The book has been designed for Engineers, Environmentalist, Technologists, process analyst and potential entrepreneurs who wish to apply adsorption technology to purify biogas. The book skilfully blends critical thinking with engineering practice to provide step by step procedure in biogas purification and characterization. Chapter 1 provides a general overview of the biogas production technology and purification while chapter 2 presents the literature review on the same subject. Techniques used for the production, purification, and characterization of the biogas were described in chapter 3. Results were discussed in chapter four while the conclusions drawn were presented in chapter five.

Abdullahi Abdulsalam is a lecturer in the school of basic science (chemistry), Maryam Abacha American University Maradi, Niger Republic while Mohammed Alhassan (Ph.D.) is a senior academic staff in the Department of Chemical Engineering, Federal University of Technology Minna, Nigeria and obtained his Ph.D. from the University of Nottingham, UK.

978-613-9-92398-4

Abdullahi Abdulsalam
Mohammed Alhassan

Studies on Biogas Purification

Using Activated Carbon and Zeolite

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Publisher:
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International Book Market Service Ltd., member of OmniScriptum Publishing Group
17 Meldrum Street, Beau Bassin 71504, Mauritius

Printed at: see last page
ISBN: 978-613-9-92398-4

DEDICATION

This book is dedicated to Almighty Allah for His infinite mercies and guidance. I also dedicate this research work to my parents and the founder of Maryam Abacha American University, Maradi, Dr Adamu Abubakar Gwarzo

ABSTRACT

Biogas generation from animal waste is inherent with a low biogas quality due to impurities such as CO_2, CO, NO_x H_2 and H_2S which requires gas clean-up. It was in view of this that the present study investigated the comparative studies on the kinetics of biogas purification using activated carbon (AC) and zeolite CBV 8014. The study focused on CO_2 adsorption using AC and zeolite CBV 8014 for the purification of the produced biogas and developed kinetic study for the AC and zeolite CBV 8014 adsorption. Surface morphology and functional group of the adsorbent before and after adsorption were also determined. Furthermore, model equations were developed for the upgraded biogas purity as a function of adsorption time and adsorbent dosage to predict biogas purity. The adsorbents and kinetic study were evaluated using a cylindrical glass column. The biogas produced from a mixture of chicken droppings substrate and cow dung substrate (1:1) were characterized and found to contain CH_4 gas (53.76%), CO_2 (33.44%) and other gases in small quantity. Characterization of adsorbents showed that AC had a better pore structure compared to zeolite CBV 8014, however, adsorption studies was found to be in the order of zeolite CBV 8014 (91.01%) > AC (84.34%) at 0 – 20 min adsorption time with adsorption increasing over time which show that zeolite CBV 8014 had strong affinity for CO_2 adsorption. The percentage adsorption of the adsorbents was evaluated using a cylindrical glass column and the model equations developed well represent the experimental data. The kinetic study of the biogas purification shows that the CO_2 adsorption onto AC and zeolite CBV 8014 obeys the pseudo-second-order model, due to its regression coefficient (R^2) value closer to unity. The equilibrium and kinetic study of CO_2 adsorption onto AC and zeolite CBV 8014 shows that the magnitude of activation energy for both adsorbent are lesser than 40 kJ/mol, indicating the occurrence of physisorption mechanism. The intra-particle diffusion model also indicates that intra-particle diffusion is not the sole rate-limiting step in the adsorption process for both adsorbent (AC and zeolite CBV 804). The zeolite CBV 8014 has higher CO_2 adsorption capacity than AC.

TABLE OF CONTENTS

CHAPTER ONE

INTRODUCTION **10**

CHAPTER TWO

LITERATURE REVIEW **15**

CHAPTER THREE

MATERIALS AND METHODS **41**

CHAPTER FOUR

RESULTS AND DISCUSSIONS **51**

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS **86**
5.1 Conclusion 86
5.2 Recommendations 87
References 88

LIST OF TABLES

Tables ***Title*** ***Pages***

Table 2.1: Potential biogas production from various Substrates 17
Table 2.2: Gases and their pore size 40
Table 2.3: Some isotherm models commonly used for adsorption of metals 42
Table 3.1: List of Materials 43
Table 3.2: List of Equipment 44
Table 3.3: Experimental Design Matrix for Factorial Analysis of Uncoded Factors 49
Table 4.1: Compositions of produced biogas 49
Table 4.2: BET Surface Area Analysis 58
Table 4.3: Composition of the upgraded Biogas using AC as Adsorbent. 67
Table 4.4: Composition of the Upgraded Biogas using Zeolite CBV 8014 68
Table 4.5: Experimental Design and Response Factors of Factorial Analysis of Biogas Upgrading using AC and Zeolite CBV 8014 72
Table 4.6: Model Coefficient for Biogas Upgrading using AC 73
Table 4.7: Model Coefficient for Biogas Upgrading using Zeolite CBV 8014 75
Table 4.8: Lagergren’s pseudo-first-order model kinetic parameters 86
Table 4.9: Lagergren’s pseudo-second-order model kinetic parameters 89
Table 4.10: Activation energy for CO2 adsorption in AC and zeolite 92
Table 4.11: Intra-particle diffusion rate constant for CO2 adsorption in AC and zeolite CBV 8014 94

LIST OF FIGURES

Figures ***Title*** ***Pages***

Figure 2.1: Composition of biogas 11

Figure 2.2: Classification of feedstocks potentially available for biogas production 15

Figure 2.3: Schematic biodegradation steps of complex organic matter 19

Figure 2.4: Scheme of fixed-dome digester 25

Figure 2.5: Scheme of floating-drum digester 26

Figure 2.6: Scheme of balloon digester 28

Figure 2.7: Scheme of a garage-type dry digestion plant 29

Figure 3.1: Biogas production setup 47

Figure 3.2: Gas adsorption setup 51

Figure 4.1: FTIR spectrum of AC before adsorption. 61

Figure 4.2: FTIR spectrum of AC after adsorption 62

Figure 4.3: FTIR spectrum of zeolite CBV 8014 before adsorption 64

Figure 4.4: FTIR spectrum of zeolite CBV 8014 after adsorption 65

Figure 4.5: The plot of the experimental against predicted responses for AC adsorbent. 74

Figure 4.6: The plot of the experimental against predicted responses for zeolite. 76

Figure 4.7: Main effect plot for biogas purity using AC. 77

Figure 4.8: Main effect plot for biogas purity using zeolite CBV 8014. 77

Figure 4.9: Four-in-One Residual plot using AC Adsorbent 80

Figure 4.10: Four-in-One Residual plot using zeolite CBV 8014 Adsorbent 80

Figure 4.11: 3D Surface plot for AC Adsorbent 82

Figure 4.12: 3D Surface plot for zeolite CBV 8014 83

Figure 4.13: CO_2 adsorption capacity in AC 84

Figure 4.14: CO2 adsorption capacity in zeolite CBV 8014 85

Figure 4.15: Pseudo-first-order kinetic model of AC CO2 adsorption 87

Figure 4.16: Pseudo-first-order kinetic model of CBV 8014 zeolite CO2 adsorption 88

Figure 4.17: Pseudo-second-order kinetic model of AC CO2 adsorption 90

Figure 4.18: Pseudo-second-order kinetic model of zeolite CBV 8014 CO2 adsorption 90

Figure 4.19: Intra-particle diffusion model for CO2 adsorption using AC 93

Figure 4.20: Intra-particle diffusion model for CO2 adsorption using zeolite CBV 8014 93

NOMENCLATURE

Symbol	***Names***
AC	Activated Carbon
AMAC	Acid Modified Activated Carbon
A^o	Armstrong
BET	Brunauer–Emmett–Teller
BMAC	Base Modified Activated Carbon
C:N	Carbon to Nitrogen
FTIR	Fourier Transform Infra-Red
GHG	Green House Gas
HRT	Hydraulic Retention Time
MW	Mega Watt
OLR	Organic Loading Rate
PPM	Part Per Million
PSA	Pressure Swing Adsorption
TS	Total Solid
UMAC	Unmodified Activated Carbon
VFA	Volatile Fatty Acids
VIF	Variance Inflation Factor
VOCs	Volatile Organic Compounds
VS	Volatile Solids
VSA	Vacuum Swing Adsorption

CHAPTER ONE

INTRODUCTION

1.1 Background to the Study

Worldwide, energy is well-known to be a major portion of any developed economy and society. It is a key factor in alleviation of poverty in any society (Aderemi*et al*., 2009). The access and availability to energy are component of national development required to improve the living standard of any nation .Moreover, worldwide energy demand continued to rise, while access and availability to energy are diminishing. The present energy systems is greatly dependent on petroleum based fossil fuel .The requirement on crude oil and it products as the only main source of energy has led to worldwide climatic changes, environmental pollution and degradation, increase in sea level as a consequence of the melting of the ice resulting from increase in temperature. This problem lead to health and environmental problems. Crude oil is finite, it destroy ecosystem in different ways, acid rain, depletion of the ozone layer, and exerting higher influences biogeochemical cycles (Eze and Agbo, 2010). These have caused the need to ofset energy systems in the direction of sustainability.

Because Africa has a weak law against environmental pollution, it is facing more environmental challenges such as water pollution, air and flooding pollution caused by dreadful conditions of the ecosystem due to pollution from crude oil based fossil fuel. Also inaccessibility to energy resources despite large deposit of petroleum based natural resource is presently facing challenge sof economic development. Mshandete and Parawira (2009), argued that < 10% of the total population of twenty one sub-SaharanAfrican countries have contact to electricity. Thus, the need for alternative renewable sources of energy from renewable and ecological locally present resources cannot be over emphasized.

In developing countries like Nigeria, lack of access to sufficient energy has continued to be a major hindrance by promoting key indicators of human growth (onafeso, 2006). At present over 60% of Nigeria population depends nearly entirely on wood as energy sources for agro-processing, heating and cooking activities. Moreover, electricity which is a major prerequisite for modern economies is not readily accessible and or better still undependable and in little supply.

As at August 10, 2017, 6803 MW was recorded as the present accessible generating capability, with a wheeling volume of 6700MW by TCN at present constrained by Discos incapacity to distribute completely, the generated power (olawoyin, 2017). Less than 4,000 MW of the over 6803 MW generated get to Nigerians (Utuk, 2007). These have led credence to the need to seek alternative energy sources to petroleum (crude oil) and turn towards sustainable and renewable sources. Thus there is an critical need to source for an alternative renewable energy before the crude oil supplies goes dry. Hence, within2008 – 2015 and between2016 – 2025, Nigeria predicts an energy conversion from petroleum to renewable energy (Highina*et al*., 2011). Nevertheless, an alternative energy must be technically achievable, economically competitive, environmentally tolerable and readily accessible and available. one fundamental and possible alternative to crude oil is the use of biofuels.

Biofuel are fundamental energy sources and fairly distributed. The generation of biofuels has become a global program. Keeney and Muller (2007) describe this global effort as “bio economy revolution”. Biofuels are biomass derived fuels which include largely agriculturally produced materials which are renewable and sustainable. Biofuel consist of, biogas, biodiesel and bioethanol .

Biogas can be generated from diverse environment including landfill and sewage sludge, during anaerobic decomposition of biomass samples. Biogas contains mainly methane (CH_4: 45 – 75% vol.), carbon dioxide (CO_2: 25-55% vol.), and other trace compound contain hydrogen sulphide s (H_2S: a couple of thousand ppm), water (H_2O) and other small gas compounds (N_2, O_2 and CO) (Zhao *et al*., 2010). Methane is greenhouse gas discharged into the air, nevertheless it also a valued renewable energy source, with the possible to reduce (GHG)releases when it is collected and exchanged for crude oil.

In Nigeria, biogas application is low despite enormous reserves of biogas feedstockin the country. For example, agricultural and animal wastes and residues produced in Nigeria amounted toa million tons per day (Eze and Agbo, 2010). This implies that from agricultural and animal wastes alone, Nigeria can produce over 4.75 x10^9mega joules per annum which means that a large portion of Nigeria's energy demand can be emanate from biogas. In order to advance raw biogas to a high level of purityof 95% CH_4,thereby ensuring that it becomes environmental benign energy source. Emission of enormous GHG and CO_2 produced from the biogas must be captured. Physical and amine based adsorptions are usually used for capture of CO_2.

Several studies shows that amine-based adsorbents for CO_2 are associated with many problems among which includes: corrosive tendency, degradation of amines and shigh regeneration energy requirement(Murshid*et al*., 2011). Choosing a suitable separation technique is determined by the activity of adsorption and diffusion which characterize sactivated carbon materials and also restricts their applications (Alhassan*et al*., 2017). However, several studies have successfully documented use of zeolite and AC for capture of CO_2. Alhasan*et al*. (2017) reported the comparative assessment of CO_2 capture via acid and base activated carbon from bagasse and found that acid and base modified bagasse AC produced have improved CO_2 adsorption capacity. Many studies reported on the use of AC for asdsorption of CO_2 have revealed that AC possesses well developed porous structure with good properties of adsorption. Consequently, the fairly abundance, cheap, low moisture sensitivity and very high thermal stability make activated carbon to exhibit distinctive characteristics and also positioned it in a strategy position as an exceptionally cheap and viable adsorbent for the CO_2 capture.

1.2 Statement of the Problems

Biogas is said to comprise of CH_4 (45-75% by vol.), CO_2 (25 to 55% vol.) andsmall quantities of H_2S, NH_3, siloxanes, volatile organic compounds, O_2, Coand H_2O (Zhao *et* *al*., 2010). The high level concentration of CO_2 in the atmosphere was estimated to surge from pre-industrial concentration of about 270ppm to 407ppm by mid-2017 (Dlugokencky, 2016). The present concentration is the highest in the history of mankind and is expected to continue to increase from the present concentration. Therefores, there is to the need to avoid the release of huge quantities of CO_2 to the atmosphere.

Carbon dioxide release to the atmosphere can be efficiently reduced through numerous methods which comprises of sequestration and extraction from GHG emission. Physical adsorption and chemical solvents approaches are commonly used. Therefore, an alternative source of energy which is friendly to the environment and affordable is very necessary to preserve our green and wild life forest. This require the need to explore and improved the purification (CO_2 removal) of biogas generated from animal waste.

1.3 Aim and objectives

The aim of this research work is the comparative studies of the kinetics of biogas purification using AC and zeolite.This aim is achievable through the following objectives;

1. To generate biogas from the mixture of poultry droppings and cow dung.
2. To upgrade the biogas produced by adsorption using zeolite CBV 8014andAC.
3. optimization of upgraded biogas purity
4. To carry out a comparative study of CO_2 adsorption from the biogas produced using AC and zeolite CBV 8014.
5. To analyze the biogass produced and upgraded biogas using gas analyzer.
6. To carry out kinetic investigation of the zeolite adsorption and AC of CO_2.

1.4 Scope of this Study

This study is restricted to the production of biogas from a mixture of chicken droppings and cow dung by anaerobic digestion of animal waste, optimization and kinetic study of the purified biogas. The study is also limited to the use of an improvised adsorption column for the gas purification.

1.5 Justification of the Study

Increase in waste disposal continues to pollute the environment, damaging the underground water and surface water. The CH_4 and CO_2 present in the waste causes global warning, hence there is an urgent need to convert the biomass into an alternative bio energy (Igboro, 2011). Biogas production will be very profitable means of reducing the problem of organic waste generated in many states in Nigeria.

It has been reported that Nigeria generates 227,500 tonnes of animal waste every day. Since one (1) kg of animal waste generates 0.03 m^3 biogas, Nigeria has the potentially generate 6.8 million m^3 of biogas daily from animal waste alone(Mshandete and Parawira, 2009). A very recent study that evaluated Nigeria's biogas potentials (least value) from livestock excrements and solid waste shown that in 1999, Nigeria's biogas future value represents a 1.382×10^9 m^3 of biogas/year or equivalent of 4.81 million barrels of petroleum (ojolo*et al*, 2007).

Currently, literature offers some of kinetic models which can commonly be classified reaction and diffusion models for adsorption (Qiu*et al*., 2009). Because of the intricacy involved in the calculation of kinetic parameters, a typical method consists in fitting experimental data to a numbers of established models, and choosing the one that offers the best fit. This study is intended to therefore add value to existing knowledge on the prediction of kinetic parameters for CO_2 removal.

CHAPTER TWO

BACKGROUND

2.1 Introduction

In general, biogas generation by anaerobic digestion and its subsequent improvement to biomethane is one of the alternatives available to meet the goal of the reduction of GHG pollutant emissions (Pöschl*et al*., 2010). The interest accorded to biogas is owing to some peculiarity in it features. Biogas is a renewable energy that is more versatile than other source such as solar and wind energy. It energy value can be determine once the composition of the biomass feedstock is known and its potential application is mainly not dependent on factors like and geographical location and seasons it is very easy to store. Furthermore the biogas, and particularly biomethane, can be used directly for electricity generation and heating or as a complement for fossil fuel uses (for example inpower generation and transportation).

Effective waste management is progressively required due to numerous environmental and economic worries such as eutrophication, climate change, and the diminishing resources for fossil based energy and initial raw materials. Anaerobic digestion can be considered a sustainable alternative for management of organic rubbishes and by-products as it generate renewable energy of the form of biogas and enables reutilizing of materials, especially nutrients (Sami and Sari, 2010). Concurrently, it has the advantage of controlled stabilization and therefore reduces emissions from the pre-treated waste materials. By replacing fossil fuel materials with digested slurry and biogas, the GHG and other pollutant emissions from production of energy and consumption and from fertilizer and petrochemical industries can be reduced.

At the present time, biogas plants in third world countries do not have upgrading facilities included in their plants. The implies that all the H_2S, CO_2, other contaminants and the combustion products such as SO_2, CO, and NO_x are released to the atmosphere. However, with the continued drive towards sustainable energy systems in Nigeria, the amount of combustion products always increase and cannot be ignored (Eze and Agbo, 2010). In addition, biogas transportation generating plants require compression, special pipes would be prerequisite if raw gas is to be distributed inside gas pipelines due to the corrosive compound of H_2S content which also cause unpleasant odour to the raw gas. Upgrading raw gas to at about 95% CH_4, putting the gas as option vehicle fuel, and decreases sstorage and compression requirements (Navaratnasamy, 2008).

2.2 Biogas

Biogas can be define as a mixture of different gases formed by the breakdown of organic substance in the absence of atmospheric air. Biogas can be generated from various raw materials such as municipal waste, agricultural waste, plant material, manure, food waste sand sewage. Biogas is a benign source of renewable energy. Biogas can be generated by anaerobic digestion with facultative organisms that digest the substance inside a secure system or via the fermentation of biodegradable substance (NNFCC, 2011).

Biogas is chiefly CO_2 and CH_4 and it may have traces of other gases such as H_2S, CO, O_2, H_2, moisture and siloxanes. CH_4, H_2 and CO can be fired or oxidized with oxygen to emit energy. This energy release permit biogas to be utilize as a fuel; it can be utilize for any heating purpose, for example cooking. It is also be utilize in a gas engine to transform the energy in the biogas to electricity generation and heat (State Energy Conservation office, 2009). Biogas can also be compressed in the same manner to as natural gas is compressed to compressed natural gas (known as CNG) and utilize to power machineries.

Animal droppings that came from pig, cow, poultry and crop residues have been utilize in different part of the world. The degree of how biogas technology has been successful varied for different part of the world that utilize biogas technology for rural energy sustainable supply. The content of CH_4 and CO_2 is a function of the matter digested and the process conditions like ionic strength or salinity, pH, temperature ,inhibitory substrates and nutrients. Biogas burns with nearly odourless flame with heat of combustion equivalent of 21.5 MJ/m^3. Figure 2.1 presents the general composition of biogas

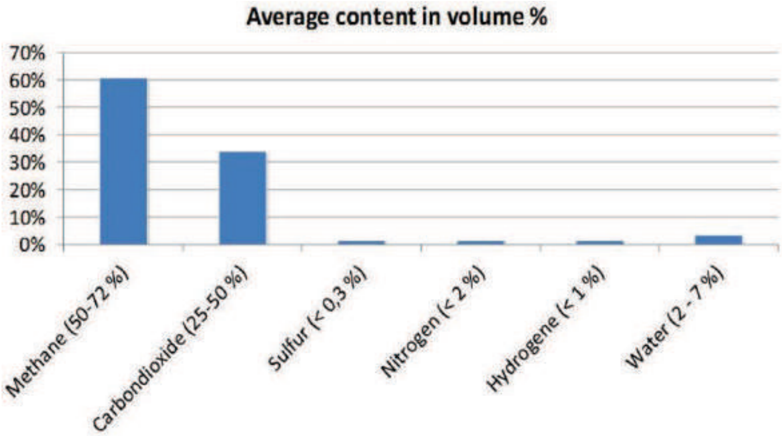


Figure 2.1: Composition of biogas (Shrestha, 2010).

2.2.1 History of the biogas

General, the existence of biogas produce from natural source date back from the 17th century and however it actual construction as a biogas plants started early in the mid-19th century (Jørgensen, 2009). The oldest biogas plant is the septic tank, which has been ultilize for the treatment of wastewater at the end of the 19th century and is still utilize for isolated properties where there is no sewerage plant. In this type of system the biogas isnot collected and utilize. Biogas was first utilize in Bombay in 1859, but biogas technology is well-known to the Chinese since 1950's and more hundred years old in India and it is fairly recent in developing countries (Dioha*et al*., 2003). The idea that decaying vegetables gives-off a flammable gas were understood since the time of ancient Persians. In recent modern times, the earlier sewage plant was constructed in Bombay in 1859; an idea that was transfer to the UK in 1895, when the gas generated was utilize to light street lamps (Lisoň*et al*., 2014).

The system of using biogas to generate electricity was develop in UK and Germany in the 1900s from sewage (Dioha*et al*., 2003). Centralized drainage systems was installed in several towns in Europe countries and anaerobic digestion was considered as a means to decrease the volume of solid material in the sewage. The gas produced will be occasionally use for source of energy, such as for motor vehicles. The utilization of farm manure to producedCH_4 was developed in Bombay, in the early 1930s. It development in Indian villagers by KVIC (Khadi Villages Industries Commission) in the 1960s. The design used a floating iron gas drum, formed the origin of an ongoing Indian Government programme to provide people living in remote villages with cooking gas fuel. China commence a similar programme to that of India in 1960s and proclaimed that 5 million plants were built by in the 1980s. The design which was based on a septic tank. The newrectangular tanks were replaced rapidly by a design based on a dome like shape (Monnet, 2003).

Until recently after the 2nd World War, there was a considerable growth in the biogas related industry, particularly in Britain, Germany and France, and the technology also progressively found its way into large scale with energy production as the chief purpose (Jørgensen, 2009). At the late 1950s, development almost stopped, due to the available of cheap fossil fuels such as crude oil and natural gas. However, the interest in biogas was not rekindle until in the mid-1970s after the oil crisis in the 1973 (Fulford, 2011).

In the early 1970s when renewable source of energy turn out to be recognized as a distinct subject, a conference on biogas was hosted at Imperial College of the University of London (Ani, 2014). The participants unanimously agreed on the potential for biogas technology in many countries of the world, particularly in the developing world. Nepal's programme commence very much in the same manner as the India one, with a government taken initiative step. Progress was firm with the aid of Agricultural Development Bank, Nepal and there was steady expansion in the late 1980s (Fulford, 2011).

Pilot biogas plant projects were executed before now in some parts of Nigeria by Energy Commission of Nigeria (ECN), Japan International Cooperation Agency (JICA),Unite Nations Development Programme (UNDP)and some Tertiary Institution. There was a 10 m^3 biogas plant at Achara area of Nsukka LGA in Enugu State which was executed by

National Centre for Education Resource Development (NCERD) and University of Nigeria Nsukka (UNN), for women in cooperative who are into garri(cassava flour) processing (Ani, 2014). The plant input include droppings of cassava peels, domestic animals, and waste from the cowpea milling and bambara nut from a very close food processing plant. There are so many other biogas plants in other parts of the country that are currently not working due to poor quality constructions. However, this has dampen people's faith in the biogas technology (Dioha*et al*., 2012).

Ifelodunfarmer's cooperative aloneojokoro, Agege, had a piggery farm of 3000 heads and inside the farm they run an abattoir which processes the pig swine to pork for sale to general public. ECN – Sokoto Energy Research Centre (SERC) inUsmanuDanfodiyo University (UDU) built a 20 m^3 fixed dome bio-digester in 1998which used pig waste to produces gas for cooking and animal manure which co-operative members use in their farm as fertilizer (Ani, 2014). Also, at National Animal Production Research Institute (NAPRI) in Zariahas a 20 m^3 biogas plant constructed in 1996 by SERC. In 1998 the centre salso constructed 30 m^3 bio-gas digester from prison in Zaria which fed from prison wastes (Ani, 2014). Also UNDP had one time sponsored the construction of 10 – 20 m^3 digesters in Yobe, Kano and Kebbi States. Unfortunately most of these biogas plants in Nigeria are not functional to this day due to lack of inadequate maintenance and advancement in the available biogass technology.

2.2.2 Feedstock for Biogas Production

Biogas can be generated from a wide range of feedstocks that are good for anaerobic digestion. Biogas can be generated from biomass and waste materials regardless of the chemical composition and over a wide range of moisture contents, with restricted feedstock preparation. Feedstocks for biogas generated may be slurries ,solid, and both dilute liquids and concentrated. In fact, biogas can even be generated from the left-over of organic material from ethanol and biodiesel fuel production. Feedstock for biogas generation includes animal wastes such as cattle piggery waste, dung, poultry droppings, municipal solid wastes (MSW) including food and kitchen residues and industrial biodegradable wastes (Eze, 1995).

Akinbami*et al*. (1996), identified some feedstock substrate which are economically feasible for biogas production in Nigeria. This includes cassava leaves, cow dung, water lettuce, water hyacinth, urban organic refuse, processing waste, solid waste (solid biomass), agricultural residues and sewage. organic, biodegradable materials that can be potentially utilized as feedstocks for biogas production are categorized in Figure 2.2 (Gilkinson*et al*., 2014).

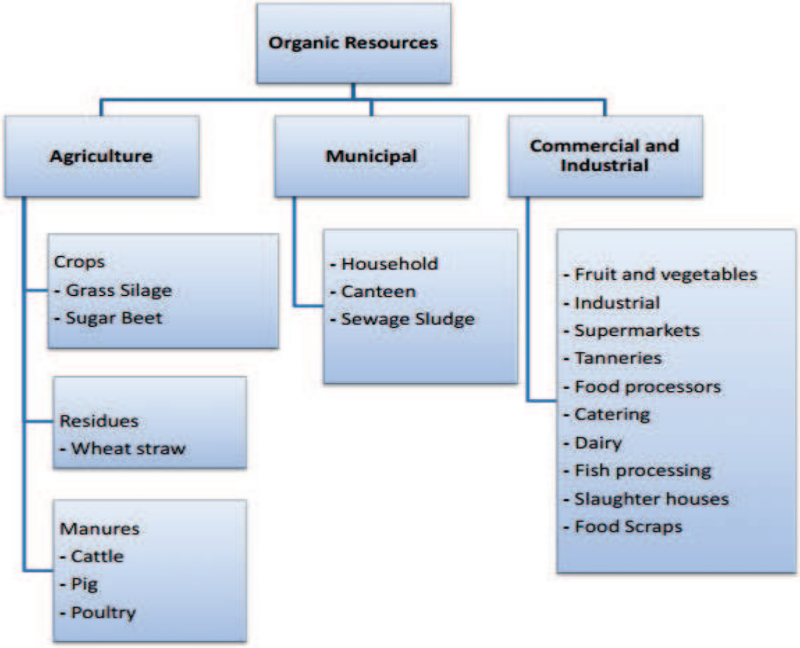


Figure 2.2: Classification of feedstocks potentially available for biogas production (Gilkinson *et al*., 2014).

Most existing biogas installations typically processes of residual sludge from wastewater purifying plants. other facilities processes wastes are from breweries, juice processing, chicken processing, brewing, and dairy production. The potential range of waste feedstocks is greatly broader which include: food waste, kitchen waste, municipal wastewater, residual sludge, food processing, wastewater, dairy manure, poultry manure, yard wastes aquaculture wastewater, seafood processing wastewater, and public solid wastes (Heo *et al*., 2004).

Furthermore, there are a lot of potential energy crops, which will be suitable for biogas manufacture including: vegetables, grass, sugarcane, corn, as well as timbered crops (tree crops) (Heo *et al*., 2004). The best crops must contain low fertility necessities, and low energy operating cost for harvesting and planting . in addition, ethanol manufacture from an energy produce will generate large volumes of waste water, which can be transformed to biogas. as well, the manufacture of biodiesel from oil vegetables gives glycerol wastewater that can be transformed to biogas (Gilkinson *et al*., 2014).

Many authors have reported the possibility to use poultry, chicken , donkey, pig, cow and wastes for biogas manufacture. Adeyanju (2008) reported seeding of pig waste and cassava and wood ash which gives significant boost in biogas manufacturing compared to unseeded combination of cassava peels and pig waste .Generation of biogas from peels of plantain and banana was investigated by the means of 10L small scale anaerobic digester, Ilori *et al*. (2007). The result show the highest amount of biogas was obtained when the banana and plantain peels were in equal size as feedstock. Various potential biogas manufacture substrates as presented in Table 2.1.

Table 2.1: Potential biogas production from various Substrates

Substrates	*Hydraulic retention time (days)*	*Solid Concentration (%)*	*Temperature (^oC)*	*Biogas Yield (m^3/kgSubstrates)*	*CH_4(%)*
Domestic garbage	30.0	5.00	35.0	0.470	-
Sewage sludges	25.0	6.00	35.0	0.520	68.0
Piggery wastes	20.0	6.5.0	35.0	0.430	69.0
wastes Poultry	15.0	6.00	35.0	0.500	69.0
Cattle wastes	20	10.0	35	0.30	58
Mixed feed of fruit wastes	20	4.0	37	0.62	50
Food wastes	30	10.0	30	0.60	50
Banana wastes	25	10.0	37	0.20	55
Citrus wastes	32	4.0	37	0.63	62

Source: Somayaji (2005)

2.3 Anaerobic Decompositions

Anaerobic digestion is a succession of controlled processes of decomposition of organic waste in an air tight in presence of anaerobic micro-organisms. The digestion process at with bacterial hydrolysis of the materials so as to break down insoluble organic polymers like protein and carbohydrates which make them obtainable for bacteria (ojolo *et al*., 2007).

The process of digestion was carried out in an airtight reactor and other equipment employed for gas retrieval and waste pre-treatment. The process produce product known as biogas that is chiefly composed of methane, CO_2, and decompost products suitable for soil conditioners on farmlands. Anaerobic digestion is used either to treat recyclable wastes or produce saleable materials such as heat and electricity (Monnet, 2003). The most important use of anaerobic digestion is to add waste management and the use ofs by-products. It is not likely that anaerobic decomposition will be a practically treated without utilization of biogas and the digestate. However, the qualities of the biogas and digestate will differ depending on substrates with s its contamination (ojolo *et al*., 2007).

According to Monnet studys (2003), anaerobic process of digestion is sub divided into four stages which includes: pre-treatment, gas upgrading, digestion, and digestate treatment. He opined that intensity of pre-treatment depends on type of substrates, for exampls, there should be mixtures of manures while requires arrangement and shredding. The digestion phase takes place in a machine known as digester. There are many types of digesters present with dissimilar temperature and combining devices. The decomposition may be wet or dry depending on the solid substance in the feedstock. This means that the substrate will require combination of water and other suitable liquid wastes like, re-circulated sludge liquid from digester runoff. The final stage which is the upgrading of the biogas is a necessary step because the biogas may contain impurities that can damage engines or devices depending on what the gas is used for. The anaerobic breakdown of organic matter occurs in four-step as shown in Figure 2.3 and are described in the following sections.

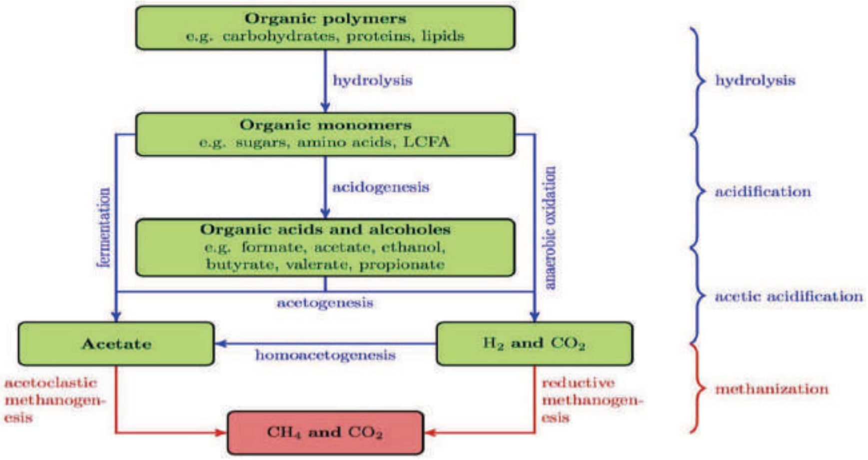


Figure 2.3: Flow diagram for biodecomposition steps of complex organic substances (Monnet, 2003)

2.3.1 Hydrolysis

This first step in biogas manufacture is typically the slowest among the four decomposition steps. Fermentative bacteria change complex organic resources like polymers , cellulose, and monomers; are transformed to soluble watery amino acids, fatty acids and monosaccharides correspondingly (Arnell *et al.*, 2007).polymeric complex matter is hydrolyzed to monomer, for example, cellulose to sugars, or alcohols and proteins to peptides or amino acids, and in the course of hydrolytic enzymes released with the aid of microbes Microbial cell is impermeable to the cellulose particle and the organism must emit extracellular enzymes in order to put together the source of carbon obtainable. sExtracellular enzyme-mediated change of higher mass organic substance into basic structural building blocks is very important as particulate organic materials are simply too large to be directly absorbed and used by microorganisms as substrate/food source (Monnet, 2003).

According to Karki *et al*. (2005), this phase is known as polymer breakdown stage because the cellulose consisting of polymerized glucose units are first broken down to dimers (disaccharides), and then to monomers (monosaccharide) such as, glucose by cellulolytic bacteria, which excrete enzyme called cellulose. The most common anaerobic cellulose fermenters in nature appear to be members of the genus Clostridium (Arnell *et al.*, 2007). Hydrolytic activity is of significant importance in high organic waste and can become rate limiting step. However, some industrial operations overcome this limitation by the use of chemical reagents to enhance hydrolysis which has been found to result in a shorter digestion time with a higher CH_4 yield (Monnet, 2003).

2.3.2 Acidogenesis

In the acidogenesis stage, acidogenic bacteria convert soluble organic monomers of sugars and amino acids to ethanol and acids (for example, propionic, lactic, formic and butyric acid), acetate, H_2 and CO_2. The degradation of amino acids also leads to production of ammonia. The specific concentrations of products formed in this stage vary with the type of bacteria as well as with culture conditions, such as temperature and pH (ostream, 2004).

2.3.3 Acetogenesis

In the acetogenesis stage, both long chain fatty acids and volatile fatty acids and alcohols are transformed by acetogenic bacteria into H_2, CO_2 and acetic acid (CH_3COOH). During this reaction the biological oxygen demand (BOD) and chemical oxygen demand (COD) are both reduced and the pH decreased (Bekker, 2007). Acetogenesis occurs through carbohydrate fermentation, with acetate as the main product, and other metabolic products. Long chain fatty acids, formed from the hydrolysis of lipids are oxidized to acetate or propionate and H_2 is formed. Hydrogen plays an important intermediary role in this process, as the reaction will only occur if the partial pressure is low enough to thermodynamically allow the conversion of all the acids. Hydrogen scavenging bacteria lead to a lower partial pressure. Thus the H_2 concentration in a digester is an indicator of its “health” (Mata-Alvarez, 2003).

However, the transition of the substrate from organic material to organic acids in the acid forming stages causes the pH of the system to drop which is beneficial for the acidogenic and acetogenic bacteria that prefer a slightly acidic environment, with a pH range of 4.5 – 5.5, they are less sensitive to changes in the incoming feed stream. According to Igboro (2011), this drop in pH is problematic for the bacteria involved in the methanogenesis stage.

2.3.4 Methanogenesis

Methanogenesis is the final stage in which methanogenic bacteria convert the H_2 and CH_3COOH to CH_4 gas and CO_2. The methanogenic anaerobic bacteria involved in this stage are the same fastidious bacteria that occur naturally in deep sediments or in the rumen of herbivores (Igboro, 2011). These bacteria carry out CH_4 formation either by means of cleavage of CH_3 COOH molecules to generate CO_2 and CH_4, by reduction of

CO_2 with H_2. CH_4 production is higher from reduction of CO_2 but limited H_2 concentration in digesters results because the acetate reaction is the primary producer of CH_4. The methanogenic bacteria include methanobacterium, methanobacillus, methanococcus and methanosarcina (Monnet, 2003).

Methanogenesis is affected by conditions in the reactor such as temperature, feed composition and organic loading rate (Parawira, 2004). Methanogens are very sensitive to changes in conditions and prefer a neutral to slightly alkaline environment. Methanogenic bacteria cannot survive a change in pH below 6. Methanogenesis is the rate-controlling portion of the process because methanogens have a much slower growth rate than acidogens (Igboro, 2011). Anaerobic digestion is considered to take place in these four stages, however, all processes occur simultaneously and synergistically because the first group has to perform its metabolic action before the next can take over, and so forth (Parawira, 2004).

2.4 Biogas Production Technologies

The choice of the basic anaerobic digester design or technology for biogas production is influenced by the technical suitability, cost-effectiveness and the availability of local skills and materials (Lohri, 2012). In developing countries, the technology and design selection is largely determined by the prevailing and proven design in the region, which in turn depends on the economic, climatic and substrate specific conditions. However, there are three main types of digesters that have been implemented in developing countries which are: fixed-dome digester, the floating-drum digester and the tubular digester. All of which are wet digestion systems operated in continuous mode under mesophilic conditions. These three types are inexpensive and can be built with locally available material, easy to handle, do not have many moving parts and are thus less prone to failure. The garage-type digester, which is operated as a dry digestion system in batch-mode, is considered as another potential biogas technology suitable for developing countries. However, this technology is being tested in Africa countries like Ghana and Uganda by converting a used shipping container into digester. This technology is however, not yet ready for commercialization as no viable low-cost design existing has been successfully tested at full-scale (Fact Foundation, 2012).

2.4.1 Fixed-dome digester

A fixed-dome plant comprised of a closed dome shape digester with an immovable, rigid gas-holder, a feedstock inlet, and a displacement pit. It is also named the compensation tank. A schematic diagram of this type of digester is shown in Figure 2.4. The gas produced in the digester is stored in the upper part of the reactor with a closed outlet gas valve in which increasing the gas production elevates the gas pressure inside the digester thereby pushing the digestate into the compensation tank (Lohri, 2012). When the gas valve is open for gas utilization, gas pressure drops and a proportional amount of slurry flows back from the compensation tank into the digester. With this design, gas pressure varies continuously depending on gas production and use. Normally, this type of plant is constructed underground which protects the digester from low temperatures at night and during cold seasons. The surrounding soil to the top of the gas-filled space, counteracts the internal pressure in the digester which is usually 0.1 – 0.15 bar (Nzila *et al*., 2012).

Though cheap, fixed-dome plants are only recommended for situations where experienced biogas technicians with specific technical skills in construction are available to ensure a gas-tight construction. Generally fixed-dome plants are characterized by modest initial cost and a long operational life of about 15 – 20 years, since no moving or corroding parts are required. However, with time, the brickwork structure may become porous and prone to cracking resulting in gas leakages. Porosity may be counteracted with the use of special sealants, however cracking often causes irreparable leaks. According to Nzila *et al*. (2012), the fluctuating gas pressure in this digester type might complicate gas utilization.

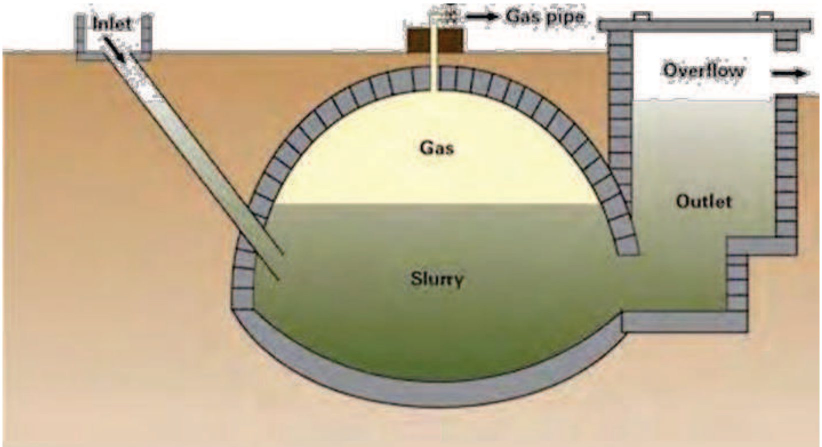


Figure 2.4: Scheme of fixed-dome digester (Nzila *et al*., 2012).

2.4.2 Floating-drum digester

Floating-drum biogas plant is made up of a cylindrical digester and a movable, floating gasholder or drum. The digester is generally constructed underground whereas the floating gasholder is above ground. Smaller household-scale systems may also be fully above ground. The digester part of the reactor is usually constructed with bricks, concrete or quarry-stone masonry and then plastered. The gas-holder is typically made of metal and is coated with oil paints, synthetic paints or bitumen paints to protect it against corrosion. Regular de-rusting is however essential to ensure sustained usage, and cover coating should be applied annually. A well-maintained metal gas-holder can last for 3 – 5 years in humid areas and 8 –12 years in a dry climate. Suitable alternative to standard grades of steel are fibre-glass reinforced plastic or galvanized sheet metal (Nzila *et al*., 2012).

The produced gas is collected in gas drum, which rises or falls again, depending on the amount of gas produced and used. The drum level thus provides a useful visual indicator of the quantity of gas available. The gas is provided at a relatively constant pressure, which depends on the weight of the drum. However, to increase the gas pressure, additional weights can be added on top of the gasholder and braces can be welded onto the inside of the drum which then help to break up the scum layer when the drum is rotated (Nzila *et al*., 2012). The gasholder floats either directly on the fermenting slurry or in a specially constructed separate water jacket which reduces CH_4 leakage as shown in Figure 2.5. A guiding frame constructed inside of the gas drum is an additional measure to avoid tilting of the drum when it rises. The design size of floating-drum plants typically ranges from 1 – 50. m^3.

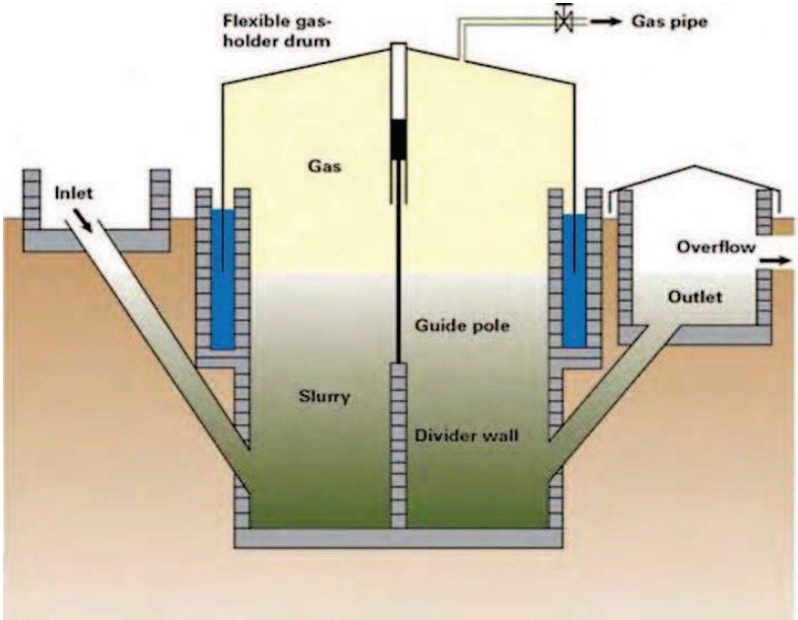


Figure 2.5: Scheme of floating-drum digester (Nzila *et al*., 2012).

2.4.3 Tubular digester

The tubular biogas plant consists of a longitudinal shaped heat-sealed, weather resistant plastic or rubber bag that serves as digester and gas holder in a single entity. The gas is stored in the upper part of the balloon while the inlet and outlet are attached directly to the skin of the balloon. As a result of the longitudinal shape, no short-circuiting occurs. But, since tubular digesters typically have no stirring device, active mixing is limited and digestate flows through the reactor in a plug-flow manner. Gas pressure can be increased by placing weights on the balloon while ensuring not to damage the ballon. Figure 2.6 shows a schematic representation of a typical tubular digester. The benefit of these digesters is that they can be constructed at low cost by standardized prefabrication and also, the shallow below ground installation makes them suitable for use in areas with a high groundwater table. However, Nzila *et al*. (2012) reported that the plastic balloon is quite fragile and are susceptible to mechanical damage with a relatively short life span of 2 – 5 years.

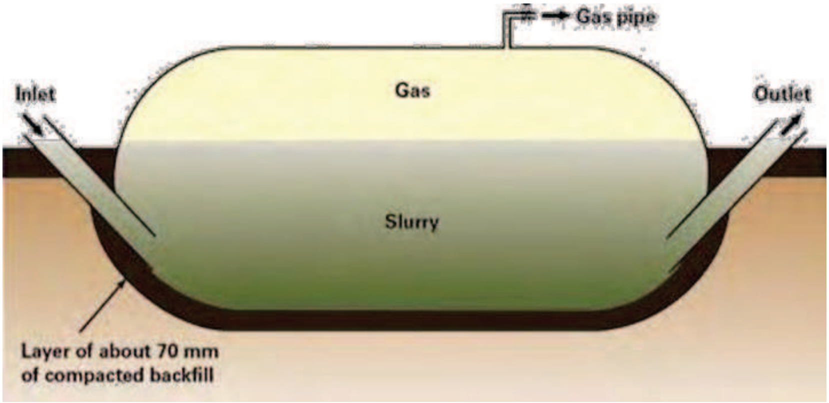


Figure 2.6: Scheme of balloon digester (Nzila *et al*., 2012).

2.4.4 Garage-type digester

In contrast to the three common type of digester described above, the garage-type digester is operated in batch-mode and in a dry digestion process (a high total solids content above 15 %). The entire organic waste stream is filled batch-wise into a simple garage-like digester with an airtight door as shown in Figure 2.7. once the door is closed, the material does not need to be transported or turned during the process (Li *et al*., 2011).

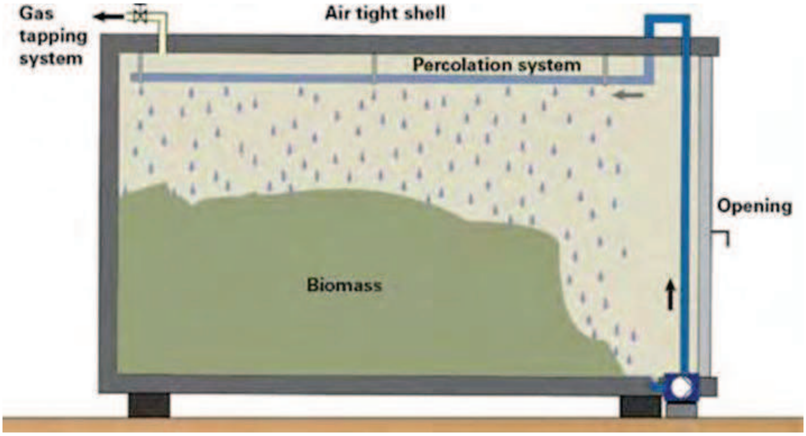


Figure 2.7: Scheme of a garage-type dry digestion plant (Li *et al*., 2011).

2.5 Operational Parameters for Biogas Production

The rate at which the microorganisms grow is of paramount importance in biogas production process. The operating parameters of the digester are therefore required to be controlled so as to enhance the microbial activity and thus increase the anaerobic digestion efficiency (Buysman, 2009). The most essential parameters are discuss subsequently.

2.5.1 Temperature

While anaerobic digestion technology is principally feasible under almost all climatic conditions, at low temperatures (mean temperature below 15 °C) the digestion process does not work satisfactorily. In low temperate conditions either a heating system has to be installed or a larger digester has to be built in order to increase retention time (Buysman, 2009). Heating systems and insulation can provide optimal digestion temperatures even in cold climates or seasons, however the required additional investment costs and fuel costs for heating may render the biogas system economically unviable. Not only is the mean temperature an important parameter for the anaerobic digestion process but large temperature variations, such as those between day and night, or seasonal variations, can also adversely affect the performance of an anaerobic digestion system (Deublein and Steinhauser, 2011). Digesters built underground help to minimize these changes by using the temperature buffer capacity of the soil. For household digesters the design should ensure that gas production remains sufficient even during the most unfavorable season of the year. Given the additional investments required in colder climates, a general rule is that the costs of biogas production increase as the temperature decreases(Buysman, 2009).

There are two ideal temperature ranges for the optimum performance of anaerobic bacteria; 30 – 40 °C for mesophilic microorganisms with optimum temperature at 37 °C and 45 – 60 °C for thermophilic microorganisms with optimum temperature at 55 °C (Mata-Alvarez, 2003). Digester operation in the mesophilic range is more stable, as the microbial communities can tolerate greater changes in environmental parameters and consume less energy. However, inhibition by ammonium is less critical in the mesophilic range as compared to thermophilic conditions due to the lower content of free ammonia at lower temperatures. on the down side however, the mesophilic microorganisms are slower and thus a longer retention time in the digester is needed to maximise biogas yield(Buysman, 2009). According to Deublein and Steinhauser (2011), the thermophilic mode of digester operation results in approximately 50 % higher rate of degradation, particularly with fat-containing materials, a better availability of the substrates to the enzymes excreted by the acidogens and thus a higher biogas yield. In lieu of the lower solubility of CO_2 at higher temperatures, a 2 – 4 % higher CO_2 concentration in biogas can be observed in thermophilic digesters. Despite some advantages of anaerobic digestion at higher temperatures, operating the digester at thermophilic ranges is generally considered less feasible in a developing country context due to the additional energy inputs required as well as the lower stability of the process (Buysman, 2009).

2.5.2 pH

The optimum pH for a generally stable anaerobic digestion process and high biogas yield lies in the range of 6.5 – 7.5 (Khalid *et al*., 2011). During digestion, the processes of hydrolysis and acidogenesis occur at acidic pH levels of pH 5.5 – 6.5 as compared to the methanogenic phase at pH level of 6.5 – 8.2 (Khalid *et al*., 2011). An alkalinity level of approximately 3 000 mg/L has to be available at all times to maintain sufficient buffering capacity. Lime is commonly used to raise the pH of anaerobic digestion systems when the process is too acidic. Alternatively, sodium bicarbonate can also be used for pH adjustment (Igoni *et al*., 2007). Lime is usually much cheaper and there might be free sources of spent lime solutions from local industry. Lime however frequently leads to precipitations and clogging of pipes when used in larger quantities. Sodium bicarbonate and sodium hydroxide are fully soluble and usually do not lead to precipitations, but on the other hand they contribute to higher costs. Additionally, the availability of sodium bicarbonate or sodium hydroxide is sometimes lower than lime. However, for immediate action, the addition of sodium salts is recommended and for back-up pH-adjustment of low pH substrates, lime might be the choice.

2.5.3 Carbon to nitrogen ratio

The relationship between the amount of carbon and nitrogen in organic materials is represented by the C:N ratio. The C:N ratio is an important parameter in estimating nutrient deficiency and ammonia inhibition in anaerobic digestion system. optimal C:N ratios in anaerobic digesters are between 16 and 25 (Deublein and Steinhauser, 2011). A high C:N ratio is an indication of rapid consumption of nitrogen by methanogens, which would results in lower gas production. on the other hand, a low C:N ratio resulted in ammonia accumulation and pH values that may exceed 8.5. Such conditions can be toxic to methanogenic bacteria. Although methanogenic bacteria can adapt to very high ammonia concentrations only if concentrations are increased gradually to allow time for adaptation. optimum C:N ratios can be maintained by mixing different feedstock materials, with high (for example organic solid waste) and low (for example sewage or animal manure) C:N ratios to achieve an ideal C:N ratio level (Buysman, 2009).

2.5.4 Inoculation and start-up

When starting the digester for the first time, there is the need to inoculate the digester with bacteria necessary for the anaerobic process. Diluted cow dung (optimally 1:1 ratio with water) is an ideal inoculate. Typically, the minimum cow dung required for good inoculation amounts to 10 % of the total active reactor volume (Khalid *et al*., 2011). In general, the more cow dung used for inoculation, the better. The bacteria population needs to be gradually acclimatized to the feedstock during start-up phase. This can be achieved by progressively increasing the daily feeding load which allows time to achieve a balanced microorganism population (Buysman, 2009). Initial overloading presents a risk to the overall anaerobic process. overloading results from either feeding too much biodegradable organic matter compared to the active population capable of digesting it, or rapidly changing digesters conditions (for example, abrupt change of temperature, accumulation of toxic substances, flow rate increase). Such disturbances specifically affect methanogenic bacteria, whereas the acidogenic bacteria, which are more tolerant, continue to work, and produce acids which eventually leads to an acidification of the digester which inhibits the activity of methanogens. Such an imbalance of acidogenic versus methanogenic bacteria can result in digester failure. Addition of manure can avoid this as it increases the buffer capacity, thereby reducing the risk of acidification (Deublein and Steinhauser, 2011).

The gas that is produced in the first weeks after start-up is mainly CO_2 and after a few days the CH_4 content of the gas will have sufficiently increased to a level that can sustain a flame ($CH_4 > 45$ Vol.%) and lead to high quality biogas (55 – 70 Vol.%) (Buysman, 2009).

2.5.5 Organic loading rate

organic Loading Rate (OLR) is a measure of the biological conversion capacity of the anaerobic digestion system. It is the substrate quantity introduced into the reactor volume in a given time. OLR is a primarily important control parameter in continuous systems because overloading leads to a significant rise in volatile fatty acids which can result in acidification and system failure. Studies of anaerobic treatment of biowaste in industrialized countries describe OLR s in the range of 4 – 8 kg VS/m^3 reactor a day, which result in volatile substance (VS) removal in the range of 50 – 70 % (Vandevivere *et al*., 2003). This is ideal for continuously stirred reactors. However, for non-stirred anaerobic digestion systems which are predominant in developing countries, an oLR below 2 kg VS/m^3 reactor a day is recommended and considered suitable (Deublein and Steinhauser, 2011).

2.5.6 Hydraulic Retention Time

Hydraulic Retention Time (HRT) is a means of measuring the time the liquid fraction remains in the reactor. It is calculated as the ratio of the reactor (active slurry) volume to the input flow rate of feedstock. HRT is required to allow complete anaerobic digestion reactions and varies with different technologies, process temperature and waste composition(Chelliapan *et al*., 2011). Recommended HRT for wastes treated in a mesophilic digester range from 10 – 40 days. Lower retention times down to a few days only, are required in digesters operated in the thermophilic range. A distinction is however made between HRT and Solids Retention Time (SRT), but for digestion of solid waste, HRT and SRT are generally considered equal(Verma, 2002).

2.5.7 Mixing

The purpose of mixing and stirring inside the digester is to blend the fresh material with digestate and thus inoculate the fresh material with microbes and it is done to avoid temperature gradients within the digester and also prevents scum formation. Scum and foam is a result of filamentous microorganisms in the digester. Low concentrations of substrate in anaerobic digestion plants can lead to an increase in the growth of filamentous bacteria compared to flocculating bacteria (Deublein and Steinhauser, 2011). As much as possible, scum in digesters should be avoided as it can result in blockage of the gas pipe and can potentially lead to a foaming over of the digester. This can result in displacement of slurry into pipes, machines and devices leading to subsequent malfunction or corrosion (Vögeli *et al*., 2014).

Loss of bacteria is usually a minor problem as they regrow. However, a constant top layer of 20 – 60 cm of foam is usually regarded as “stable” in large-scale systems and is acceptable and easy to manage. While a thicker impermeable scum layer however may prevent gas release from the liquid and eventually also lead to failure of the structure (Deublein and Steinhauser, 2011). The performance of mixing and stirring equipment varies according to reactor type and total solid (TS) content in the digester. In the three most prevalent anaerobic digestion technologies typical for developing countries (fixed-dome, floating dome, tube digester) no stirring is typically implemented. However, removing digestate outflow which is an equivalent normal daily feeding load and feeding this back into the digester through the inlet helps to achieve a passive mixing process. Such a recirculation of digestate also helps to flush the inlet pipe and improves mixing of fresh feedstock with bacteria-rich digestate (Vögeli *et al*., 2014).

2.5.8 Inhibition

When designing biogas plant, inhibition of anaerobic process require to be considered due to compounds at high concentrations can be defective to anaerobic process. In general, inhibition depends on the concentration of the inhibitors, composition of the substrate and adaptation of the bacteria to the inhibitor,s inhibitors include: oxygen hydrogen sulphide,, organic acids ammonia, metals and others dangerous substances like disinfectants from hospital, herbicides, insecticides, industry ,agriculture, market, gardens, antibiotics and houses (Deublein and Steinhauser, 2011).

Nitrogen and ammonia is frequently referred to as one common inhibiting substances of anaerobic digestion. Ammonia inhibition can take place at a broad range of concentrations. Several studies have reported ammonia inhibition between 1400 and 17 000 mg N/L of total inorganic nitrogen (Chen *et al*., 2008). In anaerobic reactors, the total inorganic nitrogen (N_2) consists mainly of NH_3 and the protonised form of ammonium (NH_4^+). At normal pH ranges, the biggest share of the total inorganic nitrogen is in the form of ammonium while increasing the pH value and temperature, the share of NH_3 increases. The un-dissociated NH_3 form diffuses through the cell membranes and inhibits cell functionality by disrupting the proton and potassium balance inside the cell (Kayhanian, 1999). This inhibition results in an imbalance and accumulation of intermediate digestion products such as volatile fatty acids (VFA) which invariably result in acidification of the digester. With long enough adaptation periods, anaerobic microorganisms can tolerate higher NH_4^+ concentrations than those typically measured. This may however, results in a reduction in CH_4 production (Vögeli *et al*., 2014).

2.6 Biogas Purification/ Upgrading

When biogas goes out of digester, it is soaked with water vapour and has high energy deficient CO_2 and unreliable quantities of acidic and poisonous H_2S. For environmental sustainability, the biogas has to be cleaned to remove the CO_2, H_2S or water vapour which may lower the rate of combustion of the biogas. This is chiefly important when using gas-driven equipment to generate electricity because CO_2 acts as diluents on the target gas CH_4, causing reduction in heating value compared with natural gas (Li *et al*., 2017).

Furthermore, CO_2 does not participate in combustion process; rather it absorbs energy from CH_4 combustion resulting in lower flame temperature and speed flame propagation. Hence, the need to upgrade the biogas quality to reduce storage problem and ensure wider application. However, there are many purification methods for biogas upgrading which includes; absorption using chemicals, water, membrane separation and pressure swing s(Li *et al*., 2017). This methods are discuss subsequently.

2.6.1 Dewatering

Produced biogas leaving the digester is usually almost 100 percent soaked with water vapour which can lead to corrosion of equipment for energy conversion and need to be capture from the biogas(Li *et al*., 2017). When biogas travels through the gas conduits from the digester to energy conversion equipment, the vapour cools down on walls s and condenses. Accumulation of condensate gradually lead to gas pipe blockage and also when the biogas is under pressure, there will be condensation of water vapours. To evade these condensation problems, a condensation separator need to be put in place at t pipeline lowest point which normally consists of valve connected to drainer where the condensate can goes off (Vögeli *et al*., 2014).

2.6.2 H_2S removal

Hydrogen sulphide is a colorless gas with a different smell of decayed eggs, which usually generated in biogas plant by transforming sulphur-containing gas. Hydrogen sulphide is hazardous and it is toxic in concentrations more than 15ppm Threshold Limit Value (TLV). However, as it can be smelled at only 0.1 ppm, its presence is frequently detected before poisonous concentrations are attained.When the concentrations are high, it will be very difficult to perceive it, which makes hydrogen sulphide very unsafe (US Department of Health and Human Services, 2006). In raw biogas, H_2S concentrations are usually between 200 – 6000ppm(Miltner *et al*., 2012).

Rremoval of H_2S is not necessary for most applications in developing countries (Miltner *et al*., 2012). When biogas is employed for heating and biogas to air percentage is correct at combustion period, Hydrogen sulphide is burned which directly converts to sulphur. Nevertheless in incomplete burning, (So_2) is produced which can cause adverse healths problems. When using biogas in powering a combustion engine, it is necessary to remove the entrained H_2S due to its corrosive natires. Several methods are obtainable for H_2S trappingss, and two relatively simple methods are: removal by ferrous materials (dry desulphurisation) and removal by water (wet desulphurisation or adsorption) (Vögeli *et al*., 2014).

2.6.3 Carbon dioxide (CO_2) removal

CO_2 is one of the major component of biogas and has about 30 to 40 % concentrations s and the removal of CO_2 increases considerably the energy available from a unit volume of biogas (Sutantoa *et al*., 2017). However, since CO_2 does not hinder when utilizing biogas for heating, it is therefore usually not adsorbed in developing countries (House, 2010). wherever pressurized storage is employed, removing the CO_2 will bring down the capital cost of storage clearly. Removal of CO_2 from the biogas can be done by bubbling the biogas through water containing some alkaline chemical (House, 2010). If biogas is emp,oyed as a motor fuel, high CH_4 content of at least 96 % need to be attained and removal of CO_2 is necessary in order to obtain quality natural gas needed (Persson *et al*., 2006). The techniques for CO_2 removal comprise of physical and chemical CO_2 absorption:

a) Pressure Swing Adsorption and Vacuum Swing Adsorption.

b) separation of membrane.

c) Cryogenic separation.

d) Biological methane enrichment.

2.6.4 Pore size of biogas gases

The pore size of an adsorbent gives an indication of the median or mean size of the pores on the adsorbent surface. It also describes the particle size that the adsorbent will be able to reject, as well as characterizing the adsorbent. The impact of adsorbent pore size on adsorption mechanism is very important because it describe the ability of the sorbate molecules to penetrate inside the adsorbent and interact with its inner surface (Qiuli and George, 2004). Table 2.2 presents the pore size of the component gases that makes up biogas

Table 2.2: Gases and their pore size

Component	***Pore Size (A°)***
Methane (CH_4)	3.751
Carbon (IV) oxide (CO_2)	3.614
Carbon monoxide (CO)	3.31
Hydrogen (H_2)	2.89
oxygen (O_2)	3.46
Hydrogen Sulphide (H_2S)	3.623

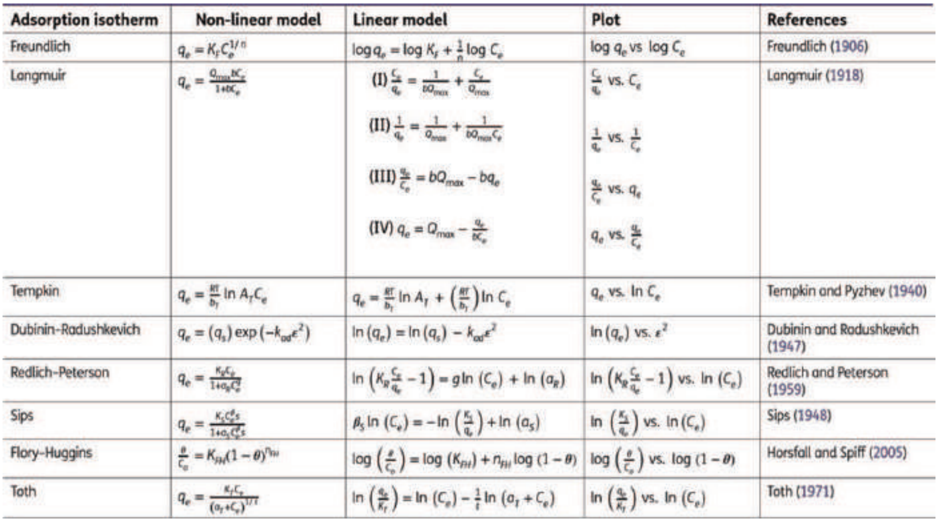
Source: Keith (2011)

2.7 Kinetics of adsorption

Kinetics of adsorption studies gives the ability of adsorbent and the stability relationships between adsorbent samples and adsorbate illustrated by adsorption isotherms which usually ratio between the amount adsorbed and the remaining left in solution at set temperature at stability (Dabrowski, 2001). Sorption isotherm (also adsorption isotherm) describes the stability of the sorption of a material at a exterior (more common at surface boundary) at stable temperature. It depicts the amount of substance bound on surface (sorbate) which represent function of the substance present within gas phase and in solution.

one way to describe the potentials of an adsorbent for the removal of pollutant is by studying the adsorption kinetics. The conclusion grafted from the kinetic studies tends to provide adequate information on the adsorption mechanism of the system (Rashidi *et al*., 2013). Table 2.3 presents some isotherm models commonly used for adsorption of materials

Table 2.3: Some isotherm models commonly used for adsorption of metals ***(Source :*** Foo and Hameed. (2010)).



Adsorption isotherm	Non-linear model	Linear model	Plot	References
Freundlich	$q_e = K_F C_e^{1/n}$	$\log q_e = \log K_F + \frac{1}{n}\log C_e$	$\log q_e$ vs $\log C_e$	Freundlich (1906)
Langmuir	$q_e = \frac{Q_{max} b C_e}{1 + b C_e}$	(I) $\frac{C_e}{q_e} = \frac{1}{bQ_{max}} + \frac{C_e}{Q_{max}}$ (II) $\frac{1}{q_e} = \frac{1}{Q_{max}} + \frac{1}{bQ_{max}C_e}$ (III) $\frac{q_e}{C_e} = bQ_{max} - bq_e$ (IV) $q_e = Q_{max} - \frac{q_e}{bC_e}$	$\frac{C_e}{q_e}$ vs. C_e $\frac{1}{q_e}$ vs. $\frac{1}{C_e}$ $\frac{q_e}{C_e}$ vs. q_e q_e vs. $\frac{q_e}{C_e}$	Langmuir (1918)
Tempkin	$q_e = \frac{RT}{b_T}\ln A_T C_e$	$q_e = \frac{RT}{b_T}\ln A_T + \left(\frac{RT}{b_T}\right)\ln C_e$	q_e vs. $\ln C_e$	Tempkin and Pyzhev (1940)
Dubinin-Radushkevich	$q_e = (q_s)\exp(-k_{ad}\varepsilon^2)$	$\ln(q_e) = \ln(q_s) - k_{ad}\varepsilon^2$	$\ln(q_e)$ vs. ε^2	Dubinin and Radushkevich (1947)
Redlich-Peterson	$q_e = \frac{K_R C_e}{1 + a_R C_e^g}$	$\ln\left(K_R\frac{C_e}{q_e} - 1\right) = g\ln(C_e) + \ln(a_R)$	$\ln\left(K_R\frac{C_e}{q_e} - 1\right)$ vs. $\ln(C_e)$	Redlich and Peterson (1959)
Sips	$q_e = \frac{K_s C_e^{\beta_s}}{1 + a_s C_e^{\beta_s}}$	$\beta_S \ln(C_e) = -\ln\left(\frac{K_s}{q_e}\right) + \ln(a_S)$	$\ln\left(\frac{K_s}{q_e}\right)$ vs. $\ln(C_e)$	Sips (1948)
Flory-Huggins	$\frac{\theta}{C_o} = K_{FH}(1-\theta)^{n_{FH}}$	$\log\left(\frac{\theta}{C_o}\right) = \log(K_{FH}) + n_{FH}\log(1-\theta)$	$\log\left(\frac{\theta}{C_o}\right)$ vs. $\log(1-\theta)$	Horsfall and Spiff (2005)
Toth	$q_e = \frac{K_T C_e}{(a_T + C_e)^{1/t}}$	$\ln\left(\frac{q_e}{K_T}\right) = \ln(C_e) - \frac{1}{t}\ln(a_T + C_e)$	$\ln\left(\frac{q_e}{K_T}\right)$ vs. $\ln(C_e)$	Toth (1971)

CHAPTER THREE

MATERIALS AND METHOD

This chapter gives a brief description of materials, chemicals and experimental procedure for biogas generation from mixture of chicken droppings and cow dung, adsorption of CO_2 impurity from the produced biogas, as well as the study of the adsorption kinetics.

3.1 Equipments, materials and chemical

Materials and the major equipments that was used in this study are presented below.

Table 3.1: List of Materials

S/N	***Materials***	***Sources***
1.	Cow dung	Gidan Kwano Farm, FUT Minna, Niger State
2.	Chicken Droppings	Gidan Kwano Farm, FUT Minna, Niger State
3.	Activated Carbon	Panlak Chemicals Minna, Niger State
4.	Zeolite	Department of Chemical Engineering FUT Minna,
5	Hydroxide of ammonia	Chemical Engineering Laboratory, Kad. Poly. Kad.
6.	Distilled Water	Chemical Engineering Laboratory, FUT Minna

Table 3.2: List of Equipment

S/N	***Equipment***	***Model***	***Manufacturer***
1.	Gas analyzer	NDIR Gas Analyzer (GASBOARD – 3100P)	Wuhan Cubic optoelectronic Co. Ltd. China
2.	Collection bag	Not Available	Not Available
3.	Tyre tube	Not Available	Locally improvise
4.	Improvised Digester	Not Available	Locally improvise
5.	Funnel	Not Available	Pyrex, England
6.	Adsorption columns	Not Available	Locally fabricated
7.	Weighing balance	Not Available	Gallenkamp, U.K
8.	Oven	Not Available	Not Available
9.	Furnace	Model No. AAF	Carbolite, UK
10.	pH meter	Not Available	Corning Ltd., U.S.A.
11.	Thermometer	Not Available	Zeal, England
12.	Measuring cylinder, beaker	Not Available	Pyrex, England
13.	Connecting tube	Not Available	Not Available
14	BET Surface Area Analyzer	Quantachrome Instrument 11.03	NoVA Instrument USA
15	FTIR	Perkin Elmer 1720.	Frontier FTIR, UK

3.2 Methodology

This section represents the methodology for the generation of biogas from cow dung and chicken droppings blended mixtures and different adsorption kinetics for the carbon (iv) oxide capture from the produced biogas.

3.2.1 Sample Collection

Cow dung was collected from the Federal University of Technology, Gidan Kwano Farm, Minna, Niger State whereas chicken droppings gotten from the poultry farm, Minna, Niger State. The zeolite CBV 8014 used for the adsorption study was collected from the Chemical Engineering Department, Gidan Kwano, Minna, Niger State while the AC used for the adsorption studies were sourced from Panlak Chemicals Minna, Niger State. Prior to usage, the zeolite was activated with ammonium hydroxide (NH_4OH) in an oven at a temperature of 550 °C for 2 hrs. The AC and zeolite CBV 8014 were characterized using Fourier Transform Infrared Spectroscopy and Brunauer-Emmett-Teller surface area investigation before usage in adsorption study. The adsorbents were sieved through a set of laboratory sieves and sieve fraction < 0.71 mm was used in the adsorption experiments.

3.2.2 Characterization of Adsorbent

BET Surface Area Analyzer

Prior to adsorption study, the surface area, volume of pores and micro-pores were obtained by N_2 physisorption (BET method) at 77K. These analyses were performed using Micromeritis Tristar 3000 surface area analyzer device using the BET method. Samples of the AC were placed in an oven at low temperature to ensure that they have as little remaining water vapor as possible. A measured quantity of the dried AC samples was introduced into the sample tube of BET Surface Area Analyzer and then de-gassed for 1 hr before starting the analysis. The AC sample was then immersed in a liquid nitrogen bath while the Quantachrome instrument performs the nitrogen adsorption tests. During the analysis, a known quantities of ultra-pure nitrogen gas is introduced into the tube while recording the pressure (P/P_0), this enables the plotting of equation 2 and determining the parameters therein. The same procedure was repeated for the zeolite CBV 8014 to determine its surface area.

FTIR Analysis

Fourier Transform Infrared Spectroscopy (FTIR) was performed using a PERKIN ELMER 1720, FRONTIER FTIR, UK. The resolution used in the FTIR collection were 2.0 cm^{-1}. The FTIR was determined using KBr pellet technique in the wavelength range 100- 4400 cm^{-1}

3.2.3 Substrate preparation and Biogas production

This research work was carried by means of an improvised small laboratory size bio-digester of ten liters gallon. A cork was used to closed the digester with small opening at the top of the cork. A tube of 10mm was passed through the opening and carefully sealed with glue to make the digester anaerobic.

The raw materials employed for this research are chicken droppings with cow-dung described above Mohammed *et al*(2016)reported that 20 percent (1:4) and 25 percent (1:3) concentration of cow- dung with chicken droppings correspondingly gave the maximum biogas yield at atmospheric temperature. Therefore, 1000g of droppings of chicken was mixed together 4000mL of treated water which give substrate concentration of 1:4. Also 1000g of cow dung with three liters(3000mL) of water which amount to 1:3 and substrate concentration of 25percent was also mixed together. Both the chicken droppings substrate and cow dung substrate were mixed together in a container. The mixing of both substrates were thoroughly carried out to ensure homogeneity and the substrate was charged into the ten liters improvised laboratory scale digester. The anaerobic digester was connected to tyre tube to collect biogas produced for about 22days. The biogas experimental setup is as shown in Figure 3.1. The anaerobic digestion took place at atmospheric temperature.

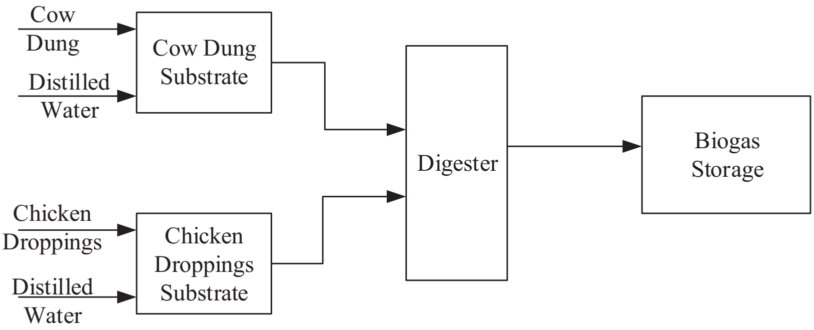


Figure 3.1: Biogas production setup

3.2.4 Test for the occurrence of methane found inside the biogas produced

The occurrence of CH_4 was tested by igniting flame on a burner connected to the biogas reservoir. Gas that came out from biogas reservoir burns smoothly with blue flame which shows that methane is found in the gas mixtures. Furthermore, sample of the biogas generate was taken to National Research Institute for Chemical Technology (NARICT), Zaria, for analysis to further confirm presence and composition of CH_4 and other gases in the produced biogas. A NDIR Gas Analyzer (GASBOARD – 3100P) was used for the analysis.

3.3 Optimization of Biogas Upgrading

In order to optimize the biogas upgrading process (output response) with adsorbent dosage and contact time as the input variables, factorial analysis was used. The factorial analysis software selected for implementing the factorial analysis methodology is Minitab 17 software. The factorial analysis experimental design matrix for the two factors was generated using Minitab 17 software as shown Table 3.3.

Table 3.3: Experimental Design for Factorial Analysis of Uncoded Factors

Runorder	***Blocks***	***Adsorption Time (min)***	***Adsorbent Dosage (g)***	***Response (Gas Purity)***	
				AC	***Zeolite***
1	1	2.5	1		
2	1	2.5	2		
3	1	2.5	3		
4	1	2.5	4		
5	1	5.0	1		
6	1	5.0	2		
7	1	5.0	3		
8	1	5.0	4		
9	1	7.5	1		
10	1	7.5	2		
11	1	7.5	3		
12	1	7.5	4		
13	1	10.0	1		
14	1	10.0	2		
15	1	10.0	3		
16	1	10.0	4		
17	1	15.0	1		
18	1	15.0	2		
19	1	15.0	3		
20	1	15.0	4		
21	1	20.0	1		
22	1	20.0	2		
23	1	20.0	3		
24	1	20.0	4		

3.3.1 Carbon (IV) oxide adsorption

An improvised glass adsorption column was used for this study while AC and Zeolite was used as adsorbents. Adsorption column fabricated was held strongly to a stand while biogas release tubes was connected from biogas storage (tyre tube) to the adsorption column that contains the adsorbent. Then the purified biogas passed through the delivery tube to a gas collection bag (purified biogas storage) for gas analysis in NARICT, Zaria, using a NDIR Gas Analyzer (GASBOARD – 3100P). In order to optimize the CO_2 capture, adsorbent dosage and contact time varied from 1g to 4g and 0 to 20 minutes correspondingly according to the experimental design presented in Table 3.3.

One gram of AC of particle size < 0.71 mm was measured and transferred into the adsorption column setup in Figure 3.2, and firmly corked. The adsorption column was then connected to the tyre tube containing the biogas produced. Then the biogas flow rate control valve was opened as the gas released into adsorption column at 60 mL/minutes, atmospheric pressure and atmospheric temperature, over time intervals of 2.5 to 20 minutess. Cleaned biogas was then collected in the storage. The weights of the activated carbon samples were carefully weighed on digital electronic weighing balance at every intervals to determine the difference in mass of the activated samples until a stable weight was determine , which indicates its highest adsorption capacity. Same procedure were repeated for other activated carbon samples of 2g, 3g and 4g respectively as shown in Table 3.3. After the completion of activated carbon sample, same procedure was also employed with Zeolite as adsorbent for 1 to 4 g Zeolite material at time intervals of 2.5 to 20 minutes. Biogas adsorption process setup is as shown in Figure 3.2.

Figure 3.2: Gas adsorption setup

The overall experiment for each adsorbent sample comprise of 24 runs as shown in Table 3.3. The amount of CO_2 adsorbed from each experimental run were calculated from Equation 3.1 (Mohammed *et al*., 2016).

$$\text{Amount of } CO_2 \text{ Adsorbed} = \frac{\qquad\qquad}{\qquad\qquad} \tag{3.1}$$

where,

Q_o = initial weight of adsorbent before adsorption

Q_t = final weight of adsorbent after adsorption at time, t

The adsorbents used (AC and zeolite CBV 8014) were characterized after adsorption using FTIR analysis do determine the functional group of the adsorbents after adsorption study.

3.4 *Adsorption Kinetics*

The adsorption kinetics for activated carbon and zeolite were studied more using the models discussed subsequently.

3.4.1 *Lagergren's pseudo-first and second order models*

Lagergren's pseudo-first and second order models were used to test the kinetic behaviour for the two adsorbents and the conformity of the experimental work and kinetic model were analyzed by the regression coefficient (R^2) data. Linearized form of Lagergren pseudo-first-order model is usually expressed by Equation 3.2 (Rashidi *et al*., 2013).

—— (3.2)

where,

qe and qt = the amount of CO_2 adsorbed inmg/g at stability and time correspondingly,

k_1 = rate constant of pseudo-first-order model per minute.

According to Rashidi *et al*. (2013), the pseudo-second -order model and initial rate of adsorption, height (mg/g.min) which is given by Equation 3.3.

– —— —— – - —— (3.3)

where,

$$h = k_2qe^2 \quad (3.4)$$

According to Rashidi *et al*. (2013), applying the pseudo-second-order kinetic model in the adsorption process outcome in the plot of $1/q_t$ vs time t which genrates a straight line plot with 1/qe and 1/h which serve as the slope and intercept sscorrespondingly.

3.4.2 *Activation energy*

According to Rashidi *et al*. (2013), the Arrhenius equation shown in Equation 3.5 can easily be employed to calculate approximately the activation energy of adsorption process.

— (3.5)

where,

k = the pseudo-second-order kinetic model rate constant (g/mg.min);

Ea= Activation energy of adsorption process (J/mol);

R = Gas constant (8.314 J/Kmol.);

T = Adsorption temperature in degree Kelvin;

K_o = Factor for independent temperature (g per mg.min).

3.4.3 Intra-particle diffusion model

Ho *et al*. (2000) gives intra-particle diffusion model which was expressed by Equation 3.6.

(3.6)

Where,

q_t = the amount of CO_2 adsorbed at any time t (mg/g),

k_{id} = the intra-particle rate constant (mg/g.min$^{1/2}$),

t = Contact time (min$^{1/2}$).

According to Rashidi *et al*. (2013), the adsorption process obeys the intra-particle diffusion model if the plot runs through the origin.

CHAPTER FOUR

RESULTS AND DISCUSSION

This chapter presents the investigational results generated from this research and the discussion of the results. This research work investigates the comparative studies of the kinetics of biogas cleansing with the help of activated carbon and zeolite CBV 8014.

4.1 Biogas Production

The composition of the raw biogas produced from the mixture of cow dung and chicken droppings substrate were presented in Table 4.1. The composition was determined using the NDIR Gas Analyzer (GASBOARD – 3100P) in NARICT, Zaria.

Table 4.1: The raw biogas Compositions produced.

Component	***Value (Vol. %)***	***Standard Value (Rakican, 2007)***
Methane (CH_4)	53.76	45 – 70
Carbon (IV) oxide (CO_2)	33.44	25 – 55
Carbon(II)oxide (CO)	1.22	0 – 2
Hydrogen (H_2)	3.52	0 – 2.5
oxygen (O_2)	8.01	0 – 3
Hydrogen Sulphide (H_2S)	0.047	0.0001 – 0.2

Table 4.1 presents the results of the raw biogas generated from the prepared blended mixtures of cow-dung and chicken droppings. The methane content found in the raw biogas was 53.76 vol. %, which is in compliance with the raw biogas composition reported by Rakican (2007) for a marketable biogas plant. From Table 4.1, the values obtained for all components were in compliance with the standard value in the literature except for hydrogen and oxygen gas which are slightly higher than the normal value. The occurrence of oxygen in the biogas is possibly due to air going into the biogas line earlier than passing through the NDIR Gas Analyzer (GASBOARD – 3100P). as well,

the little higher value of hydrogen sulphide as seen from Table 4.1 may be partially accredited to the sulphure (iv) oxide in the substrate. In clean biogas, oxygen and hydrogen sulphide content should be insignificant.

4.2 Adsorbents characterization

Activated carbon and zeolite adsorbent were characterized to determine its functional group, surface area, and pore volume using BET surface area analyzer and FTIR. The generated results from the analysis are discussed subsequently.

4.2.1 BET Analysis

Micro spongy materials have become significant in the separation or arrest of gases such as CO_2, N_2, O_2, CO, H_2 and H_2S. The exterior area and pore size of every adsorbent is a basic property for efficiency of adsorbent samples (Gor *et al*., 2012) Differences in pore sizes affect the capacity of adsorbent of different molecules sizes and shapes, and this is one of the fundamental factor in which adsorbent are selected for a specific use. BET method was used for the determination of the total pores surface area and volume. The BJH, DH and DFT method were used to determine the cumulative adsorption surface area and volume of the meso and macropores. The t-Method was used to determine the external surface area while the DR method was used to determine the micropore area.

Activated carbon and zeolite over the years have become an important adsorbent material that have been used for several purposes. The usage of these adsorbent was greatly affected by the surface area and the micro structure of the adsorbent. Porosity is classified by IUPAC into three different groups sizes of pore : micro pores with thickness < 2nm), meso pores thickness between 2 nm to 50nm) and macro pores thickness >50nm(Guo and Lua, 2003).

Table 4.2: BET Surface Area Analysis

Method	***Value (m^2/g)***	
Surface Area	***AC***	***Zeolite***
Single Point BET	729.6	639.6
Multi Point BET	1044	867.6
Langmuir Surface Area	3307	2229
BJH Method Cumulative Adsorption Surface Area	1328	1106
DH Method Cumulative Adsorption surface Area	1422	1176
t-Method External S8kurface Area	1044	867.6
DR Method Micropore area	1197	1052
Zx	289.0	263.2
Pore Volume	***(cm^3/g)***	
BJH Method Cumulative Adsorption Pore Volume	0.6489	0.5337
DH Method Cumulative Adsorption Pore Volume	0.6669	0.5458
DR Method Micropore Volume	0.4255	0.3737
HK Method Micropore Volume	0.1963	0.1837
SF Method Micropore Volume	0.05230	0.0580
DFT Method Cumulative Pore Volume	0.3449	0.3046
Pore Size	***(nm)***	
BJH Method Cumulative Adsorption Pore Diameter (Mode Dv(d))	2.144	2.072
DH Method Cumulative Adsorption Pore Diameter (Mode Dv(d))	2.144	2.072
DR Method Micropore Pore Width	5.740	5.555
DA Method Pore Diameter (Mode)	2.820	2.740
HK Method Pore Diameter (Mode)	0.3675	0.3675
SF Method Pore Diameter (Mode)	0.4523	0.4523
DFT Pore Diameter (Mode)	2.647	2.647

From Table 4.2, the volume and surface area of the pores of the activated carbon and zeolite are compared to those of the literature values for each sample. From Table 4.2, it was found that the activated is very micro porous compared to zeolite CBV 8014. The AC and zeolite that was used for the CO_2 capture possess micro porosity having surface area of 1197 m^2/g and 1052 m^2/g correspondingly which means that both adsorbents has high adsorption capacity. This further validate the declaration of Abechi *et al*. (2013) that AC prepared with potassium hydroxide activation is extremely micro porous. nevertheless, AC has a little higher surface area compared to that of zeolite CBV 8014. Corroborating the increasing adsorption surface area, the pore volume of AC and zeolite ranges from 0.6489 to 0.6669cm^3/g and 0.5337 to 0.5458cm^3/g respectively. From Table 4.2, it was observed that both AC and zeolite have high pore volume, though, the pore volume of AC are a little higher than that of zeolite CBV 8014 which could be accredited to the high growth of the pores in AC as compared to zeolite CBV 8014.

Pores with diameters less than 2nm, 2 to 50nm and greater than 50nm are classified as micropores, mesopores and macropores, respectively (Gao *et al*., 2014). From Table 4.2, it can be observed that the pores structure of the AC and Zeolite CBV 8014 comprises of the formation of a higher micropores and mesopores. Micropores are formed in the interlayer spacing with widths in the range 0.36 – 0.46 nm for both AC and zeolite CBV 8014 and it is the micropores in AC and zeolite CBV 8014 which have the greatest influence upon gas adsorption, while the mesopores formed are with widths in the range 2.1 – 5.75 nm and 2.07 – 5.56 for AC and zeolite CBV 8014 respectively. These observations indicate that AC and zeolite CBV 8014 are both suitable for adsorption of CO_2 and other impurity gases. It also indicates that adsorption takes place in the micro pores and meso pores, whereas mesopores are very important and also assist in transport of fluids to and from the micro pores.

In addition, it was noted that potassium hydroxide activated carbon is very micro porous compared to zeolite CBV 8014 or some other types of activation (Abechi *et al*, 2013). This shows that, KoH activation enhances the specific surface area, which as a result leads to the development of higher degree of micro pores and mesopores (Viswanathan *et al*., 2009), The exterior structure of zeolites are typically heterogeneous which consists limited number of various kinds of adsorption sites and the heterogeneity of the surface of zeolites led to its consideration for use in CO_2 capture and adsorption of other gases (Pakseresth *et al*., 2002). The pore structure of the zeolite CBV 8014 (Table 4.2) implies that the pore diameter of the zeolite CBV 8014 is sufficient for the CO_2 to enter into the zeolites CBV 8014 channels. However, the surface area, pore volume and pore size of AC are slightly higher than that of zeolite CBV 8014 (Table 4.2). This may be due to the fact that AC has a highly developed porous structure with good adsorption properties and high affinity for CO_2 adsorption than zeolite CBV 8014.

4.2.2 Fourier Transform Infra-Red Spectroscopy

In addition to porosity and the surface area, activities of adsorbents are influenced by the outside chemistry. Many hetero-atoms on the exterior of AC and zeolite preside over its chemistry. Hetero-atoms like oxygen, nitrogen and hydrogen are attached to peripheral carbon, aluminum Al and silicon Si are organic functional groups (El-Sayed and Bandosz, 2004). FTIR spectra obtained for the activated carbon before and after adsorption are shown in Figure 4.1 and 4.2 correspondingly. Types and arrangement of binding groups found on the surface of activated carbon and zeolite were acknowledged in the wavelength range 100 to 4400cm^{-1}.

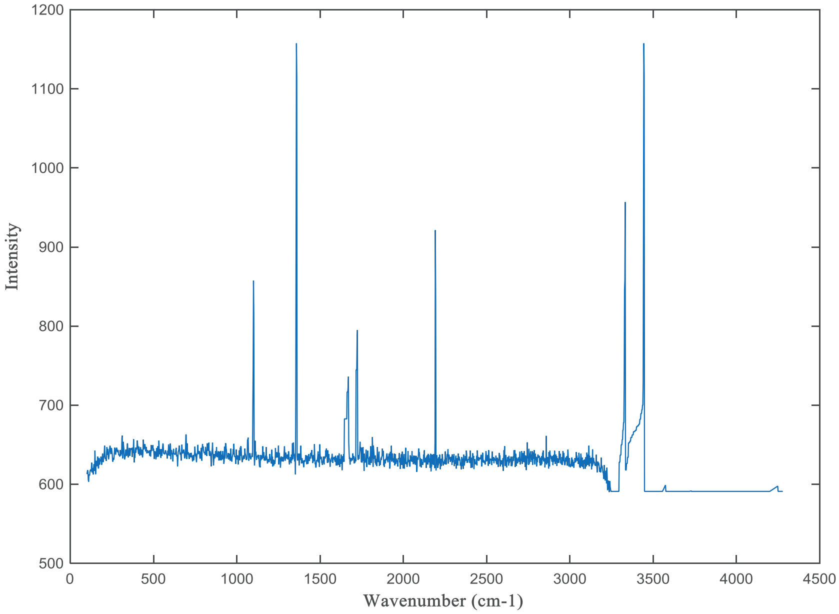


Figure 4.1: FTIR spectrum of activated carbon before adsorption.

From Figure 4.1 above, the intermolecular bonded hydroxyl groups (OH) were observed at 3300–3500 cm^{-1}. The band at 3444 $cm^{-1}$is accredited to the presence of hydrogen-bonded O-H group of phenols, alcohols and carboxylic acids. The peaks in the region of 1722 cm^{-1} could be attributed to the presence of C = O group; and peak within 1600 – 1670 cm^{-1} corresponded to C = C or symmetric and asymmetric stretching C = O sensations. A strong C-O band that was seen around 1000 to 1100 cm^{-1} was due to the existence of $–OCH_3$ group in the activated carbon samples before adsorption Peaks at 1300 to 1500 cm^{-1}shows clearly the presence of aromatics, alkynes and alkanes, hydrocarbons (Coates, 2000). Alhassan *et al*. (2017), got related results for activated carbon produced from acid modified, base modified and unmodified activated carbon.

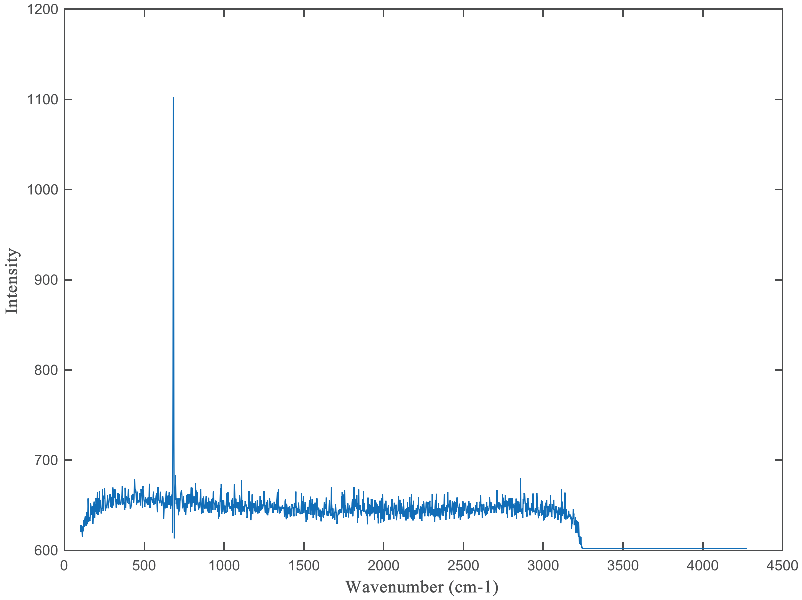


Figure 4.2: FTIR spectrum of AC after adsorption

Figure 4.2 shows the FTIR spectrum of activated carbon after adsorption. The transformation in the spectrum from Figure 4.1 (before adsorption) to that of Figure 4.2 (after adsorption) means that an interaction took place. This is due to the diminishing of some functional groups as a result of the gas adsorption. From Figure 4.2, the peaks at 682 cm^{-1} is connected with the in plane and out-of-plane aromatic ring bend vibrations (Socrates, 1994) and they are assigned to the out-of-plane C-H bending mode. These spectra can also be attributed to alkaline groups of cyclic ketones and its derivatives produced during adsorption (Guo and Lua, 1999). The vanishing of almost all the peak in the Figure 4.2 to a band of 682 cm^{-1}after adsorption clearly shows that CO_2 and other trace molecules had been adsorbed on top of the activated carbon.

The FTIR spectra of zeolite before and after adsorption are shown in Figure 4.3 and 4.4 respectively. The typical bands of zeolite representing the asymetrical and symetrical stretch are seen in the sample. From Figure 4.3, the peaks at 428 cm^{-1} is sign of tetrahedral bending peaks of zeolite CBV 8014 (omisanya *et al*., 2012).

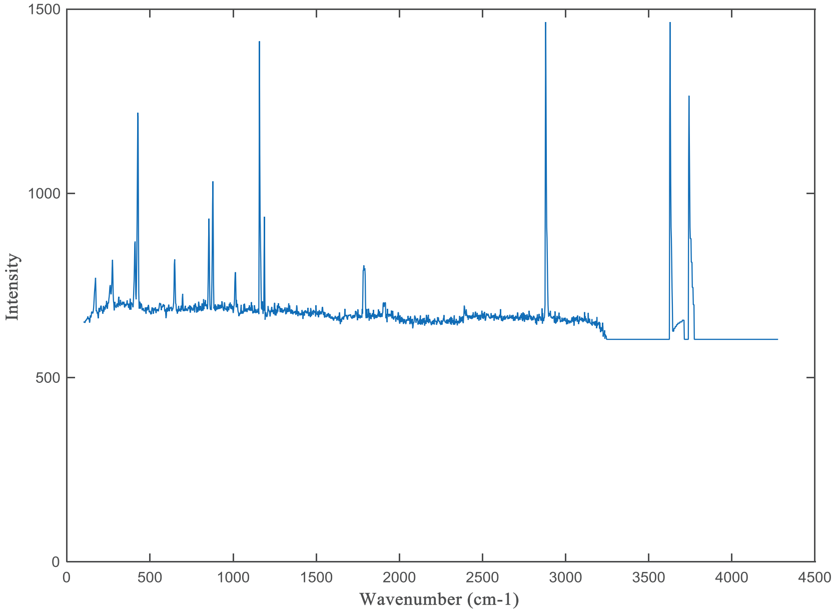


Figure 4.3: FTIR spectrum of zeolite CBV 8014 before adsorption

From Figure 4.3, the band at 500 – 670 cm^{-1} suggests the presence of Si-O-Al and Si–O–Na^{+} exchangeable. The increased strength of the band at 700 - 800 cm^{-1}is attributed to the Si-O shaking of amorphous silica. The peak at 1016 cm^{-1} are connected with the asymmetric and symmetric stretching modes of exterior linkages while the peak at 1158 is an indication of the asymmetric and symmetric stretching modes of internal tetrahedral (Misra *et al*., 2005). Also, at 1158 cm^{-1} band can be connected with asymmetric and symmetric stretching shaking (-C-O-C- ring) of ether C-O. The band can be credited to the Si-o-Si anti - symmetrical shaking mode due to the of existing silica and alumina containing minerals inside the zeolite CBV 8014 adsorbent (Calzaferri and Imhof, 1996).

The peaks at 1600 – 1800 cm^{-1} are attributed to the outer linkage stretching asymmetrically and inner tetrahedral symmetrical stretching correspondingly (omisanya *et al*., 2012). The band along 3628 cm^{-1} is assigned to hydroxyl groups attached to sodium ion, 3742 cm^{-1}depicts the silanol groups present on the outer surface of the zeolite sample. The crest at 3774 cm^{-1} equal to the isolated Aluminum oxides or Aluminum hydroxides(Misra *et al*., 2005).

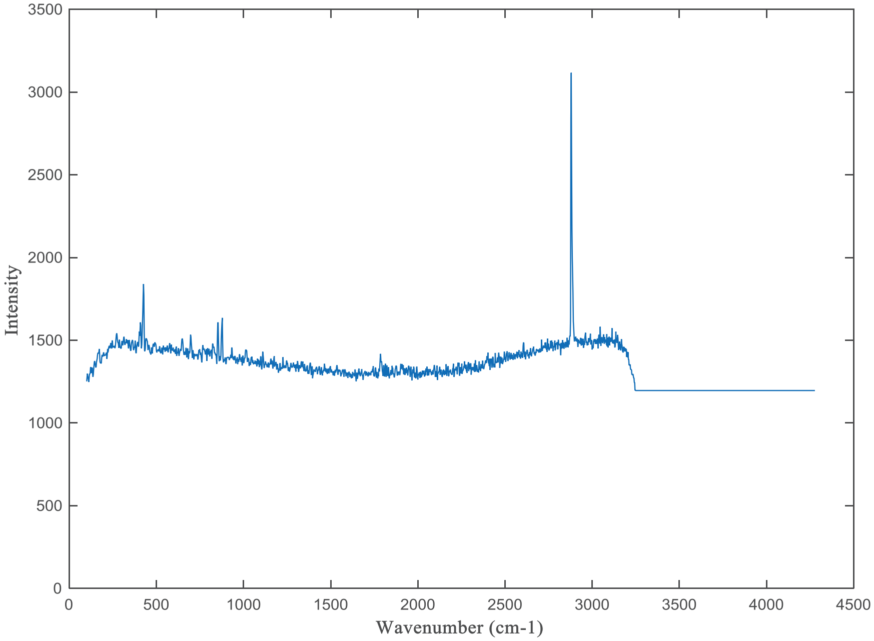


Figure 4.4: FTIR spectrum of zeolite CBV 8014 after the adsorption

Figure 4.4 clearly shows the FTIR spectrum of zeolite following the adsorption. The variations in the spectrum from Figure 4.3 (before adsorption) to that of Figure 4.4 (after adsorption) indicates that an interaction has taken place. This is because of some of the functional groups has been diminished due to the gas adsorption. From Figure 4.4, the peaks at 428 cm^{-1} is associated with the vibrations of Na+ against the framework which occur in the far infrared region (Ezzeddine*et al*., 2018). The disappearance of some of the peak due to interaction of the functional group with the gas molecule in Figure

4.4after adsorption is an indication that $CO_2$and other molecule had been adsorbed onto it.

4.3 Biogas Upgrading

Raw biogas produced from digestion is approximately 53.76% CH_4, 33.44% CO_2 and 12.8% of other gases (CO, O_2 H_2 and H_2S), it's quality is not high enough to serve as machinery fuel gas. The corrosive nature of H_2S is enough to destroy the internal components of the machinery. Therefore there is need to improve the biogas purity to above 90 percent CH_4 to ensure that the environment is safe when burn as a fuel to decrease release of large GHG produced from the gas. The biogas compositions and other gases after adsorption process were determined by the use of Gas Analyzer NDIR(GASBOARD – 3100P) . Table 4.3 and 4.4 clearly shows the gas composition of various runs in the experimental design matrix.

Table 4.3: Composition of the upgraded Biogas using AC as Adsorbent.

Sample	Percentage Composition (%)						Heating value (Kcal/m^3)
	CO	CO_2	CH_4	H_2	O_2	H_2S	
0 g, 0 min	1.22	33.44	53.76	3.52	8.01	0.0470	4286.47
1g, 2.5 min	1.19	32.63	54.13	3.59	8.01	0.0454	4451.85
1g, 5.0 min	1.15	32.11	54.70	3.59	8.01	0.0430	4650.71
1g, 7.5 min	1.11	32.01	55.12	3.54	7.82	0.0394	4793.50
1g, 10.0 min	1.07	31.98	55.36	3.52	7.69	0.0371	4885.31
1g, 15.0 min	1.03	31.88	55.80	3.44	7.50	0.0350	4835.38
1g, 20.0 min	1.01	31.87	55.96	3.38	7.45	0.0333	4875.52
2g, 2.5 min	1.15	32.11	55.10	3.47	7.74	0.0438	4518.92
2g, 5.0 min	1.07	30.81	56.67	3.34	7.70	0.0400	4752.82
2g, 7.5 min	1.08	30.06	58.04	3.19	7.27	0.0359	5020.11
2g, 10.0 min	1.01	29.32	59.11	3.09	7.12	0.0349	5160.91
2g, 15.0 min	0.98	27.79	60.63	3.05	7.21	0.0337	5192.12
2g, 20.0 min	0.93	27.45	61.15	3.00	7.15	0.0318	5240.18
3g, 2.5 min	1.12	30.87	56.51	3.48	7.59	0.0424	4563.98
3g, 5.0 min	0.93	28.13	60.53	3.29	6.76	0.0358	5024.06
3g, 7.5 min	0.63	27.04	63.67	3.27	5.20	0.0189	5970.02
3g, 10.0 min	0.58	25.42	65.99	3.29	4.57	0.0150	6213.96
3g, 15.0 min	0.50	23.63	67.87	3.31	4.57	0.0124	6293.83
3g, 20.0 min	0.47	23.16	68.39	3.29	4.57	0.0113	6313.72
4g, 2.5 min	1.09	28.41	59.84	3.69	6.59	0.0375	4628.26
4g, 5.0 min	0.89	21.87	66.99	3.60	6.39	0.0266	5214.83
4g, 7.5 min	0.39	18.59	71.79	3.48	5.64	0.0118	6441.78
4g, 10.0 min	0.27	15.83	77.24	2.80	3.80	0.0057	6651.10
4g, 15.0 min	0.21	12.04	81.93	2.60	2.76	0.0046	6803.41
4g, 20.0 min	0.17	10.74	84.34	2.27	2.45	0.0039	6867.65

Table 4.4: The results of Upgraded Biogas using Zeolite CBV 8014

Sample	Percentage Composition (%)						Heating value (Kcal/m^3)
	CO	CO_2	CH_4	H_2	O_2	H_2S	
0 g, 0 min	1.22	33.44	53.76	3.52	8.01	0.0470	4286.47
1g, 2.5 min	1.17	32.55	54.28	3.60	7.95	0.0450	4525.94
1g, 5.0 min	1.13	31.95	54.95	3.57	7.96	0.0432	4790.49
1g, 7.5 min	1.12	31.96	55.48	3.60	7.45	0.0372	4977.54
1g, 10.0 min	1.03	31.91	55.85	3.52	7.33	0.0355	4999.36
1g, 15.0 min	0.95	32.06	56.42	3.54	6.64	0.0388	5033.13
1g, 20.0 min	0.90	31.97	56.57	3.52	6.66	0.0389	5072.62
2g, 2.5 min	1.17	30.82	55.79	3.70	8.08	0.0438	4595.95
2g, 5.0 min	1.08	29.23	57.83	3.76	7.68	0.0413	4825.38
2g, 7.5 min	1.05	27.92	59.29	3.85	7.52	0.0361	5118.38
2g, 10.0 min	0.95	27.47	60.36	3.80	7.11	0.0309	5236.54
2g, 15.0 min	0.88	27.04	61.45	3.73	6.59	0.0304	5517.21
2g, 20.0 min	0.85	27.01	61.61	3.74	6.50	0.0294	5277.82
3g, 2.5 min	1.09	30.29	57.42	3.73	7.11	0.0365	4794.42
3g, 5.0 min	0.87	27.67	62.08	3.91	5.25	0.0225	5819.57
3g, 7.5 min	0.59	22.01	68.73	4.15	4.46	0.0073	6740.04
3g, 10.0 min	0.50	23.05	70.60	4.21	1.60	0.0037	7048.50
3g, 15.0 min	0.39	22.48	71.79	4.00	1.30	0.0038	7099.52
3g, 20.0 min	0.29	22.26	72.42	3.90	1.10	0.0032	7145.87
4g, 2.5 min	1.03	26.19	62.25	4.00	6.11	0.0417	4870.23
4g, 5.0 min	0.84	18.17	72.37	3.41	4.92	0.0300	6034.21
4g, 7.5 min	0.43	13.17	80.59	3.00	2.73	0.0087	7029.30
4g, 10.0 min	0.24	8.01	87.53	1.87	2.34	0.0048	7334.41
4g, 15.0 min	0.18	5.93	90.35	1.88	1.57	0.0091.	7404.12
4g, 20.0 min	0.16	5.39	91.01	1.77	1.58	0.0092	7444.84

Table 4.3 showed that the biogas responses slightly increased from 53.76% to 55.96 % for the adsorption time interval of 0 to 20 minutes using 1g of activated carbon adsorbent. As biogas purity increased from 53.76% to 61.15% for an adsorption time of 0 to 20 minutes with 2g of AC adsorbent. For equal adsorption time, biogas purity increased from 53.76% to 68.39% with 3g activated carbon adsorbent (Table 4.3). However, maximum purity of 84.3percent was observed at 20 minutes adsorption time with 4g of adsorbent (Table 4.3). This implies that purity of methane increased as adsorption time and adsorbent amount increased. 4g of activated carbon at 20 minutes has the highest purity of 84.34% with activated carbon as adsorbent. This means that more contaminant gases (CO_2, H_2, O, CO and H_2S) could be remove with more adsorbent dosage due to availability of more adsorption site (Gor *et al*., 2012).

Table 4.4 shows that adsorption time interval of 0 to 20 min, the pure biogas produced increases from 53.76% to 56.75% using 1g of zeolite .As the pure biogas increases from 53.76% to 61.61% at 0 to 20 minutes adsorption time with 2g of zeolite . At same adsorption time, biogas purity improves from 53.76% to 72.42% with 3g of zeolite. Biogas purity of 91.01% was practically observed at adsorption time of 20 minutes using 4g of zeolite. (Table 4.4). This shows that biogas purity increased as the amount of adsorbent increased with increase in time, this completely agrees with the values reported in the literature survey (Gor *et al*., 2012). For 1 g to 2 g of both activated carbon and zeolite, it was experiential observed that there was little or no significant diverse in the biogas purity for the adsorption time of 0 to 20 min. This further shows that there was large removal of more contaminant gases (CO_2, H_2, O_2, CO and H_2S) from 3 g to 4 g AC and zeolite quantity compare to maximum of 61.61percent and 61.1percent methane for 1 g to 2 g zeolite and activated carbon quantity respectively.

Comparing Table 4.3 and 4.4, it was experimentally observed from this study that the purification of raw biogas using zeolite recorded a better purity compared with the activated carbon. This is due to the fact that the adsorbates with the most great quadrupole moment like the CO_2, might relate strongly with electric field of zeolites (Bonenfant *et al*., 2008) which favours more adsorption of the impurity gases compared to AC which possess slightly higher surface area as shown in Table 4.2.Generally, it was practically seen that as the adsorption time increased from 0 – 20 min, the rate of removal of impurity gases (CO_2, CO, O_2 H_2 and H_2S) increased which invariably increases the purity of CH_4 gas. However, from 15 – 20min, it was observed that there was no major increase in the gas purity which implies that the adsorbent have reached equilibrium.

4.4 Optimization of Biogas Purity

The need to optimize the adsorption parameter (adsorbent dosage and contact time) give credence to the optimization of biogas upgrading. Biogas upgrading therefore, involves the removal of impurity in the raw biogas by absorption or scrubbing, leaving high methane volume of gas. The methane composition is used to imply biogas purity. Table 4.5 presents the experimental design, and responses (purity/CH_4 composition) for zeolite and activated carbon . Second-order model was employed in approximation of the purity variables . The second-order model is helpful in approximating part of true response using parabolic curvature. Second-order model includes all the variables in the first-order model with all quadratic terms such as $\beta_{11}x_1^2$ and every cross product variables like $\beta_{13}x_{1i}x_{3j}$ is mainly expressed as Equation 4.1;

(4.1)

®17 minitab Software was employed to do a factorial design study for the responses of the cleaned gas(Table 4.3 and 4.4). Second order polynomial equation was employed to represent the association between the parameters which are the adsorbent dosage and the adsorption time with the output response .Regression analysis , factorial plots and prediction equation as carried out.

The model correspond to the relationship of the input parameter with the corresponding response for both adsorbents was obtained by the use of experimental data presented in Table 4.3 and 4.4 for coefficients of regression for second order polynomial equation. The importance of the regression coefficients was tested by the means of t-test, Variance Inflation Factor and p-values were employed to carried out the test and the significance effect of individual variables present in the polynomial equation. The result signified that the individual term and the relations between the terms as well as the quadratic term are very import ($p<0.05$), this is in a good agreement with the trend reported in the literature. (Krishna*et al*., 2009).The responses gotten were inserted in the Minitab ®17Software and generated the models presented in Equation 4.2and 4.4.3.

Table 4.5:Experimental Design and Response Factors of Factorial Analysis of Biogas Upgrading employing AC with Zeolite CBV 8014

Stdorder	Runorder	PtType	Blocks	Adsorption Time (minute)	Adsorbent amount (g)	Response (AC)	Response (Zeolite)	FITS1	FITS2	RESI1	RESI2	SRES1	SRES2
1	1	1	1	2.5	1	54.13	54.28	53.6283	52.9544	0.50172	1.32558	0.46247	0.72862
2	2	1	1	2.5	2	55.10	55.79	53.3528	52.8181	1.74717	2.97186	1.41394	1.43415
3	3	1	1	2.5	3	56.51	57.42	56.3724	57.5385	0.13762	-0.11852	0.11137	-0.05720
4	4	1	1	2.5	4	59.84	62.25	62.6869	67.1156	-2.84693	-4.86557	-2.62423	-2.67442
5	5	1	1	5.0	1	54.70	54.95	55.1838	55.5574	-0.48376	-0.60741	-0.38991	-0.29194
6	6	1	1	5.0	2	56.67	57.83	55.9320	56.6163	0.73798	1.21367	0.55470	0.54398
7	7	1	1	5.0	3	60.53	62.08	59.9753	62.5319	0.55473	-0.45192	0.41696	-0.20256
8	8	1	1	5.0	4	66.99	72.37	67.3135	73.3042	-0.32353	-0.93418	-0.26076	-0.44899
9	9	1	1	7.5	1	55.12	55.48	56.2254	57.2887	-1.10540	-1.80870	-0.86904	-0.84793
10	10	1	1	7.5	2	58.04	59.29	57.9974	59.5428	0.04264	-0.25283	0.03198	-0.11310
11	11	1	1	7.5	3	63.67	68.73	63.0643	66.6536	0.60567	2.07637	0.45435	0.92882
12	12	1	1	7.5	4	71.79	80.59	71.4263	78.6211	0.36371	1.96891	0.28594	0.92303
13	13	1	1	10.0	1	55.36	55.85	56.7532	58.1483	-1.39321	-2.29830	-1.10484	-1.08683
14	14	1	1	10.0	2	59.11	60.36	59.5489	61.5976	-0.43887	-1.23764	-0.33412	-0.56185
15	15	1	1	10.0	3	65.99	70.60	65.6395	69.9036	0.35046	0.69636	0.26681	0.31613
16	16	1	1	10.0	4	77.24	87.53	75.0252	83.0663	2.21479	4.46370	1.75637	2.11080
17	17	1	1	15.0	1	55.80	56.42	56.2673	57.2524	-0.46730	-0.83241	-0.38310	-0.40693
18	18	1	1	15.0	2	60.63	61.45	61.1104	63.0922	-0.48038	-1.64216	-0.36644	-0.74697
19	19	1	1	15.0	3	67.87	71.79	69.2485	73.7886	-1.37846	-1.99857	-1.05150	-0.90909
20	20	1	1	15.0	4	81.93	90.35	80.6815	89.3416	1.24846	1.00835	1.02350	0.49294
21	21	1	1	20.0	1	55.96	56.57	53.7260	52.8697	2.23396	3.70026	2.35019	2.32130
22	22	1	1	20.0	2	61.15	61.61	60.6165	61.0999	0.53347	0.51010	0.44759	0.25521
23	23	1	1	20.0	3	68.39	72.42	70.8020	74.1867	-2.41202	-1.76672	-2.02375	-0.88392
24	24	1	1	20.0	4	84.34	91.01	84.2825	92.1302	0.05749	-1.12021	0.06048	-0.70275

FITS 1= simulated values for activated carbon FITS 2= simulated values for zeolite RESI 1= Residual values for activated carbon

RESI 2= Residual Values for Zeolite SRES1 = standard residual values for activated carbon SRES2= standard residual values for zeolite

Table 4.6: Coefficient model for Biogas Upgrading by means of AC

Term	*Coefficient Estimate*	*T-Value*	*P-Value*	*VIF*
Constant	56.15	25.57	0.000	
A	0.521	2.09	0.041	26.04
B	-6.24	-4.05	0.001	35.07
A^2	-0.04111	-4.26	0.000	21.04
B^2	1.648	5.67	0.000	32.25
AB	0.4095	9.37	0.000	8.82

Table 4.6, the Model equation relating the response (purity) from the contact of time and adsorbent amount during biogas upgrading using activated carbon was generated and the model equation for actual factor is given in Equation 4.2 below

$$\text{Purity} = 56.15 + 0.521A - 6.24B - 0.04111A^2 + 1.648B^2 + 0.4095AB \qquad (4.2)$$

A =The time of adsorption (min)

B = The amount of adsorbent (g)

Regression coefficient for the model equation of biogas upgrading by means of AC is as shown in Table 4.6. It was practically seen that for biogas cleansing (CH_4), the R^2, R^2 adjusted and R^2 predicted are 97.91%, 97.33% and 94.86% correspondingly for activated carbon , which simply means that 97.91% of the variable in the response could be arrested which has been explained by the purity model equation. This indicates high significance of the model. The R^2 predicted value of 94.86% indicates reasonable consistency with the R^2 adjusted value of 97.33% this means that there is good conformity between the observed and predicted value, this is in close agreement with the values reported in the literature (Sajeena *et al*., 20014).

Figure 4.5 presentes the experimental response against the predicted response. it can be practically seen from Figure 4.1 that the purity for both experimental and predicted results are closer very well with R^2 = 0.9791. Therefore the model equation design can be used to forecast the purity efficiency of activated carbon when employed to filter biogas.

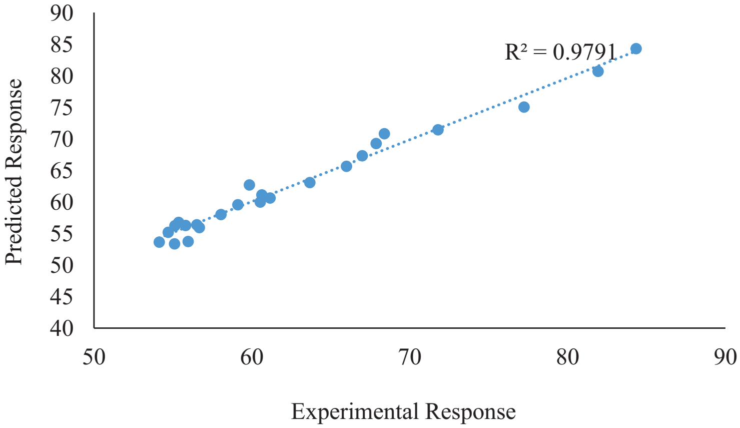


Figure 4.5: The plot of experimental vs predicted responses for activated carbon adsorbent.

Table 4. 7 present the P-values, coefficients and t-distribution and VIF of biogas upgrading by means of zeolite CBV 8014

Table 4.7: Coefficient model for Biogas upgrading with Zeolite CBV 8014

Term	***Coefficient Estimate***	***T-Value***	***P-Value***	***VIF***
Constant	55.67	15.11	0.000	
A	1.086	2.60	0.018	26.04
B	-8.62	-3.34	0.004	35.07
A^2	-0.0697	-4.31	0.000	21.04
B^2	2.428	4.98	0.000	32.25
AB	0.4781	6.52	0.000	8.82

The response equation that was used to test the biogas purity from the interaction of adsorbent amount and time variations using zeolite in term of real factor was given in Equation 4.3

$$\text{Response} = 55.67 + 1.086A - 8.62B - 0.0697A^2 + 2.428B^2 + 0.4781AB \qquad (4.3)$$

A = The time of adsorptioon (min)

B = The amount of adsorbent (g)

For the purification of biogas by zeolite CBV 801, the R^2, R^2 adjusted and R^2 predicted are as follows 96.67%, 95.74% and 91.86% correspondingly. This means that about 95.74% of the variable in the biogas purity might be captured which was explained by the model and again it indicate the high importance of the model. The R^2 predicted value of 91.86% indicates that it conform with that of R^2 adjusted value of 95.74%. This shows a very good correlation between the valus of observed and predicted, this agrees very well with the reported values in the literature (Sajeena *et al.*, 20014). nevertheless, the R^2, R^2 adjusted and R^2 predicted for activated carbon are higher than that of zeolite which means that the generated experimental data for activated carbon are well fitted than those of zeolite. Furthermore, Figure 4.6 shows that the model equation gotten for the upgrading of biogas by means of zeolite CBV 8014 can be used to forecast purity of the biogas at any convenience time as the plot of the experimental and predicted response gave a correlation coefficient (R^2) = 0.9667.

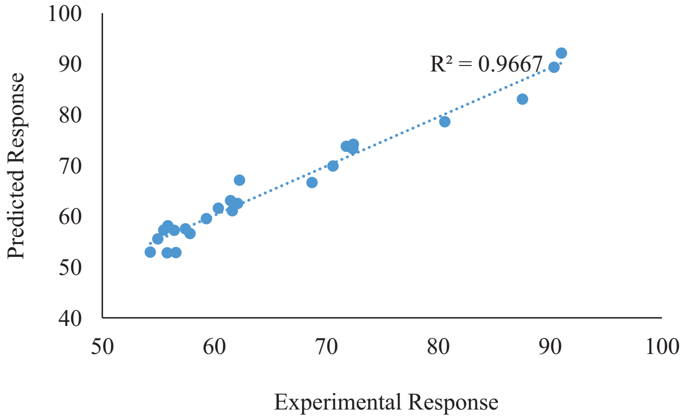


Figure 4.6: The plot of the predicted and experimental responses for zeolite.

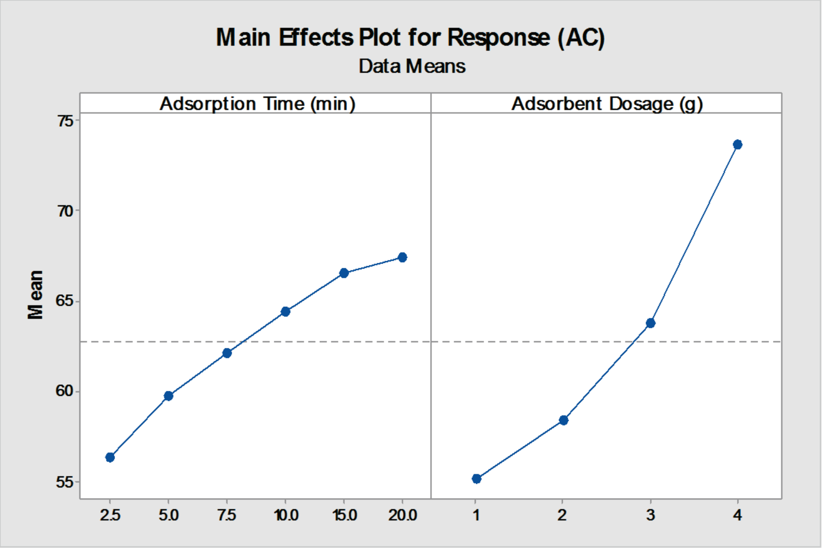


Figure 4.7: Main effect plot for biogas purity using AC.

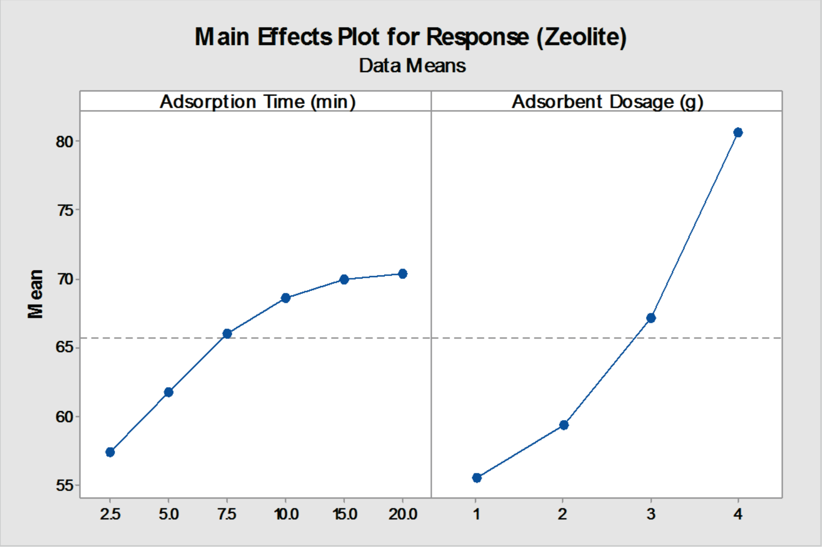


Figure 4.8: Main effect plot for biogas cleaning using zeolite CBV 8014.

Figures 4.7 and 4.8 are the major effect plot for the purification of biogas. The key effect plot was used to inspect the difference between height mean for one and more factors. It is alleged that there is a core effect when different factor levels affect the reaction in different manner (Montgomery, 2004). From Figures 4.7 and 4.8 it was practically seen that the mean responses increase a little from 15 – 20 min for both adsorbents. This implies that increase in time will not have major effect on the mean reaction which is in agreement with the result of Alhassan *et al*. (2017) which shows that impurity adsorption flattens when the time increases beyond 20 min using un modified sugarcane bagasse AC (UMAC), acid modified sugarcane bagasse AC (AMAC) and base modified sugarcane bagasse AC (BMAC). This could be attributed to the adsorbent reaching its highest adsorption capacity. The adsorbent quantity is the major parameter in biogas purity. Mean response increases almost linearly as the adsorbent dosage increase from 2 – 4 g which could be accredited to the accessibility of more adsorption spot Alhassan *et al*. (2017). However, there was no significant increase observed from 3 – 4 g of adsorbent, which may be due to the adsorbent reaching equilibrium.

From Table 4.6 and 4.7, it can be observed that the quadratic, interaction and linear term of the model equation for biogas upgrading using the adsorbents AC and zeolite CBV 8014 have major effect (p less than 0.05). and also the VIF values is gives the correlation of the predictors. The VIFs are not up to one, but higher values indicates that the predictors are well correlated. VIFs are high due to the interaction terms which are in-line with main effect terms which include the major effects terms. This also shows that the biogas improving model which was developed in Equation 4.2 and 4.3 well fit in the experimental data.

Residual design was also used to analyze the experimental and predicted responses. Residual design presents the differences among the experimental and predicted values. Figure 4.9 and 4.10, it was observed that the point in residual plot are at random dispersed around the vertical axis, this means that a linear regression will appropriate for the data, this shows that it is good for linear model (Alhassan *et al*., 2016).

The plot of normal probability is used to evaluate may be a data set is about normally distributed. For a model to be good, its residual will be normal and near to the straight line plot with little or no deviation from the line. Figure 4.9 and 4.10 can be seen as the residual plot for both adsorbents are normal and nearer to the straight line design, this indicates a good model. Figure 4.9 and 4.10 explain the values following a predicted value which designate that the model are accurate.

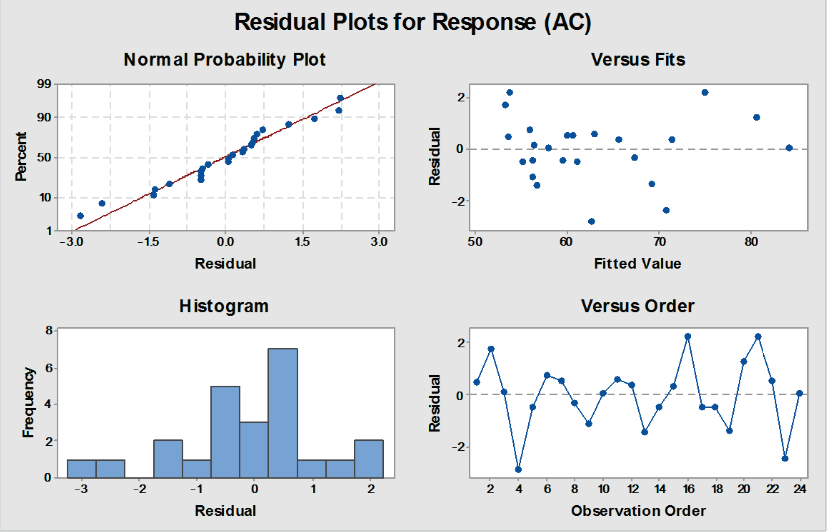


Figure 4.9: Residual plots using AC Adsorbent

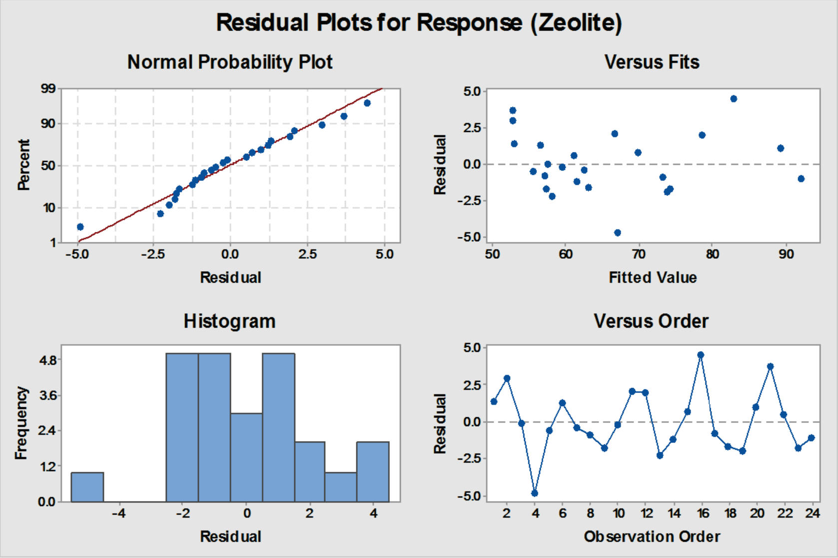


Figure 4.10: Residual plots using zeolite CBV 8014 Adsorbent

Histogram gives an irregular sense of the density of arithmetical data. The residual histogram was used to determine may be the data are skewed or may be outliers be in the data. Figure 4.9 and 4.10, shows that the histogram of residuals depicts that the residuals are evenly distributed.

Residuals against fits plot are used to confirm the assumption that the residuals have a stable variance. Residual vs fits plot is a spread out plot with residual on the vertical axis and fit on the horizontal axis. The biogas purity data (Figure 4.9 and 4.10) illustrate that the errors are randomly spread about zero which shows that the residual are not biased and well fitted. The result of this studies are in conformity with the null hypothesis in which the residuals have a stable variance (Alhassan *et al*., 2016).

Surface plot was employed to explore the connection between three variables on a single plot and to observe the combinations of x and y factors that generate desirable response values. A typically 3D surface plot consists of an x-axis and y-axis representing values of a continuous predictor variable. The surface plot for the upgraded biogas using adsorbent and adsorption time of 0 – 20 min and adsorbent of 1 – 4 g were presented in Figure 4.11 and 4.12. From Figure 4.11, it can be seen that the maximum biogas purity obtained with AC was at 20 min and 4g AC while for zeolite CBV 8014, the maximum pure biogas was found at the same 20 min and 4g AC (Figure 4.12). Figure 4.11 and 4.12 show that the adsorption time of 20 min and AC adsorbent dosage of 4g with a composite desirability of 0.999048 is required to maximize CH_4 composition for adsorption period of 20 min and the zeolite adsorbent dosage of 4g with a composite desirability of 0.999048, is required to maximize CH_4 composition.

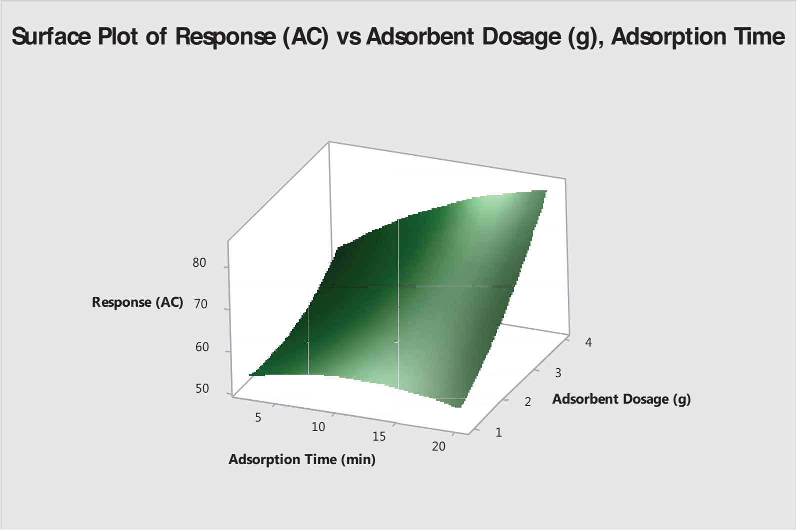


Figure 4.11: 3D Surface plot for AC Adsorbent

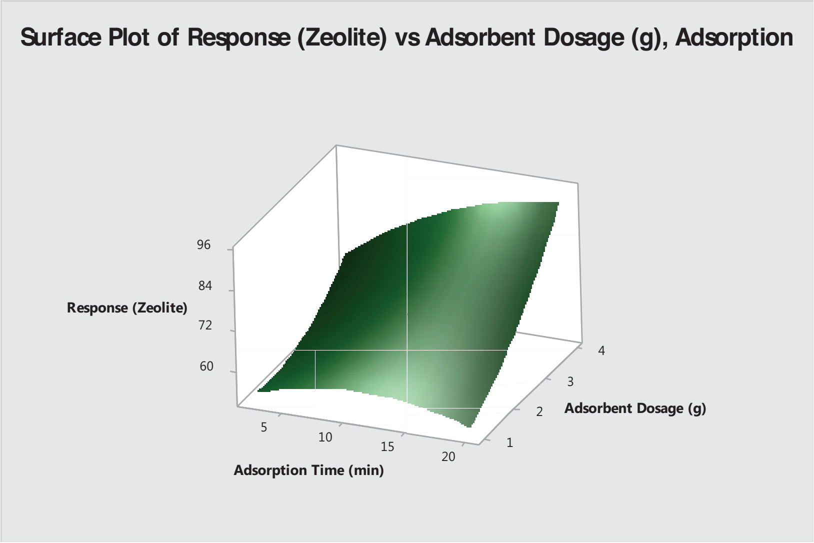


Figure 4.12: 3D Surface plot for zeolite CBV 8014

4.5 *Carbon (iv) oxide Adsorption Capacity*

Adsorption profile for the adsorbents were generated from the adsorption capacity data generated from the adsorption experiment using Equation 3.1. The data generated were presented in Appendix A and B. Figure 4.13 and 4.14 shows the adsorption profiles for different adsorbent quantity (1 g – 4 g)for both the AC and CBV 8014 zeolite. Figure 4.7 and 4.8 shows that adsorption of carbon (iv) oxide and other gases increases from 0-20 minutes. The rate of adsorption of CO_2 and other gases increases for both adsorbent up to a time of 10 min. A sharp and linear increase was noticed at 0 –10 min for all adsorbent dosage which then tends to flattens as the time increases from 10–20min.This is in conformity with the report of Alhassan *et al*.(2017) that CO_2 adsorption increases sharp at 5–20 min using UMAC,AMAC and BMAC.

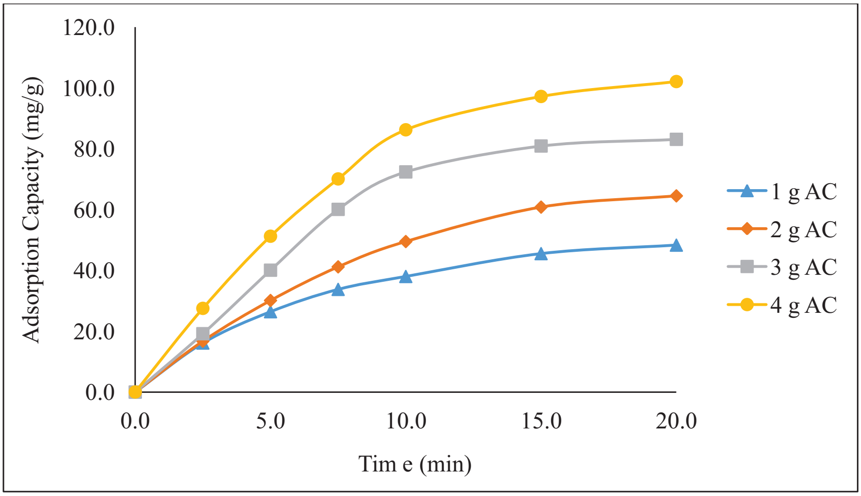


Figure 4.13: CO_2 adsorption capacity in AC

The adsorption rate of CO_2 slowly reduced from 10 – 20 min, this may be as a result of the adsorbents reaching its saturation or highest adsorption capacity. on the other hand, the speedy adsorption rate was seen at interval of 0 – 10 min while sluggish adsorption rate was noted from 10 – 20 min which could be credited to sorbent surface area been high and the micro porosity of the adsorbents(Table 4.2) which is responsible for interaction with the CO_2 and other few molecules. over time from 15 – 20 min, the adsorption rate is seen to be on the decrease because of the reduction in active sites which can reduce the adsorption process from taking place. In addition, Li *et al*. (2008) suggests that the quick adsorption at the start of the process maybe due to adsorbents external surface and is often followed by slower sinner diffusion process.

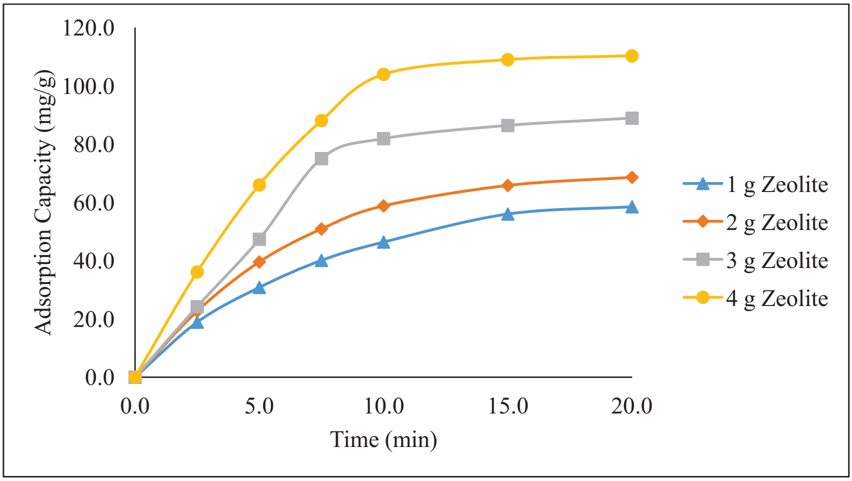


Figure 4.14: CO_2 adsorption capacity in zeolite CBV 8014.

From Figures 4.13 and 4.14, it was also seen that adsorption of CO_2 was in the order CBV 8014 zeolite greater than AC, which means that at every quantity, the adsorption capacity of CBV 8014 zeolite is greater than that of AC investigated. This high adsorption capacity observed from CBV 8014 zeolite could be attributed to its high affinity for the adsorption of the impurity gases (CO_2, CO, O_2 H_2 and H_2S) present in the biogas (Goj *et al*., 2002). This makes it satisfactory for the CO_2 to penetrate into the zeolite and AC pores. Consequently, from Figure 4.13 and 4.14, it was obvious that the adsorption rate in CBV 8014 zeolite are greater than in AC.

4.6 The Kinetic Adsorption Study

Adsorption kinetic study establishes an adsorption process rate and the residence time will be examine for the completion of the adsorption process. This is the baseline for the determination of the adsorption process and its performance in actual application. The Lagergren's pseudo first and second order model was really carefully examined in this study. The consistence of the experimental study and the kinetic model were carefully analyzed using the R^2 values. moreover, Arrhenius equation was employ to calculate approximately the activation energy of the adsorption process and again to find out if this adsorption process obeys the intra-particle diffusion model.

4.6.1 Lagergrens pseudo first-order model

Pseudo-first-order model is the model that was used to test the adsorption kinetics for the system with Equation 3.2 to estimate the adsorption dynamics. Straight line graph of log ($q_e – q_t$) vs time (t) at various adsorbent 1g – 4 g for both adsorbents was carried out using the adsorption data presented in Appendix A and B. The kinetic parameters were generated using the pseudo-first-order model as shown Table 4.8. It was practically seen that the first-order kinetic model for the adsorbents fit well with the experimental figures, with R^2 value gotten to be within the range of 0.913 - 0.9935 for AC and 0.868 to 0.9704 for zeolite. This means that AC obeyed the pseudo-first-order model very well compared to that of zeolite.

Table 4.8: The pseudo-first-order model kinetic datas

Adsorbent	*Parameter*	*1 g*	*2 g*	*3 g*	*4 g*
AC	K_1 (min^{-1})	0.0299	0.0491	0.0852	0.1895
	R^2	0.913	0.962	0.9358	0.9935
Zeolite	K_1	0.0364	0.0468	0.0824	0.2176
	R^2	0.9266	0.8987	0.868	0.9704

The straight line graph of log (qe-qt) vs time (t) gave the Lagergren's pseudo-first-order plot in Figure 4.15 and 4.16 for the adsorbents respectively. From Figure 4.15, it was seen that all AC adsorbent dosage goes in-line with the pseudo-first-order model. However, at dosage of 4g (13 cm) AC, the pseudo-first-order model fit well with the experimental data, with R^2 value of 0.9935. Likewise, for zeolite CBV 8014 adsorbent (Figure 4.12), at dosage of 4g (13 cm), the pseudo-first-order model fit well with the experimental data, with R^2 value of 0.9705

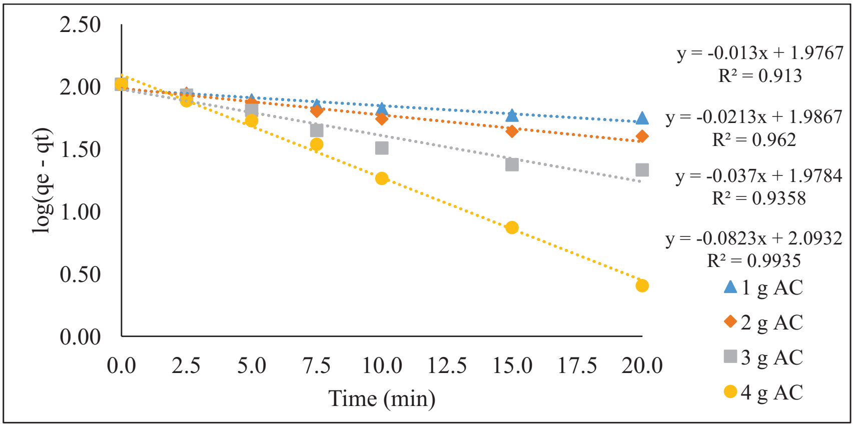


Figure 4.15: Pseudo-first-order kinetic model of AC CO_2 adsorption.

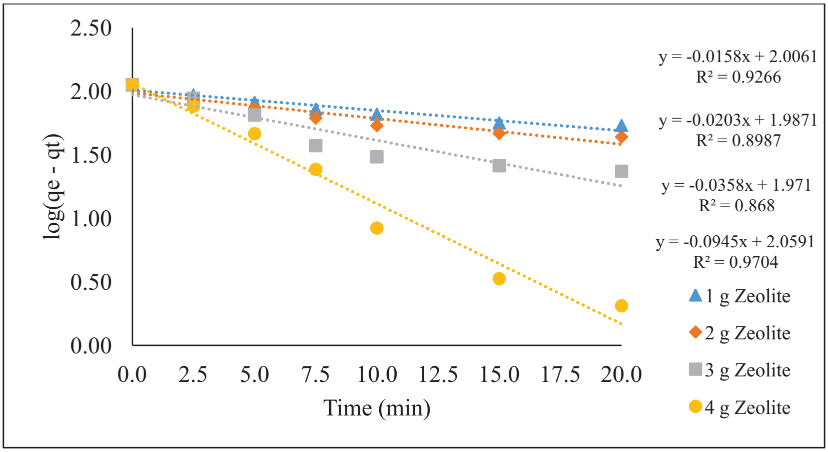


Figure 4.16: Pseudo-first-order kinetic model of CBV 8014 zeolite CO_2 adsorption.

The adsorption rate constant K_1 for the first order of the adsorbents are presented in Table 4.8, it was practical seen that K_1 for zeolite CBV 8014 are > that of the AC. though, K_1 for both adsorbents favorably compared with K_1 values of 0.097, 0.1252 with 0.1140 reported for adsorption of CO_2 using UMAC, AMAC and BMAC respectively (Alhassan *et al*., 2017).

4.6.2 Lagergren's pseudo-second-order model

The pseudo-second-order model was as well used to carry-out the adsorption studies of the system by means of Equation 3.3 to further assess the adsorption dynamics. Plot of 1/qt vs time (t) was made at different adsorbent dosage for both adsorbents using the adsorption figures in Appendix A and B. The kinetic parameters that was obtained were presented in Table 4.9. It was observed that the pseudo-second-order kinetic model for AC at 1 g, 2 g and 4 g correlate with the experimental value, with R^2 value gotten to be at the range of 0.8668 to 0.9982. similarly for zeolite CBV 8014, it was seen that the second-order kinetic model of 1 – 4g adsorbent dosage is in line with the experimental data, with R^2 rate of 0.9017– 9951.

Table 4.9: Pseudo-second-order model kinetic data

Adsorbent	*Parameter*	*1 g*	*2 g*	*3 g*	*4 g*
AC	K_2 (min^{-1})	0.00187	0.00070	0.00050	0.00056
	R^2	0.9982	0.9827	0.8668	0.9621
Zeolite	K_2	0.00136	0.00149	0.00085	0.00100
	R^2	0.9951	0.9882	0.9017	0.9621

The straight line gaph of 1/qt against time (t) gave the Lagergren pseudo-second-order plot in Figure 4.17and 4.18 for the adsorbents . From Figure 4.17, it was seen that at 1 – 4 g AC dosage well obeyed the pseudo-second-order model with R^2 value of 0.9982, 0.9827 and 0.9621 respectively. Likewise for zeolite CBV 8014adsorbent (Figure 4.18), at dosage of 1 – 4 g, the pseudo-second-order model correspond well with the experimental data, with R^2 value of 0.9951, 0.9882, 0.9017 and 9621 respectively.

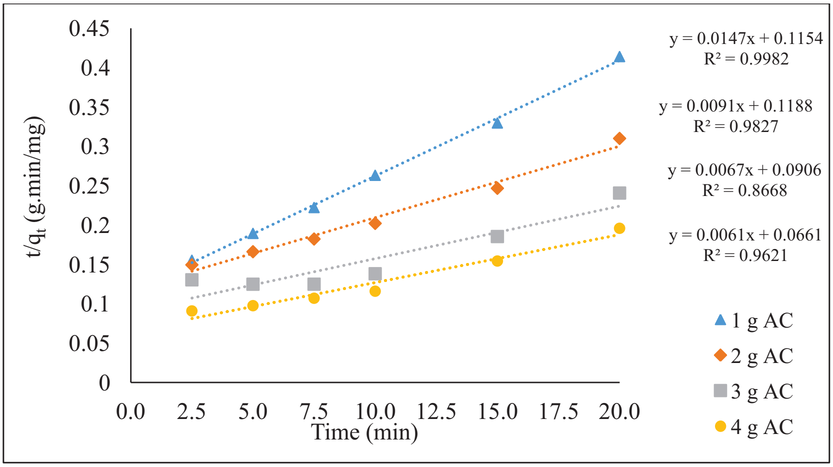


Figure 4.17: Pseudo-second-order kinetic model of AC CO_2 adsorption.

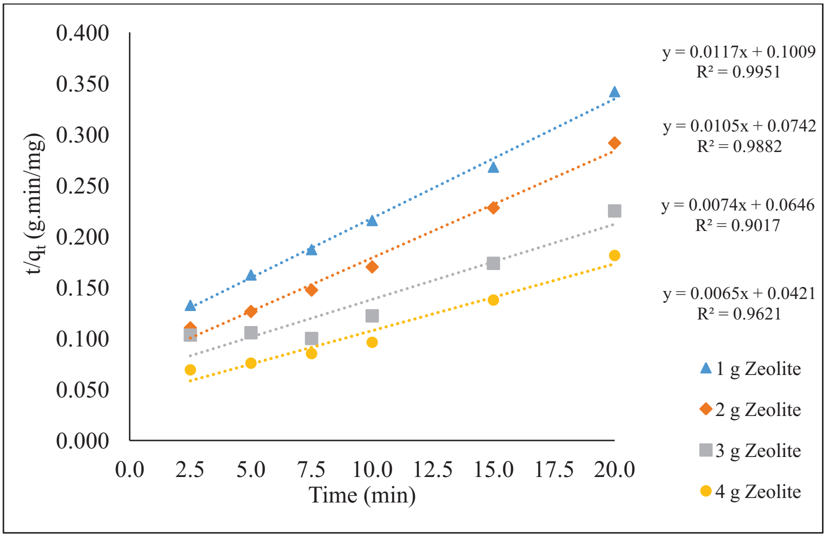


Figure 4.18: Pseudo-second-order kinetic model of zeolite CBV 8014 CO_2 adsorption.

The adsorption rate constants for the second order for the adsorbents are presented in Table 4.9. It was practically observed from Table 4.9, that zeolite K_2 are higher than that of the AC. conversely, K_2 for both AC and zeolite compared positively with K_2

values of 0.0105, 0.0052 and 0.0042 for an adsorption time interval of 0 – 25 min reported for CO_2 adsorption with UMAC, AMAC and BMAC respectively. (Alhassan *et al*., 2017).The study showed that the pseudo second order kinetics replica for AC and zeolite CBV 8014 well fitted the CO_2 adsorption kinetics data than pseudo first order kinetics model. This is because pseudo-first-order model R^2 value for both AC and zeolite CBV 8014 is within the range of 0.95– 0.998,while pseudo-second-order model R^2 value for both AC and zeolite CBV 8014 is 0.8668 –0.9982. Also it was observed from the same Figure 4.17 and 4.18 that the adsorption profiles has two regions. The first steeper region can be attributed to the surface sorption while the second region can be attributed to intra-particle diffusion. In this case, the rate of adsorption can be said to be controlled by intra-particle diffusion, since the gradient did not pass through the origin. The observation also predict that the whole adsorption process is diffusionally control and not kinetically controlled (Alhassan et al, 2017)

4.6.3 Activation energy

In adsorption procedure, the scale of the activation energy (E_a) is very important, as it gives information on adsorption mechanism .Value of E_a for physical adsorption are generally in the range of 5 – 40 kJ/mol. nevertheless, chemisorption process involves development of strong bonding linking the adsorbate (CO_2) and adsorbent through activation energy within the range of 40 – 800 kJ/mol (Özcan *et al*., 2006). Arrhenius equation that was shown in Equation 3.5 was used to calculate the Ea of the adsorption process. Table 4.10 clearly shows the activation energy for both adsorbents that was used in this research for CO_2 adsorption.

Table 4.10: Activation energies for CO_2 adsorption on AC and zeolite

Adsorbent	*Parameter*	*1 g*	*2 g*	*3 g*	*4 g*
AC	E_a (kJ/mol)	14.37	17.12	19.23	17.84
Zeolite CBV 8014	E_a (kJ/mol)	15.71	16.18	18.30	17.14

From Table 4.10, it was seen that the E_a rate for this research fall in between 5 – 40 kJ/mol for physiosorption processes which agrees well with the values reported in the literature (Özcan *et al*., 2006). The lower E_a obtained in this work shows that the CO_2 adsorption on both adsorbents are diffusion-controlled process not chemically-controlled process. The results gotten from this study were a little higher than 5.77, 13.02 and 13.55 kJ/mol that was reported for UMAC, AMAC and BMAC respectively (Alhassan *et al*., 2017). But compare positively with 17.51 and 14.27 kJ/mol that was reported for commercially and optimized available AC respectively (Rashid *et al*., 2013).

4.6.4 The intra-particle diffusion model

The intra-particle diffusion replica rate processes are usually presented with respect to square root of time. Comparing the Lagergren pseudo-first-order and pseudo-second-order model, its obvious that intra-particle diffusion model provides more clarity on adsorption mechanism process. Adsorption consists of little steps involving the transfer of adsorbate away from the bulk part to the exterior surface of solid sorbent, and followed by molecules diffusion into the inner pores. Intra-particle diffusion, usually is a rate-limiting step in most adsorption processes described as a time-consuming process. A plot of qt vs square root of time give the intra-particle rate constant. Figure 4.19 and 4.20 present the intra-particle diffusion model for this study.

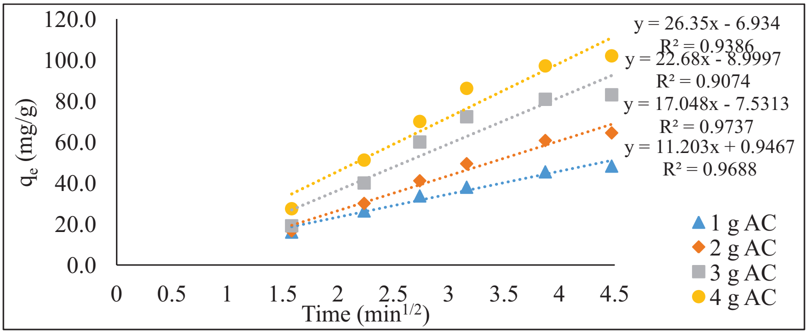


Figure 4.19: Intra-particle diffusion model for CO_2 adsorption using AC.

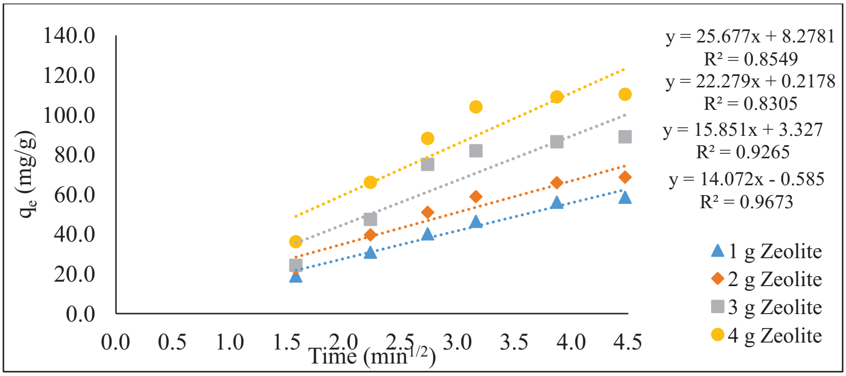


Figure 4.20: Intra-particle diffusion model for CO_2 adsorption using zeolite CBV 8014.

Theoretically, for an adsorption process to obey the intra-particle diffusion replica, a straight linear plot that start from the origin is expected. However, Figure 4.19 and 4.20 obviously shows variation of incline with respect to time. From Figure 4.19 and 4.20, two regions was observed, the first steeper area at 2–3 $min^{1/2}$ might be due to the surface sorption. And the second area at 3 – 4.5 $min^{1/2}$ may be due to the intra-particle diffusion rate controlled (Rashidi *et al*., 2013). However, as the gradients did not start the from origin, it implies that intra-particle diffusion is not the only rate-limiting step in this adsorption study. This observation is in conformity with the report of Alhassan *et al*. (2017). This confirms the observations from the first order and second order kinetic model and the estimated E_a.

Table 4.11: The rate constants for intra-particle diffusion for CO_2 adsorption in zeolite and AC.

Adsorbent	*factor*	*1 g*	*2 g*	*3 g*	*4 g*
AC	k_{id} (mg/g.min$^{1/2}$)	11.203	17.048	22.68	26.35
Zeolite CBV 8014	k_{id} (mg/g.min$^{1/2}$)	14.072	18.892	26.914	25.677

From Table 4.11, it was obvious that the intra-particle diffusion rate constant of the carbon (iv) oxide adsorption in zeolite are high at all quantity than that of the AC. This means that the intra-particle diffusion rate in zeolite is higher compared to that of AC.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

Biogas production from the blended mixture of chicken droppings and cow dung was carried out and the upgrading of the produced biogas by adsorbing CO_2 using AC and zeolite was studied. The biogas generated contains high methane gas with (53.76%), carbon (iv) oxide (33.44%) and other gases in minute quantity. This research shows the realism of using both AC and zeolite as adsorbent for CO_2 arrest in industrial applications. The structures of the surface of the adsorbents enable it to be most efficient in CO_2 trapping. From the adsorption kinetic study, the following conclusion are drawn:

1. Comparability in the carbon (iv) oxide adsorptions ability indicates the realism of the zeolite CBV 8014 and AC will be used in industrial applications.
2. The adsorption ability of the adsorbents was found to be in the order zeolite CBV 8014 greater than AC at 0 – 20 min and 1-4g adsorbent dosage
3. This kinetic study shows that the carbon (iv) oxide that was adsorbed into AC and zeolite CBV 8014 obeys the pseudo-second-order model, because of its R^2 value nearer to unity.
4. The kinetic study of carbon (iv) oxide adsorption onto of AC and zeolite shows that the size of E_a for both adsorbent are not up to 40 kJ/mol, signifying the occurrence of physical mechanism.
5. The study of intra-particle diffusion model shows that the intra-particle diffusion is the only rate-limiting step in this adsorption process for both adsorbents
6. Therefore, lower E_a obtain in this work prove that the CO_2 adsorption onto the adsorbents is a diffusion-controlled, but not chemically-controlled process.

5.2 Recommendations

From the study carried out, the following recommendations are made;

1. Further study should be carried out to investigate CO_2 adsorption capacity over a period of 0.5 – 2 hr.
2. Further study on the use of modified clay and bentonite should be investigated for feasibility of its use in CO_2 capture

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