reasons (Themelis and Priscilla, 2007). The dumpsite sites are often maintained through indiscriminate burning to reduce the volume of waste. There are no boundaries to mass transfer in form of gas, liquid and solid from the dumpsite to the environment posing major environmental and health challenges to the immediate environment. The relevance of dumpsite in low income countries may be associated to the ease associated with establishment of dumpsite, the proximity to user and no technical requirement of the practice.

1.4.3.2 Sanitary landfill

The term sanitary landfill is generally used for landfill management facility which has incorporated management scheme to curtail negative health and environmental effect of landfilled waste (Youcai and Ziyang, 2017). The concept started in 1959 with the use of waste compaction and application of soil cover to increase aesthetic and safety of landfill. In many cases, however, as much as 50 % of the operational budget is consumed on daily cover (Johannessen and Boyer, 1997).The concept as now developed into the incorporation of engineering process which focuses on the management of different potential landfill hazards.

The leachate collection and treatment plant, gas collection and flaring or reuse mechanism, impermeable baseliner and top covering and sites access control measures are essential features in a modern sanitary landfill. An evaluation carried out in 2010 by the WHO showed only a few sanitary landfills can be found in Asia, Latin America and Africa, while most of existing sanitary landfill lack one major infrastructure or the other. Deficiency in any of the required facility may pose treat to the environment. In the US and EU, resident time of wastes in sanitary landfills is been accelerated with use of bioreactors within sanitary landfills systems. The bioreactor is able to accelerate decomposition of disposed waste through the introduction of leachate recycling and addition of appropriate microbe.

1.5 Challenges of landfill management.

Landfilling may provide an initial economical means of waste disposal, but effective management of possible hazards emanating from this process is a major challenge, casting doubt on the sustainability of the method. The major environmental challenges associated with the management of landfills are the surface and ground water contamination, land contamination, generation of greenhouse gas (GHG) and odor emissions (Bolan *et al.*, 2013).

The inherent challenges persist over the period of operations and closure of the landfill site. It impacts on the quality of the environment and public health of the immediate surroundings of the landfill site. The process of waste degradation and leachate formation within the landfill are major source of both organic and inorganic contaminates for water bodies, landmass and the atmosphere.

1.5.1 Landfill water pollution

The imminent danger posed by different toxic organic and inorganic compounds generated by the waste leachate have an overbearing health effect on the surface and underground water, and human activities within the landfill environment. Landfill leachates contain contaminants, including dissolved gases, heavy metal (loids) and xenobiotic compounds (Kulikowska and Klimiuk, 2008; Bolan *et al.,* 2013). The most common organic contaminants in landfill leachates include pesticides, BTEX (Benzene, Toluene, ethylbenzenes and Xylenes), chlorinated aliphatic hydrocarbons, and chlorinated benzene compounds (Slack *et al.*, 2005).

High levels of chemicals (Cr, Mn, Ca, Mg, Na, K, NH_4, Fe, Cl^-, SO_4^{2-} and CO_3^{2-}) and bacteriological (*E. coli* and total coliform) contamination have been observed in some boreholes within 50-100 m from the landfill without contentment facility (Adeolu *et al.,* 2011). With confirmed cases of carcinogenic or co-carcinogenic potential in landfill leachate, the risk of chemically overloading hydro-geology aquifer layers with contaminants may create a major imbalance in sensitive ecosystems with diverse effect on organisms and man's source of water (Scaglia *et al.,* 2011; Foo *et al.,* 2013). In general, the interactions between groundwater resources and solid waste leachates have been reported by many researchers across the world such as: Suresh and Kottureshwara, 2009; Karunakaran *et al.,* 2009; Akudo *et al.,* 2010; Rajkumar *et al.,* 2010; Ali, 2012). Major factors which influence landfill leachate production included: the type of the wastes deposited; rainfall and other climatic factors; the degree of surface and groundwater ingress; the age of deposited waste; degree of compaction; and cover, capping and restoration (EP, 2015). Ground water pollution prevention is the main task of design and construction of impermeable underground barriers, leachate collection and treatment facility. It is estimated that landfill leachate production will continue for about 30-40 years (EP, 2015, Cossu, 2012). During this period, the problems of inadequate maintenance may pose an environmental risk in the long-term future (Johannessen and Boyer, 1997).

1.5.2 Air pollution

Landfilled organic fractions of waste when degraded generate landfill gases (LFGs), consisting mainly of methane (CH_4) and carbon dioxide (CO_2), which are the main GHG constituents. In 2010, U.S. EPA identified waste landfills as the third largest anthropogenic source of CH_4 accounting for 16 % of total CH_4 emissions (U.S. EPA, 2012). The landfill gas generation rate depends on the volume of waste, climatic factor and landfill practice. Buildup of landfill gas has also resulted in intermittent landfill fires (Liu et al 2016). Landfill gases generated from sulfur based materials are also responsible for the obnoxious odour within the vicinity of the landfill (Xu et al., 2014, Penza et al., 2015).

Landfill covers are the major methods employed for odour control. The cost implication of daily covering has limited the compliance to this practice (Johannessen and Boyer, 1997). Modified intervals of landfill covering are been adopted by respective landfill to reduce cost.

The most common mitigation strategy is the capture of LFG for flaring or combustion to recover energy, as this presents significant environmental, economic and energy gain (Yang *et al.,* 2013, Kashyap et al., 2016). However, the number of gas wells provided is limited; US average about one well per 4000m^2 of landfill (U.S. EPA, 2012). Less than 10 % of the landfill gas generation potential is been captured, utilized or flared (Themelis and Ulloa, 2007). Gas flaring is the process of combusting gas capable of generating greenhouse gas at a high altitude (U.S. EPA, 2012).Methane recovery is quite an expensive technology which is being implemented mainly in developed countries. For example, the installation costs for the gas-flaring system in Bisasar Road landfill, South Africa was 6.6 million Rand (US$1.5 million), while the operational costs may double within few years of operation. (Johannessen and Boyer, 1997). Despite huge landfill generation gas potential in landfills in the developing countries only a few landfills (less 5 %) have the provision to collect landfill gas. Motivation to collect landfill gas for flaring is poor owing to low economic benefit. The efficiency of LFG collection depends largely upon uncertain factors of waste composition and decomposition rate, which could rapidly vary across the depth. Poor waste characterization before and after disposal are factors which also inhibit adequate evaluation of landfill gas potential in abandon and active landfill in the developing countries. Figure 1.4 presents the effects of uncontrolled landfill on man.

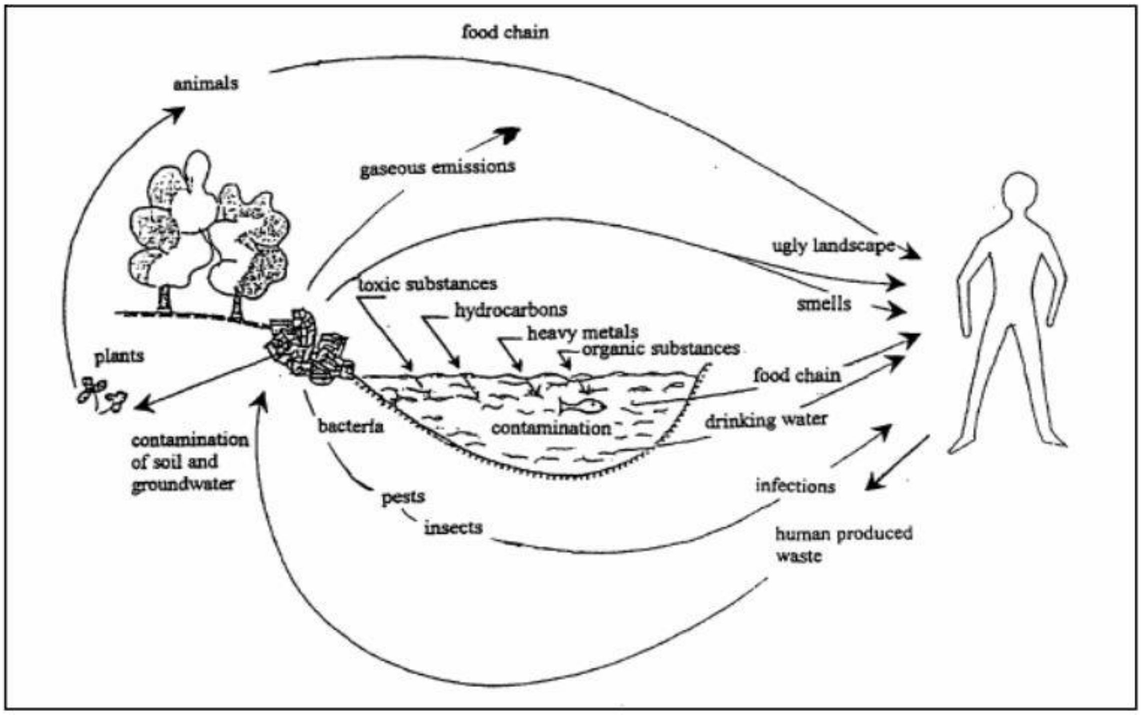


Figure 1.4: Effects of uncontrolled landfill on man (Source: Oeltzschner and mutz, 1994)

1.6 Landfill Environmental Sustainability

Sustainable landfill is a system of landfill where the disposed waste mass is managed to prevent any environmental pollution through simple, robust and cost effective measures (Batagarawa, 2011). The major driving focus is safe disposal into the landfill. Sustainability in respect to landfilling implies a multi-layer process that includes appropriate background knowledge of the waste and area geological, technical treatment plan of waste before, during and after landfilling(Cucchiella et al.,2017). Cossu (2012) defines: "a sustainable landfill as a system that should reach an acceptable equilibrium with the environment within one generation (30-40 years)".

The main aim of environmental sustainability is a well-defined resource consumption achieved by the effective waste management processes with an assurance of pollution free environment (Hung *et al.*, 2007; Roussat *et al.*, 2009). The new strategies in waste management focus on stabilization and safe final disposal of waste materials that can be integrated in a closed loop in the short term through pre–treatment of waste before landfilling. (Imran *et al.*, 2008; Batagarawa, 2011) The European Directive 75/442/EEC (The Waste Framework Directive1), and in particular Article 4, requires that waste be treated before it is landfilled.

The main objective is to ensure a carefully managed mass flow of waste to avoid the risk of creating environmental imbalance from disposed organic and inorganic substances. Converting waste into mass which does not only ensure stability in the flow of matter (liquid, gas, solid) but also help to sink possible contaminants will help in the landfill sustainability. Pollution control is ensured by inhibiting the movement of waste elements which are inimical to the environment. Based on needs we have mobilized different types of substances and elements from the geological deposits (i.e. mineral and ore deposits, oil reservoirs) where they existed in an inert non-mobile form or in a form which are not directly available to the environment (Cossu, 2012). In sustainable landfill, attempt is made to reverse the process. Immobilize substance and element of waste into the earth geology within short possible life span.

1.7 Activated Carbon Precursor and Properties

1.7.1 **Activation carbon chemistry**

Activated carbon is a crude form of graphite with a random or amorphous structure which is highly porous over a broad range of pore size cracks and crevices to cracks and crevices of molecular dimensions. The spaces between the crystallites of activated carbon constitute the micro porous structure with a large internal surface area of 250 m^2/g-2500 m^2/g. (Marsh and Rodriguez-Reinoso, 2006)

The IUPAC (International Union of Pure and Applied Chemists) define activated Carbon as: "a porous solid high in content of the element carbon in a structurally non-graphitic state, formed from a char which has been subjected to the reaction with gases, sometimes with the addition of chemicals, e.g. $ZnCl_2$, before, during or after carbonization in order to increase adsorptive properties". It is a strong adsorbent for organic materials and other non-polar compound (Marsh and Rodriguez-Reinoso, 2006)

Activated carbon is generally considered to exhibit a low affinity for water, which is an important property with respect to the adsorption of gases in the presence of moisture. The adsorption characterization of activated carbon is affected by surface chemistry of the activated carbon.

1.7.2 Surface chemistry

Surface chemistry of activated carbon is mainly influenced by the nature of the precursor and the activation process, although the functionalities of most activated carbon are often similar. It consists of condensed poly aromatic or poly aliphatic sheets as building blocks and heteroatom which influence the chemical properties of activated carbon. Oxygen is an important heteroatom that occurs in the form of carboxylic acid groups, phenolic base hydroxyl groups, and quinone carbonyl groups (Figueiredo et. al, 1999; Lei *et al.,* 2002). Other commonly found heteroatoms include nitrogen, hydrogen, sulfur, and phosphorous (Shafeeyan *et al.,* 2010). The acidic and basic characteristic of activated carbon surface is determined by the type of surface functional groups formed by heteroatoms and the delocalized electrons of the carbon structure (Laszlo and Szucs, 2001; Shafeeyan *et al.,* 2010)

The oxygen containing surface groups which are mainly found on the outer surface or edge of the basal plane mainly influence the chemical nature of the carbon. The formation of carboxylic acid or carboxylic anhydride, lactone, and phenolic hydroxyl functional groups have been reported as the sources of surface acidity, while surface functionalities such as chromene, ketone, and pyrone have been proposed to contribute to the carbon basicity (Figueiredo et. al, 1999; Laszlo *et al.,* 2001; Laszlo and Szucs, 2001; Shafeeyan *et al.,* 2010). Figure 1.5 illustrates a typical activated carbon structure showing the functional group effect on pH nature of the activated carbon (Shafeeyan *et al.,* 2010).

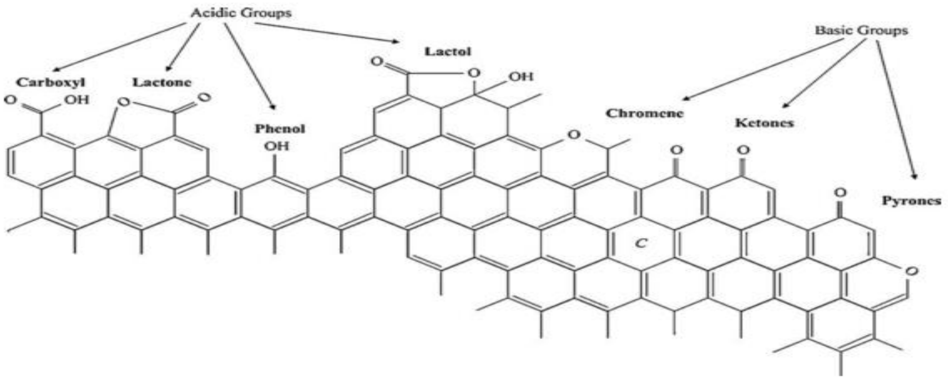


Figure 1.5: the structure of activated carbon showing the functional group and the pH effect. (Source: Shafeeyan *et al.*, 2010)

1.7.2.1 Structure of activated carbon

The structural order of activated carbon is a major feature distinguishing it from other members of the carbons family. According to Franklin (1951), activated carbon are non-graphitizable carbons which do not have long-range parallelism of grapheme layers ever after heating above 2000 °C in contrast to regular graphitizable carbon with well planarity and stacking graphene layers. Figure 1.6 shows the structure of the type of carbon

(a) **(b)**

Figure 1.6: The crystalline structure of (a) non graphitizable carbon and (b) graphitizable and (Source: Marsh and Rodriguez-Reinoso, 2006)

Non-graphitizable carbons are usually formed from precursor containing less hydrogen or more oxygen developing a strong system of cross linking of crystallites. These short-range structures of non-planar units are bonded together through carbon linkage during the carbonization stage (Marsh and Rodriguez-Reinoso, 2006).

1.7.2.2 Porosity

The activation process leads to partial removal of various carbonaceous compounds within each non-planar unit creating spaces between the elementary crystallites. The voids formed are termed as pores. (Mcdougall, 1991; Marsh and Rodriguez-Reinoso, 2006). The volume of the pores in activated carbons is opined as greater than 0.2 ml/g while the width varies from 3 Å to several thousand angstroms. Pores are often classified for in terms of their diameters. According to the IUPAC definition, pores can be distinguished in three groups (see Table 1.3) with respect to their dimensions (Marsh and Rodriguez-Reinoso, 2006, Sing *et al.,* 1985).

Table 1.3: Pore Sizes of Activated Carbon

Type of pores	Diameter
Macropores Pores	D> 50 nm (500 Å),
Mesopores Pores	2 nm < D ≤50 nm (20- 500 Å),
Micropores Pores	D < 2 nm (20 Å)

(Source: Marsh and Rodriguez-Reinoso, 2006, Sing *et al.,* 1985)

In the cross sectional view, pores appear to be of either cylindrical or rectangular in shape, but from microgram observation, they form a variety of irregular shapes: contracted entrance (ink-bottle shaped), capillaries open at both ends or with one end closed, regular slits between two planes, v-shaped, tapered pores, and other forms (Mcdougall, 1991, Marsh and Rodriguez-Reinoso, 2006)

The Macropores functions as the transitional arteries through which carbon granules access the molecules to be adsorbed. The pores account for about 5 % of the total surface area of the activated carbon. Their volume in the activated carbon is generally between 0.2 cm^3/g and 0.5 cm^3/g and their surface area about is 0.5 m^2/g to 2 m^2/g (Mcdougall, 1991; Marsh and Rodriguez-Reinoso, 2006).

The micropores account for about 95 % of pores in the internal surface area and has a volume of about 0.15 cm^3/g to 0.50 cm^3/g. Depending on the nature of the precursor employed and the activation process the percentages of the transitional pores and the micropores could vary widely.

1.7.2.3 Classification of Adsorption Isotherms for porous solid

Adsorption isotherms have been grouped into the six types according to the IUPAC classification (see Figure 2) (Sing *et al.,* 1985).The shape of the graph form due to the relationship between relative gas pressure (p/p_o) of nitrogen gas and the amount adsorbed by the adsorbent is used to determine the type of isothermal adsorption peculiar to an adsorbent.

A Type I isotherm is observed in adsorbent having small external surfaces with large microporous. It is indicative of a monolayer adsorption of adsorbate molecules. This adsorption isothermal is common to activated carbons and molecular sieve zeolites. (Sing et al. 1985, Shairafan, 2012)

The Type II isotherm is indicative of unrestricted monolayer-multilayer adsorption. This is common to adsorbent having a mixed of micro and mesopores. The point B in figure 1.7 represents the point at which monolayer adsorption coverage ends and the multilayer adsorption commence.

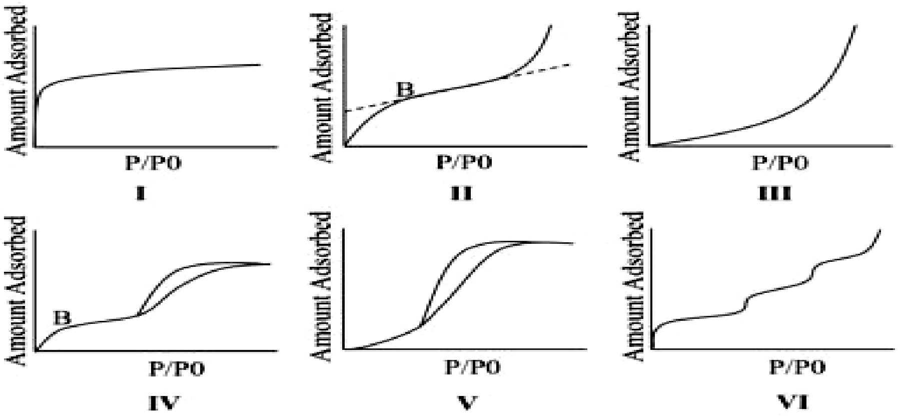


Figure 1.7 Type of adsorption isotherm by IUPAC (Sing et al., 1985)

Isotherms Type III and V have a common convex shape with the relative pressure axis. This convex shape represents the occurrence of cooperative adsorption, where there is a strong interaction between adsorbates leading to the adsorption of more molecules. The adsorption of nitrogen gas on polyethylene has observe to display a type III isothermal adsorption (Sing et al., 1985)

The Type VI isothermal occurs for mesoporous materials having monolayer-multilayer adsorption with capillary condensation thus leading to the formation of a hysteresis loop.

Hysteresis loop is formed due to differences in curvature of the meniscus on adsorption (cylindrical) and desorption (spherical) during the adsorption and the desorption. The shapes of hysteresis loops have often been identified with specific pore structures. Figures 1.8 provided the types of hysteresis loop as identify by IUPAC.

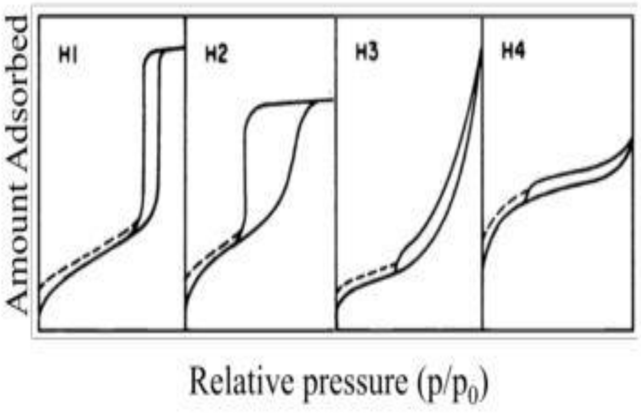


Figure 1.8: The hysteresis loop classification by IUPAC (Sing et al., 1985)

Hysteresis type H1 is associated with solids having pores of spheroidal, uniform particle size, H2 is observed in silica gels, and H3 and H4 in observed narrow slit-shape or plate-like pores (Sing et al., 1985).

1.7.3 Activation Process

There are two main steps for the preparation of Activated carbon: (1) the carbonization of the carbonaceous raw material below 800 $^{\circ}$C, in the absence of oxygen, and (2) the activation of the carbonized product (char), which is either through physical or chemical activation.

1.7.3.1 Carbonization of carbonaceous raw material

The main aim of carbonization step is to improve the carbon content of the precursor through reduction in the volatile and non-carbon content: oxygen and hydrogen in the precursor.

Precursor is subjected to pyrolytic decomposition at a temperature between 600-900 °C under the flow of nitrogen or carbon dioxide. The precursor char generated are with carbon atoms rearranged into graphitic-like structures. The carbonization of precursor has been reported to have effect on the quality of the final activated carbon products (Ioannidou and Zabaniotou, 2007).

1.7.3.2 Chemical activation

In chemical activation processes the char is impregnated with activating agents under the flow of inert gas either nitrogen or carbon dioxide (Foo and Hameed, 2012a, Rashidi and Yusup, 2017). The use of two major groups of activation agents is well reported in chemical activation. The acidic activating agent which includes the use of: H_3PO_4 (Liou, 2010), HCl (Alvarez *et* *al.*, 2007), and H_2SO_4 (Karago *et al.*, 2008) and the basic activating agent: KOH (Foo and Hameed 2012a), K_2CO_3 (Ferrera-Lorenzo et. al, 2014), NaOH (Lillo-Rodenas *et al.*, 2001, Islam et al., 2017)). Depending on the nature of the precursor the choice of the activation used is premised upon the dehydrating properties of activating reagent. Carbonization and activation can be carried out simultaneously in chemical activation, with the precursor initially mixed with chemical activating agents before application of heat at desired temperature of between 450 °C to 900 °C. This method will often lead to activated carbon of higher micropore volumes and wider micropore sizes. A major advantage of chemical activation is that the process requires lower temperature and a shorter duration of time when compared with physical activation. (Suhas *et al.*, 2007, Rashidi and Yusup, 2017). These activation conditions (chemical impregnation, reduced temperature and duration) have greatly affect the potential of generating a higher yield of activated carbon using chemical activation. The chemical agents dehydrates precursor, inhibiting the formation of tar and other volatile products leading to charring and aromatization of the carbon skeleton, with porous structure and extended surface area (Marsh and Rodriguez-Reinoso, 2006). Proper washing of the activated carbon is an essential procedure in chemical activation. Activated carbon washing is aimed at recovery of activating agent and removal of associated impurities which could affect the properties of the activated carbon produced (Mcdougall, 1991). Impregnation ratios, heating source and temperature, gas flow rate have been reported to influence chemical activation process of precursors.

1.7.3.3 Physical activation

In physical activation, the resulting char is subjected to further heating in the presence of activating agents such as carbon dioxide, steam or air within the temperature range 600–1200 °C. This results in the removal of the more disorganized carbon and the formation of a well-developed micropore structure (Suhas et al, 2007, Rashidi and Yusup, 2017).

1.7.4 Raw material/precursor

Most of the commercial activated carbons are produced from either coal based or petroleum pitch, which is prone to exhaustion due to natural limit in volume and spread of coals globally. Several researches have focus on the use of different activated carbon precursors. Agricultural materials rich in organic carbon including coal, peat, woods, fruit, nutshell and coconut shell have been used as precursor for activated carbon (Aygun *et al.,* 2003; Li *et al.,* 2008; Alslaibi et al. 2013, Zubrik et al., 2017). Recently, biomass wastes which are major constituents of some landfills have been identified as potential precursor for the production of activated carbon. A wide range of solid waste has been shown to be suitable for the production of activated carbon: plants (Tang *et. al*., 2012, Foo *et. al*., 2013a, Dieme et al., 2017), wood and sawdust (Foo and Hameed, 2012b) and industrial sludge (Fu, *et.al.*, 2013). Synthetic materials and papers have also been used as a precursor for the production of mesoporous activated carbon (Nahil and Williams ,2012). A key element is the reliability and the constancy of the resource. Most developing countries have a high percentage of organic matter in their waste stream, ranging from 40 to 85 % of the total waste, which is disposed mainly to the landfills (Hoornweg and Bhada-Tata, 2012**)**. The International Panel on Climate Change (IPCC, 2006) estimates that organic waste constitutes 89 – 92 % of waste generated in sub-Sahara Africa. De la Cruz *et al.*, 2013 work on carbon storage in the landfill indicated that excavated landfill samples had an average 64.6 ±18 % biogenic carbon. Although different waste materials have been used as activated carbon precursor the possibility of converting landfill composite directly to activated carbon have not been well reported.

1.7.5 Choice of activation heating system.

In the activation process, the heating system applied is a primary variable that can affect the activation procedure, mechanism and chemistry of the activated product. Activation heating source is broadly classified into conventional (used of electric mantles and furnace) and microwave energy (microwave oven) (Lam and Chase, 2012). The electromagnetic field from the microwave diffuses into the molecules of the bulk substance resulting in intra molecular heat generation, with about 90 % conversion efficiencies of electricity into thermal energy (Yuen and Hameed, 2009). The use of microwave radiation offers enhanced uniformed distribution of heat, effective heat transfer, and ensures a better control of experiment which represents reductions in the treatment time and energy consumption when compared to conventionally heating system. Microwave radiation provides a rapid and energy-efficient heating process about 50 % higher than using heating by natural gas, steam or electric furnace. Additionally, microwave heating provides an efficient way in the removal of oxygenated functionalities from carbon surfaces. In separate studies, Alslaibi et al. (2013) and Ferrera-Lorenzo et al. (2014) have reported that microwave treatment of precursors resulted in comparable improvement in pore size formation and chemical properties of the activated carbons.

1.7.6 Uses

Activated carbons are essential adsorbents used in many industries. There applications are majorly concerned with the adsorption of species from the liquid or gas phase for effective purification or chemicals recovery. They are used as primary or secondary cleaning agent in waste water, textile and water purification industries. They are also used as catalyst support. Activated carbon has been deployed in the removal of recalcitrant inorganic and organic compounds from landfill leachate (Foo *et al.,* 2013a; Kurniawan *et al.,* 2006; Aziz *et al.,* 2004; Heavey, 2003). Toxic compounds like aromatics and chlorinated compounds and moisture content in landfill gas haven been effectively removed using granular activated carbon (Shin *et al.,* 2002). The strong market position held by activated carbon adsorbents relates to their unique properties and low cost compared with that of possible competitive adsorbents (Girgis et. al., 2002; Yu *et al.,* 2013)

Activated carbon is a very versatile substrate with respect to its interactions with various organic and inorganic compounds. It is able to function as a simple adsorbent that is akin to synthetic polymeric adsorbents, since molecular compounds can be physically adsorbed onto its large internal surface area, and be retained there by Van der Waals forces. It can also function as a reducing agent or, in the presence of excess oxygen, as an oxidation catalyst (Marsh and Rodriguez-Reinoso, 2006).

1.8 Scope of the present study

This research work has as its overall aim: To evaluate the enrichment levels of carbon and the degree of inorganic content in selected landfills with the view to investigating the possibility of using landfill composite as a suitable precursor for activated carbon, in order to improve the environmental sustainability of the landfills.

The following specific objectives will be addressed in order to achieve the overall aim:

(1) determine the heavy metals concentrations in the landfills composite;

(2) determine the elemental composite of landfills composite in relation to depth;

(3) determine possibility of using the solid waste composite as a precursor for activated carbon production;

(4) determine the correlation of the landfill depth and age as a functionality of precursor suitability.

1.8.1 Significance of Study

Landfill remains a major means of solid waste management despite concerted efforts at reducing over reliance on this method of final waste disposal. Sustainable management of the huge tonnage of landfill waste to prevent immediate and future environmental pollution is still a challenge especially for developing countries with poor technical and financial resource to either upgrade the existing landfill or convert old landfill to energy. The huge percentages of degradable waste in these landfills pose a major challenge in the greenhouse gas generation. Alternative management option will be needed to improve eco-friendliness of these landfills.

The present research seeks to investigate the possibility of using landfill composite as a suitable precursor for activated carbon in order to improve the environmental sustainability of the landfills. It seeks to exploit the possible abundance of carbon in the landfill especially for developing countries for activation carbon production while reducing greenhouse gas emission through carbon sequestration. The effect of landfill composite composition and depth in relation to availability of carbon and the quantity of activated carbon produced will be investigated. The research finding could provide a path towards reduction of the volume of mass land used for landfill and the period of landfill maintenance after closure. It could also provide an alternative use of the large reclaimed soil and more degraded part of mined landfill.

1.8.2 Research questions

This research design was premised on the following assumptions:

A) The landfill composites were mainly household waste.

B) The composite should have good percentage of organic carbon since they are mostly domestic waste.

C) The heavy metal content of the landfill composite should be within limits and can be extracted using appropriate acid.

D) The age and depth of landfill composite should play significant role in the % yield of activated carbon to be produced.

E) The nature of landfill composite should influence the quantity of activated carbon produced

In order to verify the assumptions the following research questions were developed:

- Is there adequate information about the landfill waste composition in the landfills?
- What is the concentration level of the heavy metals in the landfill?
- Are the elemental compositions in the landfill rich in carbon and by what value?
- Are there significant change in the spread of the elemental composition of the landfill with depth and why?
- Do the age and depth of the landfill affect the elemental composition?
- What factors will affect the % yield of the activated carbon?

1.8.3 Thesis layout

This thesis has seven different chapter addressing distinct but interrelated issues with the following content:

Chapter 1: gives the background to the research and the literatures review. It evaluated the trends and challenges of Municipal Solid Waste (MSW) generation and management globally. The impacts and challenges of sustainable landfills management were reviewed. The chemistry of activated carbon, precursor options and uses of activated carbon were discussed.

Chapter 2 gives the description of the sampling location Lagos Nigeria, itemized the waste management practice, population size, climatic and anthropogenic conditions.

Chapter 3 elucidates on sampling procedure, quality control measures, analytical and instrumentation methods used in this research work.

Chapter 4 presents procedures used in evaluating the proximate properties, heavy metals, and elemental properties of the samples. The result findings were presented and discussed.

Chapter 5 presents the activation instrumentation designs for both microwave energy and conventional heating system. It discusses the activations conditions and some of the effect on % yield.

Chapter 6 this chapter presents activated carbon characterization using spectroscopic methods, BET surface analysis and adsorption studies.

Chapter 7 presents discussions on finding and deduction which reflect on current literatures leading to the overall conclusions and recommendations of the present research.

CHAPTER TWO

GENERAL FEATURES OF THE SAMPLING AREA

2.1 Geological location of sampling area

Nigeria is located in West Africa along the Gulf of Guinea and lies between 4 ° to 14 °N latitudes and 3 ° to 14 °E longitudes. It is bordered by Benin Republic, Niger Republic, and Cameroon to the west, north, and east respectively while the Atlantic Ocean in the south. (Aboyade, 2004). Its land area is about 924,000 km^2 comprising of 910,900 km^{2}of land area and 13,879 km^2 of water area. Around 40 % of the land mass covering from North West and North Central is mainly guinea savannah, while the rest is mangrove swamp at the end of southern region and Sudan savannah at the farthest northern region (NBS, 2012).

2.2 Climatic condition

Nigeria is characterized with high humidity and heavy rainfall. It has two distinct seasons: a wet season that typically occurs between April and October, and a dry season that occurs during the rest of the year (Longe and Enekwechi, 2007; NBS, 2012). The seasons are mainly controlled by two air masses: moist air coming from the Atlantic Ocean and dry continental air from the South African landmass. The total annual rainfall varies across Nigeria with the greatest total precipitation of about 4,000 millimeters average annual rainfall at the southeast and decreases towards the north to about 1,250 millimeters rainfall per year.

Nigeria maintains a relatively high temperature of between 28 °C to 40 °C throughout the year. This enhances decomposition of waste especially during wet season (Hamoda *et al.,* 1998; Sundberg and Johnsson, 2008, Batagarawa, 2011). The coastal region of the south west experiences the lowest annual temperature while the North has the highest temperatures. Temperatures across the country are at its highest peak before the commencement of the rains and drop to its lowest at inflow of cool air from December to February (NBS, 2012).

2.3 Population

Nigeria is the most populous country in Africa with a population of about 173 million and accounts for 47 % of the West Africa's population. The country's population growth rate of 2.80 % per year is one of the highest in the world. Its population had more than quintupled from 33 million in 1950 to 173 million in 2012. According to the World Bank, Nigeria was about 180.3 million in 2015 (World Bank 2015). The country's population is distributed along regional, political and commercial activities with population concentration in cities like Lagos, Kano and Rivers.

The sampling location, Lagos state, is the commercial centre of the nation with high population density and associated urban challenges. Figure 2.1 shows the location of Lagos on the Nigeria map.

Figure 2.1: Nigeria Map showing the location of Lagos State (source: Jánossy *et al.,* 2009)

2.4 Lagos State population and economy

Lagos state is the commercial nerve centre of Nigeria. It has a large costal area, bordered by 22 % of water lagoons which represents 3,577 km^2 land mass. Lagos Metropolis represents only 37 % of the state's land area and it is inhabited by more than 80 % of the state's population, resulting in a population density of about 20,000 persons/km^2 (Aboyade, 2014). Lagos city with an estimated population of 22 million is one of the most populous African city and the second fastest growing African city with annual growth rate of 4-6 % (Afolayan *et al.,* 2012; EnvironQuest, 2009). Lagos is the premier industrial city in West Africa having important sea and air port attracting large concentration of multinationals and national companies. More than 60 % of Nigeria's non-oil economy is located in Lagos. Being the industrial and commercial hub of Nigeria, there is continuous migration of people from other parts of the country. Its population is expected to grow to over 50 million by 2025 making it one of the world's largest cities (World Bank, 2009). Lagos has a total of 57 Local Council Development Areas (

LCDAs) expanding from the fringes of the southwest mouth of Lagos Lagoon to the mainland west of the lagoon and the conurbation, including Ikeja (which is the capital of Lagos State). The domestic waste generation in Lagos is estimated between 8,000 and 11,100 metric tons every day, with about 60 % of this waste derivable from food and other biodegradable components (World Bank, 2009)

2.5 Current MSW management practice in Lagos

The Lagos Waste Management Authority (LAWMA) by virtue of the LAWMA Law 2007, is the main agency charged with responsibilities of managing domestic, commercial, industrial, and medical waste streams in Lagos state while Lagos State Environmental Protection Agency (LASEPA), the Local Government Councils, (LGCs) and the Ministry of Environment and Physical Planning (MEPP) are to provide essential supportive service for the purpose of waste management. (Kofoworola, 2007; EnvironQuest, 2009)

The Lagos Waste Management Authority (LAWMA) introduced private sector participation (PSP) in the collection of waste from domestic and commercial area within the state while special firm were contracted to handle the medical waste. (EnvironQuest, 2005). Waste collection is carried out once in a week per locality with compactors trucks. Figure 2.2 shows a typical PSP trucks ready to offload at the dumpsite. Wastes are usually collected from household, commercial centres and disposed as mixed waste without segregation from source. All waste collected is disposed at the landfill within the state. The state currently has a total of six landfill sites of which three are closed landfill while two are active landfills (LAWMA, 2012). The locations of some the landfills are as indicated in Figure 2.3. There are other informal waste collectors who with the aid of pushcart or hand truck collect waste from clients and disposed at illegal dumpsites (Afon, 2007). Waste enforcement law is quite poor in the state and this is obvious in the indiscriminate waste dumping in open places, drains, streams constituting different human challenges.

Figure 2.2: Compactor truck used for waste disposal in Lagos state (taking during sampling)

As result of scarcity of land for landfill practice and the Lagos Metropolitan Development and Governance Project (LMDGP), the state is seeking alternative means to extending the life span of the present active landfills and the possibility of reclaiming landmass occupied by the closed landfill for reuse.

Figure 2.3: locations of active and closed landfills within Lagos State (source: Jánossy *et al.*, 2009)

2.6 Sampling location

2.6.1 Active landfill

The Olusoshun active landfill site is located in the northern part of Lagos within the Ojota area of Ikeja Local Government Council, within Longitude 6 ° 35' 50"E to 6 ° 36' 30 "E and Latitude 3 ° 22 ' 45 "N to 3 ° 23 ' 30 "N. It has been in operation since November 1992 with an area of 42 hectares and receives an average of 8,000 metric tons of waste daily. The site was initially used as an excavation site where sand for road construction was mined. Excavation depth was about 12 m before tipping of waste commenced but the waste height is about 18m (Longe and

Enekwechi, 2007). The area available for landfill at the site has reduced to about 37 hectares with the introduction of a landfill gas monitoring area, recycling area and leachate ponds. The solid wastes collected are not subjected to any treatment before being land filled. Wastes disposed are manually sorted by authorized waste pickers and the rest are usually spread across the landfill, compact with a waste compactors and capped at intervals. The site is expected to be closed by 2025 (Lawma, 2012).

2.6.2 Closed landfill

The Abule-Egba closed landfill is located in the Western part of Lagos, under the Alimosho Local government council, with an area of about 10.2 hectares. It started receiving waste in 1984 and has an estimated 1.3 million metric tons of waste with an average height of 12.5 metres. The site has been closed since 2009 (Lawma, 2012). The Abule-Egba site was mainly managed through burning of waste within the excavated area. There were no practice of compaction and capping of disposed waste at the landfill site. It received mainly market and household waste.

2.6.3 Anthropogenic activities around dumpsites

Initially, the Olusosun dumpsite was at the outskirts of the metropolis but due to rapid urban development the site is presently within developed locality of the metropolis. The dumpsite is surrounded by residential, commercial and industrial neighborhoods. It is bordered to the East by 'Total' Filling Station and mini-Bus Park to its West is the Oregun Industrial Estate (Housing companies like Dangote Salt, UAC, Mr. Bigg's, etc.) and to the North by LAMATA Office

(Motorways House) and Seven-Up Bottling Company and to the South by the Kudirat Abiola Way on which lies many residential as well as industrial/commercial facilities (See Figure 2.4) (EnvironQuest, 2005).

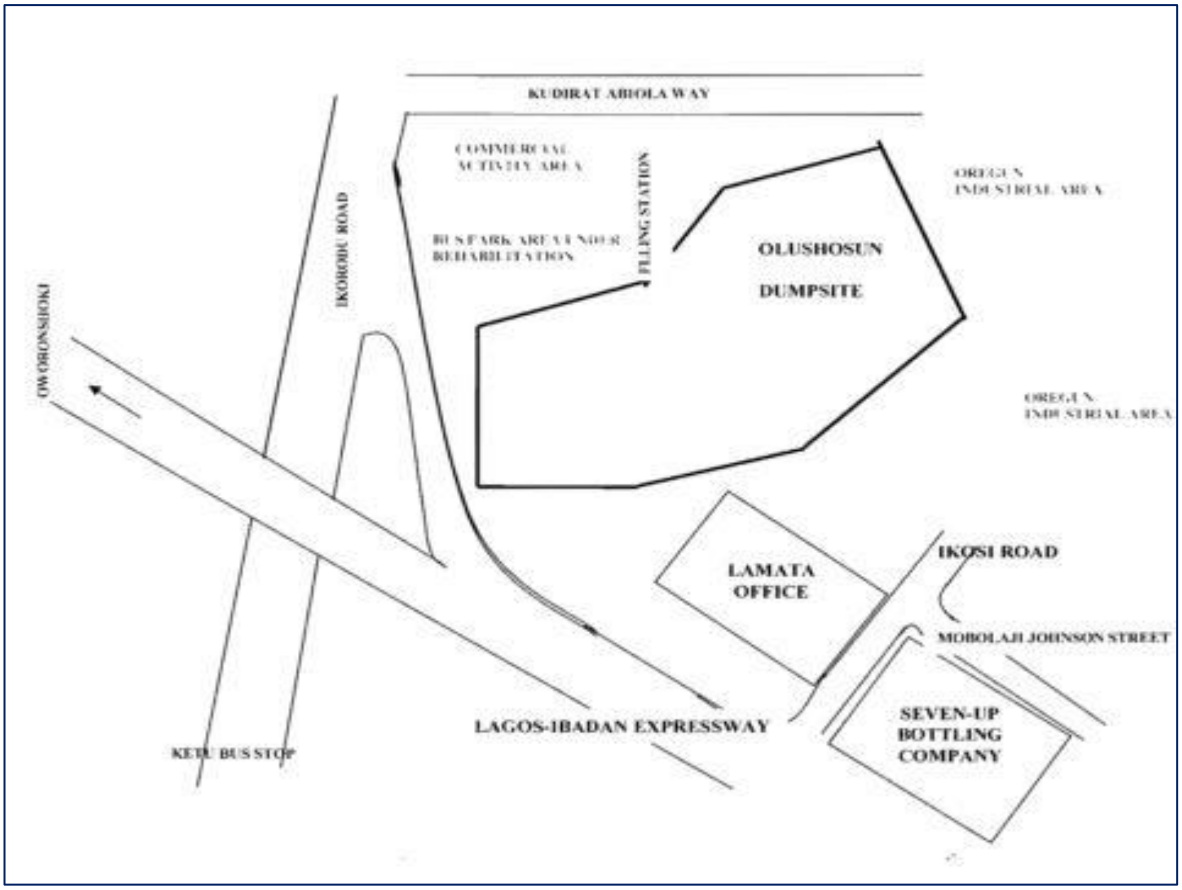


Figure 2.4: showing Olushosun landfill with relation to landmarks (EnvironQuest, 2005)

Similar to active landfill, Abule-Egba closed dumpsite is bounded by Lagos – Abeokuta expressway in the East and to the North is a large market (Ilepo market) and mini- bus stop, to its west the mini market (Katagowa Market) and residential area, by the South is an Onado filling station and metal industrial area. Appendix 1 present pictures of key features at both landfills.

CHAPTER THREE

RESEARCH METHODOLOGY

3.1 Introduction

This chapter presents the basis for the sampling plan and implementation procedure in line with RCRA Waste Sampling Draft Technical Guidance and EPA's Guidance on Choosing a Sampling Design for Environmental Data Collection and Quality Assurance Project Plan, EPA QA/G-5S (USEPA 200a). The EPA guidance provided guidelines on sampling and investigating disposed hazardous and non-hazardous solid waste for possible material recovery or reuse which is consistent with the present research work. There had been several landfill samplings, focused on deep-depth (2-30 metres) landfill mining (Jain et al., 2005, 2013; Quaghebeur et al., 2013; Kaartinen et al., 2013; Garcia et al., 2016) respectively. The procedure required the use of heavy drilling equipment, more technical personnel and huge financial demand. The basic principles of obtaining a representative sample from these procedures were however consistent with the general procedure provided by the RCRA waste sampling procedure of either systematic or stratified composite sampling. The RCRA waste sampling procedure provided guidelines which are suitable for a layer sampling of landfill informed its preference.

The solid waste evaluating methods SW 846 chapter two (inorganic) was reviewed and considered appropriate for evaluating heavy metal concentrations in samples. This chapter also presents the quality control procedure used in maintaining samples integrity throughout the analysis process. Lastly, it elucidates the different analytical instrument used during sample analysis.

3.2 Pre-sampling plan

3.2.1 Development of the project Data Quality Objectives (DQO)

Seven basic steps were taken during the Project DQO development

Step 1: Project objectives analysis

The project objectives were analyzed to aid critical decision in the sampling plans. The following specific project objectives were identified as the overall reasons of sampling:

i) Determination of heavy metals load

ii) Determination of the total organic carbon

iii) Determination of the elemental composition in the landfill layers

iv) Assessment of samples as precursor for activated carbon.

The major stakeholder that will be involved in this project was identified as the agency in charge of waste management in Lagos state: The Lagos Waste Management Authority (LAWMA). This research concept was presented and discussed with the Agency technical team and approval was given for the sampling. Presented in Appendix 2 is a copy of the approval letter.

Step 2: Identification of possible decision

The overall key decision statements regarding this research project were identified thus:

- The landfill composite should contain little heavy metal and be rich in organic carbon or other forms of carbon. Hence, its suitability for conversion into activated carbon. The conversion process is carried out straight away.
- The landfill composite contains significant concentration of heavy metals but is rich in organic carbon or other forms of carbon. It is suitable for conversion into activated carbon but the conversion process must ensure removal of the heavy metals associated with the landfill.
- The landfill composite contains less concentration of the heavy metals and is not rich in organic carbon and other related carbon. It is less suitable for conversion into activated carbon except with enrichment of the carbon content. Enrichment process could be introduced into the conversion process.
- The landfill composite contains high concentration of the heavy metals and is not rich in organic carbon and other related carbon. It is less suitable for conversion into activated carbon except with enrichment of the carbon content and proper extraction of the heavy metals. Enrichment process and strong extraction process could be introduced into the conversion process.

Step 3: Identification of inputs to the decision

Sampling will be taken with the following conditions

i) Landfill should be gridded into equal parts

ii) Each landfill cell is to be of equal land area, and is located using GPS

iii) The metals of interest are Pb, Cr, Cd, Ag, As, Ba, Se, and Hg. These heavy metals are selected based on recommendations by USEPA and Federal Environmental Protections Agency (Nigeria) that these metals are key to landfill heavy metals toxicity.

iv) Total heavy metal analysis of the sample is to be run. If the total metal analysis indicated that the concentrations of the metals are lower than USEPA threshold standard then toxicity characteristic leaching concentration is deducted from the values obtained for the total analysis (total metal concentration = 20X TCLP) (EPA method 1131)

v) If the concentration of the total heavy metals content of the samples are higher than the USEPA standard then TCLP will be prepared for all the samples.

vi)Total heavy metals content of the sample is to determined using EPA method 3051a/6020B

vii) Total organic carbon will be determined using the Walkley-Black and the dry combustion

method (Schumacher, 2002)

viii) The proximate analysis will be determined using method ASTMD 3713-5

ix) The elemental carbon will be determined using EDX analysis

x) If the total organic carbon or the total elemental carbon content of the composite is at least (TOC, fixed carbon, element carbon) ≥ 10 % then suitability for conversion may be high but if the carbon content is generally low (TOC, fixed carbon, element carbon) <10 % potentially low yield may be expected from conversion process.

xi) Activation process should be designed to low temperature range due to the degraded nature of the precursor.

xii) The products characteristic should be evaluated to determine the physical, chemical and adsorption properties.

Step 4: Defining Boundaries

i) Sampling Profile

Sampling profile depths of between 15 and 50 cm were designed to inform on early changes in the landfill waste parameters during their earlier disposal period, as recommended by International Panel on Climate Change (IPCC) guideline for countries unable to evaluate these solid waste parameters before disposal. This single layer profile sampling method was adopted to also obtain samples with similar physicochemical properties within each layer of the landfills. Sampling within this depth range also provides spatial profile information on the properties of waste within the first receptor layer of the landfills.

From evaluation of the Olusoshun landfill site some areas were covered with clayey covering while other were uncovered. Sampling design at the landfill site accommodated other structure such as the recycle facilities, offices and stores. Samplings were obtained after removal of the cap soil where necessary.

Depth	Distance	Sampling point
Upper	0- 10cm	7cm
Mid	11 – 20cm	21cm
Lower	31 – 50cm	42cm

ii) Sample Quantity

500 g of sample was obtained from each sampling point based on quantity of sample required for each analysis (300 g for heavy metal determination (SW-864), 100 g will be needed for total organic carbon analysis and 100 g for other analyses)

Landfill composite was handled and characterized based on the landfill layer and are generally assumed to have some degree of toxicity.

Samples were obtained and evaluated during the rain and dry season to accommodate for climate influence on the heavy metal distribution within each layer of the respective landfills. For each landfill layer duplicated samples were evaluated for heavy metals concentration and the average were determined. The toxicity levels of samples are compared to the USEPA threshold standard.

Step 5: Developing Decision Rules

i) Action level

The action level for all metals to be evaluated is set at the maximum limit stated by USEPA regulation for evaluating waste toxicity in term of heavy metal concentrations as stated below

Contaminant	Regulated Level(mg/l)
Arsenic (As)	5
Barium (Ba)	100
Cadmium (Cd)	1
Chromium (Cr)	5
Lead (Pb)	5
Selenium (Se)	1
Silver (Ag)	5
Mercury(Hg)	0.2

Table 3.1: Heavy metals and regulatory limits as set by the USEPA (source SW-864 Chapter 3)

Hence, any heavy metals concentration below the value of USEPA standard is considered not toxic while any above or equal to it is considered toxic.

Toxic level of samples will inform activation conditions and procedures.

ii) Sample population

The RCRA regulations for waste toxicity characterization 40 CFR 261.24 specified no regulatory population for toxicity evaluation but only specified in Table 1 of Part 261.24 the metals concentration threshold of which must not be equaled or exceeded. For the determination of the sample population the “exceedance procedure” was adopted (USEPA 1989a).

The exceedance method is a nonparametric method which requires the assumption of the number of samples in the data set that will comply with the set limit or that will exceed the standard, usually zero or one. The statistical performance criteria of the samples can be specified and the number of samples required determined. The major constrain of this method is that more samples are required compared to the parametric methods.

The USEPA regulatory concentrations of toxic heavy metals of interest stated above were taken as maximum limit. With the assumption that majority of the samples are non-toxic and none will exceed the maximum concentration limit of these metals (based on waste composition given by the regulatory body of the landfill) the statistical performance was set at 90 % confidence interval and 90th upper percentile.

The number of samples was determined from Table G-3a in Appendix G page 275 RCRA draft technical guidance 2002 which is presented as Appendix 3. The table is based on the formula $n= \log(\alpha)/\log(p)$. In which $p=0.9$ and $(1-\alpha)=0.9$, where α= confidence interval , p= upper percentiles and n= number of samples. The sample population was determined as 22.

Step 6: Specifying Limits on Decision Errors

Two potential decision errors could be made based on interpreting samples analysis in term of heavy metal content:

Error Decision (i): Concluding that the true proportion (P) of the waste that is non-toxic was greater than 0.90 when it was truly less than 0.90, and consequently heavy metals may be leached out during washing process in the activation procedure with possibility of health and environmental risk.

Error Decision (ii): Concluding that the true proportion (P) of the waste that is non-toxic was less than 0.90 when it was truly greater than 0.90 and consequently leached heavy metals during activation process (washing) will have less potential environmental implications.

Error (i) has more severe implication than error (ii), hence the baseline condition (null hypothesis) is chosen that the true proportion (P) of the waste that is non- toxic was less than 0.90

Null Hypothesis and Possible Decision Errors

"Null Hypothesis"	Possible Decision Errors	
(baseline condition)	Type I Error (α), False Rejection	Type II Error (β), False Acceptance
The true proportion (P) of the waste that is non-toxic was less than 0.09	Concluding that the composite is not toxic when it was	Concluding that the composite is toxic when it was not.

In order to set the boundaries of the Gray region, the null hypothesis (baseline condition) is assumed that the waste is toxic, hence, one limit of the Gray region is bounded by the Action Level and the other limit is set at a point where it is desirable to control the Type II (false acceptance) error. One bound of the Gray region is set at 0.90 (the Action Level) since a "no exceedance" criterion is included in the decision rule, while the other bound of the Gray region will be set at 1.

The acceptable probability of making a Type I (false rejection) error is set at 10 percent (α). Hence, only 0.1 or 10 percent chance of concluding the waste is non-toxic when at least a portion of the waste is toxic is allowed. The use of the exceedance rule method does not require specification of the Type II (false acceptance) error rate.

Step 6 output summary

Action level	0.09
Grey action	0.09 to 1 Δ 0.01
Null Hypothesis	$P<0.09$
False Rejection Decision Error Limit	
(probability of a Type I error)	0.1
False Acceptance Decision Error Limit	
(probability of a Type II error)	not specified

Step 7 Optimization of the Data Collection Design

Sampling method: Random and Systematic methods were reviewed for use. Since site operations are not the same for both landfills, and the operation also changes depending on governmental policy a systematic random sampling method was preferred. This will require gridding the landfill sites into cell and collecting equal number of samples from each cell at similar depth.

Quality Control of sample: Two groups of quality control samples have been identified as required for the project: Sampling and analysis quality controls samples

Sampling quality controls

Equipment blank: the decontaminated sampling equipment is rinsed using de-ionized water under field conditions to evaluate the effectiveness of equipment decontamination or to detect sample cross contamination.

Field blank: this sample is prepared in the field using de-ionized water to evaluate the potential for contamination by site contaminants not associated with the sample collected (e.g., airborne organic vapors).

Analysis quality control samples

Reagent blanks: this will be analyzed along with the samples but will not contain any sample of interest but will undergo all process.

Duplicate samples: selected samples will have replicate sample to evaluate reproducibility of result.

Spikes sample: Known concentration of sample will be added to determine the recovery studied and certificated reference sample will be analyzed to evaluated process accuracy.

Activation process design: A review of the samples result will initiate the activation design. Two production options will be evaluated with variation in the activation parameters: the heating source using conventional furnace and microwave oven.

3.2.2 Developing Standard Operating Procedure for Sampling

The essence of the standard operating procedure is to outline equipment and methods that will be used in obtaining a representative sample of landfill composite from selected landfill sites (Olusosun and Abule-egba landfill sites) for analysis. The procedure addressed key points - as scope and application of procedure, gridding method, checklist and quality control sample. Appendix 4 present the detailed standard operation procedure developed for the purpose of sampling.

Pre Sampling Visit

The sites were visited to evaluate site activities and factors that could influence sampling operation. The active landfill site was observed to have a number of activities which affected the choice which influence sampling point within the allocated distance point.

Waste sorting: There were large volumes of segregated wastes within some of the sampling area. The volume of the waste could influence the composition of waste within the area. Waste sorters have specific locations within the landfill which were avoided during sampling. Figure 3.1 highlight some of the activities at the active landfill.

Figure 3.1: Area having sorted recyclable waste on the active landfill

Work in progress area: Area just receiving waste could not be sampled due to health and safety concern relating to the use of heavy equipment like bulldozer and compactors.

Closed landfill: The only area avoided at closed landfill is a small area having illegal dumping of organic waste from the market just by the East side of the dumpsite (see figure 3.2). This area is capable of given wrong composition of waste compared other part of the landfill.

Figure 3.2: **Fresh organic waste in the closed landfill**

3.3 Analytical Instrument

A number of analytical instrument were used during the analysis of samples to evaluate different properties of the samples. Instruments were selected based on methods' recommendation, analyte of interest and sensitivity of instruments.

3.3.1 Inductively coupled plasma - mass spectrometry (ICP-MS)

Inductively coupled plasma mass spectrometry (ICP-MS) analytical instrument was deployed for the evaluation of inorganic content of samples (Figures 3.3). ICP-MS is a trace multi-elemental detector capable of the detecting range of metals and non-metals concentrations as low as part per trillion. It has wide application potential with high speed, precision and sensitivity above other elemental analytical instrument like atomic absorption and emission technique which had created a surge in its application in heavy metal detection.

ICP-MS has been considered more suitable for the detection of over 60 different elements in acid leachate of solid waste matrix (USEPA 6020B). The high temperature plasma heat source (5,500^{0}C) will break all types of chemical bond making it a very versatile atomizer and molecular ionizer effective for the determination of total elemental content of heavy metal. ICP-MS works by measuring the ions of analyte generated by the plasma torch. The acid digest of solid waste is nebulized and transported by argon gas to the plasma torch. The sample is ionized and drifted to the mass spectrometer which detect component by the mass to charge ratio (*M/Z*). The type of acid and heat source used for waste digestion could influence the availability of elemental content of acid digest analyzed using ICP-MS (USEPA 6020B).

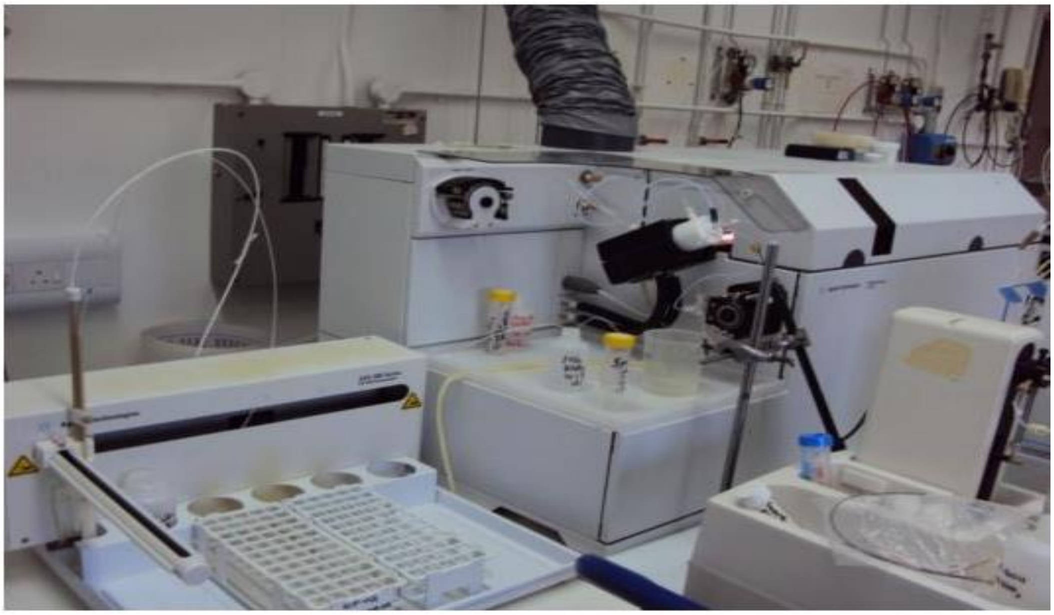


Figure 3.3 Inductively coupled plasma spectrometer (Agilent 7500 ICP-MS Agilent Technology, UK)

3.3.2 Microwave Digestion

Microwave assisted digestion system offers a fast, effective and convenient sample preparation for multi-element analytical techniques such as ICP-OES and ICP-MS. Microwave assisted digestion system provides an effective method in the determination of “total” metal analysis in a variety of matrices including organic and inorganic materials. Microwave heating source for acid digestion has been found to lead to better quantification of heavy metal toxic level in soil, waste, and food samples than conventional heating source (Poley-vos *et al.*, 1991; Zelano *et al.*, 1994, Al-Rmalli, 2012). In regards to this research, microwave assistant digestion was considered most appropriate considering the complexity associated with landfill composites. A variety of acids was chosen to verify trends in heavy metals contents in the samples. The CEM MARS X microwave digester (see Figure 3.4) has 24 sample vessels and power system range of 0 - 1800 Watts. The 20 ml samples vessels are fixed into a continuous mode turntable to ensure even distribution of microwave energy. The touch screen display provides an interface to select desired option of programme to be run.

Figures 3.4: CEM, microwave digestion MARXpress USA

3.3.3 Fourier transform-infrared (FTIR) spectroscopy

FTIR is a viable non-destructive analytical method for chemical characterization of waste. FTIR spectroscopy has been widely used in the characterization and stability assessment of waste (Smidt and Meissl, 2007). The interaction between the infrared radiation and waste components reveals its functional groups and bonding systems (Smidt and Schwanninger, 2005; Sitko *et al.*, 2004). The band position shapes and intensities are indicative of different functional groups (Ouatmane *et al*., 2000; Smidt and Meissl, 2007; Smidt et. al, 2009). FTIR spectroscopy can be adapted to different types of mode to analyze different material (gas, liquid, aqueous, amorphous and solid) from gas sensor mode to Attenuated Total Reflectance (ATR) mode (see Figure 3.5). The main advantages of (ATR) FTIR spectroscopy is that it is a faster technique suitable for most samples (solids, liquids, gels, pastes) and provides characterization with high sample reproducibility (Ouatmane *et al.*, 2000). In this research, ATR FTIR was applied to evaluate the chemical functionalities of precursors and activated carbons in order to understand the functionality of different landfills precursors and their respective activated carbon.

Figure 3.5 Alpha Fourier transform-infrared (FTIR) spectrometer (Bruker)

3.3.4 Scanning Electron Microscope with Energy Dispersive X-Ray Spectroscopy (SEM/EDX)

SEM/EDX provides a rapid and non-destructive method for the analysis of trace and major elements in solid samples. SEM/EDX is an effective analytical tool in source apportionment of environmental particulate matter (PM), evaluating size, chemistry, and morphology of particles (USEPA, 2002A; Wu et. al, 2011). It has been used to characterize the elemental composition of waste from mining areas, polluted soil sample and composite organic materials (Gonzalez-Fernandez, 2007; Kalfa, 2007; USEPA, 2002A). EDX evaluates characteristic X-ray lines of elements generated from sample as result interaction with X-ray source. SEM is ideal for imaging and analyzing the morphology of surfaces area porosity. EDX was used in this research to provide information on the elemental components of precursor and activated carbon produced. The surface morphology of precursor and activated carbons were also evaluated using SEM technique.

1: Energy Dispersive X ray spectroscope 2. Scanning electron microscope

3. Monitoring screen

Figure 3.6: Carl Zeiss EVO HD 18 SEM and Oxford EDX

3.3.5 Ultraviolet /Visible Spectrophotometer

Spectrophotometer is an essential analytical tool in quantitative analysis of sample through absorption principle. It is used to determine how much light a chemical substance absorbs when a known wavelength of light beam is passed through it. Quantitative wavelength suitable for analyte of interest could be determined through wavelength scanning. The instrument measures the amount of photons (the intensity of light) incident on the sample and amount receive by the detector after passing through the sample. Using the beer Lambert principle, the concentration of the sample is determined from the absorbance.

$A = \epsilon l c$

where

A = the measure of absorbance (no units),

ϵ = the molar extinction coefficient or molar absortivity (or absorption coefficient),

l = the path length, and

c = the concentration.

The light source of spectrophotometer could be varied from the ultra violet visible wavelength region of ultraviolet range (185 - 400 nm) and visible range (400 - 700 nm) to infrared region (700 - 15000 nm). In this research work, spectrophotometer was used to evaluate the adsorption capacity of produced activated carbon (see Figures 3.7).

Figure 3.7: G120845 Thermo Electron Helios Gamma Spectrophotometer

3.3.6 An Eltra CS800 Carbon Sulfur Determinator

The ELTRA CS-800 with induction furnace shown in Figures 3.8 offers a reliable tool for the determination of total carbon, total organic carbon and sulfur in minerals and inorganic samples(Sinha *et al.*, 2002, Zhao and Zhao, 2009, Desrochers et al ., 2015). It has 4 independent infrared (IR) cells used for precise simultaneous analysis of varying concentrations of carbon and sulfur in one measurement of combusted sample in the induction furnace. The sensitivity of the cells ranges from ppb levels to ppm depending on analyte of interest. With an average analysis time of 40 to 50 seconds, ELTRA CS-800 offer a fast and versatile application in inorganic sample evaluation. In this research, ELTRA CS-800 was used to determine the TOC of precursors.

Figure 3.8 Eltra CS800 Carbon Sulfur Determinator

3.3.7 BET surface area analyser

Micromeritics Gemini 2365 is an essential analytical instrument in the determination of surface area and porosity through gas adsorption analysis (see Figure 3.9). It has a unique identical sample balance tubes with well reproduced analytical conditions (pressure and temperature) during analysis. The interaction of pressurized gas flow into the tubes by a control valve is determined through static volumetric and mass detection analysis. The instrument has been used to determine the surface area for different porous material: nanoparticles and activated carbon (Franz *et al.*, 2000, Attia *et al.*, 2005, Ji and Zhang, 2009). The instrument was used in this research to determine the surface area, the porosity size, pores volume and adsorption isothermal of the activated carbon.

Figure 3.9 Micromeritics Gemini 2365

3.4 Sampling procedure

The sites were systematically gridded into seven sampling cells using a procedure described by Resource Conservation and Recovery Act (RCRA) waste sampling technical guideline USEPA (2002). A sampling cell was approximately 14,571 m^2 for the closed landfill and 52,857 m^2 for the active landfill. Each cell was located using the GPS and a total of three samples were obtained from each cell at different locations at the following depth: (i) upper-depth between 0-15 cm; (ii) mid-depth between 16–35 cm; and (iii) low-depth between 36-50 cm. Sampling was carried out at the end of both the wet and dry seasons, in March and August 2014 respectively. Samples were collected from areas without landfill covering. Sample collection was achieved using a bucket auger and samples were placed in decontaminated plastic containers. An average of 500 g of sample was collected from each sampling point and some parameters (pH and temperature) of the samples were determined on site according to EPA 9045D procedures. Samples were air-dried in the laboratory for three days and other sample treatments - oven drying, sieving and sorting followed. The moisture content of samples was evaluated by the ASTM D3173 procedure (ASTM, 1988).

3.5 Summary

This chapter has presented an overview of the research plans;

Highlighted sampling and implementation procedure.

Explained analytical instrument used in the research work.

CHAPTER FOUR

PRECURSOR CHARACTERIZATION

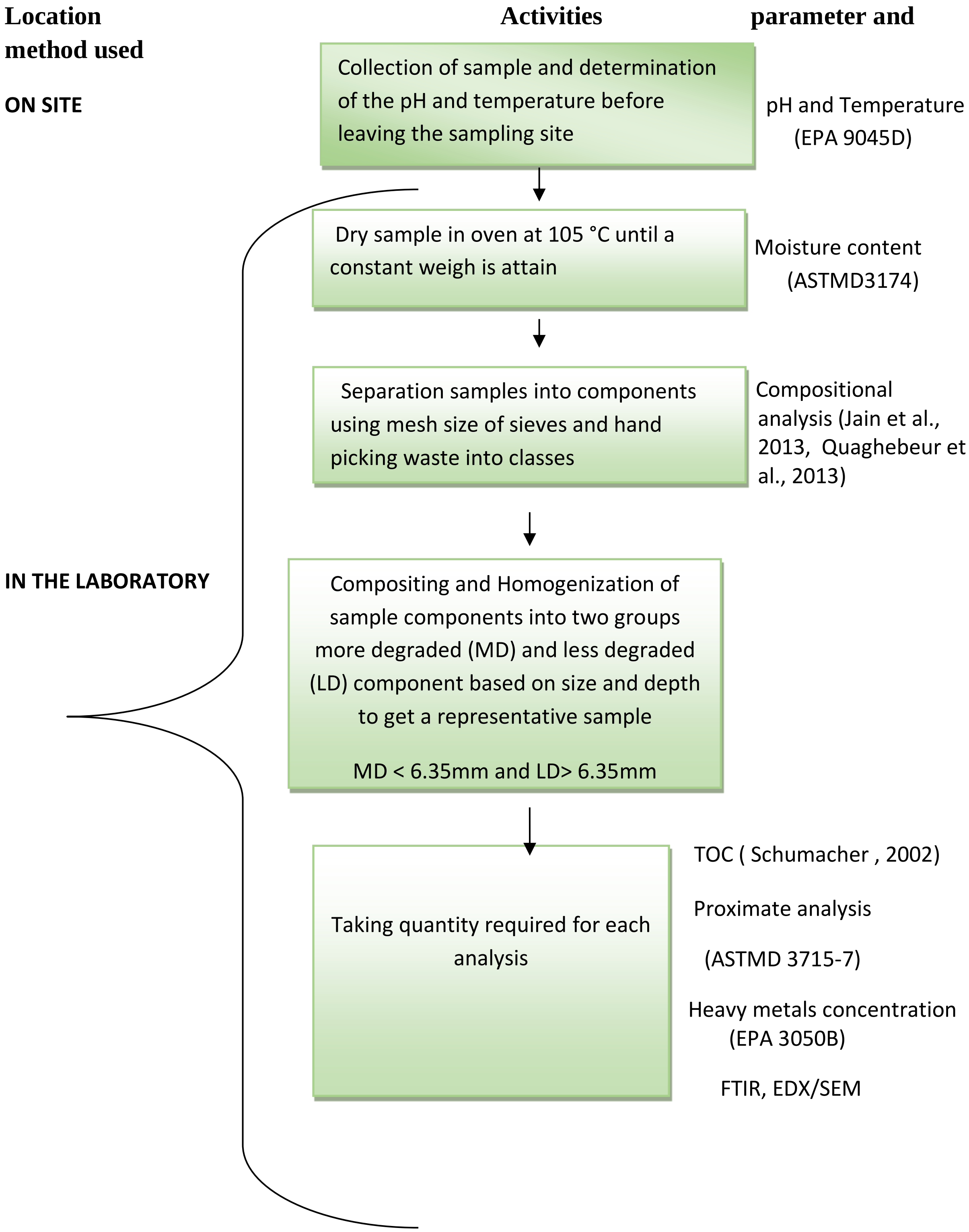
4.1 Introduction

This chapter presents results and discussions on the precursors' characterization in the following categories: compositional and physical, proximate and TOC, heavy metals, elemental and functionalities. The characterization studies were aimed at understanding different properties of the precursors that may affect the activation process. Figure 4.1 presents the flow chart on precursor treatment

4.1.1 Compositional and Physical Characterization

The landfill sites selected as precursors consist of mainly heterogeneous municipal solid waste from both closed and active landfill as explained in Chapter 2. Identifying the composition and physical properties of the waste present in landfills is important to the design of an activation process. This chapter reports on the experimental procedure taken to determine the composition of the landfill waste and their physical properties. While some physical properties were determined at the sampling sites, others were evaluated in the laboratory.

FLOW CHART OF SAMPLE TREATMENT



4.1.2 Proximate analysis and Total Organic Carbon (TOC)

Proximate properties of precursors are one of the major factors that will influence the activation process of biomass (Bolan *et al.*, 2013, Shen et al., 2010). Proximate analysis for dried sample consists of the determination of ash, volatile matter and fixed carbon contents of the raw precursor. These values essentially affect both the combustion behavior of precursor, percentage yield and nature of product formed (Bolan *et al.*, 2013). High moisture content could decrease the percentage yield while volatile matter/fixed carbon ratios of precursor influence combustion efficiency. On the other hand, ash content adds to the waste weight without enhancing the heating value and percentage yield. The organic carbon constituent in samples is determined from the TOC values. For this research, the proximate properties of sample were evaluated using ASTMD 3714-5 methods, and TOC determined using an Eltra CS800 Carbon Sulfur Determinator and by Walkley Black methods TOC (Zhao and Zhao, 2009, Schumacher, 2002)

4.1.3 Heavy metals Concentration of precursors.

Heavy metal burden of landfill is a major source of environmental toxicity (Page et al., 2014). It is responsible for the contamination of both surface and ground water. Depending on the nature, total concentrations and chemistry of heavy metal in the landfill composite, the leachate of landfill can either be a high or low risk to the environment (Jain et al., 2013). Heavy metals in the landfill site have been observed to be a major, non-volatile inorganic contamination which concentrations may not change due to landfill degradation but mobilized within and out of landfill through leachate flow. For the activation process of landfill composite, heavy metal concentrations in the precursor will be needed to design appropriate step within the conversion process to enhance heavy metal removal. Heavy metal concentrations of precursor in this work were determined using ICP-MS. The metals of interest are: As, Cd, Cr, Pb, Se, Ba, and Ag. Hg is excluded from the list of metal of interest because it is not detected by ICP-MS due its high volatility (EPA 3050B).

4.1.4 Elemental content and surface morphology of precursor

Knowing the elemental content of the precursor is essential to understanding the surface chemistry of the activated carbon that is made from it. It is important for understanding the possible ionic interaction within the activated site of carbon. It aids the explanation of the possible interaction between the available heteroatoms and the condensed poly aromatic or poly aliphatic sheets of the activated carbon. This plays a significant role in the chemical properties of the activated carbon. The spore sizes, type and distribution of precursor could play a major role in the adsorption capacity of the synthesized activated carbon. Reported here is the precursor elemental content and surface morphology in relation to the nature of the precursor (more degraded and less degraded) and sampling depth. The evaluation was carried out using Scanning electron microscope (SEM) with energy dispersive X-ray analysis (EDX) as described in Chapter 2.

4.1.5 Functionalities of the precursor

Chemical properties of precursor are largely influenced by the functional groups within the structure. Identifying the functional groups of the precursor is essential to understanding possible effect of activation parameters and possible functionality of the resulting activation product. The functional peaks will also provide information on the degradation properties and possible organic content of the precursor.

4.2 Methods

4.2.1 pH and temperature

The RCRA procedure has recommended determination of pH and temperature of waste properties on site. The EPA 9045D was used for this purpose. 20 g of each sample was collected into a plastic container and 20 mL of reagent water was added. The plastic was covered and shaken for 5 min. The solution was allowed to settle and the pH measurement and temperature was taken using Adwa AD11 pH meter. The reading of each sample was taken twice and the average determined.

4.2.2 Moisture content determination

Moisture content was determined using ASTM D 3173. Samples were spread on stainless steel container of known weight and placed in thermostatic drying oven at 105 °C and the weight of sample determined every 1 hour until a constant weight is attained.

The moisture content was determined thus

$$Mw = \frac{\text{Weight of sample on the field } (W_o) - \text{Weight of sample after drying } (W_1)}{\text{Weight of sample on the field } (W_o)}$$

4.2.3 Compositional characterization

Samples were separated into groups based on size and physical identification of the types of wastes. Separation was carried out by manual hand picking and sieve size method. Waste composites of less than 0.425mm mesh size of sieve were regarded as fine composition of the waste, while waste composites greater than 0.425mm but are less than 6.35mm were regarded as intermediate composition of the sample. Other compositions, which were greater than 6.35mm, were identified and placed in the appropriate class of waste. The fine and intermediate composition of waste - consisting of mostly soil and degraded waste - were classified as more degraded composite (MD) of the sample, while the remaining constituents were regarded as the less degraded (LD) (see Figure 4.1). Each bulk classification of waste was crushed and homogenized to make a representative samples for the analysis. The compositional procedure were design in line with methods used by Jain et al., 2005 and 2013 and Quaghebeur et al., 2013.

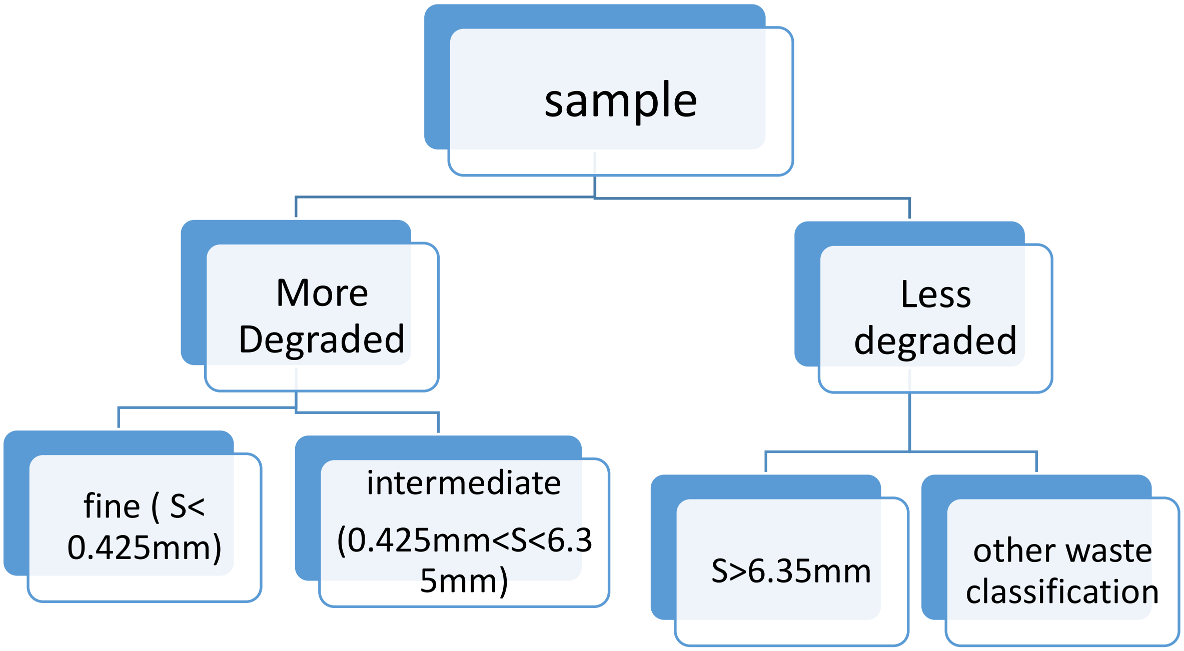


Figure 4.1: **Chart showing sample classification into components**

Eleven classes of waste were identified from the samples. They included glass, inert, metal, textile, wood, plastic, paper and cardboard, fine, intermediate, other and leather.

4.2.4 Proximate Analysis

The ash content of samples was determined using the ASTM D3174 method: representative samples (2 g) were weighed in a crucible and placed in a carbolite furnace for 1 h at 750 °C. After cooling the samples in a desiccator, the differences in weight were expressed as the percentage of the dry weights:

$\%$Ash content = $(W_o - W_{ash})/W_o)*100$ %

W_o is the dry weight; Wash is the weight of ash after heating at 750°C. The volatile carbon content of samples was determined by heating 2 g of samples at 925°C for 7 mins in a carbolite furnace (ASTM D3175), while the fixed carbon content was determined by subtracting the weight content of volatile and ash contents from the dry weight of the sample. Results were expressed as the percentage of the dry weigh (Kalanatarifard and Yang , 2011).

$\%\text{Volatile content} = (W_o - W_{VC})/W_o)*100\ \%$

W_o is the dry weight; WVC is the weight of sample after heating at 925 °C.

4.2.5 Total Organic Carbon (TOC)

4.2.5.1 Dry Method

An Eltra CS800 Carbon Sulfur Determinator was used; 1g of sample was treated with 6.5M HCl acid in an Erlenmeyer flask inside the TOC-module to remove inorganic carbon interference. Samples were placed in a crucible, and then combusted in the induction furnace at temperature of 1500 °C with a flow of pure oxygen that purges the CO_2 out of the flask, through to an infrared detector. The instrument was calibrated with reference material (3.0 % C steel) before and during the analysis.

4.2.5.2 Walkley Blacky method

Representative samples (1g) were oxidized using 0.1M dichromate and concentrated H_2SO_4. The excess $Cr_2O_7^{2-}$ was titrated with ferrous sulfate using ferroin indicator until color change from green to reddish brown. A blank sample was run using the same procedure. Triplicate titre values were determined and the average was used to calculate TOC content as thus:

$$\%C = \frac{(B-S) * M \text{ of } Fe^{2+} * 12 * 100 * 1.73}{\text{g of soil} * 4000}$$

where:

B = Volume (ml) of Fe^{2+} solution used to titrate blank

S = Volume (ml) of Fe^{2+} solution used to titrate sample

12/4000 = milliequivalent weight of C in g.

Total carbon conversion factor = 1.73(Schumacher, 2002)

4.2.6 Heavy metals concentrations in precursor

4.2.6.1 Precursor Acid Digestion

All digestion vessels were cleaned by washing with hot 6.3M hydrochloric acid at 80 °C, for a minimum of two hours followed by hot 7.3M nitric acid at the same temperature and time. The vessels were then rinsed with reagent water and dried in an oven. Homogenised samples (approximately 0.500 g) were weighed to the nearest 0.001 g into the cleaned digestion vessels. Concentrated nitric acid (10 ml) was added to each vessel containing the sample in a fume hood. These samples were pre-digested in the hood with the vessel loosely capped for 15 minutes. The digestion vessels were then tightly capped and placed in the CEM MARS Xpress digester microwave system after the power efficiency has been confirmed. The samples were digested using pre-programmed EPA3051 which digested samples by first raising temperature of each sample to 175 Electrical conductivity (EC) in 5.5 minutes and remain at 175 EC for 4.5 minutes. The heating system was at 60 % of 1600W. The vessels were allowed to cool for 1 hour before removing them from the microwave system. The vessels were vented in the fume hood for 30 minutes.

Samples were filtered and diluted with reagent water to the 50 ml mark, then centrifuge at 3000 rpm for 7 minutes. Samples were further diluted at 1:10 with reagent water. 5 ml of these samples were pipette and the heavy metal content detected using an Agilent 7500 ICP-MS. A total of 30 samples were digested using nitric acid while the remaining 31 samples were digested using the combination of nitric and hydrochloric acids (8 ml+3 ml).

4.2.6.2 Determination of heavy metals content in digested samples using ICP-MS

Agilent 7500 ICP-MS was used for the heavy metals determination. The instrument uses a collision cell for interference removal. Calibration standards for elements were prepared in the range 0.0-10 mg/l. An auto sampler (Cetac ASX-520) was used to inject the samples through the nebulizer (Thermo Fisher Scientific Inc., Waltham, MA, USA). The instrument was optimized with instrument parameters set at

PARAMETER	VALUE
RF Power (W)	1400
Cool Gas Flow (l/min)	13
Auxiliary Gas Flow (l/min)	0.8
Nebuliser Gas Flow (l/min)	0.85-0.90
Sample Uptake Rate (ml/min)	0.4 approx.
Sample Introduction System	
Concentric nebulizer	1.5mm ID injector

Instrumental calibration, reagent blank, instrument standards were run to evaluate the instrument optimum operation.

4.2.7 Elemental content and surface morphology of precursor

The homogenized samples were mounted on an aluminum stub with conductive carbon tape. The dust on the samples was removed with a spray before being placed in the sample chamber for analysis. The heterogeneous nature of these samples particles requires that multi-spot analysis of sample is carried out (USEPA 2002a). The working distance (WD) was maintained at 8.5 mm while the diameter apertures of sample were varied between 1µm and 1mm for the analysis of three different spots for each diameter. The accelerating voltage for all analysis was at 20 Kev.

4.2.8 Functionalities of the precursors

Representative samples (1 g) were additionally homogenised by means of a pestle and mortar prior to analysis using an Alpha ATR-FTIR Spectrometer (Bruker). The FTIR spectrophotometer covered a frequency range of 4000–400 cm^{-1}. In order to improve the signal to noise ratio, prior to every measurement background correction of the spectrum with a reference spectrum of the empty ATR crystal was carried out.

4.2.9 Quality Control

4.2.9.1 pH

Necessary quality control steps were taken during reading. The pH meter was calibrated using buffer 7 and 10 before use. Reagent water was used to clean the electrode after each measurement. The electrode is gently wrapped to dry using a tissue. Electrode is well covered with aqueous solution before measurement is taken.

4.2.9.2 Heavy metal determination

4.2.9.2.1 Power calibration

Three point power calibration involving measurement of absorbed power at three power setting of 400W, 800W and 1600W was carried out as thus:

1kg = 1 litre of distilled water is weighed (1,000.0 g + 0.1 g) into a beaker. The initial temperature of the water was determined a using thermometer. The beaker was covered and placed in microwave cavity and irradiated with microwave at selected power wattage for 2 minutes. The beaker was removed and the water vigorously stirred and the temperature measured within the first 30 seconds. The distilled water is disposed and the beaker allowed to cool by washing under the tap. The whole process was repeated using a fresh quantity of 1 litre distilled water and the average determine after running the calibration thrice. The power absorbed is determined by the following relationship:

$$P = (K\ Cp\ m\ \Delta T)/t$$

Where:

P = the apparent power absorbed by the sample in Watts

(W = joule sec^{-1})

K = the conversion factor for thermo chemical calories sec to watts (which equals 4.184)

Cp = the heat capacity, thermal capacity, or specific heat (cal g^{-1} °C^{-1}) of water

m = the mass of the water sample in grams (g)

ΔT = the final temperature minus the initial temperature (°C)

t = the time in seconds (s)

Using the experimental conditions of 2 minutes and 1 kg of distilled water

the calibration equation simplifies to:

$P = 47*\Delta T$

Presented below in table 4.1 is the calibration result with the efficiency range for each power rating

Table 4.1: Power calibration of the Microwave digester

S/N	Power rating (W)	Power reading (W)			Average power reading (PX)	Power limit point (PL)	difference(PX-PL)
		1st	2nd	3rd			
1	400	329	376	376	360	340	20
2	800	799	705	752	752	680	72
3	1600	1363	1457	1504	1441	1360	81

From Table 4.1 above, the microwave digester indicated highest wattage efficiency at 1600W. Although, all power rating options was above limits set for each point. The microwave digester was run using 1600W.

4.2.9.2.2 Quality control samples

Digested along with each batch of samples are other quality control samples: the spiked sample, duplicate sample, field blank, equipment blank, and reagent blank. A certified reference standard soil sample, CRM051-50G, was also analyzed to evaluated reproducibility of the extraction system.

4.2.9.2.3 Spiked sample procedure

Analyte grade chromium standard was used for the spiking process. The spiking concentration was determined to be 20 mg/l which is more than 20 times the quantification limit for chromium (20 X 0.75 mg/l = 15mg/l). Chromium standard solution (2 ml) was dissolved in 10 ml standard flask and made to mark. 2ml aliquots of the solution were added to 0.5g of the sample and allowed to dry in the oven at 50°C. The dried sample was digested as stated in Section 4.2.3 above

4.3 Result and discussion

4.3.1 pH values

A total of 44 and 33 samples were evaluated for the active landfill and closed landfill respectively. The pH values of samples in both landfills during the wet and dry seasons were mainly within the range of 7.2-7.6, with an average pH of 7.2 and 7.5 for the active landfill and 7.5 and 7.2 for the closed landfill respectively (Table 4.2). Landfill waste with pH >7 is considered as intermediately stable and the age to be >5 years (Kurniawan *et al.*, 2006, Kulikowska, and Klimiuk, 2008). At this pH, methanogenesis should be enabled through methanogenic microorganisms convert volatile fatty acids (VFA) to biogas (Sormunen *et al.*, 2008). This accession confirms Ogunyemi *et al*. (2010), who reported high population counts of bacteria and fungi at an active landfill (Olusosun) and a closed landfill (Abule-egba) while evaluating the microbial content of soil from the landfills at pH of 7.5 and 7.8 respectively. In the present study, pH also had different relationships with depth for the two landfills. The upper depth in the active landfill showed higher pH during both season with an average of 7.6, while the upper depth in the closed landfill showed the lowest during both season with an average of 7.3.

4.3.2 Temperature

Both landfills samples exhibit similar trend in the temperature values across the depth and with seasonal variation. The average temperature for all depth in both landfills sample were higher in the dry seasons (active landfill: dry season 33.3 °C, wet seasons 26.7 °C, closed landfill: dry season 34.9 °C, wet season 28.2 °C). For both landfills, the temperature increased with increase depth during the dry seasons while having no definitive trend in the wet seasons. This observation may indicate the effect of precipitation which tends to affect the heat content on the landfill through moisture movement across the depth.

Table 4.2: Comparison of measured parameters for active and closed landfills

	Active landfill N= 44						Closed landfill N= 33					
Depth	**Upper**		**Mid**		**Lower**		**Upper**		**Mid**		**Lower**	
Seasons	**Wet**	**Dry**	**Wet**	**Dry**	**Wet**	**Dry**	**Wet**	**Dry**	**Wet**	**Dry**	**Wet**	**Dry**
Average moisture (%)	31.1	25.8	40.4	23.8	33.4	28.0	29.5	19.7	36.2	24.1	30.38	31.0
Average TOCMD (%)	5.9	4.8	5.3	5.2	7.1	6.1	8.5	3.9	7.2	4.8	7.6	3.8
Average TOCLD (%)	9.8	ND	10.2	ND	7.6	ND	14.3	ND	13.3	ND	10.3	ND
Average pH	7.5	7.5	7.4	6.7	7.6	7	7.6	6.9	7.4	7.5	7.4	7.1
Temperature (°C)	25.6	33.5	27.7	31.2	26.9	40.4	28	34.6	28.1	34.9	28.5	35.1

TOCMD, TOC of more degraded samples; TOCLD, TOC of less degraded samples; ND, not determined: N, number sample.

4.3.3 Moisture content

The moisture content in both landfills varied with depth and seasonal condition. The major source of water flow in both landfills is from precipitation during the wet season. The water system of the landfills ensures that no other external water gets into the landfills and excess runoff water from the rain is collected in the leachate ponds at active landfill, while in the closed landfill it forms water logs at low level areas within the landfill. The active landfill had moisture content during both seasons at an average of 34.9 % during wet season and at 25.8 % during the dry seasons, compared to 31.9 % and 24.4 % respectively for the closed landfill. The difference in the average moisture content can be attributed to low absorption capacity associated with older waste in the closed landfill.

During the wet season, both landfills showed similar trend in moisture content (see Table 4.2) despite differences in waste composition. The variation in the more degraded composition in the upper depth of the landfills (82.6 % closed landfill; 63.9 % active landfill) had little impact on the moisture contents, at 29.1 % and 33.1 % for the closed and active landfill respectively. The more degraded components possess pores which can be filled with liquid during precipitation. As the volume of liquid increases within pores, the liquid is able to move by gravity to the next layer (Booth and Price, 1989; Munawar, 2014). The more degraded component seems to provide a water infiltration path within the landfill rather than absorption of moisture. At mid-depth, however, there was a higher percentage of less degraded components (35.5 % (w/w) closed landfill; 38.8 % (w/w) active landfill), which are less porous waste components (nylon, glass, metal, stone and leather). This slows the gravitation movement of the liquid, which may be responsible for the accumulation of moisture in the mid layer, at 31.2 % and 40.4 % for closed and active landfills respectively. Table 4.3 below shows the statistical regression analysis of the relationship between the more and less degraded components with moisture content of both landfills; moisture content in both landfills had a positive significant statistical relationship with less degraded weight ($p<0.01$), and a negative relationship with more degraded weight percentage ($p<0.05$).

Table 4.3: Regression analysis of waste parameters for both landfills

	Active landfill		Closed landfill	
Parameters	#MD Weight	## LD Weight	#MD weight	## LD weight
Moisture content (%)	- 0.86*	0.81*	-0.99*	0.96*
pH	0.89^	0.88^	- 0.31^	0.26^
# MDTOC	0.42^		-0.11^	
## LDTOC	0.59^		0.15^	

* Values have $p<0.01$ # more degraded
^ Values have $p>0.05$ ## less degraded

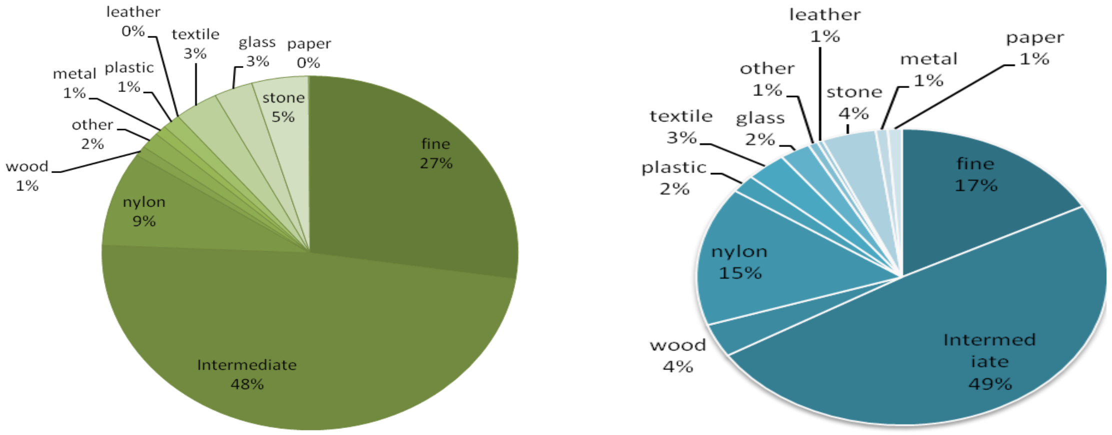
4.3.4 Composition

The compositions of samples from both landfills were similar in that three constituents are the major component in the entire cell sampled: fine, intermediate and Nylon. Figure 4.2 shows the average distribution of waste type in the landfills samples. Fine and intermediate components of waste constituted an average of 66.1 % and 75.3 % (w/w) of waste in both active and closed landfills respectively. There was a clear trend in the depth distribution of fine and intermediate components of waste in the active landfill: with increasing depth the intermediate constituent progressively decrease from 55.8 %(w/w) to 43.5 % (w/w), while the fine constituent increased from 13.6 % (w/w) to 24.2 % (w/w). Conversely, for the closed landfill, the intermediate constituent increased from 45.0 % (w/w) to 54.7 % (w/w) with increasing depth, while the fine component decreased from 37.8 % (w/w) to 21.2 % (w/w) (see Table 4.4). Generally, the volume of waste and soil in the landfill will be determined by the local practices, the landfill age, and the ratio of decomposed organic waste (Møller et al 2009). Jain *et al*. (2013) and Quaghebeur *et al*. (2013) have reported that 75 % of the fine and intermediate components of excavated waste were from the daily soil cover and degraded part of the waste. However, daily landfill covering was not practiced for the sites in the present study and the most likely source of the fine and intermediate constituents will be from the point of generation and from the degraded part of the waste. Nylon constituted an average of 15.1 % (w/w) of waste in the active landfill and 8.6 % in the closed landfill. Unlike other reported waste compositions from Thailand and Belgium (Quaghebeur *et al.,* 2013), nylon weight was not combined with plastic weight in the present study because of the large volume of nylon compared to other forms of plastic, and the need to recognize it as major stream of waste onto the landfills. The relatively high volume of nylon at the active landfill can be trace to the increasing use of polythene bags in household and commercial activities, as reported by Umara *et. al*, (2012).

Table 4.4 Composition (%) of samples with depth for both landfills

	Active landfill N = 44			Closed landfill N= 33		
Depth:	upper	mid	lower	upper	mid	lower
Fine	13.6	13.4	24.2	37.8	22.7	21.2
Intermediate	55.8	47.8	43.5	45.0	44.8	54.7
Nylon	12.4	21.8	11.3	5.5	16.0	4.4
Wood	5.6	0.6	4.6	0.1	0.2	2.3
Metal	1.5	0.7	0.5	0.2	0.3	2.4
Plastic	2.5	1.5	1.8	2.5	1.3	0.5
Leather	0.2	0.9	0.3	0.0	0.2	0.2
Textile	4.2	2.3	3.2	4.9	0.8	4.6
Glass	1.1	2.0	4.2	0.4	4.5	4.2
Stone	2.8	6.7	3.4	3.3	6.7	3.2
Paper	0.0	1.3	2.0	0.1	0.2	0.0
Other	0.3	1.0	1.0	0.2	2.3	2.3
Total	100	100	100	100	100	100

N: number of sample



Closed landfill **Active landfill**

Figure 4.2 Average distribution waste compositions in the closed and active landfills samples

In both landfills the paper constituent was a low proportion of the compositions; an average of 1.1 % (w/w) of the waste in the active landfill and a very minor constituent (0.1 % w/w) of the whole waste mass in the closed landfill. Paper constituent was lowest at lower depth (0.1% for active landfill and 0 % for the closed landfill). The low volume of paper in the samples could be due to the degradation of paper in the landfill. A similar observation was made on the decomposition of paper/cardboard by Quaghebeur *et al*. (2013), who reported a decrease from 14 % (w/w) of landfilled waste to 4 % (w/w) of the waste during evacuation. Also, Sormunen *et al*. (2008) observed that the proportion of paper and cardboard decreased towards the bottom of the investigated landfills, indicating their degradation.

4.3.5 Total organic carbon (TOC)

TOC determination indicated that 24 % of the samples had above >10 % TOC by mass, while 32 % had above the recommended quantity (IPCC 2006; DEFRA, 2010) for waste to be landfilled (6 % TOC). The less degraded component of the samples had more TOC than the more degraded samples in both landfills, with an average of 12.6 % for closed landfill and 9.2 % for active landfill. The TOC for both landfills varied with season but there was little evidence of a relationship with moisture content of samples (see Figure 4.3). TOC of samples showed no pattern with depth, with the exception of average TOC of the more degraded samples which increased with depth from 4.8 % to 6.1 % during the dry season in the active landfill. Similar observation was made by García *et al.,* 2016 evaluation of organic carbon content in excavated landfill waste who observed no linear relationship between depth of waste sample and availability of degradable organic fraction for a depth of 2- 30 m.

This result indicates that the non-degraded organic carbons are present in the less degraded components of both landfills. Stricter regulation is considered for these types of waste due to their recalcitrant nature on the landfill (Renou *et al.,* 2008). TOC of samples obtained during the wet season were greater than those of the dry season (7.8 % and 4.7 % for closed landfill; 6.1 % and 5.4 % for the active landfill). This may be due to the possibility of increased dissolved organic carbon within the landfill during the wet season. During the wet season increased precipitation washes out the degraded organic carbon forming leachate containing dissolved organic compound complex and colloid particulates, which move through layers within the landfills. The transport of leachate is affected by a variety of chemical and hydrologic factors, which enhance or impede the re-absorption of the organic carbon complex through the waste profile (Ogundiran and Afolabi, 2008).

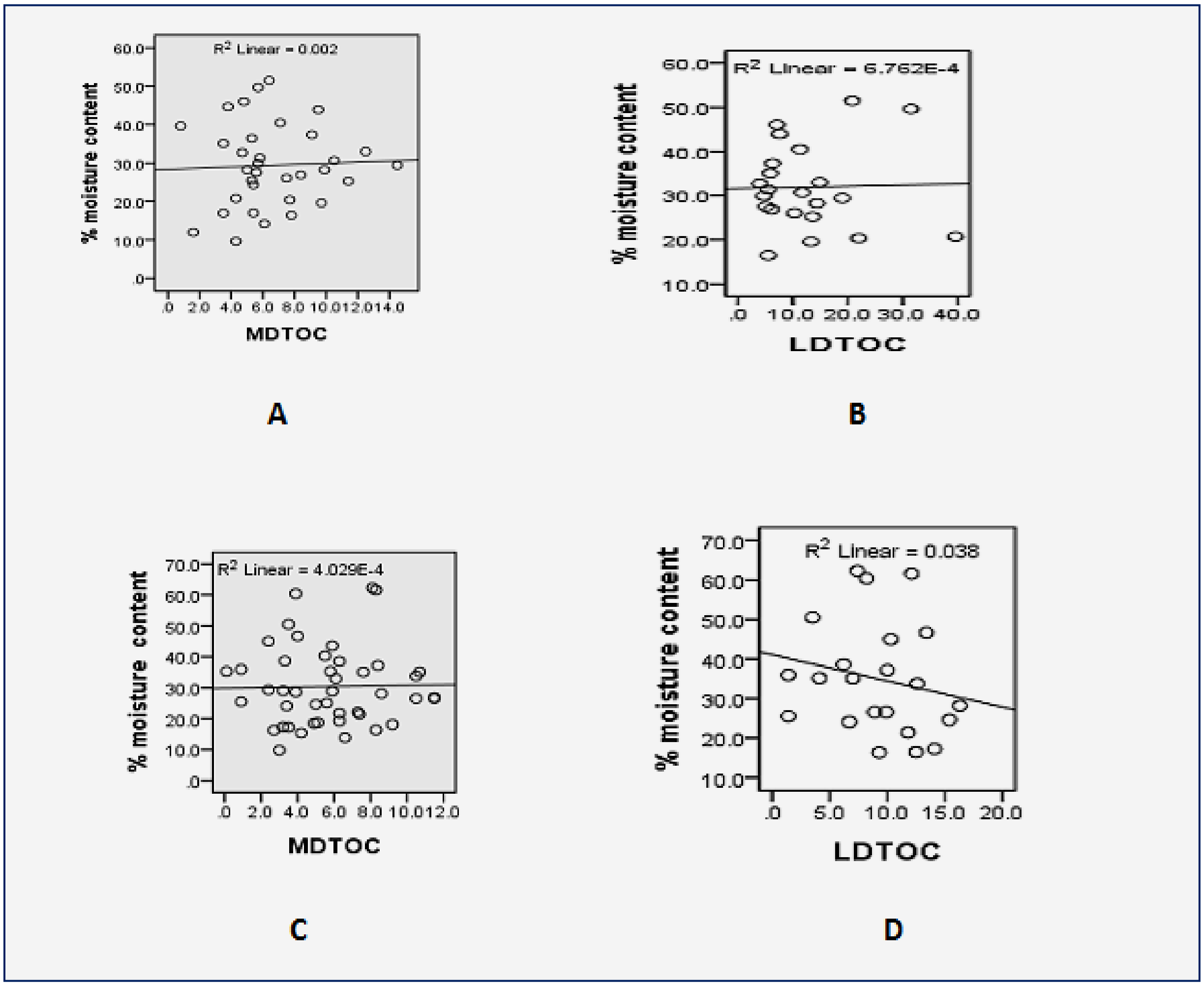


Figure 4.3 Correlation studies between moisture content and TOC

MD: More degraded, LD: Less degraded, TOC: Total organic content.

4.3.6 Proximate analysis

The proximate constituents of most samples from both landfills showed the same trend: ash content>volatile carbon>fixed carbon (Table 4.5). The more degraded samples of both landfills had very similar proportions of ash and fixed carbon (closed landfill, 58.8 and 17.0 % respectively; active landfill 57.2 and 17.2 % respectively). This reflects stability in the material composition of these components of waste due to degradation. Degraded waste and biomass are often high in ash and fixed content compared with fresh material (Simkovic *et. al.,* 2008)

Statistical analysis (ANOVA) of the proximate constituents of the more degraded and less degraded samples revealed that the differences between the active and closed landfill samples were not significant (p>0.05). There were no evident trends for proximate constituents, with sampling depth for the closed landfill. However, for the active landfill, volatile carbon of the more degraded sample increases progressively from 23.1 to 25.4 % with increased depth, while the ash content decreases from 60.2 to 56.2 %. In evaluating wastes for thermal conversion,

Proximate properties are the essential characterization used. The high average ash content (51 %) of these wastes is a limiting factor for their utility in heat generation. Ash content adds to the waste weight without enhancing the heating value, and also increases the ignition temperature of the waste which can reduce plant output and result in increased operating costs.

Table 4.5: Comparison of the average Proximate Composition (W/W %) of Samples from the Active and Closed landfills with depths

Closed landfill												
Depth	Upper layer				Mid layer				Lower layer			
Sample	volatile	ash	fixed	total	volatile	ash	fixed	total	volatile	ash	fixed	total
MD	20.8 (9.71)	61.2 (12.67)	18 (5.73)	100	33.4 (12.25)	52.4 (12.29)	14.2 (6.44)	100	23.4 (3.8)	58 (7.07)	18.6 (7.1)	100
LD	43.8 (20.51)	45.2 (17.57)	11 (4.56)	100	49.3 (22.71)	41.3 (19.6)	9.4 (4.79)	100	41.6 (13.99)	46.3 (12.74)	12.1 (4.27)	100
Active landfill												
MD	23.1 (8.95)	60.2 (10.97)	16.7 (4.89)	100	23.7 (9.95)	59.9 (8.49)	16.4 (12.45)	100	25.4 (13.43)	56.2 (12.95)	18.4 (6.5)	100
LD	39.6 (21.18)	46.1 (16.78)	14.3 (5.79)	100	40 (25.8)	47.4 (18.84)	12.6 (8.45)	100	39 (15.68)	44.6 (10.43)	16.4 (7.26)	100

More degraded samples (MD); less degraded samples (LD). The values in parentheses are the standard deviation based on 33 samples for each layer.

4.3.7 Heavy metal concentrations

4.3.7.1 Quality control sample

The detection limits for samples were evaluated by analyzing replicate determinations of the reagent blank. The results of blanks for each digestion were used to calculate the limit of detection (LOD) and limit of quantification (LOQ) using the equations.

LOD = 3 X SD and LOQ = 10 X SD (see Table 4.6) where SD is the standard deviation of the blank

Table 4.6 Detection limit using Aqua Regia and HNO_3

Detection limit using Aqua Regia

Blank Sample	Cr	As	Se	Ag	Cd	Ba	Pb
MDL (mg/l)	0.68	0.01	0.11	0.00	0.00	0.52	0.19
SD	0.75	0.00	0.04	0.01	0.00	0.14	0.05
LOD=3XSD	2.25	0.01	0.12	0.04	0.00	0.41	0.16
LOQ=10XSD	7.48	0.02	0.41	0.15	0.02	1.37	0.54

Detection limit using HNO_3

Blank Sample	Cr	As	Se	Ag	Cd	Ba	Pb
MDL (mg/l)	0.33	0.01	0.05	0.00	0.00	0.91	0.28
SD	0.08	0.01	0.02	0.01	0.00	0.24	0.04
LOD=3XSD	0.23	0.02	0.07	0.02	0.00	0.71	0.13
LOQ=10XSD	0.75	0.08	0.23	0.08	0.01	2.37	0.44

For the elements of interest As, Cd, Cr, Pb, Se, Ba, and Ag, 65 % of elements in the four duplicate sample replicated well with variation within limit (relative percentage difference (RPD) <20 %). The recovery study of spiked sampled was between 88 % and 99 % for the three spiked samples. Concentration of certificated referenced sample analyzed was within predicted interval for 60 % of the metals and replicated at (RPD< 8 %) for all elements except Ag. Table 4.7- 4.9 presents the values of the quality control samples.

Table: 4.7 Duplicate studies of samples using Aqua regia and HNO_3

Duplicate sample digested using aqua regia								
Sample\metal	Cr (mg/l)	Zn(mg/l)	As(mg/l)	Se(mg/l)	Ag(mg/l)	Cd(mg/l)	Ba(mg/l)	Pb(mg/l)
sample 1	50.3	7032.4	4.8	1.0	0.9	6.9	119.3	306.6
sample 2	56.5	8515.3	5.5	1.1	1.1	8.3	121.4	404.0
RPD	12 %	19 %	14 %	10 %	25 %	18 %	2 %	27 %

Duplicate sample digested using HNO_3

sample\metal	Cr (mg/l)	Zn(mg/l)	As(mg/l)	Se(mg/l)	Ag(mg/l)	Cd(mg/l)	Ba(mg/l)	Pb(mg/l)
sample 1	26.9	256.5	1.0	0.30	0.2	0.4	32.1	34.6
sample 2	16.9	257.9	1.0	0.25	0.1	0.6	32.6	27.7
RPD	46 %	1 %	0 %	15 %	46 %	29 %	2 %	22 %

Table 4. 8 Recovery studies of samples

Sample ID	number of sample	conc. of sample(mg/l)	conc. of spiked sample (mg/l)	spiked conc.(mg/l)	% recovery	acid used
CMD Lower	1	28.3	46.2	20	89.5	HNO_3
AMD upper	1	33.1	52.8	20	98.5	HNO_3
AMD upper	1	32.6	52.2	20	98	Aqua reiga

Closed landfill more degraded lower depth (CMD lower); Active landfill more degraded upper depth (AMD upper); Relative percentage difference (RPD)

Table 4.9 Certified reference sample

Acid Used	Cr (mg/l)	As (mg/l)	Se (mg/l)	Ag (mg/l)	Cd (mg/l)	Ba (mg/l)	Pb (mg/l)
Aqua regia	112.7	48.4	142.0	1.4	234.7	707.2	355.9
HNO_3	149.5	56.2	175.0	43.9	264.0	798.0	423.7
RPD	7 %	4 %	5 %	47 %	3 %	3 %	4 %

4.3.7.2 Acid extraction effect

Six of the seven USEPA-defined toxic heavy metals investigated, microwave digestion with Aqua regia resulted in higher concentration of metals than with HNO_3. Only Pb showed a higher average concentration of 150.9 mg/l for HNO_3 compared to 135 mg/l for aqua regia. Concentrations of heavy metals in samples varied with type of acid used. A student T-test was used to investigate if there are significant statistical differences in the concentrations of metals of each acid. The concentrations of metals in the acid digest had no significant statistical difference with $p > 0.05$. Both acids indicated a higher burden of heavy metals (>10 %) in closed landfill samples than active landfill samples, except for Cd and As. For both acids, five of the metals of interest had elevated concentrations in the more degraded component than the less degraded samples of both landfills (see table 4.10-4.13). The combination of nitric acid and hydrochloric acid was found suitable for the extraction of more metal from samples

Table 4.10 Toxic metals concentrations of closed landfill samples using aqua regia

More degraded N=2							
depth	Cr(mg/l)	As(mg/l)	Se(mg/l)	Ag(mg/l)	Cd(mg/l)	Ba(mg/l)	Pb(mg/l)
upper	23.1(0.7)	3.1(0.4)	0.8(0.1)	0.5(0.2)	5.4(0.1)	75.3(26.5)	184.0(52.4)
mid	31.0(15.1)	4.9(2.0)	0.5(0.1)	0.6(0.3)	4.1(1.8)	145.0(15.2)	154.2(61.5)
lower	31.1(18.3)	3.6(2.5)	0.4(0.1)	0.6(0.6)	11.8(11.4)	210.6(118.9)	157.6(117.6)
	Less degraded						
upper	23.0(12.1)	2.4(0.6)	0.3(0.1)	1.0(0.1)	2.2(2.1)	126.3(76)	177.2(154.7)
mid	20.5(6.8)	2.4(0.4)	0.4(0.1)	0.4(0.2)	3.2(0.9)	70.3(16)	118.6(74.7)
lower	35.2(22.4)	4.6(1.5)	1.1(0.9)	1.0(0.6)	6.4(1.7)	311.6(42.5)	380.1(81.6)

Table 4.11 Toxic metals concentrations of closed landfill using HNO_3 acid

More degraded N=2							
Depth	Cr(mg/l)	As(mg/l)	Se(mg/l)	Ag(mg/l)	Cd(mg/l)	Ba(mg/l)	Pb(mg/l)
upper	23.5(6.7)	2.2(1.2)	0.5(0.2)	0.4(0.1)	4.5(2.3)	58.7(1.5)	184.8(36.6)
mid	30.8(2.9)	5.2(3.1)	0.6(0.3)	0.6(0.5)	5.2(0.6)	202.6(51.2)	211.4(25.3)
lower	22.4(7.8)	2.1(0.3)	0.4(0.1)	1.0(1.2)	4.9(0.3)	99.1(23.0)	140.1(51.5)
Less degraded							
upper	18.4(9.0)	2.1(0.8)	0.3(0.1)	0.6(0.1)	3.3(0.3)	138.7(27.7)	183.0(146.7)
mid	21.2(7.4)	2.1(0.7)	0.3(0.0)	0.7(0.1)	7.3(3.1)	106.3(7.7)	195.6(45.1)
lower	25.1(16.7)	2.4(1.2)	0.3(0.1)	0.9(0.8)	4.2(2.9)	229.0(240.8)	355.5(123.8)

Values in parentheses are the standard deviations; N: Number of sample

Table 4.12 Toxic metals concentrations(mg/l) of active landfill samples using aqua regia

More degraded							
depth	Cr(mg/l)	As(mg/l)	Se(mg/l)	Ag(mg/l)	Cd(mg/l)	Ba(mg/l)	Pb(mg/l)
upper	39.4(9.6)	2.4(0.4)	0.3(0.0)	0.6(0.2)	1.7(0.5)	68.0(2.4)	66.1(22.0)
mid	21.1(2.6)	1.8(0.3)	0.3(0.0)	0.3(0.1)	2.1(0.2)	66.6(6.9)	71.6(6.3)
lower	20.2(6.9)	2.1(0.3)	0.3(0.0)	5.9(5.2)	4.1(0.4)	68.5(15.3))	59.6(21.6)
	Less degraded						
upper	27.3(0.5)	1.6(0.8)	0.3(0.0)	0.3(0.2)	1.0(0.9)	50.0(25.4)	60.0(36.0)
mid	34.3(9.1)	2.1(0.8)	0.3(0.1)	0.5(0.1)	6.0(3.0)	48.6(13.9)	127.8(10.3)
lower	16.0(4.5)	1.6(0.5)	0.3(0.0)	0.3(0.1)	1.2(0.5)	54.9(20.9)	63.9(38.1)

Table 4.13 Toxic metals concentrations of active landfill using HNO_3 acid

More degraded							
depth	Cr(mg/l)	As(mg/l)	Se(mg/l)	Ag(mg/l)	Cd(mg/l)	Ba(mg/l)	Pb(mg/l)
upper	22.6(14.4)	1.8(0.3)	0.1(0.0)	0.7(0.0)	2.0(0.7)	109.2(37.6)	76.1(41.3)
mid	15.8(2.7)	16.4(20.4)	0.2(0.0)	2.6(3.3)	3.0(2.3)	75.0(14.2)	81.3(12.4)
lower	23.9(10.4)	2.0(1.0)	0.2(0.0)	0.3(0.2)	1.9(0.8)	75.4(25.2)	68.7(34.0)
less degraded							
upper	14.7(0.8)	1.2(0.3)	0.1(0.0)	0.2(0.1)	1.3(0.2)	45.1(12.5)	68.3(38.9)
mid	28.7(1.5)	1.3(0.1)	0.2(0.0)	0.5(0.0)	8.8(9.1)	48.2(0.7)	121.4(68.5)
lower	31.0(20.2)	1.3(0.1)	0.2(0.1)	0.3(0.0)	1.5(0.0)	58.6(0.6)	121.4(75.0)

Values in parentheses are the standard deviations, N: Number of sample

4.3.7.3 Availability of heavy metals

The profile of heavy metals in both landfills samples showed the trend that the concentrations of metals was in the order Pb> Ba> Cr> Cd > As > Ag >Se. The elemental concentrations of these metals in the two landfills samples were mostly below both the USEPA toxic waste values and Flemish limit standards for waste soil reuse as agricultural compost and fertilizer, as reported by Quaghebeur et al. (2013) exept for Pb which were above limit the in the closed landfill (Table 4.14).

TABLE 4.14: Comparison of the average concentrations (mg/l) of toxic metals of samples from Active And Closed landfills to the Flemish Regulations Limit and the USPEA Toxic Metal Standards

Sample / Element	As	Cd	Cr	Hg	Pb	Se	Ba	Ag
Closed-MD (n=12)	2.69 (1.64)	4.84 (1.9)	23.87 (8.01)	ND	212.00 (94.76)	0.44 (0.20)	69.50 (27.0)	0.70 (0.50)
Closed-LD (n=12)	3.50 (1.50)	5.50 (4.8)	27.34 (12.06)	ND	195.28 (114.30)	0.57 (0..37)	156.53 (98.63)	0.68 (0.38)
Active-MD (n=12)	4.01 (8.43)	3.08 (3.9)	23.11 (10.31)	ND	89.87 (43.87)	0.20 (0.03)	134.0 (97.48)	0.76 (1.31)
Active-LD (n=12)	1.92 (0.51)	2.69 (2.1)	26.37 (9.83)	ND	74.84 (31.28)	0.32 (0.03)	59.42 (14.84)	1.32 (2.67)
Flemish limit values [a]	150	6	250	5	300		100	5
USEPA TCLP concentrations [b]	5	1		0.2	5	1		

More degraded samples (MD); less degraded samples (LD); number of samples (n); standard deviations are shown in parenthesis; United States Environmental Protection Agency USEPA; toxicity characteristic leaching procedure concentrations (TCLP).

[a] for use of soil waste as fertilizer and compost as reported by Quaghebeur *et al.*2013

[b] USEPA TCLP heavy metal concentrations limit for municipal waste.

Total elemental Concentration is 20 TCLP concentrations, according to method 11311 USEPA.

Boron and selenium were rarely detected in the entire sample analyzed. The availability of metals bears no definite trend with the depth for both landfill samples regardless of the acid used in digestion.

4.3.8 Elemental characterization

Tables 4.15 and 4.16 below presents the elemental concentrations for samples at each depth. The two landfills had similar major elemental constituents, representing 96.5 % and 98.4 % of the elemental composition for the closed (O > C > Si > Fe > Ca >Al) and active (C > O > Si > Al > Ca > Fe) landfills respectively. For both landfills, Mn and Ni were rarely found: their occurrence was less than 5 % and 1.4 % for closed and active landfill samples respectively. When comparing across the two landfills, each of these major elemental constituents were within the same range for (C, O) and (Al, Fe, Ca, Si).

The elemental composition of the more degraded samples varied with depth of landfills. For the active landfill, O, Al and K concentrations progressively decrease from the upper to the lower layer (Al, 4.36 to 1.13 %; O, 42.09 to 36.78 %; K, 0.21 to 0.12 %), while Ti and C increased down the layers (Ti, 0.21 to 1.2 1%; C, 35.25 to 47.66 %). For the closed landfill, Ca, Cu and Ti concentrations increased with depth of sampling. There was no clear trend in the elemental composition of less degraded samples with depth for both landfills. The depth distribution of the elemental concentrations in the more degraded samples could be associated with a leaching effect on the degraded components of waste. Leachate is able to flow through the more degraded component of waste interacting with the elemental components, which could change the redox of the liquid present and thus influence mobility of constituents. A similar observation was made by Kaartinen *et al*. (2013), who reported a decrease in the concentrations of Cl and S down layers of degraded waste samples due to a leaching effect.

The concentrations of Al (1.5 % w/w), Si (5.0 % w/w) and Ti (0.36 % w/w) reported for a closed landfill in Finland (Kaartinen *et al.,* 2013), of the same age range and for fine components < 20mm mesh, were similar to values obtained for degraded samples from the closed landfill in the present study. The concentrations of Fe for the more degraded samples from the closed landfill were also similar to levels reported by Quaghebeur *et al*. (2013) who reported concentrations of Fe between 1.7 and 3.9 % (w/w) for the fine fraction (<10 mm of municipal solid waste).

Table 4.15: Descriptive analysis of the elemental constituents of closed landfill samples in each layer (w/w %)

Element	C	O	Mg	Al	Si	P	S	Cl	Ca	Fe	Zn	K	Ti	Cu	Na	Mn
MORE DEGRADED SAMPLES																
Upper layer																
Mean (7)	39.07	38.76	0.14	1.69	8.23	2.89	0.14	0.04	6.8	0.96	0.91	0.22	0.08	ND	0.06	ND
Median	37.94	43.99	0	0.59	2.25	0.33	0.16	0	4.14	0.93	0.93	0	0		0	
SD	21.39	12.03	0.24	3.19	9.77	3.57	0.14	0.08	7.17	0.96	0.55	0.47	0.16		0.15	
Range	19.39-81.69	18.31-51.88	0.0-0.65	0-8.91	0-26.45	0.0-7.89	0.0-0.31	0.0-0.16	0.0-14.37	0.0-2.88	0.0-1.83	0.0-1.26	0.0-0.42		0.0-0.39	
Mid layer																
Mean (12)	36.26	39.93	0.16	1.31	3.82	0.1	0.04	0.01	8.37	9.18	0.35	0.04	0.31	0.11	0.01	ND
Median	31.89	43.43	0	1.09	3.04	0	0	0	1.84	1.64	0	0	0	0	0	
SD	22.55	13.69	0.28	1.26	4.3	0.17	0.09	0.03	11.99	14.89	0.48	0.1	0.65	0.16	0.04	
Range	15.17-84.21	15.79-58.15	0.0-0.79	0.0-3.96	0.0-14.69	0.0-0.45	0.0-0.29	0.0-0.1	0.0-31.3	0.0-35.46	0.0-1.2	0.0-0.27	0.0-2.13	0.0-0.37	0.0-0.14	
Lower layer																
Mean (9)	40.96	32.5	0.11	1.95	4.47	0.21	0.9	0.11	10.43	2.33	0.57	0.21	0.35	0.92	0.04	ND
SD	6.55	8.86	0.18	0.81	5.65	0.32	1.8	0.3	10.12	2.86	0.9	0.47	0.63	1.63	0.08	
Median	40.34	36.12	0	1.67	2.58	0.15	0	0	7.98	1.23	0	0	0	0	0	
Range	32.28-51.78	14.81-41.41	0.0-0.53	0.0-2.74	0.0-17.82	0.0-1.03	0.0-5.01	0.0-0.9	0.48-25.28	0.0-7.82	0.0-2.03	0.0-1.45	0.0-1.79	0.0-4.29	0.0-0.2	
LESS DEGRADED SAMPLES																
Upper layer																
Mean (11)	40.92	38.42	0.13	2.83	4.93	0.31	0.07	0.03	1.84	8.14	0.73	0.57	0.34	0.03	0.03	0.67
Median	41.22	36.56	0.07	2.9	3.42	0.26	0	0	0.95	4.97	0.31	0.11	0.27	0	0	0
SD	7.79	8.32	0.19	1.8	4.05	0.16	0.08	0.07	1.76	7.53	0.96	1.18	0.41	0.09	0.09	2.22
Range	23.91-31.95	26.5-54.18	0.0-0.54	0.24-5.24	0.49-13.58	0.11-0.67	0.0-0.23	0.0-0.23	0.33-5.85	0.15-19.06	0.0-2.78	0.0-3.98	0.0-1.4	0.0-0.29	0.0-0.29	7.35
Mid layer																
Mean (12)	39.42	39.5	0.39	1.03	13.02	1.04	0.07	0.02	3.61	0.81	0.66	0.12	0.08	0.07	0.04	0.04
Median	34.31	41.93	0.2	0.69	6.83	0.23	0	0	1.06	0.5	0	0	0	0	0	0
SD	18.08	9.19	0.85	0.98	12.84	2.88	0.12	0.06	6.18	0.95	1.86	0.27	0.14	0.24	0.13	0.09
Range	19.05-73.42	22.92-51.88	0.0-3.06	0.0-2.91	0.84-30.91	0.0-10.16	0.0-0.38	0.0-0.21	0.0-19.05	0.0-2.66	0.0-6.51	0.0-0.86	0.0-0.38	0.0-0.82	0.45	0.32
Lower layer																
Mean (11)	22.81	49.22	0.08	2.82	10.89	0.22	0.18	0.02	1.44	10.4	0.24	0.29	0.55	ND	0.03	ND
Median	23.45	48.94	0	0.32	7.21	0	0	0	0.59	3.49	0	0	0		0	
SD	9.87	5.37	0.12	3.51	14.18	0.41	0.33	0.08	2.23	12.25	0.39	0.61	1.3		0.11	
Range	6.5-37.12	41.45-60.49	0.0-0.28	0.15-9.56	0.58-43.47	0.0-1.34	0.0-1.11	0.0-0.26	0.0-7.11	0.0-28.08	0.0-1.09	0.0-2.09	0.0-4.34		0.0-0.36	

SD = standard deviation; ND = not detected; values in parentheses are the number of sample. Elemental composition was determined by SEM/EDX analysis

Table 4.16: Descriptive analysis of the elemental constituents of Active landfill samples in each layer (w/w %)

Element	C	O	Mg	Al	Si	P	S	Cl	Ca	Fe	Zn	K	Ti	Cu	Na	Mn
MORE DEGRADED SAMPLES																
Upper layer																
Mean (12)	35.25	42.09	0.36	4.36	9.63	0.05	0.13	ND	5.57	2.11	ND	0.21	0.24	0.02	ND	ND
Median	30.1	44.01	0	1.57	9.27	0	0		0.7	1.81		0.05	0	0		
SD	21.73	13.45	0.66	4.09	7.22	0.12	0.3		13.75	1.89		0.39	0.36	0.05		
Range	10.19-71.22	17.96-57.76	0.0-2.19	0.63-10.27	1.05-22.63	0.0-0.38	0.0-0.9		0.0-48.49	0.0-5.79		0.0-1.37	0.0-1.14	0.0-0.18		
Mid layer																
Mean (12)	42.86	39	0.09	4.02	6.77	0.31	0.23	0.06	1.88	3.46	0.78	0.17	0.3	0.04	0.03	0.02
Median	44.71	37.86	0	2.09	2.95	0.24	0.07	0	0.64	3.21	0.25	0.12	0.12	0	0	0
SD	22.02	12.52	0.13	4.18	8.25	0.31	0.4	0.15	2.68	3.06	1.03	0.23	0.41	0.09	0.11	0.05
Range	13.5-70.95	23.38-56.54	0.0-0.42	0.57-13.58	0.73-28.98	0.0-0.98	0.0-1.35	0.0-0.42	0.0-7.77	0.3-10.14	0.0-2.53	0.0-0.79	0.0-1.24	0.0-0.27	0.0-0.37	0.0-0.19
Lower layer																
Mean (12)	47.66	36.78	0.42	1.73	8.51	0.08	0.04	0.04	2.18	1.07	0.02	0.12	1.21	0.03	0.02	ND
Median	54.66	30.68	0.11	1.24	3.17	0	0	0	0.71	0.53	0	0.1	0	0	0	
SD	22.06	11.84	1.08	2.08	10.39	0.13	0.07	0.06	4.82	1.1	0.06	0.12	3.99	0.08	0.05	
Range	13.79-70.26	22.42-55-43	0.0-3.84	0.23-8.11	0.7-29.41	0.0-0.41	0.0-0.23	0.0-0.15	0.19-17.19	0.13-3.39	0.0-0.22	0.0-0.29	0.0-13.87	0.0-0.24	0.0-0.13	
LESS DEGRADED SAMPLES																
Upper layer																
Mean (12)	44.82	37.68	0.71	3.04	7.31	0.05	0.07	0.06	4.93	0.96	ND	0.19	0.11	0.01	0.04	ND
Median	53.39	35.83	0	1.82	3.35	0	0	0	0.35	0.8		0.05	0.04	0	0	
SD	23.45	9.74	2.3	2.85	9.22	0.19	0.17	0.17	9.91	0.42		0.33	0.14	0.04	0.1	
Range	11.71-71.66	26.06-52.56	0.61-9.38	0.64-29.47	0.0-28.83	0.0-0.65	0.0-0.51	0.0-0.57	0.0-28.98	0.59-1.93		0.0-1.11	0.0-0.38	0.0-0.13	0.0-0.28	
Mid layer																
Mean (11)	39.8	43.25	0.05	5.05	7.41	0.08	0.07	0.02	0.64	2.27	0.07	0.17	0.6	0.02	0.47	ND
Median	30.7	47.91	0	6.47	7.96	0	0	0	0.34	2.56	0	0.11	0.24	0	0	
SD	23.22	14.47	0.11	3.66	5.62	0.14	0.21	0.07	0.85	1.83	0.23	0.24	1.4	0.05	1.37	
Range	19.47-85.48	14.43-55.89	0.0-0.32	0.0-9.43	0.09-20.17	0.0-0.37	0.0-0.71	0.0-0.23	0.0-2.67	0.0-5.91	0.0-0.75	0.0-0.83	0.0-4.79	0.0-0.18	0.0-4.58	
Lower layer																
Mean (12)	48.21	37.09	0.21	3.21	5.98	0.08	0.15	0.18	2.47	1.65	0.09	0.35	0.14	0.02	0.18	ND
Median	50.79	35.03	0.11	3	5.05	0	0.16	0.17	1.43	0.92	0	0.27	0.12	0	0.21	
SD	19.14	11.69	0.3	2.67	6.04	0.12	0.12	0.14	3.37	1.96	0.16	0.32	0.15	0.06	0.15	
Range	16.83-82.43	17.44-55.19	0.0-1.05	0.0-8.55	0.0-22.5	0.0-0.31	0.0-0.36	0.0-0.47	0.0-12.07	0.0-6.65	0.0-0.42	0.0-0.93	0.0-0.49	0.0-0.16	0.0-0.48	

SD = standard deviation; ND = not detected; values in parentheses are the number of sample. Elemental composition was determined by SEM/EDX analysis.

However, the concentrations of K, Fe, Ti and Mn for both landfills were lower than those obtained for soil contaminated with recyclable urban waste in Brazil (Anjos *et al.,* 2002). A comparison of elemental medians of both landfills using a non-parametric Mann-Whitney U-test indicated that there were no significant statistical differences ($p>0.05$) in concentrations between active and closed landfills for C, O, Mg, Si, P, S, Cl, Fe, Zn, Ti, Cu and Na. However, Al was found to be significantly higher ($p=0.024$) in the active landfill, while Ca was significantly higher ($p=0.023$) in the closed landfill.

4.3.8.1 Cluster analysis for elemental constituents

Hierarchical agglomerative cluster analysis was performed using Ward's method, and squared Euclidean distances as a measure of similarity. Ward's method was considered more appropriate agglomerative technique for the data analysis as it partitions data set into cluster by computing sum of squared distances within each set with minimum increase in the overall sum of squares partitions (Punj & Stewart, 1983; Liao, 2005).

Average linkage and centroid methods are other methods which measure either minimum or maximum distance between the data sets (Liao, 2005). The cluster analysis was used as an unsupervised exploratory technique to investigate similarities among the elemental composition of the two landfills. The analysis of the closed landfill samples generated two main clusters (Figure 4.4): one comprised mostly of more degraded samples (5 of the 7 cluster members), while the other comprised mostly of less degraded samples (4 of the 5 cluster members). The analysis of the active landfill samples also generated two main clusters, but with an equal number of more degraded and less degraded samples in each cluster (Figure 4.5). A Mann-Whitney U-test analysis was conducted on the mean levels of elements to establish potential significant difference between the main clusters for each landfill. Levels of C, O, Si and Ti showed significant difference ($p<0.05$) between the main clusters for each of the landfills. This suggests that more samples from the closed landfill had similar trends in their element composition based on sample composition (more degraded / less degraded) than other associated factors such as depth and sampling seasons. For the active landfill, however, the elemental composition of samples showed no clear similarity trend in relation to sample composition, depth and sampling season.

The elemental composition of samples will largely depend on the nature of waste material, which can be influenced by interaction with the complex heterogeneous environment of the landfill (Shen et *al.*, 2010, He *et al.*, 2011). Discrimination analysis revealed that C, O and Si were the major discriminators of the clusters for both landfills (Wilks' lambda <0.5, F > 58.516 (see Table 4.17). Wilk's lambda value shows how well each level of the independent variables contributes to the model. The scale ranges from 0 to 1, where 0 means total discrimination, and 1 means no discrimination. The significance of the change in the model is measured with an F-test; if the F-value is greater than the critical value, the variable is kept in the model. Hence, the smaller the Wilk's lambda values and the higher the F-test result, the greater the discriminating capacity of the variable (Rodrigues et al., 2010).

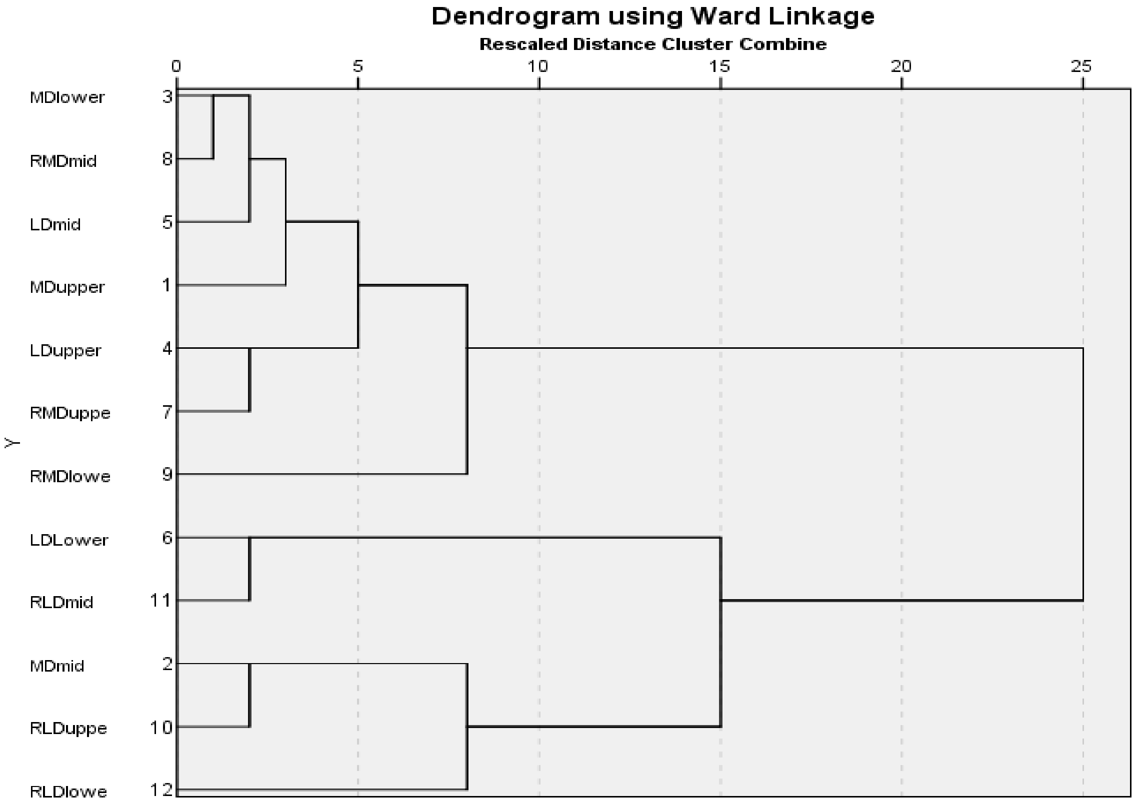
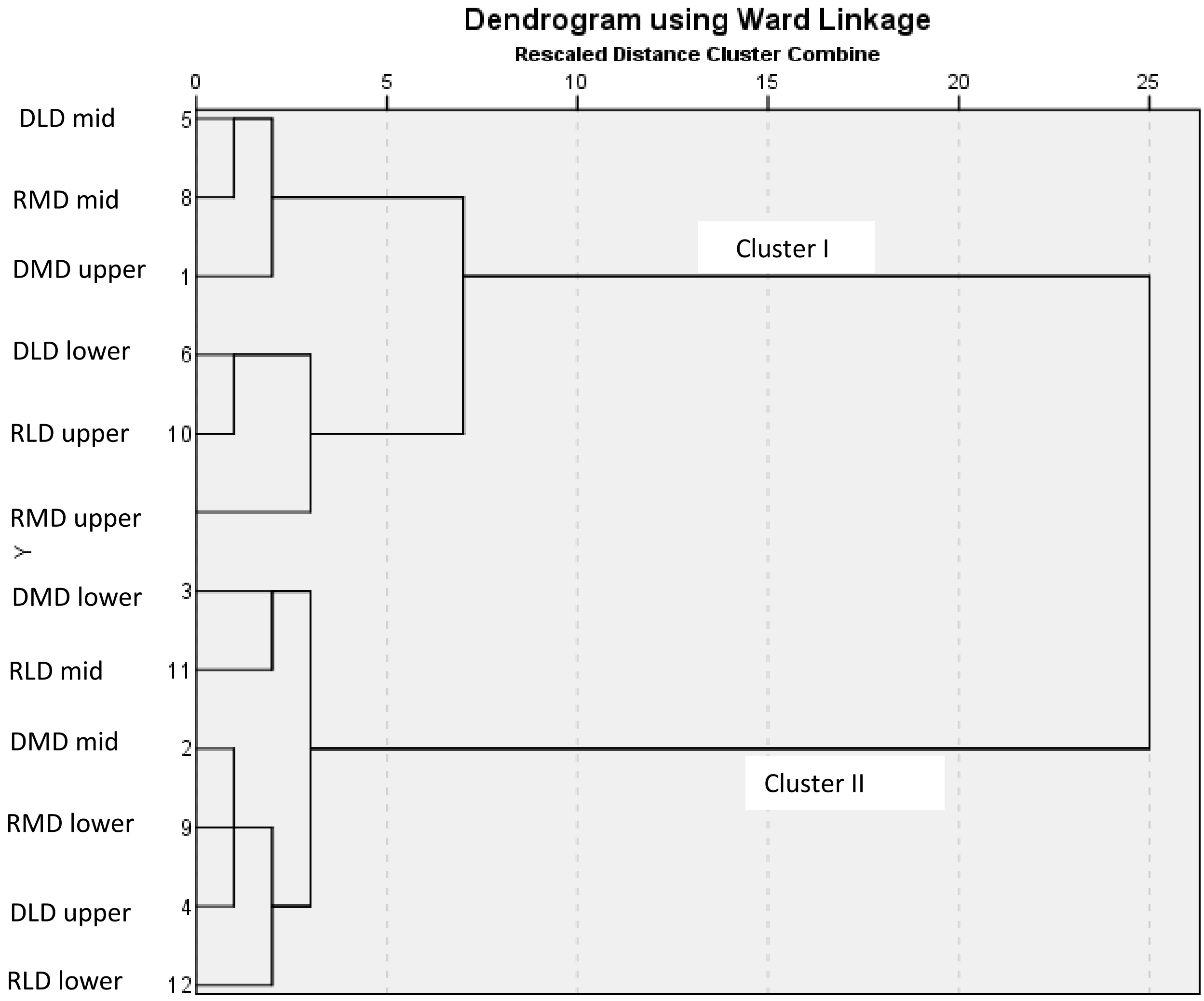


Figure 4.4: Dendrogram showing similarity in the closed landfill samples based on elemental composition data. Dry season (D); rain season (R); more degraded samples (MD); less degraded sample (LD); depth of sampling (lower, mid, upper)



Figures 4.5: Dendrogram showing similarity in the active landfill samples based on elemental composition data. Dry season (D); rain season (R); more degraded samples (MD); less degraded sample (LD); depth of sampling (lower, mid, upper).

TABLE 4.17: Discrimination capacities of elemental components in the detected clusters of closed and active landfills samples

Element	Closed landfill (Fig.4.4)		Active landfill (Fig4.5)	
	Wilks' lambda	F	Wilks' lambda	F
C	**0.201**	**274.841**	**0.484**	**63.685**
O	**0.244**	**213.394**	**0.452**	**72.696**
Mg	0.954	3.176	0.991	0.533
Al	0.908	28.468	0.993	0.429
Si	**0.541**	**58.517**	**0.851**	**10.530**
P	0.997	0.190	0.999	0.0542
S	0.996	0.287	0.991	3.358
Cl	0.991	0.649	0.969	1.89
Ca	0.967	2.338	0.997	0.200
Fe	0.976	1.705	0.993	0.422
Zn	0.942	4.260	1.000	0.482
K	0.971	2.087	0.971	1.767
Ti	0.992	0.539	0.995	0.287
Cu	1.000	0.010	0.951	3.117
Na	0.989	0.776	0.999	0.080

The most discriminating elements are shown in bold

4.3.9 Functionalities of the precursor

Figure 4.6 presents representative FTIR spectra of the different samples analyzed. The characteristic fresh waste peaks for organic functional group were absent in all analyzed samples (24 samples) of both landfills, *vis*: at 1740 cm^{-1} and 1760 cm^{-1} for esters and carboxylic respectively; carboxylic acids at 1260 –1240 cm^{-1}; and aromatic primary and secondary amines at 1320 cm^{-1} (Wu *et. al*, 2011). The spectra of samples from both landfills shared some common characteristic peaks, while other peaks were only associated with either active or closed landfill samples. No remarkable differences were observed when comparing the FTIR peaks of samples based on depth or sampling season. However, the FTIR of fresh municipal waste obtained before landfilling showed all major peaks of organic functional groups: 1240 cm^{-1}, 1320 cm^{-1},1538 cm^{-1} 1638cm^{-1}, 1742 cm^{-1} (Figure 4.6).

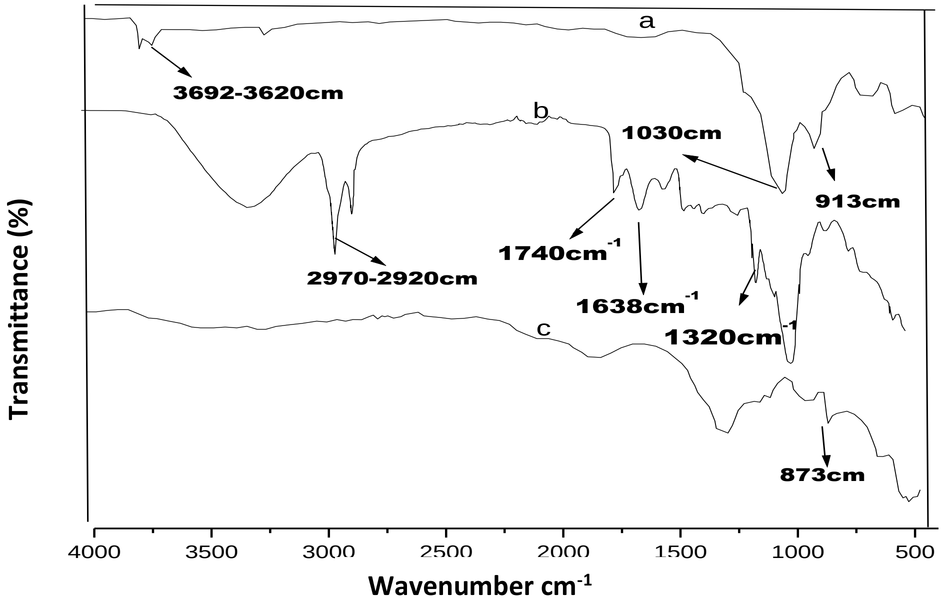


Figure 4.6: Typical infrared spectra of (a) active landfill, (b) fresh municipal waste, and (c) closed landfill samples

4.3.9.1 FTIR peaks common to both landfills

A small peak of carboxylic acid group (C–O stretch vibration and C–O of plane vibration) at 1420 cm^{-1} (Smidt *et al.,* 2002) was found in samples from both landfills. Very weak aliphatic methyl and methylene peaks, at 2960 cm^{-1} and 2920 cm^{-1} respectively (Smith,1999), were only found in a few samples from both landfills (40 % of active and closed landfill samples). Taken together, these findings indicate that samples from both landfills comprised non-fresh waste. Smidt & Meissl (2007) have attributed weakness or disappearance of aliphatic methyl and methylene peaks, at 2920 cm^{-1} and 2850 cm^{-1} respectively, as an indicator of waste degradation. The organic functional groups spectral peaks are known to decrease in intensity or disappear with progressive degradation of waste (Smidt and Schwanninger, 2005).

The prominent peaks common to the active and closed landfill samples spectral were peaks of inorganic compounds. The intense peaks at around 1030-3 cm^{-1} and 1000-9 cm^{-1} can be attributed to silica, clay minerals (Si–O–Si and Si–O stretching vibration) and quartz (Madejova, 2013); particularly strong absorption at 1032-3 cm^{-1} and 1006-9 cm^{-1} was evident for samples from the closed landfill. The peaks have been attributed to reflect the degree of soil, silica content or degradation in waste (Ouatmane *et al.,* 2000, Reig, 2002, Smidt and Meissl, 2007). Increasing decomposition of the organic matter within waste will lead to a relative increase of mineral compounds that is responsible for the increase in the corresponding absorption peaks (Grube *et al.,* 1999, Ouatmane *et al.,* 2000, Reig, 2002, Smidt *et al.,* 2002, Smidt and Meissl K, 2007).

A peak at 910-15 cm^{-1} attributed to the vibrations of inner and surface OH groups of clayey mineral (kaolin) (Reig, 2002) and a carbonate peak at 875 cm^{-1} attributed to C–O out of plane, were also observed for both landfills (Reig, 2002). The latter peak (carbonates) was prominent in all the FTIR spectra of closed landfill samples, but was either weak or absent in FTIR spectra of active landfill samples (presence in 5 out of 12 samples of active landfill samples). Wu *et al.* (2011) and Smidt & Meissl (2007) observed a sharp peak at 875 cm^{-1} for abandoned landfill and decomposed food waste compost, which was associated with increase in mineralization of organic matter. The weakness or absence of carbonates peaks at 873 cm^{-1} in most active landfill samples may be caused by interference from other mineral material within the waste.

4.3.9.2 Differential FTIR peaks

The major distinguishing peaks of the active landfill samples were at 3690 cm^{-1} and 3619 cm^{-1}, attributed to O-H vibration of clayey (kaolin) materials (Madejova ,2013). The 3619 cm^{-1} peak arose from interaction between the inner hydroxyl groups with the tetrahedral and octahedral sheets (Madejova, 2013; Reig, 2002) while that at 3695 cm^{-1} was related to the in-phase symmetric stretching vibration of hydroxyl groups (Madejova, 2013; Reig, 2002). These peaks have been observed by Smidt *et al.* (2013) as the major peaks common to samples of compost of abandoned landfill, when compared to a compost of yard/kitchen wastes during the evaluation of waste stability after 42 days.

The peak at 1113 cm^{-1}, found only in active landfill samples, has been attributed to the C-O stretching vibration of carbohydrates such as polysaccharides (García-Gil *et al* .,2008, Grube *et al.*, 2006). A few samples (3 of 12 samples analysed) from the active landfill also showed a peak at 1389 cm^{-1}, which canbe attributed to N-O stretching vibration of nitrates (García-Gil *et al.,* 2008). In most of the closed landfill samples (8 of 12 samples analysed) peaks at 1640-50 cm^{-1} and 1540-80 cm^{-1} were observed, which can be attributed respectively to the amide I and amide II groups of proteins (Grube *et al.,* 1999). These peaks could be due to decomposition of proteins leading to the formation of small compounds with amide bonds in the active landfill and closed landfills.

A quartz doublet of peaks at 775-9 cm^{-1} and 750-9 cm^{-1} was also prominent in the less degraded samples of active landfill samples, which can be attributed to the presence of silicate mineral. Reig *et al*. (2002) considered that a peak at 779 cm^{-1} is best attributed to quartz.

4.4 Conclusion

4.4.1 Compositional and physical characterization

It can be inferred that for both landfills, the distribution of less degraded composition plays a significant role in the moisture content at each depths. The pH and temperature values reflect the effect of rainfall and possible filtration during seasonal variations. This is consistent with Quaghebeur *et al*. (2013), who reported a significant difference in moisture content in the sampled landfill layers due to the presence of poor-draining or impervious layers in the landfill. Kim and Townsend (2012) reported that degradation of waste will vary with variation in the moisture content of waste in the landfills. The moisture content of the waste are indication that the waste precursor will required heating process that will ensure moisture contents are removed. Dry weight of sample will be used to prevent error in the weight of the precursor before conversion. Moisture of sample may have also influenced the degradation level which may consequently affect the yield.

4.4.2 Proximate analysis and TOC

The TOC content of less degraded sample of both landfills (>10 %) indicates that this set of precursors may be more suitable for the activation process than the more degraded. The seasonal variations in the TOC content of precursors portent a possible loss of precursors' organic carbon content as dissolve organic carbon which may affect % yield. The high ash content (> 51 %) of these wastes is a factor that could reduce the yield, require increased carbonization temperature and also increase the ash content of produced activated carbon. Activated carbon precursors are often rated according to their low ash on their low content in ash content and high fixed carbon. Fixed carbon content of more degraded precursors was higher than the less degraded precursors and comparable to fixed carbon of other biomass previous used for activation process. This may influenced the yield of more degraded sample positively.

4.4.3 Heavy metals concentrations

The heavy metal analysis reveals that the closed landfill and more degraded samples have higher concentrations of heavy metals than the active and less degraded samples respectively. The heavy metal level of both landfills was below set thresholds limit for most metals expect Pb in the closed landfill. Aqua regia extraction capacity was higher than the nitric acid.

The result indicated that landfill composite of both landfills may be suitable as precursor with heavy metal toxicity below set thresholds. Aqua regia will be preferred for the acid extractive process in the conversion process. The concentration and time for extraction process may also be essentially reduced because of the low content of heavy metals in the samples.

4.4.4 Elemental composition

Both landfills consist of three major elements (C, O, Si) which can potentially influence the chemistry and activation process of the precursors. Oxygen was identified as the major heteroatom consisting of 37.1 % and 42.4 % for more and less degraded precursors in the closed landfill and 39.3 % for both more and less degraded precursors in the active landfill respectively. The elemental constituents of the closed landfill were influence by the nature of precursor (less degraded or more degraded) than other factors such the depth and sampling seasons.

4.4.5 Functionalities of Precursors

The spectral analysis of samples from both landfills indicated a high level of mineralisation, which is indicative of stability in both landfills. The presence of mineral peaks, which were particular high in the active landfill, indicated the present of calcite (1420 cm^{-1}) and clayey material (3690, 3620, 1031, 1009, 912 cm^{-1}) (Reig et al 2002). The practice of covering the active landfill with clayey material may have elevated these mineral peaks; the clayey landfill covering material could drift within the active landfill during the rainy season. The FTIR spectra indicate that the composite of both landfills is not best suited to use as compost or soil enrichment since essential organic peaks are absent, *vis*: 1740 cm^{-1} and 1760cm^{-1} for esters and carboxylic respectively; carboxylic acids at 1260 cm^{-1} and 1240 cm^{-1}; and aromatic primary and secondary amines at 1320 cm^{-1}. The absence of these peaks also indicates limited potential for biogas generation from the landfills. However, this does not preclude consideration of the waste composite as a landfill covering after adequate toxicity evaluation.

4.5 Overall chapter conclusions

The following conclusions are made:

- The compositions of samples from both landfills were similar, consisting largely (>65 %) of three main constituents: fine, intermediate and Nylon.
- More degraded components in both landfills represents > 52 % of most sample constituents.
- The moisture content of the waste indicates that a heating process to remove/reduce moisture contents would be required prior to use of the waste for activated carbon production. Dry weight of sample should be used to prevent error in the weight of the precursor before conversion.
- There is a linear relationship between the moisture content of landfill samples and the distribution of the less degraded component of the waste.

- The high ash content (>51 %) of these samples is a factor that could affect the activation carbon process. It will require the use of high heating temperature during activation process which may influence the yield.
- The heavy metal concentrations of samples were generally below set thresholds expect for Pb in the closed landfill. Aqua regia acid extracted higher concentrations of most metals content making it the preferred acid for the activation process.
- The two landfills had similar major elemental constituents (O , C ,Si, Fe , Ca and Al), representing 96.5 % and 98.4 % of the elemental composition for the closed and active landfills respectively
- The elemental compositions of samples were largely depend on the nature of sample (more degraded and less degraded).
- The spectral analysis of samples from both landfills indicated a high level of mineralization (degradation) with prominent silica, clay minerals (Si–O–Si and Si–O stretching vibration and quartz, carboxylic acid group (C–O stretch vibration and C–O of plane vibration functional groups and absent of major organic peaks.

There are similarities in most landfill composite properties which may enhance the use of a single activation process for all samples regardless of the type of dumpsite. The major challenge is the heating source which should ensure activation whilst minimizing loss of carbon through decomposition. The TOC and Fixed carbon content of the precursors may also have a favorably effect on the activation process. Based on the evaluated precursor properties, the ash content is considered as a major factor which can negatively impact on the activation process.

CHAPTER FIVE

ACTIVATION PROCESS OF PRECURSOR

5.1 Introduction

This chapter presents the activation instrumentation design, conditions and the AC yield. Three activation routes were proposed to accommodate observed properties of the precursor which can influence the activation process. These methods were identified after reviews of previous research works. Nagano et al. (2000) had observed that municipal refuse derived fuel pre-treated with nitric acid had porosity suitable for the adsorption of dioxin just like commercial activated carbon. Karago et al. (2008) prepared activated carbon from sunflower oil cake by washing the biowaste in sulfuric acid before activation. Liou (2010) also leached sugar cane bagasse and sunflower seed hull with 0.5M NaOH before impregnation with phosphoric acid and zinc chloride. These pre-activation treatment processes are intended to remove impurities from the precursors and produce chars that have initial pore structures (Yuen and Hameed, 2009). In the present research work, acid leaching of sample before activation was intended to reduce the inorganic load of sample before activation. A number of researchers had reported production of microporous AC from biowaste with carbonization between 450-500 °C, and decomposition of organic matter and reduction in BET surface above 500 °C (Fu *et al.*, 2013; Girgis *et al.*, 2002). A conventional heating source using a two steps activation procedure was used in this study to ensure effective carbonization despite limiting ash content. Conventional heating source refers to use of combustion furnace for the activation process. Table 5.1 highlights some other literatures review which inform the selection of some of the activation procedures.

Precursor	**Activation parameters**					**Reference**
	Activating agent	Carbonization condition	Optimum activation conditions*			
		temperature (°C)/ time (hrs)	temperature (°C)	time (h)	impregnation ratio (IR)	
Rubber wood sawdust	H_3PO_4	200/1	500	0.75	1.5	Srinivasakannan and AbuBakar, 2004
Olive seed waste	KOH	800/1	900	2	4	Stavropoulos and Zabaniotou, 2005
Rice straw	KOH	700/1	800	2	4	Oh and Park, 2002
Cassaval peel	KOH	nil	750	1	5:02	Sudaryanto *et al.*, 2006
Corn	KOH	500/2	550	1	2	Bagheri and Abedi, 2009
Olive stone	KOH	600/1	900	1	1	Martinez *et al.*, 2006
Coconut shells	NaOH	500/2	700	1.5	3	Cazetta *et al.*, 2011
Rice bran	H_2SO_4	nil	850	1.5	1	Suzuki *et al.*, 2007
Paper black liquor	Steam	450/1	725	0.67	Nil	Fu *et al.*, 2013
Peanut hull	KOH	500/2	700	3	1.1	Girgis *et al.*, 2002
	ZnCl	300/6	750	6	0.5	
	H_3PO_4	500/3	500	6	0.75	

Table 5.1: Literature Review of some activities optimum conditions

* Activation was under N_2 gas flow for all process.

Lastly, a microwave heating source with one step activation was used to reduce the potential loss of carbon common to conventional heating systems, as reported by Suhas et al. (2007), Yuen and Hameed (2009) and Wu et al. (2014). The influence of some of the activation parameters on the activation carbon yield was also investigated. Figure 5.1 presents the flow chart for the activation process while table 5.2 present the aim of each activation process and the choice of sample for each process

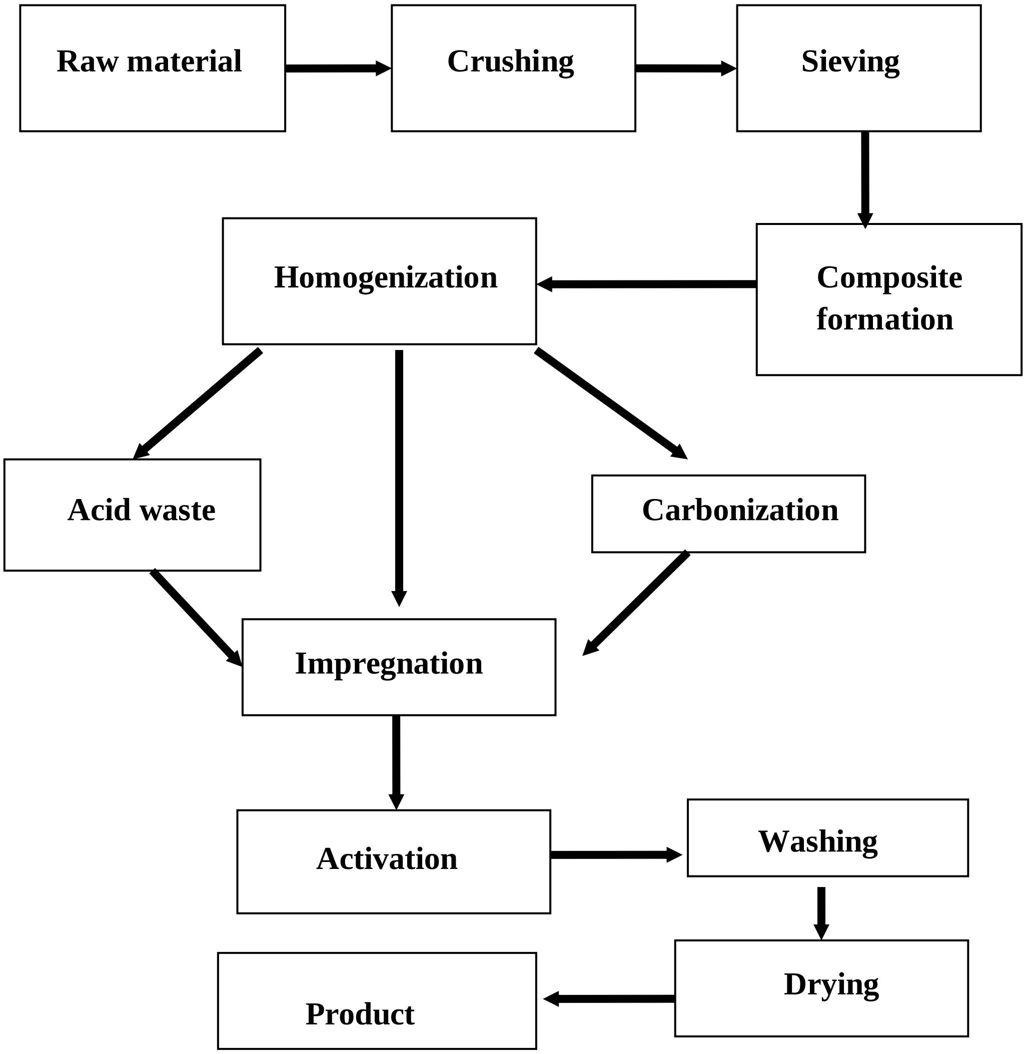


Figure 5.1: Flow chart of the activation process

Table 5.2: The activation process and the choice of precursors used

S/N	Aim of activation	No of samples	Basis for the selection of samples	Total number samples for activation
1.	To compare the suitability of precursor based on depth	3 samples of active landfill (less degraded and upper , mid, lower 3 samples of closed landfill (less degraded of samples: Upper, Mid, Lower depth	i) less degraded samples of both landfills had high TOC (65 % of samples with TOC> 10 %) ii) 64 % of yield in the first activation were of less degraded samples iii) the number of samples represent 50 % of all less degraded samples	6 samples
2.	To evaluated reproducibility of activation process	3 samples of active landfill (more degraded sample: upper, mid, lower)	i) the proximate analysis result indicated that more degraded samples had closed properties. This	12 samples

		3 samples of closed landfill(more degraded sample: upper, mid, lower)	will reduce the possible variation that could arise from precursor difference. ii) it also provide an evaluation of suitability of more degraded samples for activation carbon iii) the number of sample represent 50 % of all more degraded samples	
3.	To evaluated activating agent ratio effect on activated carbon produced	2 samples of active landfill (less and more degraded sample at the upper depth) 2 samples of closed landfill (less and more degraded samples at Upper depth)	To be able to compare result with result obtained from (1) above	12 samples

4.	To evaluate the wattage effect on activated carbon produced	1 sample of active landfill (less degraded sample :upper) 1 sample of closed landfill (less degraded samples: Upper)	To be able to compare result with result obtained from (1) and (3) above	6 samples

5.2 Material and method

5.2.1 Activation instrumentation

5.2.1.1 Conventional heating system

Two steps activation was carried out in carbolite tubular furnace. The diagrammatic sketch of the instrument set up is shown below.

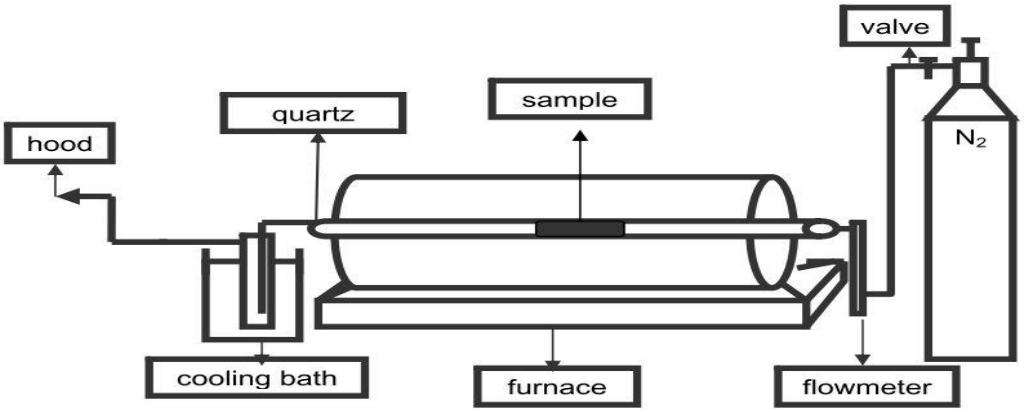


Figure 5.2: Schematic diagram of the convectional activation instrumentation

5.2.1.2 Instrumentation component

The furnace dimension (65cm length and internal diameter 20.8 mm) determined the length and the diameter of the quartz tube to be use. A quartz tube of 19 mm internal diameter, 1.5 mm thickness and 75 cm in length was found to fix into the furnace opening with no space to prevent heat loss, and also long enough to allow connection of other fitting to both ends of the quartz tube. A cast clamps (aluminum) and centering rings were fixed at the end of the tubes to prevent gas and heat escape during activation process. Gas flow was ensured through the use of a Parker A-Lok fitting which was connected to 1/4" outer diameter stainless tube to deliver nitrogen to the system. A flow meter was connected to the gas outlet of the nitrogen cylinder to measure the gas flow rate, while the pressure of the gas cylinder was measured using the pressure gas connected at the top of the cylinder. The tube outlet was connected into adsorption solution placed in the fume cupboard. The major instruments used during the activation process are shown in Figure 5.3

A: Carbolite furnace B: Quartz tube C: Cast clamps D: Parker A-Lok E: Power button F: Power indicator G: Flow meter H: Pressure gauge I: Nitrogen Cylinder

Figures 5.3: Showing major instrument using in conventional activation process

5.2.2 Microwave instrumentation

The design and set up of the microwave instrumentation had to be developed from scratch as there was no initial instrument on ground. Effort was devoted to the review of microwave oven design and safety issues. Advice on the construction and operation of the microwave was obtained from (1) the Microwave Unit, Electrical Department, University of Lagos, Nigeria and (2) a microwave technical expert at De-Monfort University waste water laboratory.

From review of past research work, instrumentation for microwave activation using a modified domestic oven can be classified into: i) microwave cavity design ii) temperature device and iii) gas flow design.

5.2.2.1 Microwave cavity design

The microwave design entails the choice of electromagnetic radiation source to be use, the cavity to be installed within the microwave and the sample holder selection.

Source of electromagnetic radiation wave (EMW): The microwave source could be purposely built microwave cavity or modify domestic microwave (Yuen and Hameed, 2009). The use of domestic microwave with different modification was prevalent in most reported work. The major concern with a domestic microwave was the issue of safety during modification, the prevention of EWM leakage to the environment and the lack of a rotating reactor system, which may affect uniform heating of precursor in the reactor (Sharifan, 2014; Menendez *et al.,* 2012). An LG intellowave domestic microwave (model no MB-382W/03) with the following specification: frequency rating: 2.5 KHz, time rating: 1- 60mins, voltage: 240V, wattage range of 90, 180, 360, 600, 800 W was selected for the process. The specifications were considered suitable for the purpose of activation. During modification narrow diameter opening outlet of 60 mm were used to prevent leakage. For safety assurance, microwave edges and duct area were covered with Teflon tape to prevent leakage. The choices of sample holder and quantity of sample to be run were also selected to ensure better contact with microwave radiation.

Reactor cavity: The reactor cavity is the compartment where the activation process takes place within the microwave radiation area. The cavity should be of material that allow microwave radiation pass through it (transparent to microwave). Quartz tube has been largely used in most journals, but Teflon and glass are considered as also transparent to microwave (Yuen and Hameed, 2009). The reactor cavity either has a horizontal or a vertical orientation depending on the magnetron position and the gas flow direction. Foo and Hameed (2012) activation of sugarcane was carried in a horizontal cavity, while Menendez *et al.* (2010) had used vertical cavity respectively. Teflon has been used in industrial microwave systems, such as Marx5 and Marx6, therefore, a vertical reactor cavity design with the use of Teflon plastic was employed. Although the controlled run (without sample) was successful, on introduction of sample into the cavity it could not withstand the heat generated from the sample which melted the cavity. The option of using quartz tube of 4 cm internal diameter which runs vertical through the microwave area with gas inlet and outlet at each end of the tube was considered and found to be stable during control and trial runs (see Figure 5.4)

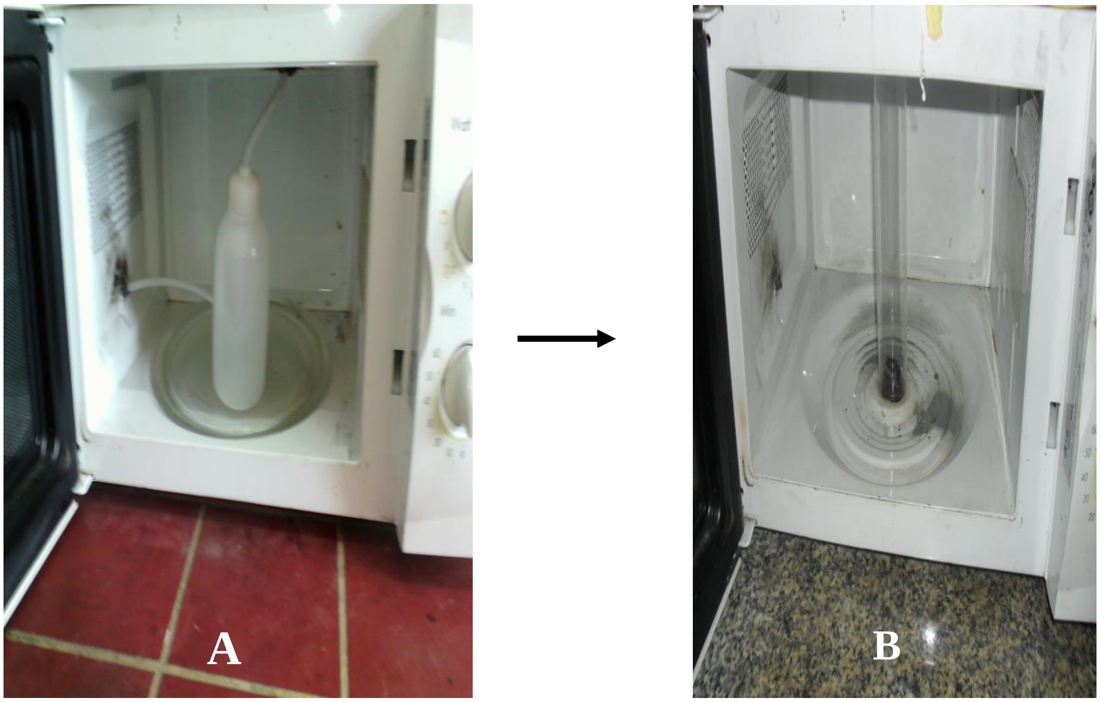


Figure 5.4: Reactor cavity design A: Teflon cavity B: Quartz cavity

<u>Sample holder</u>: An emphasis was placed on choice of sample holder since it can impact on the degree of radiation reaching the sample. Salema and Ani (2011) and Ji *et al.* (2007) have previous used perforated stainless and crucible as sample holder, respectively. In the present research, the used of Pyrex glass, stainless steel and combustion crucible as sample holders were explored to observe the effect on samples At wattages of 360, 600 and 800 an electric arc, known has a 'hot spot' (Menéndez *et al.,* 2011), was generated with used of either pyrex glass or combustion crucible. The non-formation of hot spot after 15 min radiation of samples at 600 or 800 W, with the use of stainless steel holder, indicated the possibility that microwave radiation was prevented from reaching the sample. The heat generated within 1-3min of run

cracked all the glasses when run with samples, but the combustion crucible was able to hold sample and withstands the radiation for 15 minutes. The large electric arc usually referred to as Hot Spot or Microsplasmas are observed when carbon based material are heated using microwave. These sparks last only a fraction of a second (Menéndez *et al.,* 2011). The carbon content of samples has delocalized π-electrons which are free to move in relatively broad regions; the movement is constricted by the microwave radiation resulting in high dielectric loss tangent: $\tan \delta = \varepsilon''/ \varepsilon'$. This causes molecular heat generation where some excited electrons are able to jump out of the material, resulting in the ionization of the surrounding atmosphere (Menéndez *et al.*, 2011). Unlike the glass holder, the stainless steel holder did not generate any spark but glowed during radiation. (See Figures 5.5 a-c). The combustion crucible was used as sample holder for the activation process.

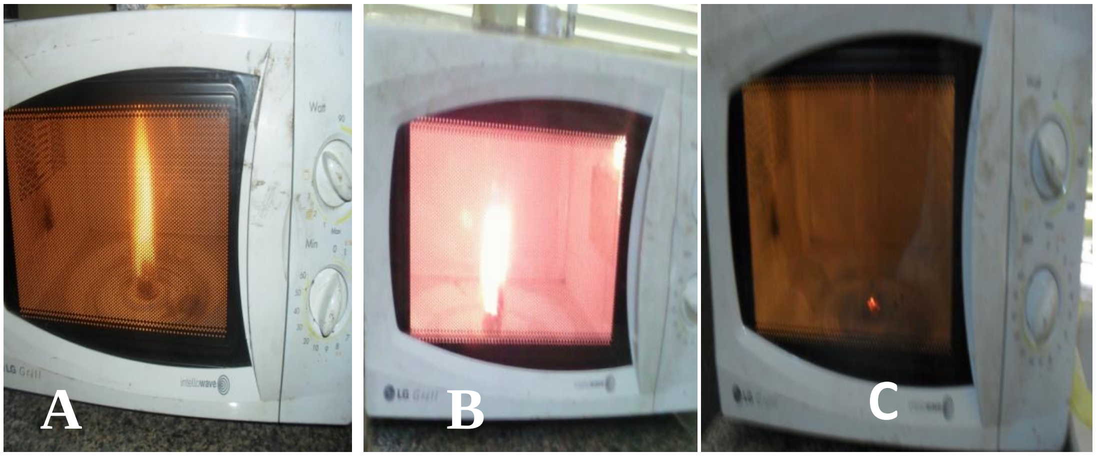
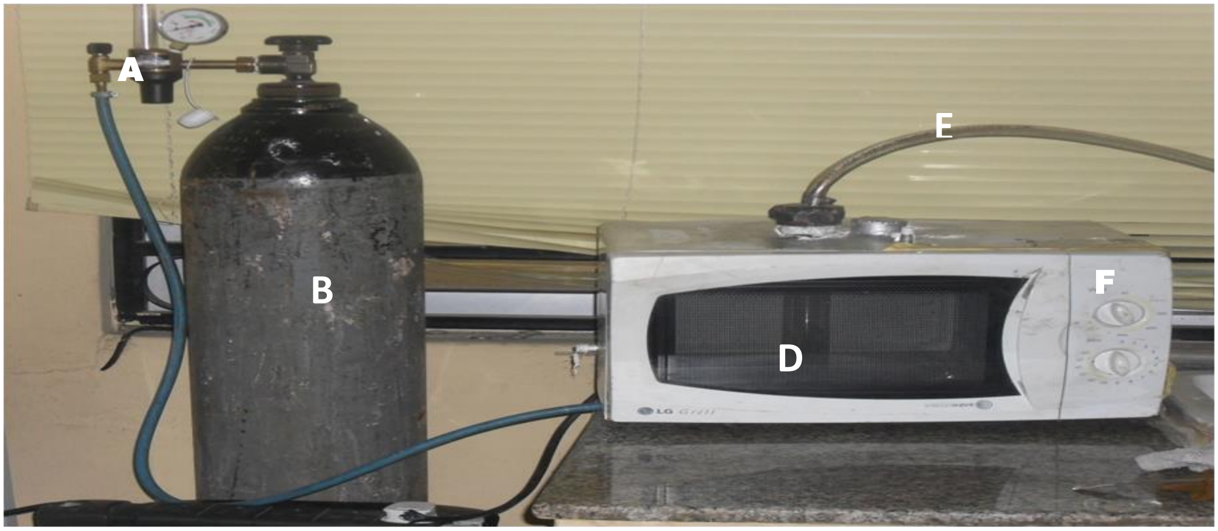


Figure 5.5: Generation of hot spot using different sample holder. A: Pyrex glass, B: combustion crucible, C: stainless steel

5.2.2.2 Temperature measure device and gas flow design

Determination of the sample temperature during radiation is a major challenge with microwave activation. The cavity environment is often determined using a pyrometer or thermocouple. The actual temperature of the sample could be a hundred degrees higher. An infrared pyrometer (BENETECH GM 300) with laser probe was used to monitor temperature during and after each irradiation of sample and the average determined. It is recognized that the barrier of glass may affect the temperature reading.

Gas flow design: The nitrogen gas was designed to flow from the bottom to the top of the cavity. The direction of the nitrogen will aid the outward flow of generated gaseous component during activation. Also, nitrogen gas is intended to create an inert environment throughout the activation process. The microwave cavity is often constructed to ensure prevention of microwave leakage to the environment which will also prevent oxygen inflow. An inert environment was maintained by purging the cavity with nitrogen before running. Figures 5.6 shows the microwave set up.



A: Flow meter and pressure gauge B: Nitrogen cylinder C: Gas inlet connector D: Reactor

E Gas outlet connector F: Wattage regulator G: Time regulator

Figure 5.6: Microwave instrumental set up

5.3 Activation parameters

5.3.1 Convention activation

The activation parameters used for the process varied based on intended parameter of interest and the instrumentation set requirement. Parameters which are key to the nature of activated carbon produced are thus:

Activation temperature: The activation temperature has been highlighted as an essential factor in the activation process (Pastor-Villegas and Durán-Valle, 2002; Aygün *et al.*, 2003; Wigmans, 1989). It is attributed to enhancement of the reactivity between the carbon and activating agent (Baçaoui et al, 2001). For a two steps activation process, the carbonization temperature had been reported to affect the optimum activation temperature (Fu at al., 2013; and Girgis *et al.*, 2002). For example, the temperature studied by Tsai *et al.* (1997) for the preparation of ACs from corn cob observed that char yield from carbonization process decreases with increase in temperature from 500 to 800 °C. Coupled with the observation made by Fu at al. (2013) and Girgis *et al.* (2002) on the negative effect of carbonization temperature above 500 °C, the carbonization temperature for the conventional heating system was kept at 500 °C for 1.5 hours ,while the activation temperature was increased from 700 to 800 °C for two hours.

Activating agent: The impregnation ratio of activating agent to the precursor has been reported as another significant factor in the activation process (Njoku *et al.*, 2014; Foo and Hameed, 2012). Studies by Suhas et al. (2007) have shown that the use of KOH at high carbonization temperature leads to enhanced pore formation in activation carbon produced from biomass, due to formation of water vapour which evaporates during heating process. Guo et al. (2002) have proposed a possible reaction mechanism between KOH and carbon material as thus:

$4\ KOH + C \rightarrow K_2CO_3 + K_2O + 2\ H_2$ ....(1)

KOH reacts with disordered or amorphous carbon at high temperatures to form K_2CO_3 as well as the decomposition product K_2O along with the evolution of hydrogen. Considering the decomposition of KOH into K_2O as well as the reducing ability of carbon, additional reactions do take place during the process of activation as shown:

$2\ KOH \rightarrow K_2O + H_2O$ .... (2)

$C + H_2O$ (steam) $\rightarrow H_2 + CO$ .... (3)

$CO + H_2O \rightarrow H_2 + CO_2$ .... (4)

$K_2O + CO_2 \rightarrow K_2CO_3$ .... (5)

$K_2O + H_2 \rightarrow 2\ K + H_2O$ .... (6)

$K_2O + C \rightarrow 2\ K + CO$ .... (7)

$K_2CO_3 + 2C \rightarrow 2\ K + 3\ CO$ .... (8)

The steam generated in (step 2) causes removal of amorphous carbon as CO as shown in (step 3) leading to formation of pores. Additional carbon is also consumed for reducing K+ to K as shown in steps (7) and (8)

The elemental composition of the precursor shows low content of potassium (< 0.25 %), which should reduce formation of K_2O and enhance reaction 3 above. In the present research, KOH was used as the activation agent and the quantity was varied during the activation process to study the effect on activation yield.

<u>Gas flow</u>: An inert gas mixture (N_2/CO_2) is introduced at a flow rate that can drift the vapour and volatile content off the reactor during the activation to avoid re-condensation and possible secondary reactions with the precursor (Sharifan, 2014). The gas flow rate effect has not been widely reported due to the possible influence of precursors' properties and temperature on gas

flow rate (Sharifan, 2014). At higher flow rate of N_2 gas, Lua et al. (2004) observed a decrease in volatile matter from char produced and a corresponding increase in the fixed carbon yields from pistachio nut shells precursor. In the present study, 99.5 % nitrogen gas was for the activation process. The flow rate of N_2 gas was kept constant at 400 cm^3/ minutes throughout the activation process.

5.3.2 Development of activation parameters for the microwave activation

Preliminary runs of sample were carried out to evaluated suitable condition for microwave activation of samples. Table 5.3 shows the how the conditions were varied in the preliminary runs, and inference made.

Table 5.3: Preliminary run of samples and inference made in respect to activation parameters

	Activation parameters varied	**Sample used**	**Observations**	**Inference**
1.	Ratio of activating agent to sample. Reasons for the variation: - Sample holder could only take small quantity of sample (1 -2.1g) which should be properly dried to avoid splashing within the cavity. The activating agent was mixed with sample at ratios of 1:1, 2:1, 3:1 and subjected to oven dried at 105°c till a constant weight was attained	Coconut, ALD upper CMD upper	Ratio 3:1 did not dry after 48hours of oven drying for all samples used. Ratios 2:1 and 1:1 dried within 12hours but attained a constant weight after 24 hours.	Ratio 3:1 could not be used for activation for these samples. Ratio 1:1 is considered a suitable ratio for the purpose of sample loading. A lower ratio of 0.5:1 was also considered. 24hours drying period was used for all samples

2.	Wattage selection Reasons for variation: - Wattage rating of microwave is expected to vary in the intense and interaction with samples. Selecting suitable wattage for activation is important. Samples were run at 180, 360, 600 or 800W	Coconut, ALD mid CMD mid	At 180W, after 5 minutes irradiation of samples in microwave no visible reaction could be observe (no generation of microplasmas nor gaseous build up). At 360, 600 or 800W there was intense gaseous build up within the cavity for coconut and active landfill samples, while microplasma occurred within 1-5seconds for all samples. At 800W sample holders cracked within 15minutes of run.	600W was preferred as sample holder could withstand 15mins radiation without cracking and closest to wattage previously reported
3.	Duration of radiation Reasons for variation: - Exposure period may affect the sample carbonization and vaporization volatile carbon in the sample. - The samples were run for 20mins, 15mins or 10mins	AMD Upper CMD upper	At 20mins all sample holder cracked and sample could not be effectively recovered. At 15mins and 10mins samples were recovered.	10mins was preferred as the run time for samples to reduce possibility of sample holder cracking and lost of samples.

Active landfill less degraded sample (ALD); Closed landfill more degraded sample (CMD); Active more degraded sample (AMD).

5.4 Activation process

5.4.1 Conventional activation

Method one (carbonization and activation):

Dried sample (2-5g) was carbonized at a temperature of 500°C under nitrogen gas flow of 400cm^3 /min for 1:30mins in a tubular furnace. The resulting char and activating agent was dissolve (ratio 1:1 or 1:2) in 10 ml distilled water and dried in the oven at 105°C for 3 hours. The sample was then activated at 700°C for 2hours under the flow of nitrogen gas at 400cm^3/minutes.

Method two (acid wash):

Sample (2-5g) and activating agent at ratio of 1:1 or 1:2 (w/v) to the sample were homogenized using a Griffin flask shaker for 5 minutes. The mixture was heated on the hot plate for 30minutes at temperature of 105 °C using 6.3M aqua regia acid. The mixture was filtered and the residue dried at 105 °C in the oven for 3hours before activation at the same condition in method one.

Method Three (one step):

This was a single step activation process in which samples were directed activated without initial carbonization. Weighed sample (2-5 g) and activating agent was dissolved in 10ml of water at a ratio 1:2 or 1:1. The slurry was agitated with Griffin shaker for 10 mins. The slurry was allowed to dry in the oven for 3hours at 105 °C and then transfer to the tube furnace and activated at 800 °C for 2hrs. The product was washed with distilled water and dried in the oven.

5.4.2 Microwave activation

Samples were further homogenized using a mortar and pestle to an average particle size of 0.25mm. An aliquot (5 g) of sample was impregnated with 10 ml 10 M KOH solution. The mixture was agitated on a stirrer at 80 rpm for 1 hour. The mixture was dried in an oven at 105°C for 24 hours to attain a constant weight. Dried sample (2g) was loaded into a sample holder (combustion tube) in the reactor fixed within the microwave cavity. Pure nitrogen gas (99.5 %) was passed through the microwave cavity at a flow rate of 15 cm^3/minutes for 1 minute to purge the oxygen, then the sample was irradiated for 10 minutes under the stream of nitrogen gas. The sample was allowed to cool while under nitrogen gas flow. An Infrared Pyrometer (BENETECH GM 300) with laser probe was used to monitor temperature during and after each irradiation of sample and the average determined.

The activated samples were first washed with 5 % HCl to remove the KOH and then continuously washed with distilled water until the pH was within a neutral range (6-7). The activated sample was then dried in the oven at 105 °C to a constant weight. The % yield (dry sample) was determined as:

$$\%\ \text{yield} = \frac{(\text{weight of precursor before activation - weight of precursor after activation})}{\text{Weight of precursor before activation}} * 100 \qquad \text{Eq. (5.1)}$$

5.4.3 Comparing the activation processes

The conventional activation process took an average of 4 hours and the use of 24,000 ml volume of nitrogen gas per sample compared to microwave activation with less consumption of nitrogen (225 ml per sample) and faster activation period of an average of 15 minutes per sample. Conventional heating was only used to evaluate a single run of sample while the microwave system was used to carry out studies of samples reproducibility and characterization.

5.5 Result and discussion

5.5.1 Microwave activation

5.5.1.1 Activation conditions, yield

Table 5.4 presents the activation conditions for each precursor, together with the associated yield and reproducibility for the activated carbon produced. Reproducibility was assessed to determine if the heterogeneous nature of the precursor affected the activated carbon yield and its adsorption properties. At the same activation condition of 600 W and impregnation ratio of 1:1, the average yields of samples from active landfill were higher than closed landfill for all sampling depths (upper, 23.8 % and 19.3 %; mid, 52.4 % and 34.7 %; lower, 35.7 % and 27.0 %).

Table 5.4: The activated carbon reproducibility with depth

S/N	Samples names		% yield[a]	RPD %yield of sample 1 and 2		pH
1	AMD Upper	1	23.8	0		6.2
		2	23.8			6.3
2	AMD Mid	1	57.1	18		6.4
		2	47.6			6.5
3	AMD Lower	1	47.6	17		6.7
		2	23.8			7.1
4	CMD Upper	1	30.8	30		6.7
		2	7.7			6.8
5	CMD Mid	1	30.8	5		6.7
		2	38.5			6.9
6	CMD Lower	1	38.5	21		6.2
		2	15.4			6.5
7	ALD upper^		57.1			6.4
8	ALD Mid^		47.6			6.4
9	ALD Lower^		47.6			6.4
10	CLD upper^		34.6			6.4
11	CLD mid^		15.4			6.9
12	CLD lower^		23.8			6.8

[a] Activation condition power =600W, impregnation ratio =1:1, duration = 10mins ,

^ Samples without reproducibility studies, Closed landfill (C); More degraded (MD); Active landfill(A); Less degraded(LD):, Upper depth (Upper); Mid depth (mid), lower :lower depth

More degraded samples of the active landfill showed better reproducibility in the percentage yield (up to 18 % RPD) compared to those more degraded sample of the closed landfill (up to 30 % RPD). For both active and closed landfills, the activation yield did not show a definitive trend with depth or with the extent of organic content (TOC) of the initial samples; high TOC samples did not produce relatively higher yields. The pH of samples from both landfills samples were within the same narrow range, pH 6.2 - 7.1. These data indicated that under the same set of activation parameters the percentage yields from the heterogeneous precursor used (landfill composite) were reasonably reproducible (<30 % RPD).

Proximate and ultimate properties, together with ignition temperature, are considered to be key characteristics of biomass for dry conversion processes (Garcia *et al.,* 2013; Garcia *et al.,* 2012). The precursors at each depth of both landfills maintained close proximate properties.

5.5.1.2 Effect of irradiation power

The closed landfill yield of AC progressively decreased from 42.9 % to 33.3 % with increased irradiation power, while the active landfill had the lowest yield of 33.3 % at 800 W (Table 5.5). The low yield at 800 W may be attributed to increased gasification of precursor. During the activation process at 800W, intense build-up of gaseous components within the reaction cavity was observed within the 1-5 seconds of exposure to microwave radiation. The process of precursor degradation, volatilization and decomposition is known to increase with rising microwave power (Foo and Hameed, 2012a; Guo and Lua, 2000; Foo and Hameed, 2012).

Table 5.5: Percentage yield of AC with variations in irradiation power and impregnation ratio

Samples	Ma/Ms	wattage (W)	% yield	pH
1.ALD upper	1:1	360	38.1	6.6
2.ALD upper	1:1	600	57.1	6.4
3.ALD Upper	1:1	800	33.3	6.4
4. CLD upper	1:1	360	42.9	6.5
5. CLD upper	1:1	600	34.6	6.4
6. CLD upper	1:1	800	33.3	6.3
7. ALD upper	0.5:1	a	47.6[a]	6.2
8. ALDupper	1:1		57.1	6.4
9. ALD upper	2:1		33.3	6.4
10. ALD upper	0.5:1		14.3	6.4
11. CLD upper	0.5:1		28.6	6.3
12. CLD upper	1:1		42.9	6.4
13. CLD upper	2:1		47.6	6.2
14. CLD upper	0.5 : 1		28.6	6.5
15. CMD upper	0.5:1		38.1	6.3
16. CMD upper	1:1		19	6.7
17. AMD upper	0.5:1		42.9	6.2
18. AMD upper	1:1		23.8	6.2

Ma: weight of activating agent: Ms: weight of sample; a:activation condition duration =10mins, wattage = 600W; Closed landfill (C); More degraded (MD);

Active landfill(A); Less degraded(LD):, Upper depth (Upper); Mid depth (mid), lower :lower depth

5.5.1.3 Effect of activation reagent ratio

Effect of impregnation ratio (activating reagent: precursor) on the AC yield was evaluated by varying the ratio of the chemical reagent from 0.5:1 to 3:1.

The percentage yields of less degraded samples of active landfill in respect to impregnation ratio were in order of 1:1 > 2:1 > 0.5:1, while for the closed landfill samples the order was 2:1 > 1:1 > 0.5:1. More degraded samples of both landfills had a ratio in the order of 0.5:1> 1:1. At a ratio 3:1 the samples did not solidify after 24 h drying at 105°C and this ratio was considered not suitable for activation.

Activating agent impregnation ratio is an important parameter in a chemical activation process, which influences both quantity and quality of the AC produced (Liou, 2010; Njoku *et al.,* 2014; Ferrera-lorenzo *et al.,* 2014). A ratio of 0.5:1 was observed to be more suitable than 1:1 for more degraded sample, with yield enhancement from 19 to 38 % and from 24 to 43 % for the closed and active landfill respectively. This suggests that the degraded nature of precursor, with increased surface area, was more able to absorb activating agent. For less degraded sample of both landfills, increase in impregnation ratio from 0.5:1 to 1:1 led to increase in percentage yield (active 47.6 to 57.1 %, closed 28.6 to 42.9 %). Similarly, Foo and Hameed (2012) observed that an increasing ratio of activation chemical reagent from 0.25-1.25 for Mangosteen peel precursor increased yield of AC from 76.03 to 88.01 %.

5.5.2 Conventional activation

As shown in Table 5.6, five of the 16 samples activated using the convectional heating source either vapourised during activation (3 samples) or dissolve during washing (2 samples). Vapourization of samples during activation was only peculiar to sample activated using acid wash method. The acid wash may have led to oxidation of both organic and fixed carbon of the precursor to carbon IV oxide and weaken the carbon matrix, which can vapourize during activation. Similar observation was made by Foo *et al.*, 2012b that the addition sulfuric acid to coconut husk led to low AC due to the water vapour formed from the dehydration by H_2SO_4 which increased the carbon burn off.

Table 5.6: Percentage yield of AC and activation condition for the conventional activation

Sample number	sample name	method	IR	% yield	pH	activation condition*
1	CLDlower	Acid wash and activation	1	8	6.3	HNO_3 washing at 105°C for 30mins, activated temperature 700°C for 2hours.
2	CLDmid		1	13	6.5	
3	AMDupper		2	vapourizes		
4	AMDmid		2			
5	AMDlower		2			
6	CMDlower	Two steps activation	1	11	6.5	Carbonized at 500°C for 1.5hours under N_2 at 400ml/min and activated at 700°C
7	CMDmid		1	12	6.5	
8	CMDmid		2	19	6.7	
9	CMD lower		2	dissolve		
10	AMD mid		2			
11	ALDupper	One step activation	2	8	6.7	impregnation and activated at 800°C for 3hrs
12	ALDlower		2	13	6.9	
13	CLDmid		2	18	6.9	
14	ALDlower		2	16	6.9	
15	AMDupper		1	10	6.7	
16	AMDmid		1	14	6.9	

* Activation was under N_2 at 400ml/min IR: impregnation ratio; C: closed landfill; MD: more degraded; A: active landfill; LD: less degraded; Upper: upper depth; mid: mid depth ; lower: lower depth

All samples (2) lost during acid wash method were more degraded samples, one from the closed landfill and the other from the active landfill. This may also indicated the effect of heat on the degraded nature of carbon in these set of samples. The AC % yields were between 8-19 % for all samples evaluated, while the pH was within the range 6.3 - 6.9.

The thermal heating source was found to have a negative effect on the % yield of activated carbon produced, possibly due to loss of carbon. Carbon lost as result of increase in carbonization and activation temperature has previously been reported by Lua and Guo (2000). Based on the result of the activation process the convection heating source was less preferred to the microwave energy; the latter was used for further characterization studies.

5.6 Conclusion

The conventional activation process had a major challenge: sample loss associated with carbon loss during activation. The vapourization of acid washed precursor indicated possible oxidation of precursor during washing. The conventional activation results suggest carbon matrix may not be able to withstand further increase in temperature in carbonization and activation temperature. This could be associated with the degraded nature of the precursor, as other fresh biowaste has been subjected to higher activation temperature of 850-950 °C with less loss of carbon (Stavropoulos and Zabaniotou, 2005; Martınez *et al.*, 2006). Also, Ioannidou and Zabaniotou (2007) recommendation of carbonization temperature range between 500 and 850 °C and activation temperature range between 800 and 900 °C may not apply to this type of precursor. Microwave activation provided a faster and higher yield for most samples than the convection method. Increase in impregnation ratio or microwave power decreased the percentage yield of AC. More degraded samples of the active landfill showed better reproducibility of percentage yield (up to 18 % RPD) compared to those more degraded sample of the closed landfill (up to 30 % RPD).

CHAPTER SIX

ACTIVATED CARBON CHARACTERIZATION

6.1 Introduction

It has been established that the adsorption capacity of activated carbons (ACs) can be identified through the physical characteristics such as porosity, pore volume, surface area pore size and the surface chemistry (Ahmad *et al.,* 2007). This chapter presents the surface, functional and adsorption characterization of produced activated carbon. The characterization was carried out to evaluate the surface area, pore formation and distribution of the produced activated carbon. The functionalities and adsorption potentials properties were also evaluated. The adsorption kinetics of the activated carbons were studied to understand the factors influencing the adsorption capabilities of the activated carbon. The adsorption isotherm was studied using both aqueous and gas adsorbates.

6.2 Methods

6.2.1 Surface morphology

The ACs were mounted onto an aluminum stub with conductive carbon tape and coated with gold reflective layer before sputtering with gold. Gold dust on the AC was removed with air spray before being placed in the ionization chamber of the SEM (Carl Zeiss, EVO HD15) for analysis. The working distance was varied between 8.0 to 8.5 mm. An aperture diameter of 1 or 2 µm was used for the analysis. The accelerating voltage for all analysis was between 20 and 10 keV.

6.2.2 Adsorption studies

Assessment of the adsorption capacity of activated carbon samples was carried out using methylene blue (MB). A 25 mg/l solution of MB in distilled water prepared from a 100 mg/l stock solution. An aliquot (10 ml) of the 25 mg/l MB solution was added to 10 mg of activated carbon. The mixture was agitated in a Brunswick C76 water bath shaker at 200rpm for two hours at 23°C. Supernatant solution (2 ml) was pipetted off after the solution was allowed to settle and MB concentration in the supernatant was determined by measuring absorbance at 664 nm. The amount of adsorbed MB at equilibrium, q_e (mg/g), was calculated by:

$$q_e = \frac{(C_o - C_e)V}{W} \qquad \text{Eq. (6.1)}$$

Where C_o and C_e (mg/l) are the initial and final concentrations of MB before and after equilibrium, respectively. V is the volume of the solution (l), and W is the mass of dry adsorbent used (g).

The % uptake of MB was determined by:

$$\%\text{ uptake of MB} = \frac{C_o - C_e}{C_o} \times 100 \qquad \text{Eq. (6.2)}$$

The experimental procedure used to determine the adsorption equilibrium of AC, described above, was modified to investigate the effect of adsorbent dosage at 50 mg, 25 mg and 10 mg. The pH effect on adsorption rate was evaluated by adjusting the pH of the solution to 2-3 or 11-12, through the addition of 5 % HCl or 0.1M of KOH respectively. The temperature effect on adsorption rate was determined by varying the temperature in a Labline orbit environ shaker (model 3527) at 23, 30 and 50°C. Adsorption capacity of an activated carbon at other time t (q_t) during the analysis was determined as follows:

$$q_t = \frac{(C_o - C_t)V}{W} \qquad \text{Eq.} \quad (6.3)$$

where q_t (mg/g) is the amount of MB adsorbed at time t (min), C_o (mg/l) is the initial concentration of MB, C_t is the concentration of MB (mg/l) at time (t), V (l) is the volume of the solution and W (g) is the weight of activated carbon.

6.2.3 Surface area characterization

The surface area and pore structure parameters of an activated carbon sample were obtained by nitrogen adsorption–desorption isotherm, determined using a Micromeritics Gemini 2365 surface area analyzer. AC (0.2g) was purged at 20°C for 18 hours under a constant flow of Helium *gas* using a Micromeritics Flowprep 060 at 77.5 K. The AC was outgassed at 250°C. The surface area was calculated by the BET (Brunauer, Emmett and Teller) equation using N_2 adsorption values within 0.1 to 0.3 relative pressure (p/p0) (Sing *et al.*, 1985). The pore size distribution was determined by the Barrett-Joyner-Halenda (BJH) method. Nitrogen adsorption isotherm was measured over a relative pressure (p/p0) range from approximately 10^{-2} to 1. The total pore volume (V) was measured by converting the amount of N_2 gas adsorbed (expressed in cm^3/g STP) at a relative pressure of 0.99 to liquid volume of the nitrogen adsorbate (Guo and Lua, 2000; Li *et al.,* 2008).

6.2.4 Functionalities of AC

The functionalities of the AC were determined using FTIR, as described in section 4.2.8

6.3 Result and Discussion

6.3.1 Scanning electron microscopy (SEM)

SEM micrographs of some the precursors and AC obtained are shown in Figure 6.1. The precursors' surface morphology depicts a compact and covered surface texture, while the AC surface displayed well defined porosity distributed across the surface area. Comparison of the surface morphology of the four micrographs indicates modification in the surface area after microwave radiation. The AC surface morphology could not however give sufficient information on the influence of the precursor used on the nature of pore formed. Also, the relationship between the nature of the pore formation and adsorption capacity could not be inferred from the microphotographs. An adsorption study on the AC was therefore carried out (see Section 6.3.2). SEM micrographs of other AC samples are presented as Appendix 5.

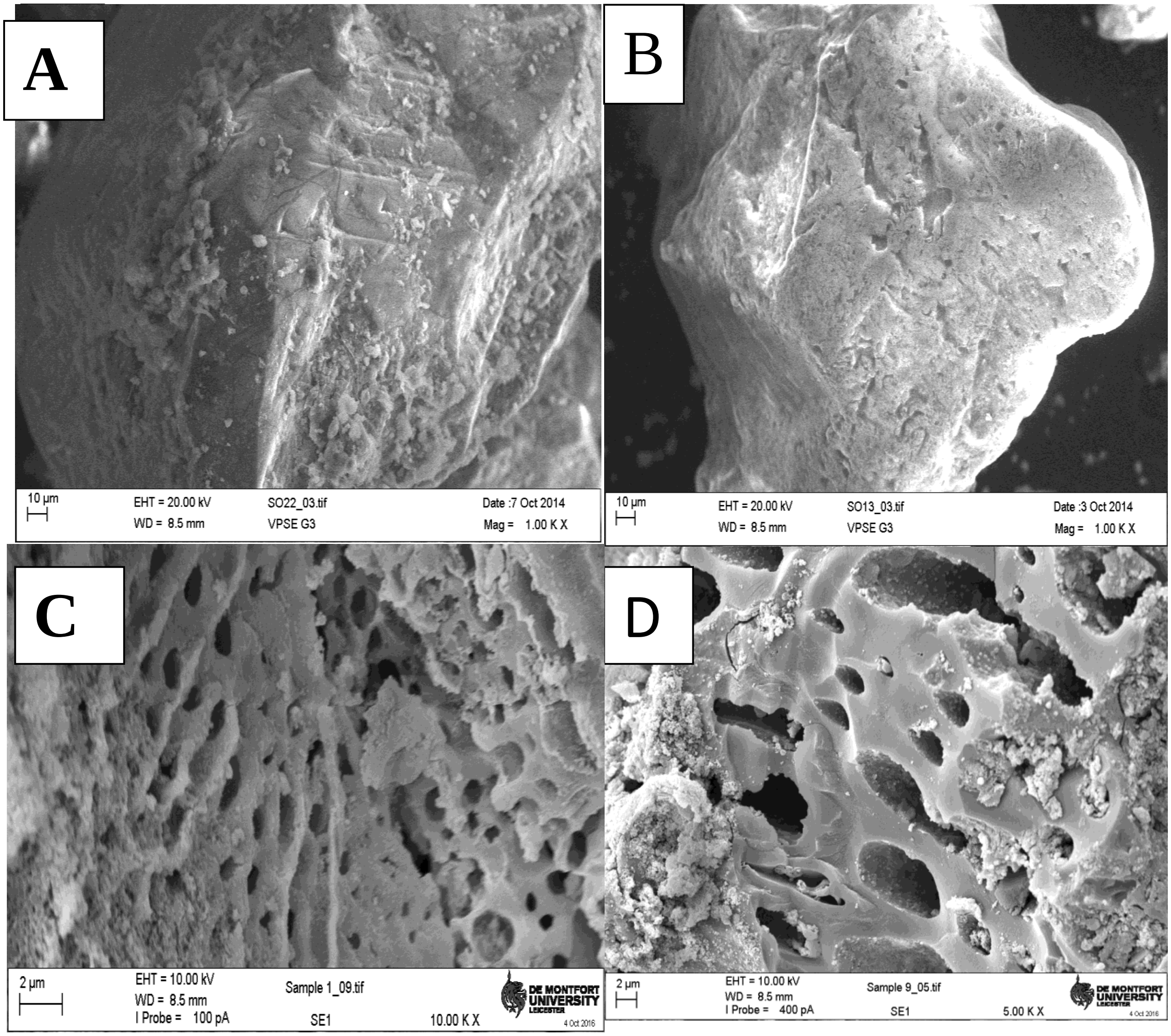


Figure 6.1: SEM image of precursors and of activated carbon
A and C: precursor and AC of less degraded active landfill lower sample
B and D: precursor and AC of more degraded active land lower sample
Activation condition: wattage (600W); impregnation ratio (1:1); duration (10minuntes)

6.3.2 Adsorption studies

6.3.2.1. Effect of adsorbent quantity

Figure 6.2 shows the adsorption capacity of AC produced from the precursor of samples from both landfills at 23°C. The adsorption capacities of the AC decreased with increase in weight of AC; the adsorption capacity was 36 – 190 mg/g for 10 mg AC, 59-82 mg/g for 25 mg and 38- 45 mg/g for 50 mg of the absorbent. For 10ml of MB at 25 mg/l concentration, an optimum adsorbent dosage of 10 mg was selected to use for the equilibrium experiment. The decrease in adsorption capacity of AC could be due to the splitting effect in the flux (concentration gradient) between the adsorbate and adsorbent (Beekaroo and Mudhoo, 2011). As the quantity of adsorbent increase from 10mg to 50mg with MB concentration kept constant at 25mg/l, there is an increase in the number of surface sites of adsorbent available for the adsorbate adhesion leading to lower number of adsorbate molecule per site. Only AC from less degraded closed landfill precursor had the optimum adsorption capacity of 58 mg/g at 25 mg and a reduced adsorption capacity of 36mg/g at 10mg, properly due to decrease in adsorbent sites with reduction in weight.

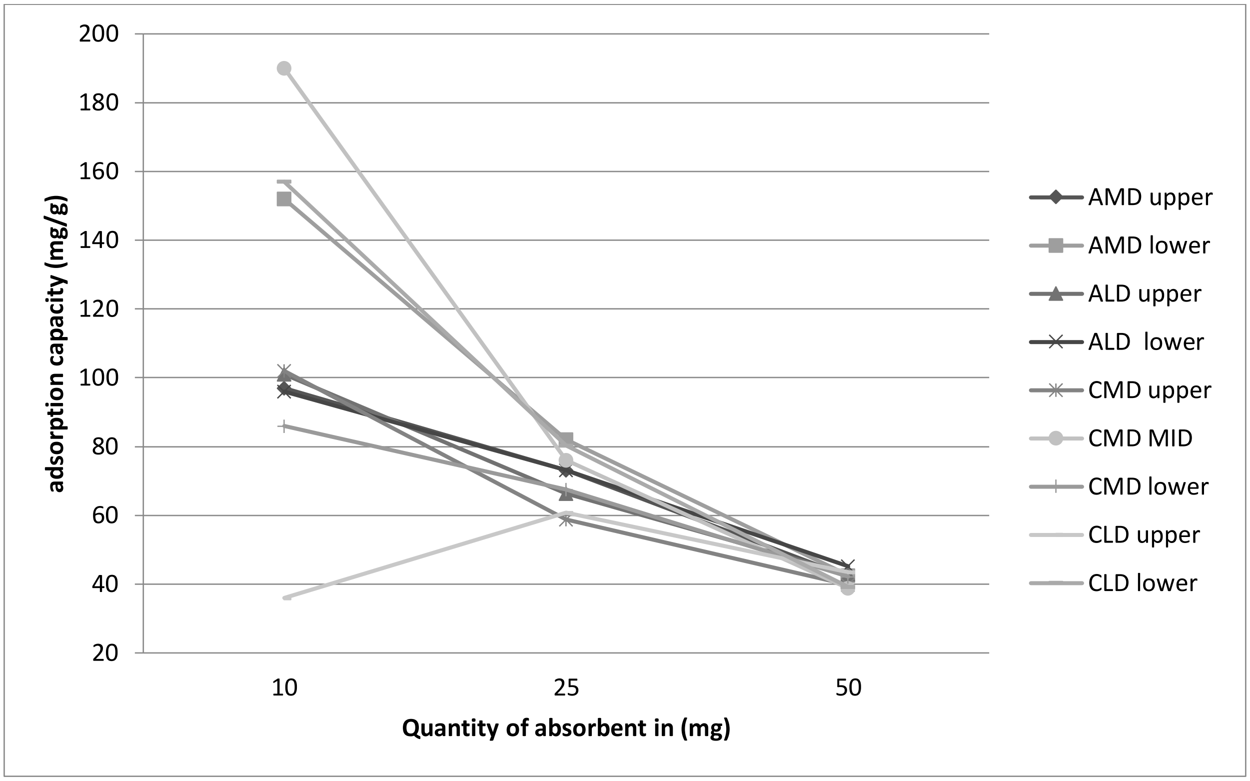


Figure 6.2: Effect of concentration of adsorbent on methylene blue adsorption capacity of absorbent.

Active landfill (A); closed landfill (C); more degraded (MD); less degraded (LD); upper depth (upper); mid depth (mid); lower depth (lower)

6.3.2.2 Adsorption capacity with depth of sampling

The adsorption capacity of AC produced from less degraded active landfill decrease with depth from (upper: 43 mg/g, mid: 32 mg/g, lower: 16 mg/g), while adsorption capacity of the AC from more degraded precursor of closed landfill increases with depth (upper: 35 mg/g, mid: 39 mg/g, lower: 42 mg/g) at a temperature of 23°C using 50mg absorbent. This trend may reflect the elemental content of carbon in the precursor. The adsorption capability of 9 out of 12 of the AC follows the same trend as reported for elemental content of carbon in the elemental characterization studies of the precursors reported in chapter four, i.e. active degraded: upper > mid > lower, closed degraded: lowe r> upper > mid. For both landfills the average adsorption capacity AC from more degraded precursors was higher than AC from less degraded precursors (active landfill 42 to 30 mg/g, closed landfill 41 to 36 mg/g). This may be due to a higher fixed carbon content in the more degraded samples than the less degraded samples. Fixed carbon of a biomass represents the carbon content available for fuel and energy conversion (García et al, 2013). Table 6.1 compares the average optimum absorption capacity of the AC with AC from other biogenic waste. The optimum adsorption capacity of AC generated from both landfills was within the values reported for AC from oil palm and tea waste.

Table 6.1: Comparison of the optimum adsorption capacities of MB onto different biogenic waste adsorbents.

Adsorbents		Adsorption capacity (mg/g)	Reference
Cotton waste		24	McKay *et al.* (1986)
Coconut husk based activated carbon		66	Prauchner and Rodríguez-Reinoso, (2012)
Tea waste		85.16	Uddin *et al.* (2009)
Activated carbon from oil palm wood		90.9	Tamai *et al.* (1996)
black lignin liquor		92.51	Fu *et al.* (2013)
Mangosteen peel **this study**		345	Foo and Hameed (2012a)
closed landfill composite activated carbon	More degraded	152	
	less degraded	101	
active landfill composite activated carbon	More degraded	190	
	less degraded	157	

6.3.2.3 Temperature effect on adsorption

There was an increase in the percentage uptake of MB with increase in temperature from 30 to 50 °C, for all AC samples tested. However, only 60 % of the AC samples indicated an increase in the percentage uptake of MB with increase in temperature from 23 to 30 °C (see Figure 6.3). The AC from more degraded precursor of active landfill (upper and lower layer) showed higher uptake of MB at 23 °C than at 30 °C. An ANOVA statistical analysis was used to investigate if there is a significant difference in % MB uptake at the three temperatures: 23, 30 and 50 °C. Taking the landfill type (closed and active) and sample nature (more degraded and less degraded) as the fixed factors, the ANOVA analysis showed that there is no significant statistical difference in % MB uptake at each of temperature point for the AC of both landfill with $p > 0.2$ (see Table 6.2).

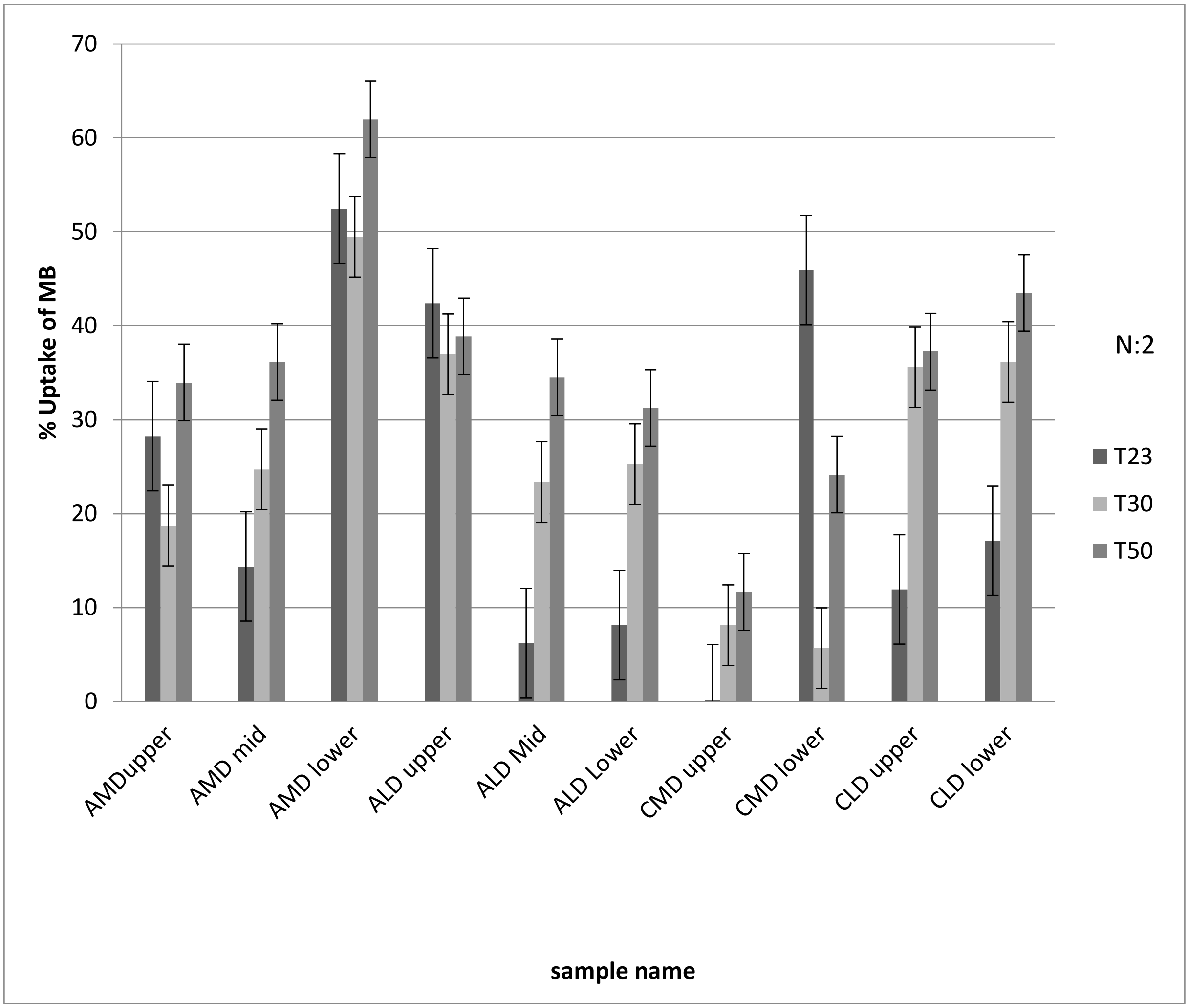


Figure 6.3: Effect of temperature on the uptake of MB (methylene blue)

T23, temperature at 23°C; T30, temperature at 30°C; T50, temperature at 50°C. Active landfill (A); closed landfill (C); more degraded (MD); less degraded (LD); upper depth (upper); mid depth (mid); lower depth (lower); N:number of replicate sample.

Table 6.2: ANOVAs analysis of adsorption capacity at different temperatures

temperature	F value	P value	N*
23°C	0.276	0.614	10
30°C	.901	0.370	10
50° C	1.644	0.236	10

N* number of samples; sample analyze: AMD Upper – AMD Lower, ALD Upper –ALD Lower, CMD Upper; CMD Lower, CLD Upper and CLD Lower .Active landfill (A); closed landfill (C); more degraded (MD); less degraded (LD); upper depth (upper); mid depth (mid); lower depth (lower); N:number of replicate sample.

6.3.2.4 pH effect on adsorption

The percentage uptake of MB onto the activated carbons was affected by solution pH. For all the AC investigated (6 samples), uptake of MB was found to be optimal at a solution pH within 6-7 (Figure 6.4). This is similar to the observation made by Gercel *et al.*, 2007 and Karago *et al.*, 2008 who observed an optimum adsorption of MB at the pH of 6 for activated carbon produced from Euphorbia Rigida and sunflower oil cake respectively. Solution pH and ionic strength are major factors that can influence the adsorption process in solution (Foo and Hameed 2012; Njoku *et al.*, 2014).

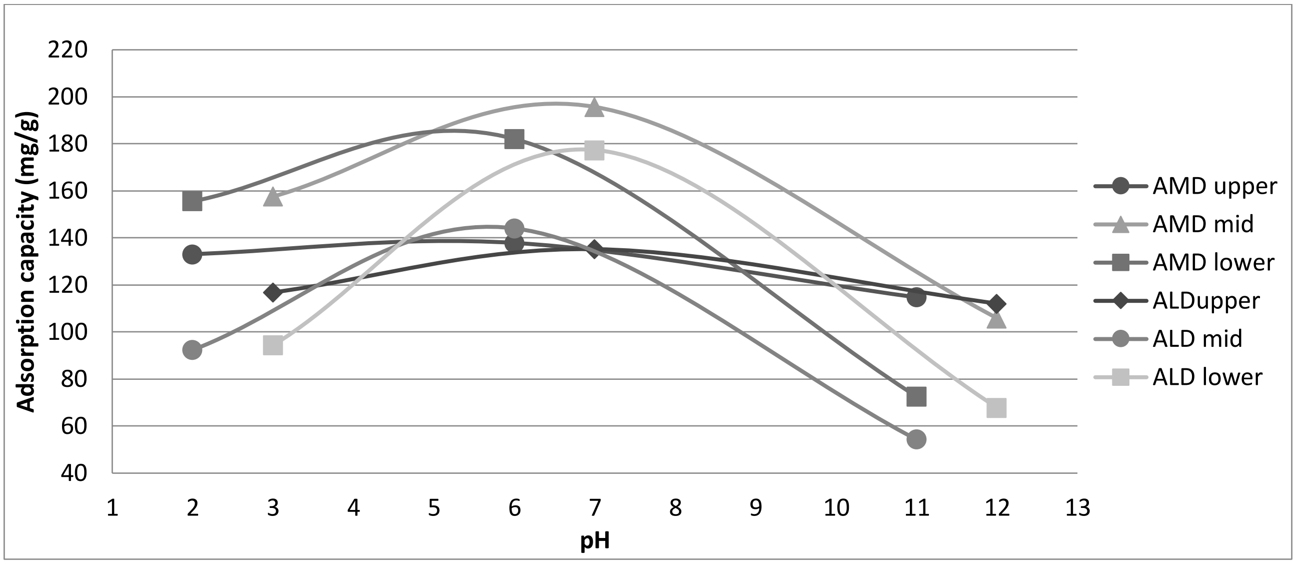


Figure 6.4: Effect of pH on the adsorption capacity of AC Active landfill (A); closed landfill (C); more degraded (MD); less degraded (LD); upper depth (upper); mid depth (mid); lower depth (lower).

Solution pH effect on adsorption capacity is controlled by the electrostatic interactions between the charged surface adsorbents and the adsorbates present in the solution (Moreno-Castilla 2004; Karago *et al.*, 2008; Foo and Hameed, 2012). In acidic medium, the presence of excess H^+ ions and protonated MB compete with MB cations for the adsorption sites. At neutral pH, AC becomes more negatively charged and consequently increasing MB cations uptake on the adsorption site. In the basic medium, the drop in adsorption capacity could have been due to electrostatic repulsion between OH^- in the medium and the surface functional group of the adsorbent. Moreno-Castilla (2004) reported low adsorption in *ortho*-chlorophenol due to electrostatic repulsions between the negative surface charge and phenolate–phenolate anions in solution at basic pH medium.

At pH 11-12, the adsorption capacity of AC of more degraded active landfill precursor progressively decreased with depth: 114mg/g -upper, 106mg/g-mid and73mg/g –lower. There was no clear trend in MB adsorption with pH or with depth of sampling for other AC samples.

6.3.2.5 Adsorption equilibrium isotherms

Adsorption equilibrium isotherms are important in the explanation of the dynamics between absorbates on the adsorbents and their distribution in liquid phases when attaining equilibrium state (Weng and Pan, 2007; Karago et al, 2008). Langmuir and Freundlich isotherm models were used to analyze the equilibrium data for the adsorption of MB onto the respective AC. Langmuir models' central assumption is that adsorption occurs only at the homogeneous adsorbent surfaces sites, which are equally available and have equivalent energy to adsorb equal numbers of molecules with no interaction between these molecules (Weng and Pan, 2007; Karago et al, 2008).

The model is expressed by the equation

$$\frac{C_e}{Q_e} = \frac{C_e}{q_m} + \frac{b_L}{q_m} \qquad \text{Eq.} \quad (6.4)$$

Where C_e is the concentration of MB solution (mg/l) at equilibrium. q_m and b_L are Langmuir constants related to the maximum adsorption capacity (mg/g) and energy of adsorption (L/mg). The plot of C_e/Q_e versus C_e should give a linear graph when the adsorption follows

Langmuir isotherm with the slope equal to $1/q_m$ and intercept b/q_m (Weng and Pan, 2007; Karago et al, 2008; Foo and Hameed, 2012).

Samples were also evaluated using Langmuir isothermal dimensionless constant (R_L), which evaluates the type of absorption as either unfavorable when ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$) Weng and Pan, 2007; Kavitha and Namasivayam, 2007; Foo *et al.*, 2013).

R_L is expressed as:

$$R_L = \frac{1}{(1+bC_o)} \qquad \text{Eq. (6.5)}$$

Where b is the Langmuir constant and C_o is the initial dye concentration (mg/l).

Of nine AC samples evaluated, six (67 %) conformed to the Langmuir model, showing a linear trend with coefficient of determination values (R^2) within the range 0.8-0.9 (Figure 6.5). Two of the three activated carbon samples from less degraded sample conformed to the Langmuir model. Details of the Langmuir values for each sample are given in Table 6.3. The Langmuir equilibrium constant values were within 0.2-0.8, which fall within the favourable range $R_L = 0 < R_L < 1$.

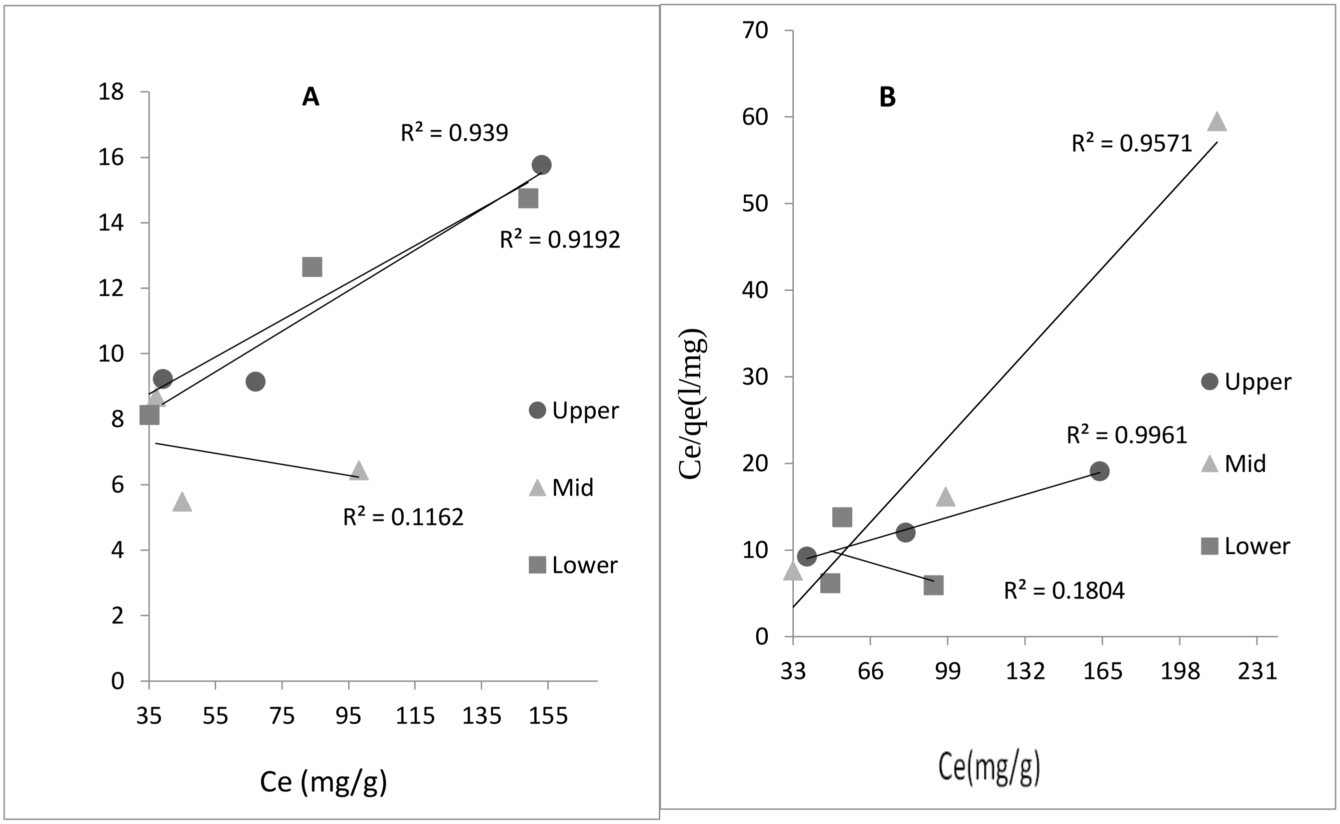


Figure 6.5: Langmuir plots for the adsorption of methylene blue onto the activated carbons

A: AC from active landfill more degraded precursor B: AC from closed landfill more degraded precursor.

Table 6.3: Comparing the Langmuir and Freundlich model parameters of AC

Depth	Langmuir				Freundlich		
	Q_0(mg/g)	R^2	b	R_L(L/mg)	R^2	n	k_f(L/g)
AMD* upper	16.2	0.939	0.10216	0.281	0.9984	1.1737089	0.1569
AMD mid	59.3	0.1162	0.02138	0.652	0.9375	1.618123	0.0605
AMD lower	17.7	0.919	0.08324	0.325	0.9606	1.1290505	0.1676
ALD$^{\#}$ upper	12.2	0.9991	0.23646	0.145	0.9805	0.8755801	0.1929
ALD mid	51.7	0.1557	0.01488	0.729	0.9328	1.5432099	0.1448
ALD lower	-0.045	0.825	-0.1597	-0.334	0.6779	24.630542	-0.0995
CMD$^{\wedge}$ upper	12.6	0.9961	0.13456	0.229	0.9919	1.1286682	0.1748
CMD mid	3.37	0.9571	-0.4644	-0.094	0.9698	0.8730574	0.2331
CMD lower	12.5	0.1804	0.05812	0.408	0.6952	2.8034763	0.0149

AMD * : Active more degraded , ALD$^{\#}$:Active less degraded, CMD$^{\wedge}$: Closed more degraded

The Freundlich isotherm model assumes that adsorption occurs on heterogeneous surfaces with interaction between the adsorbed molecules. The model is expressed by

$$\log_{10}(X/M) = \log_{10} K_f + 1/n \log_{10} C_e \qquad \text{Eq. (6.6)}$$

Where X is the amount of MB adsorbed (mg), m is the weight of the adsorbent used (g), C_e is the equilibrium concentration of MB in solution (mg/l), K_f (mg/g) $(l/mg)^{1/n}$ and 1/n are Freundlich constants. A plot log Ce and log (x/m) was used to evaluated AC conformance to Feundlich model (see Figure 6.6).

All nine AC samples evaluated conformed to the Freundlich model with the R^2 >0.9 for 7 samples (78 %) of AC (see Table 6.4). This suggests that adsorption by the activated carbons is best explained by Freundlich model. Figure 6.7 shows the adsorption effect of AC at equilibrium.

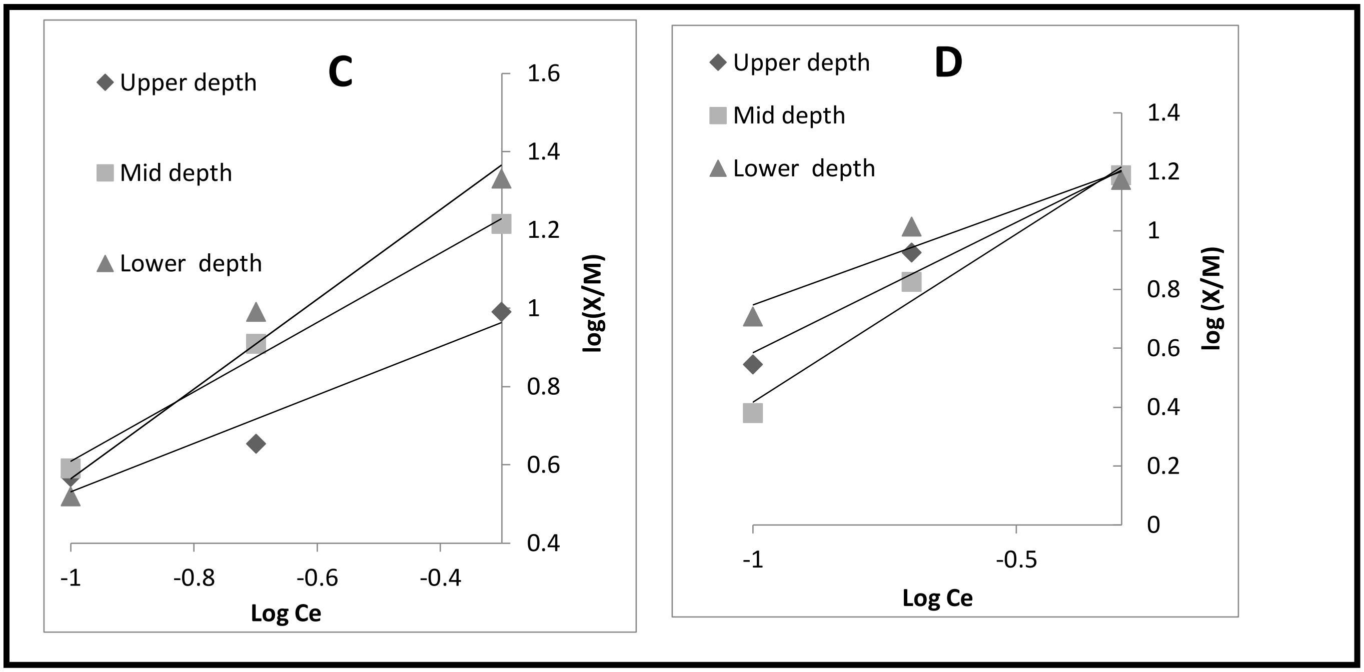


Figure 6.6: Freundlich plots for the adsorption of methylene blue onto the activated carbons. C: AC from closed more degraded precursor D: AC from active less degraded precursor

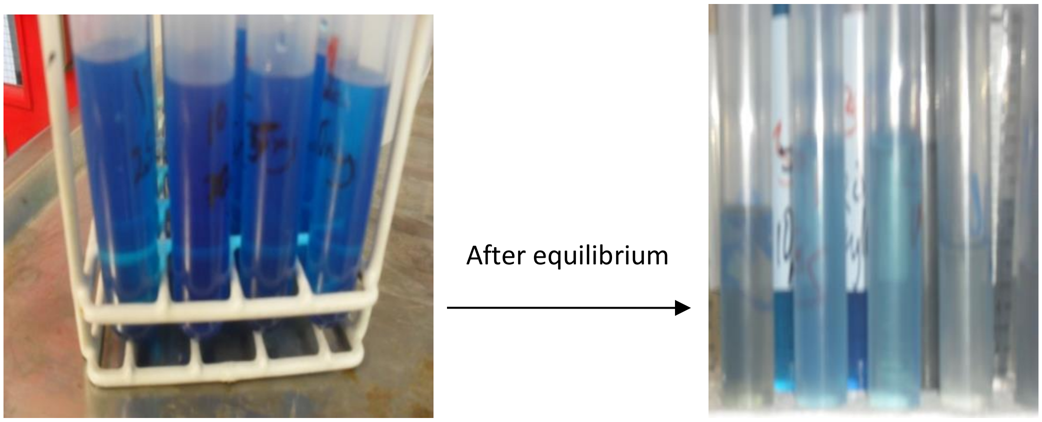


Figure 6.7: Shows the AC adsorption effect at equilibrium

6.3.2.6 Adsorption dynamics

The kinetic rate orders of MB adsorption onto the AC were evaluated using the pseudo first order and pseudo second order kinetic models. The expression for the first order given by Lagergren expression (Dogana *et al.*, 2006):

$$\text{Log}\ (q_e\text{-}q_t) = \log q_e - \frac{K_1}{2.303t} \qquad \text{Eq.} \quad (6.7)$$

Where q_e and q_t are the amounts of MB adsorbed (mg/g) at equilibrium and at time t (min), respectively, and k_1 is the rate constant of adsorption (min^{-1}). The plot of log (q_e-q_t) versus t gave a poor linear graph of $R^2 < 0.4$ for 67 % (8 of 12) of the AC evaluated. The kinetic adsorption of AC did not conform to the first order rate order. The values of K_1 and q_e were determined from the slope and intercept respectively (Table 6.4)

The second-order kinetic model given by Dogana *et al.*, 2006 expressed as

$$\frac{t}{q_t} = \frac{1}{hq_e^{\ 2}} + \frac{1}{q_e^{t}} \qquad \text{Eq. (6.8)}$$

the initial adsorption rate, h is defined as

$$h= k^2q_e^2$$

Where (h) is the initial adsorption rate, the equilibrium adsorption capacity (q_e), and the second-order constants k_2 (g/mg min). The plot of t/q versus t (Fig 6.8) gave a linear graph with R^2 value higher than 0.9 for 75 % of the AC evaluated. The q_e experimental and q_e calculated had relative percentage different < 10 % for 67 % of AC (see Table 6.4). Thus, the adsorption kinetics of MB onto AC was more favorably described by second-order kinetic model.

Table 6.4: Comparing the first and second order parameters

Sample	**2nd order**				**1st order**	
	R^2	**q_e^{cal}(mgg^{-1})**	**k^2(gmg^{-1}min^{-1})**	**q_e^{exp}(mgg^{-1})**	**R^2**	**k^1(min^{-1})**
AMDupper	0.9859	169.2047	0.001656	144	0.5488	-0.0509
AMD mid	0.9924	89.28571	0.002798	69.9	0.0699	-0.00368
AMD lower	0.995	183.1502	0.003506	167.2	0.5687	-0.03201
ALDupper	0.9888	118.2033	0.009209	112.7	0.5379	-0.04721
ALD mid	0.0048	588.2353	1.79E-07	42	0.1296	-0.01359
ALD lower	0.7082	87.0322	6.69E-06	97.1	0.4603	-0.01313
CMDupper	0.4455	-03.1092	0.022428	36.5	0.3418	0.013818
CMDmid	0.9177	344.8276	0.000232	185.6	0.8781	-0.00806
CMDlower	0.9177	158.296	0.002657	133	0.7532	-0.0251
CLDupper	0.786	161.5509	0.000838	112	0.9096	-0.0251
CLDmid	0.995	105.2632	1.09E-05	146	0.7909	-0.00898
CLDlower	0.998	207.4689	0.003821	191.7	0.5`56	-0.04744

AMD: Active more degraded , ALD :Active less degraded, CMD: Closed more degraded CLD: Closed less degraded

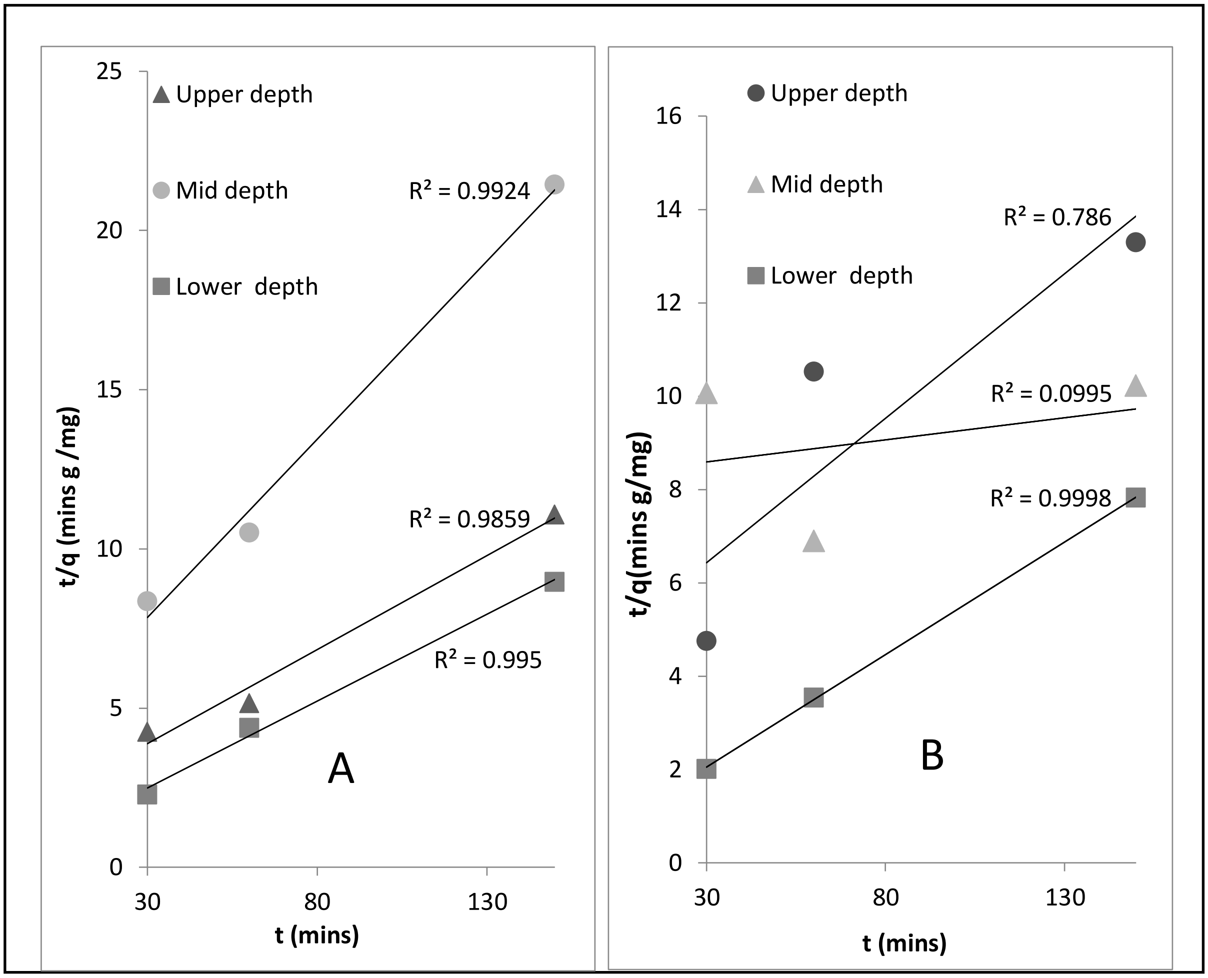


Figure 6.8: second order kinetic for the adsorption of methylene blue onto ACs

(A) AC from closed landfill less degraded precursor; (B) AC from active more degraded precursor

6.3.3 BET surface analysis

The BET surface area of the AC samples is as presented in Table 6.5. For both closed and active landfills, the BET surface area of more degraded samples increases with depth (closed landfill 72.53 m^2/g, 86.07 m^2/g and 132.51 m^2/g) and (active landfill 34.02 m^2/g, 38.08 m^2/g and 105 m^2/g). AC surface area of less degraded samples had no definite depth relationship. The surface area of AC of more degraded closed landfill samples follow the same trend as the adsorption capacity of MB (adsorption increased with depth as explain in section 6.3.2.2)

Table 6.5: BET surface area and pore surface area of AC

Sample name	BET surface area (m^2/g)	Pore surface area(m^2/g)
CMD upper	72.53	5.8
CMD mid	86.07	3.85
CMD lower	132.51	5.19
AMD upper	34.02	7.49
AMD mid	38.08	1.38
AMD lower	105.15	ND
ALD upper	51.64	0.87
ALD lower	92.89	11.33
CLD upper	31.75	2.58
CLD mid	89.33	4.59

*ND: not determined

A further study of the pore distribution in three selected samples (AC from closed landfill more degraded lower depth sample (CMD lower), AC from active landfill less degraded upper depth sample (AMD upper)and AC from active landfill more degraded upper depth sample (ALD upper)) is shown Figure 6.9. The graph shows the distribution of mesoporous, with most pores diameters of the AC were within the range 2-5 nm.

The average pore size of 3.7 nm, 4.6nm, 5.9 nm for analyzed AC further confirms the graphic observation that the AC consist of mostly mesopores. The AC had average pore volumes of 0.102, 0.160 and 0.126 cm^{3}respectively.

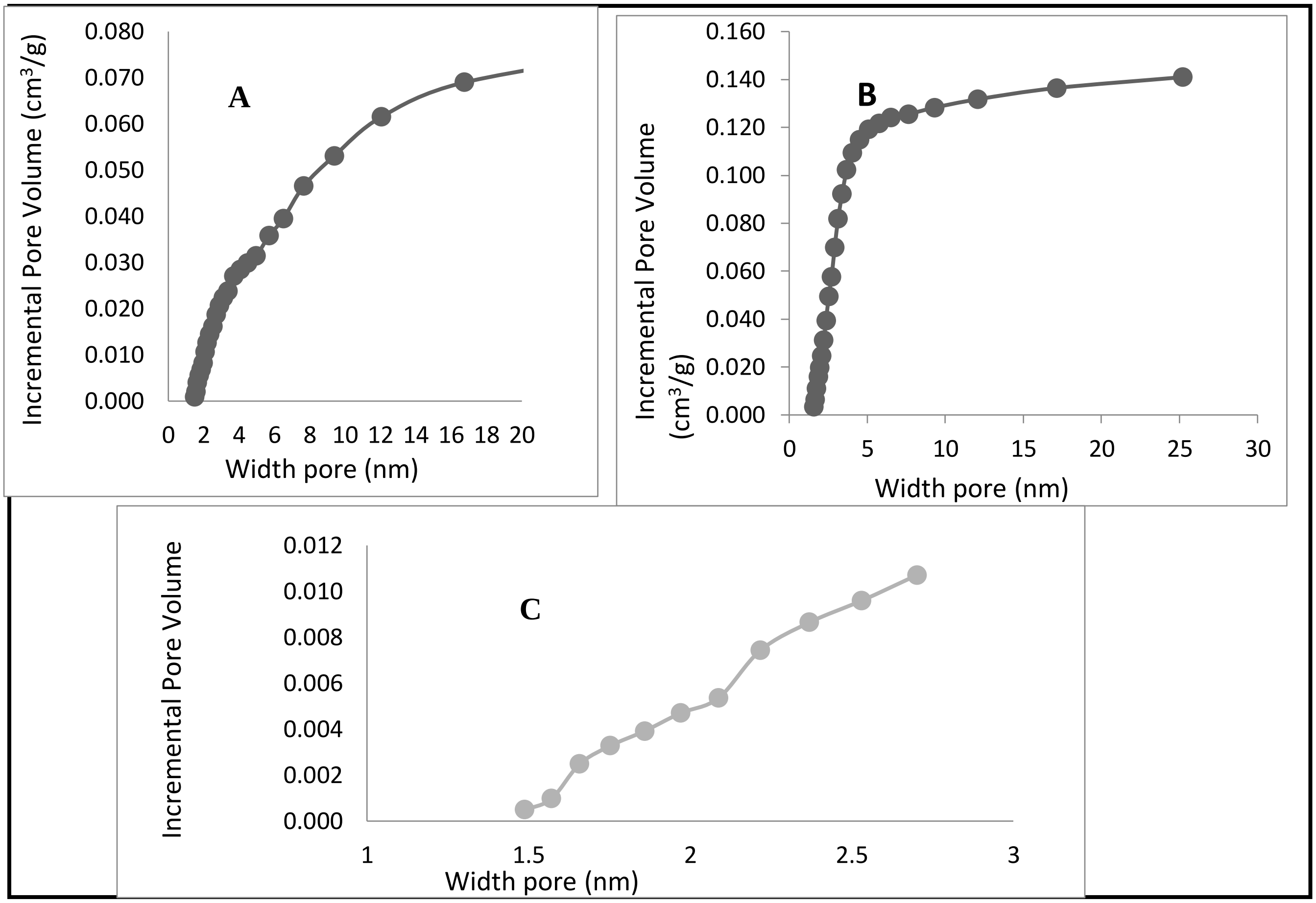


Figure 6.9: pore size distributions of the activated carbon. A, AC of closed landfill more degraded sample; B, AC of active landfill more degraded sample; C, AC of active landfill less degraded sample.

The adsorption isothermal was determined by the plot of relative pressure (P/P_o) and N_2 volume at STP in cm^3/g (see Figure 6.10). For all plots in figure 6.10, the quantity of N_2 adsorbed increases with the increase in the relative pressure indicating the adsorption of second layers with a characteristics hysteresis formation peculiar to Type IV isothermal adsorption. (Sing *et al.,* 1985; Teng *et al.*, 2000). Type IV adsorption process conforms to the Freundlich adsorption models of unrestricted monolayer - multilayer adsorption with the adsorbate-absorbate interaction playing the major role. Hysteresis appearance at above 0.4 can be associated with capillary condensation in mesopore structures (Sing *et al.,* 1985). The hysteresis has a type H4 loop which is attributed to narrow slit-like pores (Sing *et al.,* 1985). The large Langmuir area of 636 m^2/g, 466.1 m^2/g, 361.8 m^2/g further strength the high adsorption potential of the activated carbon. Hu et al. (2001) observed adsorption isothermal of type I and II for the AC from coconut shells as the ratio of activating agent impregnation increased.

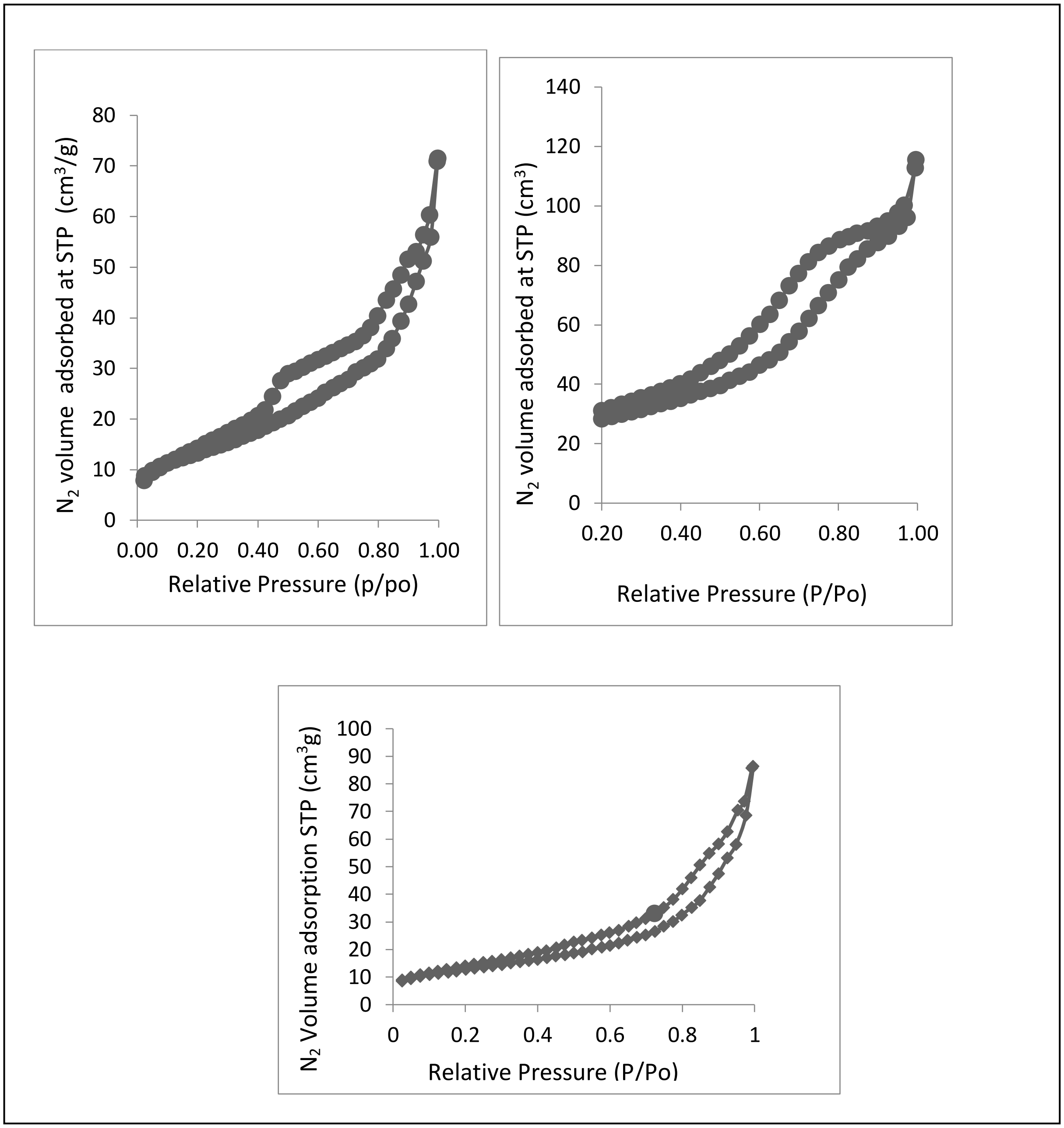


Figure 6.10: Nitrogen isotherms adsorption of the AC. A: AC of closed landfill more degraded sample, B: AC of active landfill more degraded sample C: AC of active landfill less degraded sample.

6.3.4 Functionalities of AC

A total of 42 FTIR spectra were reviewed to investigate the nature of functional group common to ACs. Major peaks located at 3320-3380, 1635-1694, 990-998, 770-779 and 699 cm^{-1} were prominent in most (8 of 12) of the AC samples. The peak at 3320-3380 cm^{-1} was identified as stretching vibration of hydroxyl group from alcohol or phenol (Kaartinen *et al.,* 2013; Ferrera-Lorenzo et al.; 2014a, Weng and Pan, 2007; Karago *et al.,* 2008; Kavitha and Namasivayam, 2007), which may reflect –OH from residual KOH. The 1635-1694cm^{-1} peak is attributed to C=C stretching vibration of olefin groups **(**Weng and Pan, 2007; Karago et al.; 2008, Kavitha and Namasivayam, 2007), while the peaks at 990-998, 779, and 699 cm^{-1} were ascribed to C-H out of plane bending of aliphatic groups (Suhas *et al.,* 2007; Weng and Pan, 2007; Karago *et al.,* 2008).

The FTIR spectra of the AC of both landfills showed significant changes in functional groups when compared to spectra of their respective precursors. Figure 6.11 compares typical FTIR spectra of the precursor to those of their respective AC.

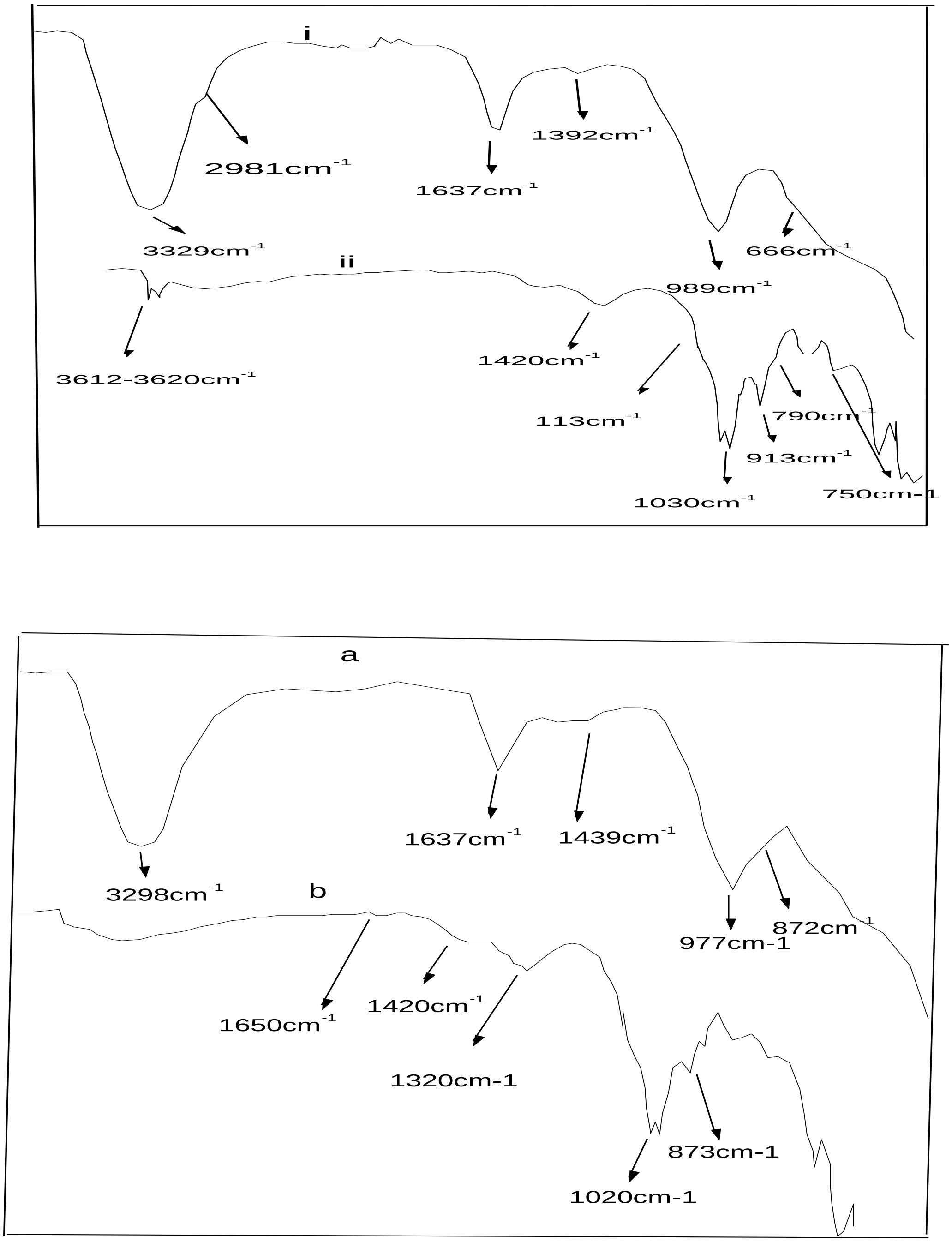


Figure 6.11: Typical spectra of AC and precursor. (i). active landfill AC, (ii) active landfill precursor, (a) closed landfill AC, (b) closed landfill precursor.

Prominent peaks of active landfill precursor at 3690 and 3619 cm^{-1}, attributed to O–H vibration of Si-OH of clayey materials (Quaghebeur *et al.,* 2013; Madejova, 2003) (see section 4.3.9.1), was absent in all AC samples of the landfill. This could be attributed to oxidation of the OH group during activation. OH vibration of clayey material (Si-OH) become less stable with increase in temperature and could be oxidized to carboxyl or aldehyde (Suhas *et al.,* 2007). Suhas et al. (2007) observed that with increased heating deeper oxidation of OH containing groups takes place leading to formation of carboxyl and aldehydes.

The intense peaks at around 1030–3 and 1000–9 cm^{-1} were attributed to silica, clay minerals (Si–O–Si and Si–O stretching vibration) (Quaghebeur *et al.,* 2013; Ouatmane *et al.,* 2000), which were present in the precursors of both landfill but absent in AC of the active landfill, except for the upper layer. In most (60 %) of the closed landfill AC, however, these peaks were retained but were less intense. This suggests that the source of these peaks in AC differs for each landfill. The AC peaks for active landfill sample could be mainly from clay mineral which is less resistant to heat, while those of the AC from closed landfill could be largely due to Si-O-Si stretching of silica, which is more stable to heat.

A very weak aliphatic methyl peak at 2980-4 cm^{-1} was found in 95 % of AC samples from the closed landfill, but was completely absent in all AC of the active landfill. Other peaks at 1558-1560 cm^{-1} were ascribed to C-O groups conjugated with aromatic rings (Foo *et al.*, 2013). The peaks at 1440-12 cm^{-1} were attributed to C–O–H in-plane bending of carboxylic carbon (Kaartinen *et al.*, 2013; Suhas *et al.,* 2007), while those at 1340-1395 cm^{-1} were ascribed to conjugated moieties of oxygen functional group of C=O stretching and C-O stretching in carboxylic group (Ji *et al.*, 2007). The peaks located at 1165 and 874cm^{-1}, attributed to C–O and C–H vibrations (Liou, 2010) respectively, were found in AC from both landfill types but were more prominent in the closed landfill than the active landfill.

6.4 Conclusion

The AC generated from different precursors had different characteristics and adsorption potentials. The nature of landfill (closed and active), the nature of sample (degraded and less degraded) and the depth were factors observed to have influenced some properties of the produced ACs. Precursors from both landfills generated AC with different adsorption capacity and BET area but had similar functionalities and pore size distribution. For both landfills, more degraded precursors generated AC had higher adsorption capacity with higher surface area (active landfill, 131 mg/g and 59.1 m^2/g; closed landfill, 126 mg/g and 97.0 m^2/g). The more degraded sample of both landfills showed similar trends in the character of the produced AC (surface increase with depth). AC of the less degraded precursor of active landfill had higher adsorption capacity with higher surface area compared to the closed landfill precursor, with no definite trend with depth. The AC exhibited a monolayer-multilayer adsorption isothermal of type II order. The AC shows less presence of micropores, which indicates that it may not be suitable for the absorption of some gaseous pollutants (pore size < 1nm). However, with the AC consisting of mainly of mesopores and adsorption capacity of 34 mg/g – 190 mg/g for methylene blue, the AC could be used to adsorb a range of cationic dyes and pollutants.

CHAPTER SEVEN

CONCLUSION AND RECOMMENDATION

7.1 Conclusions

This chapter presents an overview of the research objective and findings in order to draw conclusion on the observations made during the course of this research work.

The practice of waste landfilling is a long age practice which is still an integral part of Municipal solid waste system despite associated environmental challenges (Bolan *et al.*, 2014). Sustainable Management of active and closed landfill is desirable to preserve our ecosystem from pollution and optimize land utility. The first step to a successful sustainable landfill management system is undertaking a compositional characterization of waste disposed to understand the potential alternative uses (Armijo *et al.*, 2008). This research has been able to provide strategic information on the composition of samples in a closed and active landfill in Lagos, Nigeria. Both landfills showed similarity in waste constituent despite age difference (active: 1-2 years; closed: 5-6years). Polythene waste was found to be the predominant non-biodegradable component representing 45 % and 35 % of less degraded waste in the active and closed landfill respectively. Recovery practice of polythene from landfill has been poorly reported and may not economically viable due to the intense cleanup process it would require before reuse. However, the use of polythene and polyethylene terephthalate waste as activated precursor has been reported by Laszlo *et al.* (2001) and Mendoza-Carrasco *et al.* (2016). The virgin wastes of the remaining constituents of the less degraded samples in the landfills have been previously investigated as precursors for activated carbon: plants (Tang *et al.,* 2012; Foo *et al.,* 2013), wood (Fu, *et al.,* 2013;Foo and Hameed, 2012) and synthetic materials and papers (Nahil and Williams, 2012). Degraded components constitute above 55 % of landfill composite for both landfills. Degraded or soil component of mined landfill are often above 50 % of extracted waste Jain *et al.,* (2013 and 2014) and Frandegard (2013) made similar observation of degraded or reclaimed soil, consisting of 52 % and 53 % of mined landfill in Florida and Sweden respectively. The compositions of waste in the two landfills were considered to have good potential as activated carbon precursor.

The inorganic contents of both landfills were generally below regulatory standards, except for Pb in the more degraded closed landfill samples. The closed landfill with no leachate collection pond has a high risk of Pb leaching into the environment as runoff water from the landfill. Levels of inorganic contaminants (Cr, Cu, As, and Ag) were generally within the same magnitude as in household wastes reported for Finland (Vesanto *et al.* 2007; Kaartinen *et al.* 2013).

Both landfills were rich in C, O, S, Fe, Al and Ca elemental content. This identifies O and S as the prominent hereatoms that could affect the surface chemistry of the produced activated carbon. The ratio of carbon and oxygen content throughout the depths in both landfills were within 1:1, providing coordination between the poly aromatic or poly aliphatic sheets and the heteroatom.

Total Organic carbon (TOC) is one of the major contrasts between the two landfills. The distribution of TOC could be affected by the nature of waste, precipitation and landfill practice

(Jain *et al.,* 2005; Quaghebeur *et al.,* 2013). Although the TOC of more degraded samples of both samples were similar (active: 5.9 % and closed 5.7 %), the TOC of less degraded samples in the closed landfill was more than 10 % higher the active landfill for all the depths. Kaartinen *et al.* (2013) evaluated the TOC of mined waste and reported a low TOC of 5.3 – 4.8 % for waste of size < 20 mm, while waste of size >70 mm had a TOC of 11 %. The possibility of TOC loss as dissolved organic carbon (DOC) during the wet season was also observed in both landfills. In term of suitability for used as activated carbon based on the TOC content, the samples of closed landfill were favoured.

Fixed carbon of a biomass represents the carbon content available for fuel and energy conversion (García *et al.,* 2012 and 2013). The proximate properties of samples in both landfill were in order Ash > volatile > fixed carbon. The fixed carbon of precursors (average 17 %) for both landfills was considered suitable for activation despite the limiting ash content. Biomass having fixed carbon of 17.1, 16.3 and 14.8 %, has been previously used as precursor for AC activation, by Guo and Lua (2000) and Liou (2010).

Precursors from both landfills had peaks which indicated mineralized nature of the constituent with the absence of aliphatic methyl and methylene peaks at 2920 cm^{-1} and 2850 cm^{-1} and prominent inorganic peaks attributed to silica, clay minerals (Si–O–Si and Si–O stretching vibration) and quartz at 1030-3 cm^{-1} and 1000-9 cm^{-1}. Smidt & Meissl (2007) and Smidt & Schwanninger (2005) characterized degraded waste using these peaks. The precursor's degraded nature is considered a major factor in the heating source to be used for the activation process. The use of conventional heating source resulted in low % yield of activated carbon due to vaporization during activation process. The degraded nature of precursor may have influenced vapourization of elemental carbon. Carbon loss during carbonization using combustion furnace was attributed to thermal decomposition of carbon bond at high temperature 400 °C. The use of a microwave oven provided a heating system that enhanced molecular heating with less possibility of carbon loss. Increase in impregnation ratio above 1:1 or microwave power above 600W decreased the percentage yield of AC. This was consistent with the observation made by Ferrera-Lorenzo *et al.* (2014) ,Njoku, *et al.(*2014) and Foo and Hameed,2012 that impregnation ratio and microwave power influenced the quantity of activated carbon produce.

The AC of both landfills differ in properties based on depth and type of landfill. Generally, AC showed good pore formation when compared to their respective precursors. The BET surface area of AC increased with depth for both landfills. A similar trend was observed in the MB adsorption capacity of AC of the more degraded samples of the closed landfill. AC from the more degraded samples had higher adsorption capacity than that from the less degraded samples. At equilibrium, the isothermal adsorption of MB onto AC conformed more to the Fredulich's model than to Langmuir's model. The adsorption kinetics of MB onto AC was more favorably described by second-order kinetic model. AC of more degraded samples showed distribution of both micropores and mesopores with most pores of the AC between 1-5nm. The BET isothermal adsorption graph further confirmed the multilayer adsorption properties of AC.

The landfill composite properties and the AC formed can be compared to some other biomass: oil palm stone and black liquor lignin which have been identified as having potential of been sustainably managed by conversion to activated carbon (Guo and Lua, 2000; Fu et al., 2013). Considering this reuse option for landfill composite could provide a means for use of large percentage of degraded and mixed resource from the landfill which cannot be easily separated. It could increase the integrated resource management of landfill with potential reuse as landfill liner and leachate pond adsorbent. Organic and inorganic mass transfer within the landfill could be curtailed with the reuse of the landfill composite AC as daily landfill covering. This could reduce huge budget on landfill covering and close the loop for virgin soil on landfill. The potential generation of greenhouse gas will be further reduced and weight of waste left in the landfill will be reduced thus increasing the life span of the landfill. Studies by Jain *et al.* (2013 and 2014) indicated that landfill mining for resource reuse, recycle and recovery is environmental beneficial and economical cost effective than doing nothing throughout the closure period.

In conclusion, these research findings provide essential information on the potential used of municipal landfill composite as a precursor for AC generation and its characterization. Landfill composites were considered suitable for AC activation, except for the degraded nature and inorganic content in the closed landfill. The AC quality in terms of surface area and adsorption capacity increases with depth. With a Langmuir surface of 636 m^2/g and MB adsorption capacity of 190 mg/g, the AC could be used to adsorb a range of cationic dyes and pollutants.

7.2 Contribution to knowledge

- The first part of this research work had shown that both active and closed landfill investigated consist largely of decomposed materials across the sampled depth. This is a strong indication that aerobic landfill condition existed within these layers. The degradation process of waste within this depth is expected to be accelerated due to temperature range above 25 °C and moisture content above 32 %. The use of SEM/EDX and FTIR for precursor characterization present a faster and non-destructive method applied for the first time to these samples been investigated.
- The landfill composite of both landfills were found suitable for used as a precursor for the generation of activated carbon. This represent a novel source of precursor for the activation carbon production and possible novel reuse option for landfill composite. It creates a possible window for an integrated landfill management system.
- The depth of both landfill composites made a significant difference on the adsorption capacity and surface area of the generated activated carbon, while age difference play no definite role. Increase in the depth of precursor resulted largely to higher quality of activated carbon. This is a new research finding indicating relationship between depth of landfill composite and the quality of activated carbon produced.

7.3 Limitation of Result

The major limitation of the present results as with most landfill parameters is that is highly dependent on the type of waste disposed, climatic condition and the landfill management practice. It is difficult to generalize results for all landfills.

7.4 Recommendations and future research

The finding reported here present a single profile evaluation of the landfills to create the basis for an in-depth look at resource potential in the landfill located in Lagos, Nigeria. A deeper sampling of the landfill to establish spatial trend between profiles is necessary in order to design a robust landfill mining strategy and activation conditions. A study of quality optimization conditions for the activation process using landfill composite is necessary to enhance the use of this management option.

The using of anaerobic landfill composite as a precursor is necessary to assess its suitability for the production of activated carbon. It will help establish the possible application of this conversion strategy to both anaerobic landfill composite common in the developed countries and aerobic composite peculiar to developing countries.

AC regeneration studies are necessary to enable better understanding of management strategy for the exhausted AC. Evaluating adsorption potential of the landfill leachate content onto the activated carbon is highly desired to determine the possibility of deploying it for this purpose. There is need for the government to enact policy and strategy to prevent continuous buildup of non–biodegradable waste (Polythene) in active landfill. This type of waste is best recycled rather than disposed on the landfill.

REFERENCE

AbdAlqader, A., Hamad, J. (2012). municipal Solid Waste Composition Determination Supporting the Integrated Solid Waste Management in Gaza Strip. *International Journal of Environmental Science and Development*, 3:172- 176.

Aboyade, A. (2004). The Potential for Climate Change Mitigation in the Nigerian Solid Waste Disposal Sector: A Case Study from Lagos. Master's Thesis. Lund University, Sweden.

Adeolu, A. O, Ada, O. V., Gbenga A. A., Adebayo, O. A. (2011). Assessment of groundwater contamination by leachate near a municipal solid waste landfill. *African Journal of Environmental Science and Technology*, 5:933-940.

Afolayan, O.S., Ogundele, F.O., Odewumi, S.G. (2012). Spatial Variation in Landfills Leachate Solution in Urbanized Area of Lagos State, Nigeria. American International. *Journal of Contemporary Research*, 2:178-184.

Ahmad, A., Loh, M., Aziz, J. (2007). Preparation and characterization of activated carbon from oil palm wood and its evaluation on methylene blue adsorption, *Dyes Pigm.* 75 263–27

Akudo, E. O., Ozulu, G.O. and Osogbue, L.C. (2010). Quality Assessment of Groundwater in Selected Waste Dumpsites Areas in Warri, Nigeria. *Environmental Research Journal*, 4(4): 282-285.

Ali, A. F. (2012). Groundwater Pollution Threats of Solid Waste Disposal in Urban Kano, Nigeria: Evaluation and Protection Strategies PhD thesis submitted to the Department School of Mechanical, Aerospace and Civil Engineering, University of Manchester, UK.

Al-Rmalli, S.W. (2012). Arsenic and Other Trace Elements in Bangladeshi Foods and Non-Foods and Their Relationship to Human Health. PhD thesis, De Montfort University, Leicester, UK.

Alslaibi, T.M., Abustana, I., Ahmad, M.A., AbuFoul, A. (2013). A review production of activated carbon from agricultural by products via conventional and microwave heating. *J Chem Technol Biotechnol*, 88: 1183–1190.

Armijo de Vega C., Benítez, S.M., Barreto, E.R. (2008). Solid waste characterization and recycling potential for a university campus, *Waste Management.* 28: S21-S28.

Attia, A.A.,Girgis, B.S., Tawfik, N.A.F.(2005). Porosity and Liquid-phase Adsorption Characteristics of Activated Carbons Prepared from Peach Stones by H3PO4, Carbon Science, 6:89-95.

Aygün, A., Yenisoy-Karakaş, S., & Duman, I. (2003). Production of granular activated carbon from fruit stones and nutshells and evaluation of their physical, chemical and adsorption properties. *Microporous and Mesoporous Materials*, *66*: 189–195.

Aziz, H.A., Adlan, M.N., Zahari, M. S.M., Alias, S. (2004). Removal of ammoniacal–nitrogen (N–NH3) from municipal solid waste leachate by using activated carbon and lime stone, *Waste Manage*. 22: 371–375.

Baçaoui, A., Yaacoubi, A., Dahbi, A., Bennouna, C., Phan Tan Luu, R., Maldonado-Hodar, F. J., Rivera-Utrilla, J. & Moreno-Castilla, C. 2001.Optimization of conditions for the preparation of activated carbons from olive-waste cakes. *Carbon*, 39: 425-432.

Bagheri N., Abedi J. (2009).Preparation of high surface area activated carbon from corn by chemical activation using potassium hydroxide. *ChemEngResDes* 87: 1059–1064.

Batagarawa, R.L. (2011). Sustainability appraisal of waste management in Nigeria: development and evaluation of an index Based tool. PhD thesis, Department of Civil Engineering, University of Portsmouth, UK.

Beekaroo, D., Mudhoo, A. (2011). Adsorption of reactive red 158 Dye by chemical treated Coos nuferal shell powder. *Springer Dordrecht Heidelberge*, New York.

Bolan, N.S., Thangarajan, R., Seshadri, B., Jena, U., Das, K.C., Wang, H., Naidu, R. (2013). Landfills as a biorefinery to produce biomass and capture biogas, *Bioresource Technology*. 135,578–587.

Buenrostro, O., Bocco, G., Cram, S., (2001). Classification of sources of municipal solid wastes in Developing countries. *Resources, Conservation and Recycling* 32, 29– 41.

Cazetta A.L., Vargas A.M.M., Nogami E.M., Kunita M.H., Guilherme M.R., Martins A.C., Silva T.L., Moraes J.C.G and Almeida V.C. (2011). NaOH-activated carbon of high surface area produced from coconut shell: kinetics and equilibrium studies from the methylene blue adsorption. *Chemical Engineering Journal*, 174:117–125.

Cossu, R. (2012). The environmentally sustainable geological repository: The modern role of landfilling. *Waste Management,* 32: 243–244.

DEFRA -Department for Environment, Food and Rural Affairs (2012). Guidance on the legal definition of waste and its application (2012) available on https://www.gov.uk/government/uploads/system/uploads/attachment_data/file/69590/pb13813-waste-legal-def-guide.pdf (accessed July 2015)

DEFRA -Department for Environment, Food and Rural Affairs.(2010).The Landfill Directive for the Environmental Permitting Regulation. Department for Environmentfoodandruralaffairs.UK<https://www.gov.uk/government/uploads/system/uploads/attachment_data/file/69347/pb13563-landfill-directive-100322.pdf (accessed September 2014).

De la Cruz, F. B., Chanton, J. P., & Barlaz, M. (2013). Measurement of carbon storage in landfills from the biogenic carbon content of excavated waste samples. *Waste Management*, *33*:2001–5.

Desrochers, A. N. K., Paulson, M. A. K., Ptacek, C. J. , Blowes, W. D. , Gould, D. W. (2015). Effect of Electron Donor to Sulfate Ratio on Mercury Methylation in Floodplain Sediments under Saturated Flow Conditions. *Geomicrobiology Journal*, 32: 924-933

Dogana, M., Alkana, M., Demirbas, O.,Yasemin, O., Ozmetin, C. (2006). Adsorption kinetics of maxilon blue GRL onto sepiolite from aqueous solutions, *Chemical Engineering Journal.* 124, 89–101.

Friedrich, E., Trois, C. (2013). GHG emission factors developed for the collection, transport and landfilling of municipal waste in South African municipalities. *Waste Management* 33: 1013–1026.

Environment Agency UK.(2015). Waste classification, Guidance on the classification and assessment of waste (1st edition 2015) Technical Guidance WM3.https://www.gov.uk/government/publications/waste-classification-technical-guidance (accessed July, 2016)

EnvironQuest. 2005. *Resettlement policy framework*. S.L.; EnvironQuest. http://documents.worldbank.org/curated/en/767521468291898557/Resettlement-policy framework. (accessed May 2016)

EnvironQuest. 2009. *Solid waste management component: environmental and social impactassessment*.s.l.;s.n..http://documents.worldbank.org/curated/en/132331468290441565/Solid-waste-management-component-environmental-and-social-impact-assessment.(accessed May 2016)

EPA,Environmental Protection Agency.(1997). landfill manuals, landfill operational practices. Ardcavan, Wexford, Ireland.

European Union Council directive 1999/31/EC;http:// ec.europa.eu /environment /waste/ landfill_index.htm (accessed August 2016).

Ferrera-Lorenzo, N., Fuente , E., Suárez-Ruiz, I., Ruiz, B. (2014a). Sustainable activated carbons of macroalgae waste from the Agar–Agar industry. Prospects as adsorbent for gas storage at high pressures *N. Chemical Engineering Journal,* 250: 128–136.

Ferrera-Lorenzo, N., Fuente, E., Suárez-Ruiz, I., Ruiz, B. (2014). KOH activated carbon from conventional and microwave heating system of a macroalgae waste from the Agar–Agar industry. *Fuel Processing Technology,* 121: 25–31.

Figueiredo, J.L., Pereira, M.F.R., Freitas, M.M.A., Orfao, J.J.M. (1999). Modification of the surface chemistry of activated carbons. Carbon 37: 1379–1389.

Foo, K.Y., Hameed, B.H. (2012a). Factors affecting the carbon yield and adsorption capability of the mangosteen peel activated carbon prepared by microwave assisted K_2CO_3 activation. *Chemical Engineering Journal,* 180: 66– 74.

Foo, K.Y., Hameed, B.H. (2012b). Mesoporous activated carbon from wood sawdust by K_2CO_3 activation using microwave heating. *Bioresource Technology* 111: 425– 432.

Foo, K.Y., Hameed, B.H. (2012). Coconut husk derived activated carbon via microwave induced activation: Effects of activation agents, preparation parameters and adsorption performance. *Chemical Engineering Journal* 184: 57– 65.

Foo, K.Y., Lee, L.K., Hameed, B.H. (2013). Preparation of activated carbon from sugarcane bagasse by microwave assisted activation for the remediation of semi-aerobic landfill leachate. *Bioresource Technology,* 134:166–172.

Foo, K.Y., Lee, L.K., Hameed, B.H. (2013a). Preparation of tamarind fruit seed activated carbon by microwave heating for the adsorptive treatment of landfill leachate: A laboratory column evaluation, *Bioresource Technology.* 133, 599–605.

Frändegård, P. Krook J., Svensson N., Eklund M. (2013). Resource and Climate Implications of Landfill Mining A Case Study of Sweden, 2013. *Journal of Industrial Ecolog,.* 17: 742-755.

Franz, M., Arafat, H. A., Pinto, N. G. (2000). Effect of chemical surface heterogeneity on the adsorption mechanism of dissolved aromatics on activated carbon. *Carbon*, 38: 1807–1819.

Friedrich, E., & Trois, C. (2013). GHG emission factors developed for the collection, transport and landfilling of municipal waste in South African municipalities. *Waste Management (New York, N.Y.), 33*(4), 1013–26.

Fu, K., Yue, Q., Gao, B., Sun, Y., & Zhu, L. (2013). Preparation, characterization and application of lignin-based activated carbon from black liquor lignin by steam activation. *Chemical Engineering Journal*, *228*: 1074–1082.

García, J. , Davies, S., Villa,R., Gomes, D.M. , Coulon ,F., Wagland S.T. (2016). Compositional analysis of excavated landfill samples and the determination of residual biogas potential of the organic fraction. Waste management, 55:336–344.

García-Gil , J.C., Plaza, C.J., Fernández , M., Senesi, N., Polo A. (2008). Soil fulvic acid characteristics and proton binding behaviour as affected by long-term municipal waste compost amendment under semi-arid environment. *Geoderma,* 146: 363–369.

García, R., Pizarro C., Lavín, A. G., Bueno, J.L. (2012). Characterization of Spanish biomass wastes for energy use, *Bioresource Technology*, 103:249-258

García, R., Pizarro, C., Lavín, A. G., Bueno, J.L. (2013). Biomass proximate analysis using thermogravimetry. *Bioresource Technology,* 139:1–4.

Gercel, O., Ozcan, A., Ozcan, A.S., Gercel, H.F.(2007). Preparation of activated carbon from a renewable bio-plant of Euphorbia Rigida by H_2SO_4 activation and its adsorption behavior in aqueous solutions. *Appl. Surface Sci.* 253: 4843–4852.

Girgis, B. S., Yunis, S. S., Soliman A. M. (2002). Characteristics of activated carbon from peanut hulls in relation to conditions of preparation, *Materials Letters* 57: 164–172.

GOI. (2008). Waste Management Act, Jakarta, Indonesia.

Gonzalez-Fernandez O, Queralt I, Carvalho ML & Garcia G (2007) Elemental analysis of mining wastes by energy dispersive X-ray fluorescence (EDXRF). *Nuclear Instruments and Methods in Physics Research B* 262: 81–86

Guo, J., Lua, A.C. (1999). Textural and chemical characterizations of activated carbon prepared from oil palmstone with H_2SO_4 and KOH impregnation, *Microporous and Mesoporous Materials,* 32: 111–117

Guo, J., Lua, A.C. (2000). Preparation of activated carbons from oil-palm-stone chars by microwave-induced carbon dioxide activation. *Carbon*, 38: 1985–1993

Guo, Y., Yang, S., Yu, K., Zhao, J., Wang, Z., and Xu, H. (2002). The preparation and mechanism studies of rice husk based porous carbon, *Materials Chemistry and Physics*, 74: 320-323

Hamoda, M. F., Abu Qdais, H. A., & Newham, J. (1998). Evaluation of municipal solid waste composting kinetics. Resources, Conservation and Recycling, 23: 209-223.

Heavey, M. (2003). Low-cost treatment of landfill leachate using peat, *Waste Manage.* 23: 447–454.

Hockett, D., Lober, D.J., Pilgrim, K.(1995). Determinants of Per Capita Municipal Solid Waste Generation in the Southeastern United States. *Journal of Environmental Management*,45: 205-217.

Hoornweg, D. and Bhada-Tata, P. (2012). What a waste: a global review of solid waste management, World Bank, Washington DC, USA

Hu, Z., Srinivasan, M.P, Ni, Y.(2001). Novel activation process for preparing highly microporous and mesoporous activated carbons. Carbon 39: 877–886.

Hung, M., Ma, H., & Yang, W. (2007). A novel sustainable decision making model for municipal solid waste management. *Waste Management*, 27:209-219.

International Standard Industrial Classification of All Economic Activities Revision 4.(2008).ST/ESA/STAT/SER.M/4/Rev.4, Department of Economic and Social Affairs, Statistics Division, United Nations, New York.

Ioannidou O., Zabaniotou A. (2007). Agricultural residues as precursors for activated carbon production—A review, *Renewable and Sustainable Energy Reviews*, 11: 1966 – 2005.

IPCC - international Panel on Climate Change, 2006, Guidelines for National Greenhouse Gas Inventories Vol. 5-Waste < http://www.ipcc-nggip.iges.or.jp/public/2006gl/vol5.html> (August 2014).

Irwan, D., Basri, E. A., Watanabe, K. (2011). Interrelationship between affluence and household size on municipal solid waste arising: evidence from selected Residential areas of putrajaya. *Journal of Asian Scientific Research,* 2:747-758

Islam, A. Md., Ahmed, M.J., Khanday,W.A., Asif.,M., Hameed, B. H.(2017). Mesoporous activated carbon prepared from NaOH activation of rattan (Lacosperma secundiflorum) hydrochar for methylene blue removal. *Ecotoxicology and Environmental Safety*, 138:279-285.

Jain, P., Kim, H. and Townsend, T.G. (2005). Heavy metal content in soil reclaimed from a municipal solid waste landfill. *Waste Management*. *25*: 25–35.

Jain, P., Powell, J. T., Smith, J. L., Townsend, T. G., & Tolaymat, T. (2014). Life-Cycle Inventory and Impact Evaluation of Mining Municipal Solid Waste Landfills. *Environ Sci Technol.,* 48:2920-7

Jain, P., Townsend, T. G., & Johnson, P. (2013). Case study of landfill reclamation at a Florida landfill site. *Waste Management. 33*: 109–16.

Ji, L. and Zhang, X. (2009). Generation of activated carbon nanofibers from electrospun polyacrylonitrile-zinc chloride composites for use as anodes in lithium-ion batteries. *Electrochemistry Communications*, 11: 684–687.

Ji,Y., Zhu,T.L., Wang, X., Lin, Q. (2007). Preparation of activated carbons by microwave heating KOH activation. *Applied Surface Science*, 254: 506–512.

Johannessen, L. M., Boyer, G. (1997). Observations of Solid Waste Landfills in Developing Countries: Africa, Asia, and Latin America, Urban Development Division, Waste Management Anchor Team, The World Bank, Washington, D.C.

Kaartinen, T., Sormunen, K. and Rintala, J. (2013). Case study on sampling, processing and characterization of landfilled municipal solid waste in the view of landfill mining. *Journal of Cleaner Production*. 55: 56–66.

Kalfa, O.M, Ustundag., Z, Ozkirime, I., & Kadioglu, K.Y. (2007). Analysis of tincal ore waste by energy dispersive X-ray fluorescence (EDXRF) technique. *Journal of Quantitative Spectroscopy & Radiative Transfer* 103: 424-427.

Karago, S., Tay T., Suat U., Erdem M. (2008). Activated carbons from waste biomass by sulfuric acid activation and their use on methylene blue adsorption .*Bioresource Technology*. 99: 6214–6222.

Karunakaran, K., Thamilarasu, P. and Sharmila, R. (2009). Statistical Study on Physicochemical Characteristics of Groundwater in and around Namakkal, Tamilnadu, India. *E-Journal of Chemistry,* 6:3.

Kawai, K., Tasaki, T.(2016). Revisiting estimates of municipal solid waste generation per capita and their reliability. *Journal of Material Cycles and Waste Management,* 18(1):1-13.

Kavitha, D., Namasivayam, C. (2007). Experimental and kinetic studies on methylene blue adsorption by coir pith carbon, *Bioresource Technology*. 98, 14–21

Kofoworola, O.F. (2007). Recovery and recycling practices in municipal solid waste management in Lagos, Nigeria. *Waste Management*. 27: 1139–1143

Kulikowska, D., Klimiuk, E., (2008). The effect of landfill age on municipal leachate composition. *Bioresource. Technology*. 99: 5981–5985.

Kurniawan, T.A., Lo, W., Chan, Y.S.G. (2006). Physico-chemical treatments for removal of recalcitrant contaminants from landfill leachate. *Journal of Hazardous Materials*. B129: 80–100.

Lagos Waste Management Authority (LAWMA), (2012), MSW PROJET OPPORTUNITY, Lagos State, Nigeria Available from <http://www.lawma.gov.ng/lawma_landfill.html. > (21 July 2014.)

Lam, S. S., Chase, H. A. (2012). A Review on Waste to Energy Processes Using Microwave Pyrolysis. Energies 5: 4209-4232.

Laszlo, K., Tombacz, E., Josepovits, K. (2001b). Effect of activation on the surface chemistry of carbons from polymer precursors. *Carbon*, 39: 1217–1228.

Laszlo, K., Szucs, A. (2001a). Surface characterization of polyethyleneterephthalate (PET) based activated carbon and the effect of pH on its adsorption capacity from aqueous phenol and 2,3,4-trichlorophenol solutions. *Carbon*. 39: 1945–1953.

Lei, L., Patricia, A., Knappe, D. R.U. (2002). Effects of activated carbon surface chemistry and pore structure on the adsorption of organic contaminants from aqueous solution, *Carbon*. 40: 2085–2100.

Li, W., Zhanga, L., Penga, J., Lia, N., Zhua, X. (2008). Preparation of high surface area activated carbons from Tobacco stems with K_2CO_3 activation using Microwave radiation, *Industrial crops and products*. 27: 341–347

Liao T. W. (2005). Clustering of time series data—a survey, *Pattern Recognition*, 38: 1857- 1874

Lillo-Rodenas M, Lozano-Castello D, Cazorla-Amoros D, Linares-Solono A. (2001). Preparation of Activated Carbons from Spanish Anthracite: II Activation by NaOH. *Carbon* 39: 751-759.

Liou, T. (2010). Development of mesoporous structure and high adsorption capacity of biomass based activated carbon by phosphoric acid and zinc chloride activation. *Chemical Engineering Journal* 158: 129–142.

Longe, E. O., and Enekwechi, L. O. (2007). Investigation on potential groundwater impacts and influence of local hydrogeology on natural attenuation of leachate at a municipal landfill. *International Journal of Environmental Science & Technology*. 4: 133–140.

Lua, A. C., Yang, T. & Guo, J. (2004). Effects of pyrolysis conditions on the properties of activated carbons prepared from pistachio-nut shells. Journal of Analytical and Applied.*Pyrolysis*, 72: 279-287

Madejova, J., (2003). FTIR techniques in clay mineral studies, *Vibrational Spectroscopy*, 31: 1–10.

Marsh, H., Rodriguez-Reinoso, F. (2006). Activated Carbon. *Elsevier Science & Technology Books*, Amsterdam.

Martínez M.L., Torres M.M., Guzmán C.A., Maestri D.M. (2006). Preparation and characteristics of activated carbon from olive stones and walnutshells. *Ind Crops Prod*, 23: 23–28.

McDougall, G.J. (1991). The physical nature and manufacture of activated carbon. *J. S. Afr. Inst. Min. Metal*. 91:109 - 120.

McKay, G., Ramprasad, G. Mowli, P.P. (1986). Equilibrium studies for the adsorption of dyestuffs from aqueous solutions by low-cost materials, Water Air Soil Pollut. 29, 273–283.

Medina, M. (1999). Globalization, Development, and Municipal Solid waste Management in the Third World Cities. Tijuana, El Colegio de la Fronera Norte.

Mendoza-Carrasco, R.E.M., Alexandre-Franco M.F., Fernandez-Gonzalez, C., Gomez Serrano, V. (2016). Preparation of high-quality activated carbon from polyethyleneterephthalate (PET) bottle waste .Its use in the removal of pollutants in aqueous solution. *Journal of Environmental Management* 181: 522-535

Menéndez, J.A., Jua´rez-Pérez, E.J., Ruisánchez, E., Bermúdez ,J.M., Arenillas A. (2011). Ball lightning plasma and plasma arc formation during the microwave heating of carbons. *Carbon*, 49: 339–351

Menéndez, J.A., Arenillas A., Fidalgo B., Fernández Y., Zubizarreta L., Calvo E.G., Bermúdez, J.M. (2010). Microwave heating processes involving carbon materials. *Fuel Processing Technology*. 91: 1-8.

Menikpura, S.N.M., Janya Sang-Arun, Magnus Bengtsson. (2013). Integrated Solid Waste Management: an approach for enhancing climate co-benefits through resource recovery. *Journal of Cleaner Production*, 58: 34-42

Moreno-Castilla, Carlos. (2004). Adsorption of organic molecules from aqueous solutions on carbon materials. *Carbon*. 42, 83–94

Munawar, E. (2014). “Modelling the degradable organic carbon in municipal solid waste.” Doctoral Thesis. Vienna University of Technology, Wien, Austria.

Nagano, S., Tamon, H., Adzumi, T., Nakagawa, K., & Suzuki, T. (2000). Activated carbon from municipal waste. *Carbon*, *38:* 915–920.

Nahil, M. A., & Williams, P. T. (2012). Surface chemistry and porosity of nitrogen-containing activated carbons produced from acrylic textile waste. *Chemical Engineering Journal*, *184*: 228–237

NBS- National Bureau of Statistics. (2012). Annual abstract of Statistics. http://www.nigerianstat.gov.ng/report/253 (accessed August 2016)

Njoku, V.O., Foo, K.Y., Asif, M., Hameed, B.H. (2014). Preparation of activated carbons from rambutan (Nephelium lappaceum) peel by microwave-induced KOH activation for acid yellow 17 dye adsorption. *Chemical Engineering Journal*. 250,198–204.

OECD .2013. Glossary of stastical term, waste, organization for Economic Co-operation and Development. https://stats.oecd.org/glossary/detail.asp?ID=2896 Accessed september 2015.

Oeltzschner H., Mutz D. (1994). Guidelines for an Appropriate Management of Domestic Sanitary Landfill Sites. Division water, waste management and protection of nature resource. Deutsche Geselischaft für Technische Zusammenarbeit (GTZ), Eschborn, Germany.

Oh, G.H., Park C.R. (2002). Preparation and characteristics of rice-sraw-based porous carbons with high adsorption capacity. *Fuel*, 81:327–36.

Ouatmane, A., Provenzano, M.R., Hafidi, M., and Senesi, N. (2000).Compost maturity using calorimetry, spectroscopy and chemical analysis. *Compost Science and Utilization*, 8:124–134.

PAHO. (2010). Regional evaluation on urban solid waste management in Latin American and the carribbean pan American Health Organization washinton DC, USA.

Pastor-Villegas, J., & Durán-Valle, C. J. (2002). Pore structure of activated carbons prepared by carbon dioxide and steam activation at different temperatures from extracted rockrose. *Carbon*, 40: 397-402

Poley-vos, C.H., Nieuwenhuize, J., Van den Akker, H. A., Van Delft, W. (1991). Comparison of microwave extraction techniques for the determination of metals in soil, sediment and sludge sample by atomic spectrometry. *Analyst* 116: 347-351

Prauchner, M.J. Rodríguez-Reinoso, F. (2012). Chemical versus physical activation of coconut shell: a comparative study, Microporous Mesoporous Mater. 152: 163–171

Punj G., Stewart, D.W. (1983). Cluster Analysis in Marketing Research: Review and Suggestions for Application, *Journal of Marketing Research*, 20:134 – 148.

Quaghebeur, M., Laenen, B., Geysen, D., Nielsen, P., Pontikes, Y. (2013). Characterization of landfilled materials: screening of the enhanced landfill mining potential, *Journal of Cleaner Production*, 55, 72–83

Rajkumar, N., Subramani, T. and Elango, L. (2010). Groundwater Contamination Due to Municipal Solid Waste Disposal - A GIS Based Study in Erode City. *International Journal of Environmental Sciences*, 1: 20-10.

Rashidi, N. A., Yusup, S. (2017). A review on recent technological advancement in the activated carbon production from oil palm waste. *Chemical Engineering journal,* 314: 277-290

Renoua, S., Givaudan, J.G., Poulain S., F. Dirassouyan, Moulin, P. (2008). Landfill leachate treatment: Review and opportunity. *Journal of Hazardous Materials,* 150:468–493.

Rodrigues, P.M.S.M, Rodrigues, M.M., Costa, B.H.F, Martins, A.A.L.T, Esteves da Silva, J.C.G. (2010). Multivariate analysis of the water quality variation in the Serra de Estrela (Portugal) natural park as a consequence pf road deicing with salt. *Chemometrics and intelligent laboratory systems*, 102: 130-135.

Roussat, N., Dujet, C., & Méhu, J. (2009). Choosing a sustainable demolition waste management strategy using multicriteria decision analysis. *Waste Management,* 29: 12-20.

Salema, A. A., Ani, F. N. (2011). Microwave induced pyrolysis of oil palm biomass, *Bioresource Technology,* 102: 3388–3395

Scaglia, B., Orzi, V., Artola, A., Font, X., Davoli, E., Sanchez, A., Adani, F. (2011). Odours and volatile organic compounds emitted from municipal solid waste at different stage of decomposition and relationship with biological stability. *Bioresource. Technology*. 102:4638–4645.

Schumacher, B. A. (2002). Methods for the Determination of Total Organic Carbon (Toc) In Soils and Sediments**.** NCEA-C- 1282, EMASC-001. United States Environmental Protection Agency Environmental Sciences Division, Las Vegas.

Shafeeyan, M., S., Wan Daud, W. A., Houshmand, A., Shamiri, A. (2010). A review on surface modification of activated carbon for carbon dioxide adsorption, *Journal of Analytical and Applied Pyrolysis*. 89: 143–151.

Sharifan, S. (2013). A Comparative Optimization Study of Activated Carbon Production from Hazelnut Shells by Thermal and Microwave Heating Methods. PhD thesis, Imperial College London, UK.

Shen, J., Zhu, S., Liu, X., Zhang, H., Tan, J. (2010).The prediction of elemental composition of biomass based on proximate analysis. Energy Convers. Manag. 51: 983–987.

Shin H., Park, J.,Park K., Song H. (2002). Removal characteristics of trace compounds of landfill gas by activated carbon adsorption. *Environmental Pollution* 119: 227–236.

Sing, K. S. W., Everett, D. H., Haul, R.A.W., Moscou, L., Pierotti, R.A., Rouquerol, J. & Siemieniewska, T. (1985). Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity. *Pure and Applied Chemistry*, 57, 603-619

Sinha, A·, Mahata, T., Sharma, B.P. (2002). Carbothermal route for preparation of boron carbide powder from boric acid–citric acid gel precursor. Journal of Nuclear Materials, 301: 165-169

Sitko, R., Zawisza, B, Jurczyk, BF & Zielonka, U. (2004). Determination of High Zn and Pb Concentrations in Polluted Soils Using Energy-Dispersive X-ray Fluorescence Spectrometry. *Polish Journal of Environmental Studies.* 13: 91-96.

Sjöström, M., and Östblom G. (2010). Decoupling waste generation from economic growth - CGE analysis of the Swedish case. *Ecological Economics*, 69, 1545–1552.

Slack, R., Gronow, J., Voulvoulis, N., 2005. Household hazardous waste in municipal landfills: contaminants in leachate. *Sci.Total Environ*. 337, 119–137.

Smidt, E., & Meissl, K. (2007). The applicability of Fourier transform infrared (FT-IR) spectroscopy in waste management. *Waste Managemen*t 27:268–276.

Smidt, E., & Schwanninger, M. (2005). Characterization of waste materials using FT- IR spectroscopy – process monitoring and quality assessment. *Spectroscopy Letters* 38:247–270.

Smidt, E., Meissl, K., Tintner, J., & Ottner, F. (2009). Interferences of carbonate quantification in municipal solid waste incinerator bottom ash: evaluation of different methods. *Environmental Chemistry Letters* 8: 287-222.

Srinivasakannan, C., Zailani A. M. (2004). Production of activated carbon from rubber wood sawdust. *Biomass Bioenergy*, 27:89–96.

Stavropoulos, G., and Zabaniotou, A. (2005). Production and characterization of Activated carbons from olive-seedwaste residue. *MicroporMesopor Mater*, 82:79–85.

Sudaryanto, Y., Hartono, S.B., Irawaty, W., Hindarso, H., Ismadji, S. (2006). High surface area activated carbon prepared from cassava peel by chemical activation. *Bioresource Technology,* 97:734–9.

Suhas, Carrott, P. J. M., & Ribeiro Carrott, M. M. L. (2007). Lignin--from natural adsorbent to activated carbon: a review. *Bioresource Technology*, *98,* 2301–12.

Sundberg, C. & Johnson, H. (2008). Higher pH and faster decomposition in biowaste composting by increased aeration. *Waste Management*, 28, 518-526.

Suresh, T. and Kottureshwara, N.M. (2009). Assessment of groundwater quality of borewells water of hospet taluka region, karnataka, India. Rasayan. *J. Chem.,* 2: 221-233

Suzuki, R., Andrade A., Sousa J., Rollemberg, M. (2007). Preparation and characterization of activated carbon from rice bran. *Bioresource Technology*, 98: 1985-1991.

Tamai, H., Kakii, T., Hirota, Y., Kumamoto, T., Yasuda, H. (1996). Synthesis of extremely large mesoporous activated carbon and its unique adsorption for giant molecules, *Chem. Mater.* 8, 454–462.

Tang, Y., Liu, Q., & Chen, F. (2012). Preparation and characterization of activated carbon from waste ramulus mori. *Chemical Engineering Journal*, *203,* 19–24.

Teng, H., Lin, Y., & Hsu, L. (2000).Production of Activated Carbons from Pyrolysis of Waste Tires Impregnated with Potassium Hydroxide, *50*, 1940–1946.

Themelis, N. J., Ulloa A. Priscilla. (2007). Methane generation in landfills, *Renewable Energy.* 32: 1243–1257

Tsai, W T, Chang, C, Y, Lee, S L. (1997).Preparation and characterization of activated carbons from corn cob. *Carbon,* 35:1198–200.

Uddin, M.T. Islam, M.A. Mahmud, S. Rukanuzzaman, M. (2009). Adsorptive removal of methylene blue by tea waste. *J. Hazard. Mater.* 164, 53–60.

UNEP. (2009). Developing an integrated solid waste management plan training manual Volume 2: Assessment of current waste management and the Gaps therein,Osaka/ShigaJapan.*www.unep.or.jp/ietc/Publications/spc/ISWMPlan_Vol2.pdf (accessed August 2016).*

U.S. EPA, (2012). US. EPA (United States Environmental Protection Agency), (2012). Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990 -2010.

USEPA. (2002). *RCRA Waste Sampling Draft Technical Guidance. Planning, Implementation and Assessment*. EPA530-D-02-002. Office of Solid Waste, Washington, DC.

USEPA. (2002A). *Guideline for the application of SEM/EDX analytical techniques to particulate matter samples*. EPA68-D-002-206. Office of research and development. New York. USEPA.

USEPA. 1998. "Method 6020B (SW-846): Inductively Coupled Plasma-Mass Spectrometry," Revision 1. (http:www.epa.gov/sites/production/files/2015-07/documents/epa-6020b.pdf) (accessed July 2013).

Weng, C., Pan, Y. (2007). Adsorption of a cationic dye (methylene blue) onto spent activated clay .*Journal of Hazardous Materials*. 144, 355–362.

Wigmans, T. (1989). Industrial aspects of production and use of activated carbons. Carbon, 27:13-22.

World Bank. 2009. *Environmental impact assessment of the proposed earthcare compost facility at Odogunyan farm settlement, Ikorodu, Lagos state*. s.l.; s.n.. http://documents.worldbank.org/curated/en/295231468290728796/Environmental-impact-assessment-of-the-proposed-earthcare-compost-facility-at-Odogunyan-farm-settlement-Ikorodu-Lagos-state (accessed May 2016)

World Bank Country Report 2015- Nigeria. www.worldbank.org./en/country/nigeria. (accessed May 2016).

Wu, C., Budarinb, V. L.,1, Gronnow, M. J., Bruyn, M. D., Onwudilia, J. A., Clark, J. H., Williams P. T.(2014). Conventional and microwave-assisted pyrolysis of biomass under different heating rates. *Journal of Analytical and Applied Pyrolysis*, 107: 276–283

Wu, H., Zhao, Y., Long, Y., Zhu, Y., Wang, H., & Lu, W. (2011). Evaluation of the biological stability of waste during landfill stabilization by thermogravimetric analysis and Fourier transform infrared spectroscopy. *Bioresource Technology.* 102: 9403-9408

Yang, N., Zhang, H., Shao, L.M., Lü, F., & He, P.J. (2013). Greenhouse gas emissions during MSW landfilling in China: influence of waste characteristics and LFG treatment measures. *Journal of Environmental Management*, *129*, 510–21.

Yu, M., Gong, H., Chen, Z., Zhang, M. (2013). Adsorption characteristics of activated carbon for siloxanes, *J. Environ. Chem. Eng.* M., 1:1182–1187.

Yuen, F. K., Hameed B.H. (2009). Recent developments in the preparation and regeneration of activated carbons by microwaves Advances in Colloid and Interface Science 149: 19–27.

Zelano, V., Ostacolia, G., Gulmini, M., Torazzo, A. (1994). Comparison between microwave and conventional haeating procedure in Tessier extraction of calcium, copper, iron and manganese in a lagoon sediment, *Analyst* 119: 2075 -2082.

Zhang, K., Cheung, W.H., Valix M. (2005). Roles of physical and chemical properties of activated carbon in the adsorption of lead ions. *Chemosphere*, 60 1129–1140.

Zhao, X.H., Zhao, Y.Q. (2009). Investigation of phosphorus desorption from P-saturated alum sludge used as a substrate in constructed wetland, Separation and Purification Technology, 66: 71-75.

Appendix 1

Key features of the sampling area

Active landfill Olushosun

Main entrance to Olusosun landfill and the reserve area for energy from waste project

The height of disposed waste at active landfill

Covering of some area of the dumpsite for access

Closed Landfill Abule egba

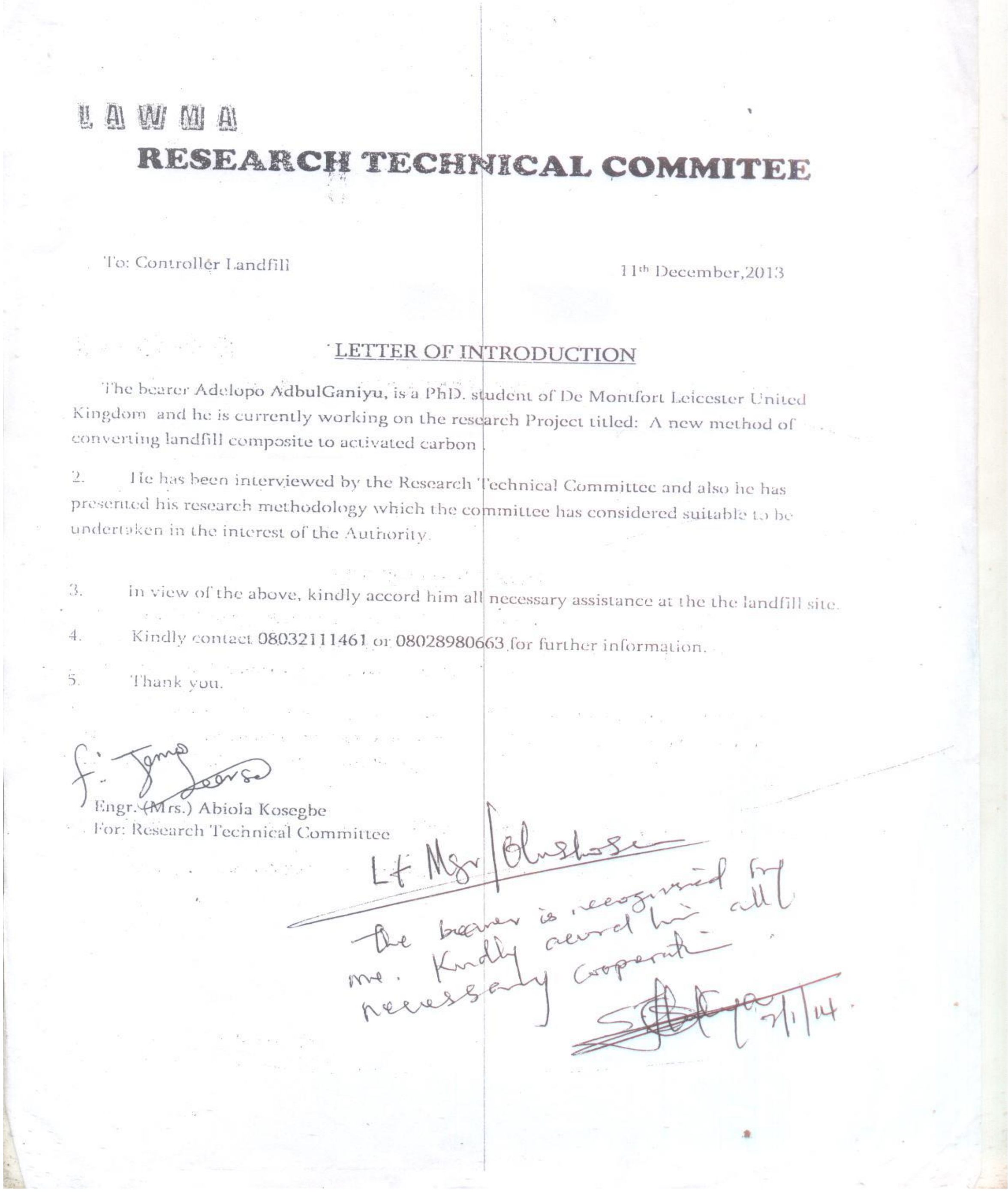
Closed landfill proximity to a petrol station and a major high way

Water logged section of the closed landfill

Vegetation covering some section of the landfill

Appendix 2

Approval letter for sampling



LAWMA

RESEARCH TECHNICAL COMMITEE

To: Controller Landfill

11th December,2013

LETTER OF INTRODUCTION

The bearer Adelopo AdbulGaniyu, is a PhD. student of De Montfort Leicester United Kingdom and he is currently working on the research Project titled: A new method of converting landfill composite to activated carbon .

2. He has been interviewed by the Research Technical Committee and also he has presented his research methodology which the committee has considered suitable to be undertaken in the interest of the Authority.

3. In view of the above, kindly accord him all necessary assistance at the the landfill site.

4. Kindly contact 08032111461 or 08028980663 for further information.

5. Thank you.

Engr. (Mrs.) Abiola Kosegbe
For: Research Technical Committee

Lf Mgr / Olushose

The bearer is recognised by me. Kindly accord him all necessary cooperation

7/1/14

Appendix 3

RCRA draft technical guidance statistical table on no exceeding sampling procedure

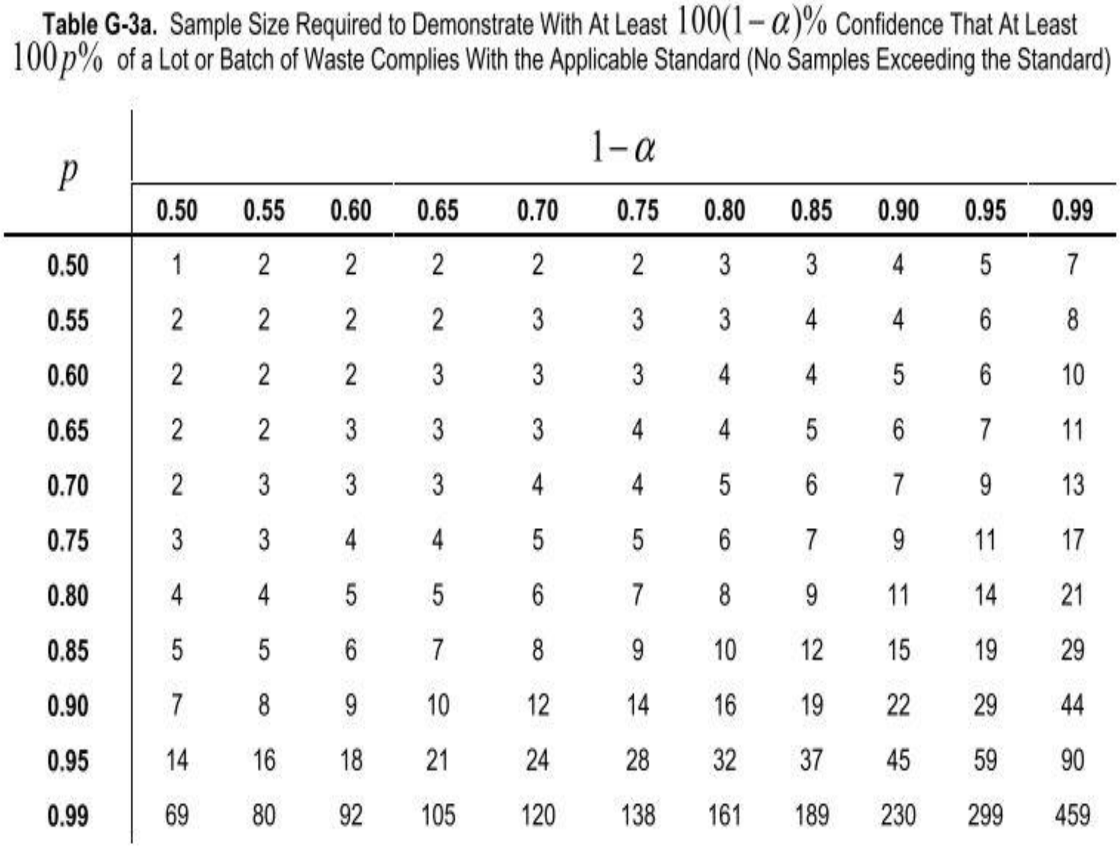


Table G-3a. Sample Size Required to Demonstrate With At Least $100(1-\alpha)\%$ Confidence That At Least $100p\%$ of a Lot or Batch of Waste Complies With the Applicable Standard (No Samples Exceeding the Standard)

p	$1-\alpha$										
	0.50	**0.55**	**0.60**	**0.65**	**0.70**	**0.75**	**0.80**	**0.85**	**0.90**	**0.95**	**0.99**
0.50	1	2	2	2	2	2	3	3	4	5	7
0.55	2	2	2	2	3	3	3	4	4	6	8
0.60	2	2	2	3	3	3	4	4	5	6	10
0.65	2	2	3	3	3	4	4	5	6	7	11
0.70	2	3	3	3	4	4	5	6	7	9	13
0.75	3	3	4	4	5	5	6	7	9	11	17
0.80	4	4	5	5	6	7	8	9	11	14	21
0.85	5	5	6	7	8	9	10	12	15	19	29
0.90	7	8	9	10	12	14	16	19	22	29	44
0.95	14	16	18	21	24	28	32	37	45	59	90
0.99	69	80	92	105	120	138	161	189	230	299	459

Appendix 4

STANDARD OPERATING PROCEDURE FOR SAMPLING

1.0 Scope and application: the essence of this standard operating procedure is to outline equipments and methods that will be used in obtaining a representative sample of landfill composite from selected landfill sites for analysis.

2.0 Purpose of sampling: to determine the heavy metals concentrations and total organic carbon concentrations of landfill composite samples

3.0 Method Summary:

An appropriate sampler (decontaminated bucket auger) is used to obtain a landfill composite sample at different specific depth measured with a stainless steel meter rule. The sample is weigh and kept in a plastic container before being transfer to the laboratory for appropriate analysis.

4.0 Sampling Locations: Olushosun and Abule Egba, landfill Sites in Lagos State, Nigeria

5.0 Sample Method: systematic grid sampling method is to be used.

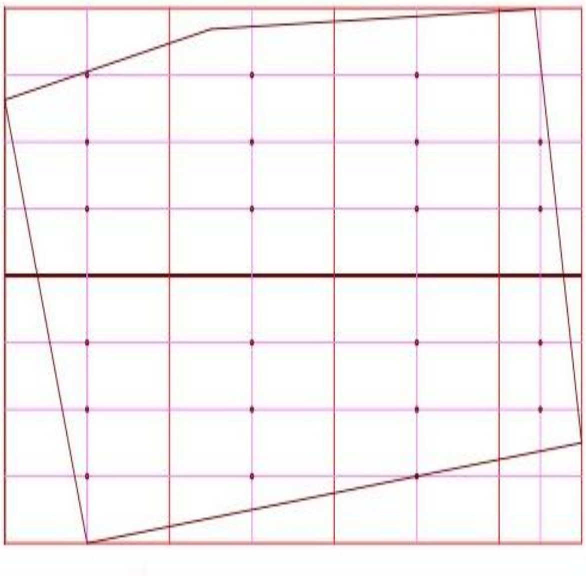
5.1Gridding method

Each Site is divided into 7 equal cells on the map and three locations of equal distance within each cell are located with help of a Global Position Satellite (GPS) as sampling point.

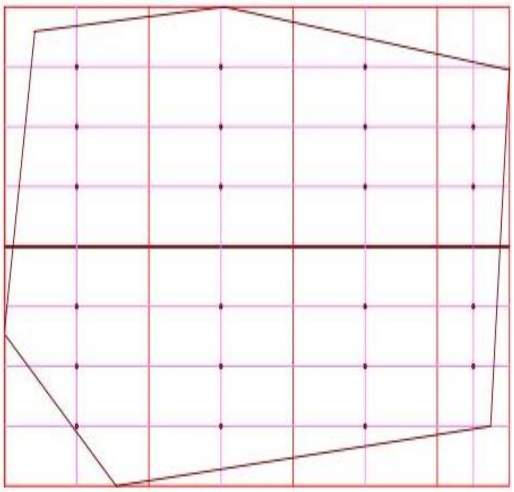
Olushosun: Area capacity 42.7 hectares cell size 42.7/7= 6.1hectares sampling distance 8.5/3=2.03hectares

Abule egba: Area capacity 10.2 hectares cell size10.5/7 = 1.5 sampling distance 2.04/7= 0.5hectares

5.2 Gridded map of the sampling sites



Active land landfill



Closed landfill

A systematic grid map of each landfill is drawn as a guide.

6.0 Sampling equipment: One Sampler/ bucket auger which is made up of non contaminating material and can scoop a volume of 500g and a distance of 50cm , 50 plastic containers, pH meter, GPS, Conductivity meter, chest cooler, labels, sampling log notes, de-ionized water, weigh balance, tissue paper, video and camera , survey stakes or flags, one homogenization container

7.0 Preservative: None for now

8.0 Sampling codes: the code for each sample will be First letter of sampling site name, depth range and the number on the grid. for example:

OLUSHOSUN

Upper sample code: OU 1, OU2 OU3-------------OU8

Mid sample code: OM1, OM2,OM3--------OM8

Low sample code: OL1 , OL2, OL3--------OL8

9.0 Sample label SAMPLE LABEL

Sample code ---

Location /location coordinate ------------------------------

Sample type---

Sampling Date --

Sampling Time --

Preservatives used---

10.0 Field note Content

10.1 Site record

Sampling site date ---- time ----

Site Observations

Constrain and modification in activities

Reasons

Duration of sampling on the site

11.0 Procedure

11.1 pre sampling

Review all information available on the landfills site

Carry out the site survey to determine health and safety issue

Obtain necessary sampling and monitoring equipment as stated above.

Clean sampler as directed by the manufacturer and ensure dryness of instrument

Clean and calibrate all measuring instrument e.g PH meter, GPS, weighing balance

Check all label and sampling log note for conformity in inform and adequacy for sampling

Confirm purity level of reagent and solvents to be used.

Carry out a checklist of materials and equipment to be used for sampling.

11.2 Sampling

Convey all materials and instruments to sampling site in a compartment free of possible contamination

Locate sampling points based on the grid map and consideration for the following:

I. time/ age variation years.>Month> as given by the authority

ii. Anthropogenic activities of interest

iii. Information received from operators

iv. Observed contamination

Locate the sampling point

Record the coordinates

Update the sampling note

Fill the sampling label

Disinfect the sampler by wiping the samplers with clean tissue paper twice

Check the plastic container for cleanliness and free from contaminants

Place the plastic container on the weighing balance

Take the sample at appropriate depth and weigh 500g with sampler operated to specification.

Take the PH, temperature and conductivity reading of the samples.

cover the sample and keep in the chest cooler

Prepare the field blank and the equipment blank.

Place the containers in a contamination free area

Convey samples to the laboratory.

13.0 Quality Control of sampling

Prepare:

Equipment blank: the decontaminated sampling equipment is rinsed using de-ionized water under field conditions to evaluate the effectiveness of equipment decontamination or to detect sample cross contamination.

Field blank: this sample is prepared in the field using de-ionized water to evaluate the potential for contamination by site contaminants not associated with the sample collected (e.g., airborne organic vapors)

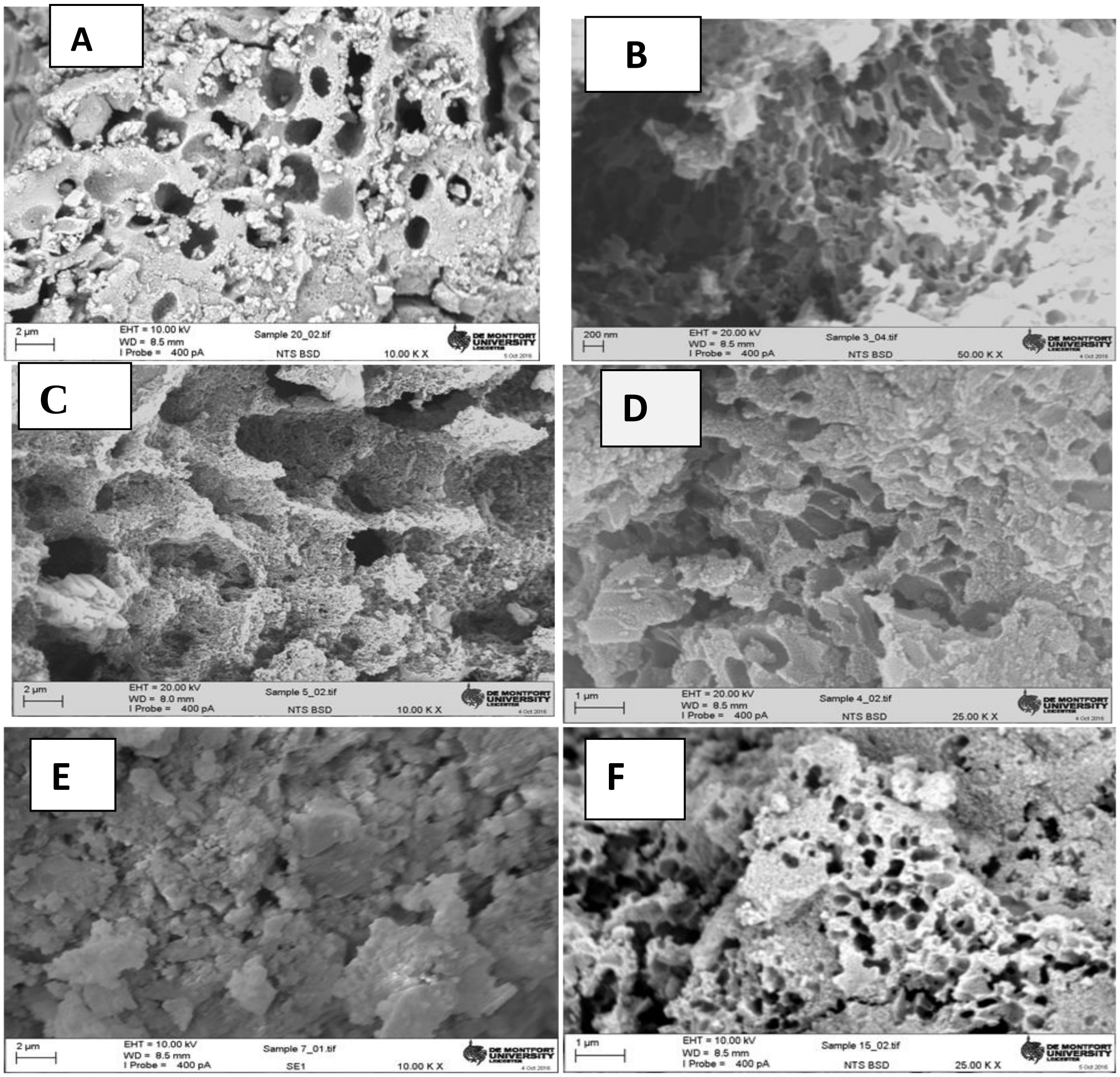
Sample of Field Record

	DATE	SITE NAME	SAMPLE TYPE	SAMPLE CODE	COORDINATE	pH	TEMP. (°C)	CONDUCIVITY	WEIGHT OF EMPTY CONTAINER	WEIGHT OF SAMPLE + CONTAINER
1.	18-01-14	OLUSO SUN	SOLID	Os$_1$	N06°35.743’ E003°22.687’	7.80	36.2	1049µs	61.2g	599.5g
2.	18-01-14	OLUSO SUN	SOLID	OM$_1$	N06°35.771’ E003°22.625’	7.65	35.0	1162µs	58.2g	628.3g
3.	18-01-14	OLUSO SUN	SOLID	OL$_1$	N06°35.807’ E003°22.581’	7.12	36.8	1290µs	53.5g	683.2g
4.	18-01-14	OLUSO SUN	SOLID	OS$_2$	N06°35.761’ E003°22.587’	7.20	34.2	383µs	53.0g	1,040.0g
5.	18-01-14	OLUSO SUN	SOLID	OM$_2$	N06°35.722 E003°22.660	6.87	32.5	772µs	58.5g	769.1g
6.	18-01-14	OLUSO SUN	SOLID	OL$_2$	N06°35.686’ E003°22.647’	7.28	36.7	414µs	51.6g	986.6g
7.	25-04-14	OLUSO SUN	SOLID	OS$_3$	N06°35.611 E003°22.647	76.0	25.3	1385µs	63.3g	1000.5g
8.	25-04-14	OLUSO SUN	SOLID	OM$_3$	N06°35.549’ E003°22.662’	6.95	28.2	672 µs	71.8g	1213.9g
9.	25-04-14	OLUSO SUN	SOLID	OL$_3$	N06°35.499’ E003°22.774’	8.61	31.8	1812µs	63.8g	1177.6g
10.	25-04-14	OLUSO SUN	SOLID	OS$_4$	N06°35.580’ E003°22.708’	8.26	34.0	1304µs	63.6g	1092.0g
11.	25-04-14	OLUSO SUN	SOLID	OM$_4$	N06°35.580’ E003°22.759’	7.14	31.1	2010µs	70.9g	1494.5g
12.	25-04-14	OLUSO SUN	SOLID	OL$_4$	N06°35.419’ E003°22.769’	7.52	32.1	1032µs	69.7g	2343.0g
13.	25-04-14	OLUSO SUN	SOLID	OS$_5$	06°35.561’ E003°22.811’	7.23	31	347µs	64.9g	1234.5g

14.	24-01-14	OLUSO SUN	SOLID	OM_5	06°35.670’ E003°22.698’	7.27	33.8	715µs	64.3g	1331.8g
15.	24-01-14	OLUSO SUN	SOLID	OL_5	06°35.671 E003°22.775’	7.20	34.8	1174µs	64.3g	1177.6g
16.	24-01-14	OLUSO SUN	SOLID	OS_6	N6°35.675 E003°.22620’	7.65	37.3	3999µs	73.5g	1363.6g
17.	24-01-14	OLUSO SUN	SOLID	OM_6	N06°.770 E003°22.747’	8.30	32.8	860µs	75.5g	824.0g
18.	24-01-14	OLUSO SUN	SOLID	OL_6	N6°35.784 E003°22.657’	7.60	33.9	1520µs	71.6g	1192.9g
19.	24-01-14	OLUSO SUN	SOLID	OS_7	N06°35.776° E003°22.607’	7.40	37.1	926µs	75.5g	1115.0g
20.	25-01-14	OLUSO SUN	SOLID	OM_7	N06°35.772 E003°22.557’	7.62	33.7	329µs	73.1g	1009.8g
21.	25-01-14	OLUSO SUN	SOLID	OL_7	N06°35.664’ E003°22.536’	7.77	33.7°C	1092µs	70.0g	1050.1g
22.	25-01-14	OLUSO SUN	SOLID	OS_8	N06°35.800’ E003°22.816’	7.22	31.4^0C	654µs	70.2g	995.5g

Appendix 5

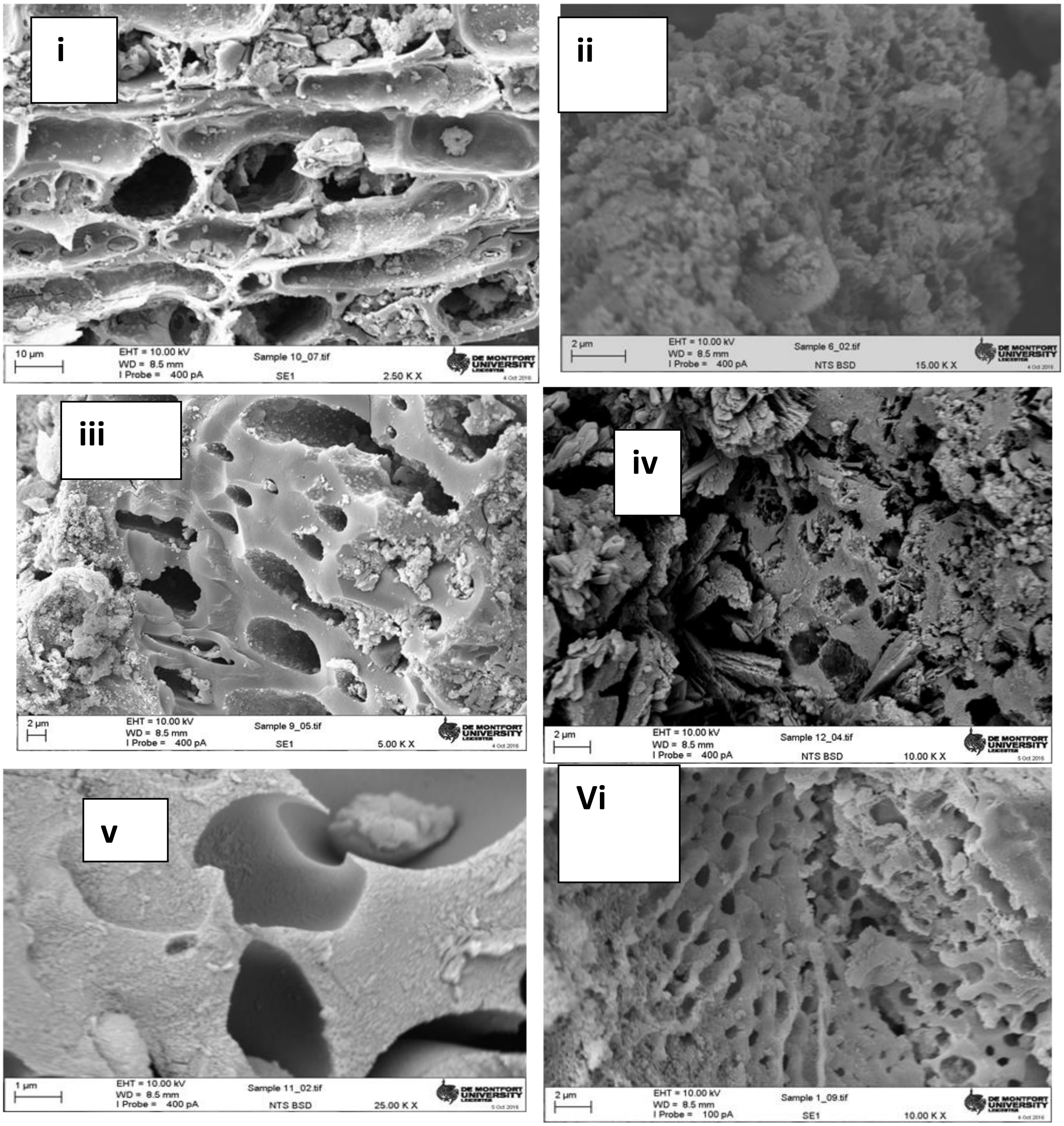
Scanning Electron Microscopy micrographs of AC samples



SEM image of AC from Close landfill sample

Depth of sampling for more degraded precursor: (A)upper; (B) mid; (c) lower

Depth of sampling for less degraded precursor: (D) upper (E) mid (F) lower



SEM image of AC from active landfill sample: I , ii, iii :upper – lower more degraded

iv, v, vi : upper – lower less degraded