DURBAN UNIVERSITY OF TECHNOLOGY

EVALUATION OF KAOLINITE AND ACTIVATED CARBON PERFORMANCE FOR CO_2 CAPTURE

by

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Submitted in fulfilment of the requirements for the degree of Master of Engineering: Chemical Engineering in the Faculty of Engineering and The Built Environment at the Durban University of Technology

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DECLARATION

I declare that this dissertation is my own unaided work. It is being submitted for the degree of Master of Engineering to Durban University of Technology, South Africa. It has not been submitted before for any degree or examination to any other University.

Akpasi, S. O.

Date: .....09 March 2021.....

CERTIFICATION

This is to certify that the work contained in the thesis entitled "**Evaluation of kaolinite and activated carbon performance for CO_2 capture**", submitted by **Stephen Okiemute Akpasi (Student No.: 21958199)** for the award of the degree of **Master of Engineering (MEng)** to the **Durban University of Technology, South Africa** is a record of original research works carried out by him under my direct supervision and guidance.

I consider that the thesis has reached the standards and fulfilling the requirements of the rules and regulations relating to the nature of the degree. The contents embodied in the thesis have not been submitted for the award of any other degree or diploma in this or any other university.

19 03 2021

Prof. Yusuf Makarfi Isa (Supervisor) Date

ABSTRACT

Global climate change is one of the major threats facing the world today and can be due to increased atmospheric concentrations of greenhouse gases (GHGs), such as carbon dioxide (CO_2). There is also an immediate need to reduce CO_2 emissions, and one of the potential solutions for reducing CO_2 emissions is carbon capture and storage (CCS). This work investigated the performance assessment of kaolinite and activated carbon (AC) adsorbent for CO_2 capture. In particular, the effect of operating parameters such as temperature, bed height, inlet gas flow rate etc. on CO_2 adsorption behaviour of the adsorbents was also investigated. Extensive research on the development of adsorbents that can adsorb large amounts of CO_2 with low energy consumption has recently been carried out. In CO_2 adsorption technology, the challenge is to develop an adsorbent that is not only non-toxic, eco-friendly, and cost-effective, but also has the potential to extract CO_2 gas from a mixed gas stream selectively and effectively. Due to the possibility of a potential adsorbent due to its low cost, rich natural abundance and high mechanical and chemical stability, this study proposes kaolinite. As the presence of clay minerals in soils serves as a pollutant collector to enhance the atmosphere, kaolinite has the potential to be an efficient adsorbent for CO_2 capture. Kaolinite was investigated as an adsorbent in this research to confirm if it is suitable for CO_2 capture. Kaolinite/activated carbon composite adsorbents were synthesized. Sugarcane bagasse was used in preparing the activated carbon (AC). $ZnCl_2$ was impregnated onto sugarcane bagasse during the preparation of activated carbon (AC) to improve the physical properties (surface area, pore size and pore volume) and the CO_2 adsorption capacity of the activated carbon (AC) adsorbent developed. The materials were characterized and tested for CO_2 adsorption (activated carbon and kaolinite). BET, FTIR and SEM studies were used to classify the adsorbents for their surface area and pore properties, functional groups, and surface morphology, respectively. BET analysis was conducted and the pore volume, pore size and surface area of the adsorbent materials were reported. Functional groups were actively present in the adsorption process. This was verified using FTIR spectroscopy. The kaolinite adsorbent was not feasible for CO_2 capture. BET, SEM, and custom-built CO_2 adsorption equipment have confirmed this. In contrast to literature, the CO_2 adsorption capacity of kaolinite was low. This is due to the fact that kaolinite used in this study is not suitable as adsorbent for CO_2 capture as they exhibited a low CO_2 adsorption capacity. The results obtained in this study show that temperature, bed height and inlet gas flow rate influenced the adsorption behaviour of activated carbon (AC), kaolinite and kaolinite/activated carbon composite adsorbent during CO_2 capture. At 30 ºC,

activated carbon (AC) exhibited an adsorption capacity of 28.97 mg CO_2/g, the highest capacity among all the adsorbents tested. Kaolinite-activated carbon composite adsorbent offered CO_2 adsorption capacities of 18.54 mg CO_2/g. Kaolinite provides the lowest capacity of 12.98 mg CO_2/g. In conclusion, this research verified that CO_2 adsorption with kaolinite and activated carbon is favoured at low temperatures, low operating CO_2 flowrates and high column bed height.

ACKNOWLEDGEMENTS

Life itself is a journey, and according to a popular English saying, "*the journey of a thousand mile begins with a step".* When one embarks on a journey of this kind in search of knowledge, it is normal and natural to come across some benefactors. In the light of the above, my profound gratitude goes to God almighty the giver of life, the helper to the fatherless, his greatness no one can fathom, the one who is able to do immeasurably more, and my strong deliverer who sustained me throughout my postgraduate studies at the Durban University of Technology. He is indeed the creator of heaven and earth and 'El-Shaddai' is his name. You are my chief benefactor Lord, and I am a debtor of your grace and mercies.

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Lastly, I would like to acknowledge all those that I cannot name individually who contributed to this project materially or otherwise. Without you all, this project would not have been a success.

PUBLICATIONS AND PRESENTATIONS

A few conference papers and journal have emanated from this research project and are as listed below:

Publications:

1. **S.O Akpasi, Y.M Isa,** (2020). Carbon dioxide Capture and Sequestration: A Review. *Manuscript in preparation.*
2. **S.O Akpasi. Y.M Isa,** (2020). Preparation and characterization of adsorbents for CO_2 adsorption. *Manuscript in preparation.*
3. **S.O Akpasi. Y.M Isa,** (2020). Effect of operating variables on the CO_2 adsorption capacity of kaolinite and activated carbon. *Manuscript in preparation.*

Conference presentation and proceedings:

1. **S.O Akpasi. Y.M Isa,** (2020). Preparation and characterization of adsorbents derived from sugarcane bagasse and kaolin clay for CO_2 capture. **Oral presentation**. 5^{th} Interdisciplinary Research and Innovation Conference 2020, 15^{th} – 17^{th} September, Durban, South Africa.
2. **S.O Akpasi. Y.M Isa,** (2020). Preparation and characterization of adsorbents for CO_2 adsorption. **Oral presentation**. 18^{th} Johannesburg International Conference on Science, Engineering, Technology & Waste Management 2020, 16^{th} – 18^{th} November, Johannesburg, South Africa.
3. **S.O Akpasi. Y.M Isa,** (2021). Effect of operating variables on the CO_2 adsorption capacity of activated carbon, kaolinite, and kaolinite / activated carbon composite adsorbent. **Oral presentation**. Green Technologies for Sustainable Development (GTSD -2021), 9^{th} – 11^{th} March, India.

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NOMENCLATURE

AC – Activated carbons

ASU – Air Separation Unit

BET – Brunauer-Emmett-Teller

CCS – Carbon Capture and Storage

CCSTP - Carbon Capture and Sequestration Technologies

CMS – Carbon Molecular Sieves

CNT(s) – Carbon Nanotube(s)

CO – Carbon Monoxide

CO_2 – Carbon Dioxide

EOR – Enhanced Oil Recovery

EPA – Environmental Protection Agency

ESA – Electric Swing Adsorption

FTIR – Fourier Transform Infrared Spectroscopy

GDP - Gross domestic product

GHG – Greenhouse gas

HCl – Hydrochloric Acid

H_2 – Hydrogen

H_2O – Water

H_2S – Hydrogen Sulphide

IEA – International Energy Agency

IPCC – Intergovernmental Panel on Climate Change

IUPAC – International Union of Pure and Applied Chemistry

MEA – Monoethanol Amine

MOF(s) – Metal Organic Framework(s)

NaOH – Sodium Hydroxide

NASA - National Aeronautics and Space Administration

NH_2 – Amine Functional Group

NOAA - National Oceanic and Atmospheric Administration

N_2 - Nitrogen

O_2 – Oxygen

NOx – Nitrous Oxides

PEI - Polyethyleneimine

PM – Particulate Matter

PSA – Pressure Swing Adsorption

RSM – Response Surface Methodology

SACCCS – South African Centre for Carbon Capture and Storage

SCADA - Supervisory Control and Data Acquisition

SEM – Scanning Electron Microscopy

SOx – Sulphur Oxides

SO_2 – Sulphur Dioxide

TSA – Temperature Swing Adsorption

UN – United Nations

UNFCCC – United Nations Frameworks Convention on Climate Change

USA – United States of America

VSA – Vacuum Swing Adsorption

$ZnCl_2$ – Zinc Chloride

CHAPTER ONE

Introduction

1.1 Background and Motivation

Environmental problems related to enormous fossil fuel consumption are raising serious global concerns today; especially carbon dioxide emissions, a significant anthropogenic greenhouse gas that results in global warming that causes global climate change (Chu *et al.* 2016). Human activities increase the chemical composition of the atmosphere with carbon dioxide, methane and chlorofluorocarbons, and this aggravates the increase in greenhouse effect (Barbalace 2006). Modern methods of energy production that do not utilize fossil fuels, including nuclear electric power and various types of renewable energy including solar and wind power have been developed since the transition in industry. Figure 1.1 produced by the International Energy Agency (IEA) in 2015 and covers a period of 1971 to 2013, compares the energy supplied by fossil fuels to non-fossil fuels worldwide (Heubaum and Biermann 2015). Non-fossil fuel energy generation methods still do not feature significantly for an energy generation. Consider that in 1971, 86 % of energy was produced from fossil fuels and in 2013 this decreased only slightly by 1 % to 82 % (Heubaum and Biermann 2015). Despite the development of non-fossil fuel energy generation methods, the proportion of energy provided by fossil fuels has not been substantially reduced.

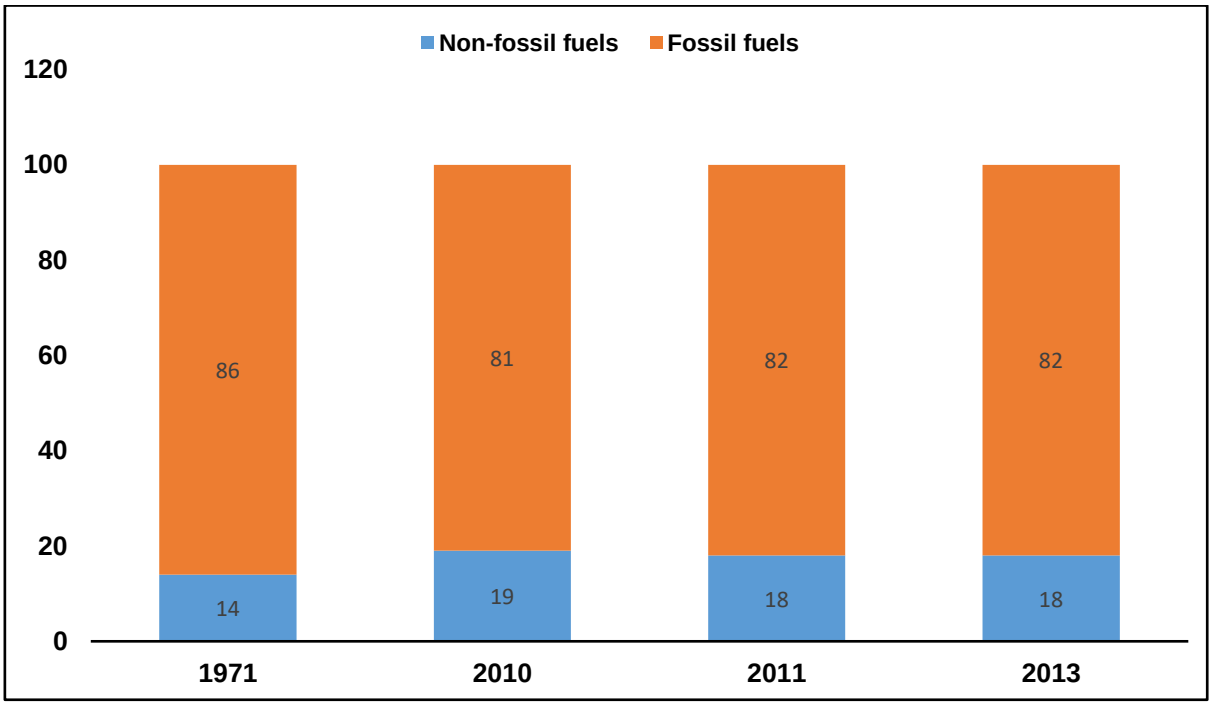

Figure 1.1: World energy supply proportions (Adapted from International Energy Agency, 2015).

Carbon dioxide's life span as a greenhouse gas can be up to 200 years. The most common greenhouse gas released into the atmosphere in significant quantities is considered to be CO_2 (Lim *et al.* 2013). Carbon dioxide emissions can be minimized in two ways; by reducing the consumption of fossil fuels and moving towards technologies not emitting CO_2 or by capturing and storing the CO_2 produced to close the carbon cycle. The first approach would involve the introduction of alternative renewable energies or the improvement of current systems' energy efficiency. But the second approach may involve the introduction of technologies for carbon capture and sequestration. The second method that speculates that CO_2 capture is the best solution for reducing atmospheric CO_2 emissions is discussed in this report. In this context, adsorption technology is envisaged to be a viable technology for CO_2 capture.

According to the International Panel on Climate Change (IPCC) Studies, global CO_2 emissions are predicted to be increased by the IPCC by at least 50 percent in 2007 by reducing global warming or restricting global average temperatures to 2 °C by 2050. South Africa depends heavily on coal to generate electricity (Comfort 2017). In 2013, 72% of the primary energy in South Africa came from coal and the rest from natural, nuclear, petroleum and renewable sources. (see Figure 1.2) (EIA, 2015).

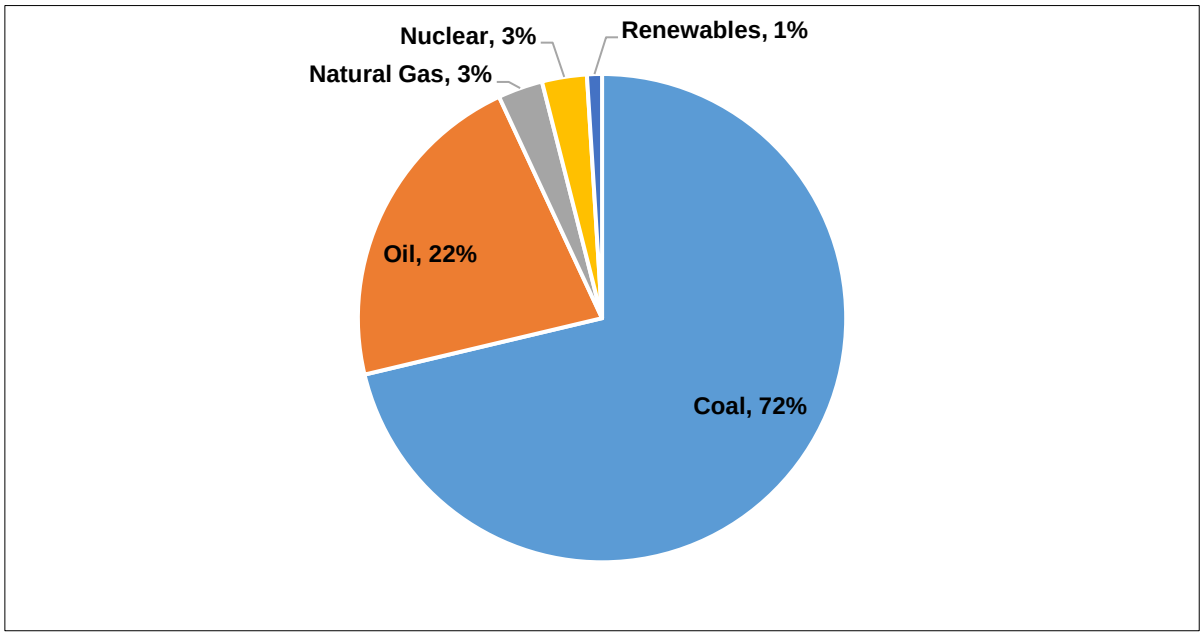

Figure 1.2: South Africa's total primary energy consumption, 2013 (adapted from EIA (2015))

To date, coal provides approximately 90 % of the energy needs of South Africa (Comfort 2017). In the next decade, due to the inherent lack of viable options to coal as a source of energy, this is unlikely to change significantly (Eskom, 2015). For power generation, coal is incinerated.

These activities release significant amounts of atmospheric carbon dioxide (CO_2). CO_2 significantly emits greenhouse gases, creating the greenhouse effect, that is considered to be the primary contributor to global warming. Consequently, global warming leads to climate change and environmental hazards. A lot of work has been done to focus on reducing the quantities of CO_2 discharged into the atmosphere. In view of this, a range of options that could help reduce CO_2 emission into the atmosphere is being considered worldwide and this includes carbon capture and storage (CCS). CCS is regarded as the foremost and proper way to lessen atmospheric carbon emissions (Yoro 2017). Currently, CO_2 capture via adsorption technology has drawn keen attention globally contributing to relatively low energy consumption, and the high purity CO_2 streams it produces (Serna-Guerrero and Sayari 2010). Consequently, a variety of adsorbents have been developed and evaluated for such purposes (Choi, Drese and Jones 2009).

Adsorbents play a very significant role in any CO_2 capture process that uses the adsorption technology. For instance, in vacuum swing adsorption technology, the type of adsorbent determines the overall CO_2 capture performance (Chaffee *et al.* 2007). An effective adsorbent for CO_2 capture must have a high capacity to adsorb CO_2 in any industrial application, good selectivity as well as easy regeneration of adsorbents with less energy requirement and a rapid CO_2 adsorption rate i.e. fast kinetics of adsorption (Song *et al.* 2016). In addition, satisfying these requires a deep and proper knowledge of the behaviour of the adsorbent via the CO_2 capture process. On this note, the possibility of having cost-effective and efficient adsorbents for post-combustion CO_2 capture needs to be examined. The work presented in this dissertation was targeted at investigating the CO_2 adsorption behaviour of kaolinite and sugar cane bagasse based activated carbon for CO_2 capture using adsorption column and experimental approaches.

1.2 Mitigation of Climate Change

During the United Nations Framework Convention on Climate Change (UNFCCC) in Cancún in 2010, the rise in mean global surface temperature was debated. The conclusion from this conference was that it is necessary to avoid such dire climate change consequences and to sustain our current lifestyle. To do this the global mean surface temperature rise must be stabilized at 2 °C. The Paris Agreement, from COP 21 in Paris 2015 raised this agreement to 1.5 °C. To have at least a 50 % chance of meeting this target, the ambient CO_2 concentration should be kept below 450 ppm (UNFCC, 2010). If target of maintaining the atmospheric CO_2

concentration to below 450 ppm is to be realized it is crucial to implement a plan of action to combat CO_2 emissions immediately.

The IEA (International Energy Agency) has laid out an energy deployment system which is published in Energy Technology Perspectives 2015. That gives a pathway and emissions trajectory that will allow this target to be reached. The perspective only allows for a cumulative emission levels of approximately 1 000 Gt CO_2 from 2013 to 2050. The perspective identifies changes that need to be made to reduce emissions.

Figure 1.3 graphically depicts this energy deployment system. These changes show that switching to renewables could be used to reduce emissions by 32 %, increasing efficiency in power generation and fuel switching could be used to reduce emissions by 1 %, end use fuel switching could be used to reduce emissions by 10 %, end use efficiency could be used to reduce emissions by 38 %, nuclear power generation methods could be used to reduce emissions by 7 %. With all these changes in place it is still not possible to reduce emissions enough to reach target of maintaining the atmospheric CO_2 concentration below 450 ppm, particularly for developing countries who lack the financial support.

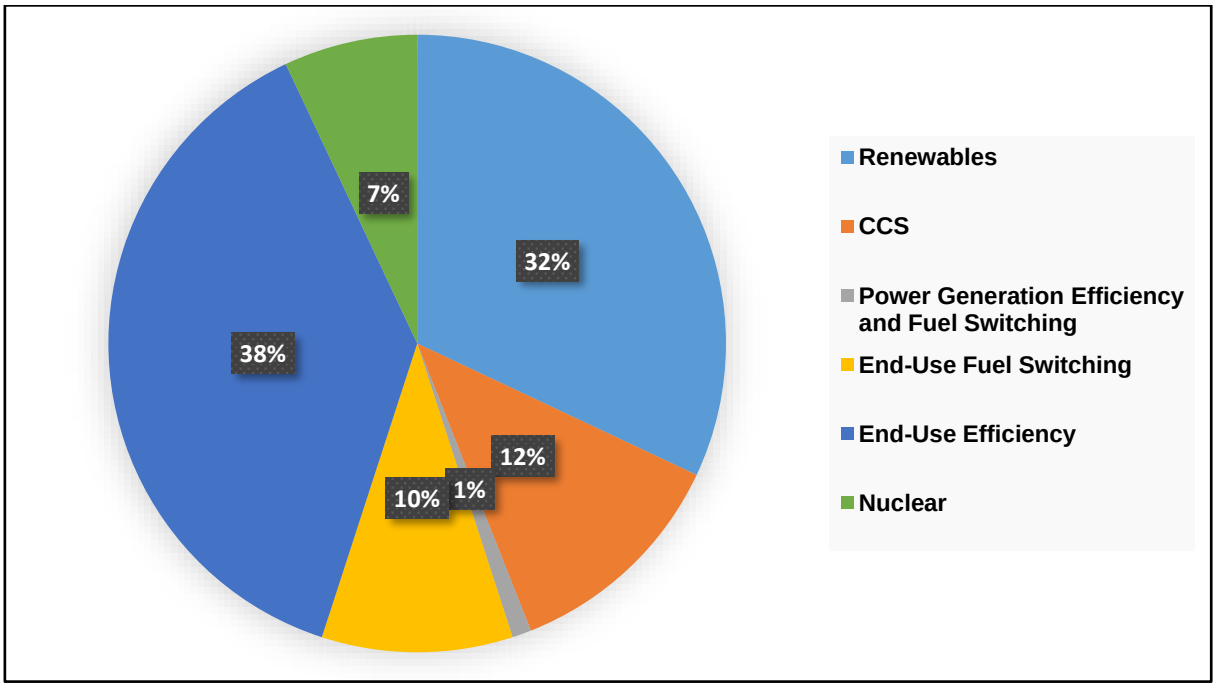

Figure 1.3: IEA Strategy to reduce CO_2 emissions (Adapted from (International Energy Agency, 2015))

Since as early as 1800, when coal was used in the Kimberly Diamond Fields, coal dominated the South African energy supply market. Eskom estimates that the combustion of coal in the 16

coal-fired power plants owned by the nation meets 77% of the country's primary energy needs. Eskom is the world's 7th largest producer of electricity (Eskom, 2015).

To put this into a worldwide CO_2 emissions perspective, in 2014 South Africa was reported to be the 12th most significant CO_2 emitter worldwide and it accounts for almost half of Africa's CO_2 emissions (Osler 2017). To meet energy demands, South Africa clearly relies on fossil fuels. Installation of two existing power plants powered by coal (Medupi and Kusile), it is uncertain that the country will be able to economically move away fossil fuels for energy generation soon enough to meet the target of maintaining CO_2 emissions.

To meet the CO_2 emissions target, the practice of venting anthropogenic CO_2 gas into the atmosphere needs to cease. With a lifestyle so dependent on energy and all the necessary infrastructure already in place to produce this from fossil fuels, this seems an impossible task. The Energy Deployment System creates a problematic situation for not only South Africa but also for other developing as well as developed countries. There becomes a need for a method of energy generation from fossil fuels that can avoid CO_2 emissions while still providing the advantages of fossil fuels. One proposed method is carbon capture and storage (CSS). For this method, CO_2 is captured from large sources, like power generation plants, and then stored for several years. CCS is widely considered the solution to this CO_2 emissions problem (International Energy Agency, 2016). The Energy Technology Perspectives 2015 laid out by the IEA and shown in Figure 1.4, thus incorporates CCS to reduce CO_2 emissions by a further 12% which will allow for the 450-ppm atmospheric CO_2 concentration target to be reached.

1.3 Possible Effects of Global Warming

According to Mustafa *et al.* (2020), there is no doubt that anthropogenic greenhouse gases (GHG's) would lead to global warming, as their atmospheric presence intensifies the greenhouse effect. However, the expansion of global warming and its effects remain unknown (Mustafa *et al.* 2020). The stabilization of GHG concentrations was called for by Mustafa *et al.* (2020) and the Intergovernmental Panel on Climate Change (IPCC) as a precaution as the consequences of climate change can be catastrophic in various regions of the world (Metz 2010). According to Tao *et al.* (2014), it is estimated that warming of the atmosphere might result in pest management challenges and ultimately food security issues; outbreaks in pests are expected particularly during periods of long drought with heavy rainfall following the drought. In China, there have been studies on wheat growth from 1981-2009, and the results from the study show that lengths of growth periods had significantly become shorter. This was correlated

to significant changes in the climate during the wheat growing period (Tao *et al.* 2014). From the aforementioned, mitigation of climate change causes is necessary as it will impact positively on food security in different regions. In addition, climate change could contribute to an increase in global surface temperatures, hydrological cycle changes, ocean acidification and an increase in mean sea levels. Greater occurrences of severe weather incidents, such as heavy rainfall, storm surges, and heat waves, amongst others (Mustafa *et al.* 2020). These harsh weather occurrences will most likely have impacts on supply and generation of power with detrimental effects on world economies and the growing global population (Chandramowli and Felder 2014). For the power plant production side of the power industry, warming temperatures may result in higher surface temperatures and higher cooling water temperatures which will lead to lower equipment efficiencies and lower equipment life spans (Chandramowli and Felder 2014). This will impact the consumers, with more power cuts being experienced as there will be production cuts due to insufficient production.

Water bodies on the planet such as oceans act as sinks for CO_2 and participate in the world carbon cycle (Czaun *et al.* 2013). If atmospheric CO_2 concentrations increase, much CO_2 dissolves into the bodies of water lowering water pH making the water acidic (Czaun *et al.* 2013). In oceans, coral reefs and shell making organisms are destroyed by the acidic water, leading to crumbling of food chains and possible extinction of some aquatic living organisms (Czaun *et al.* 2013). Mitigation of CO_2 emissions will therefore alleviate the destruction of such eco-systems. In addition, the predicted effects of rising atmospheric CO_2 concentrations have significant effects on the atmosphere and human well-being and will need strategies to minimize CO_2 emissions (Metz 2010).

1.4 Problem Statement

CO_2 emissions need to be reduced. South Africa's government has committed to using carbon capture and storage to minimize CO_2 emissions. The South African Centre for Carbon Capture and Storage (SACCCS) has been put in place to develop and implement the application of CCS in South Africa. Currently CCS has not been developed on a large scale in South Africa but is at the research stage with a particular emphasis on storage. SACCCS, the Council for Geosciences, and a few academic institutions are in charge of much of the research. There is a need to place more focus on the capture component as CO_2 must be captured before it can be stored.

Many distinct capture technologies are currently being researched worldwide. Most of these technologies are inefficient at capturing CO_2, are expensive, and have been shown to pose health risks (Pires *et al.* 2011). Resulting in CCS being economically unviable, especially for developing countries. For CCS to be applied on a large-scale industrial scale around the world, it is important to develop more acceptable capture technologies that are both cost effective and reliable.

CCS will only gain public acceptance and implementation in industry once it has been confirmed to be viable economically. There are many factors that affect the economic viability of CCS. One of these factors is the lack of inexpensive technology and high-performance materials for selective CO_2 separation from flue gas. For this reason, various novel materials for the post combustion CO_2 capture have been developed and studied (Osler 2017), (International Energy Agency, 2016). Examples of these are solvents for absorption, solid adsorbents for adsorption, materials for cryogenic separation and membranes for membrane separation. The most mature and established of the proposed technologies for CO_2 capture is chemical absorption utilizing liquid amine-based solvents (e.g., monoethanolamine (MEA)). The use of Amines can pose health risks when released into the air from CO_2 capture plants; although there are some disadvantages to this process, including the high energy requirements for the regeneration step and the high corrosivity of the amine species. As a result, a variety of potentially more efficient and energy-efficient second and third generation capture technologies have been proposed (Pires *et al.* 2011). Adsorption is one such technology that appears promising due to its low energy consumption, as well as its improved health and environmentally benign properties. This is due to the ability to work at mild temperatures and pressures. Recently, extensive research has been conducted on designing adsorbents that can adsorb large amounts of CO_2 with Low energy consumption while not posing additional health and environmental risks (Pires *et al.* 2011).

This study proposes kaolinite, a biodegradable non-toxic polymer as an adsorbent that has the potential to be one such material. The benefit of kaolinite is that it can retain significant quantities of CO_2, thus releasing it quickly after a brief period of heating. The most challenging aspect of using kaolinite as a starting material to synthesize competitive adsorbents for CO_2 capture processes is adjusting it to produce microporous adsorbents using low-cost methods. This problem is difficult to consider because kaolinite is a raw material where even a great amount of physiochemical and environmental parameters influences its formation and hence its textural properties, which are the main parameters of its capacity for CO_2 adsorption. However,

there is little information in open literature concerning the use of kaolinite for CO_2 capture. Against this background, this study aims at investigating kaolinite and activated carbon material for the selective post combustion capture of CO_2 and to study the effect of operating parameters on its adsorption capacity via custom-built CO_2 adsorption equipment.

1.5 Research Questions

This study aims to address the questions below.

1. How effectively can an adsorption experiment be used to describe the behaviour and performance of kaolinite and activated carbon as an adsorbent for CO_2 capture?

2. What is the effect of the operating parameters, including flow rate, operating temperature, and height of column bed on the adsorption capacity of kaolinite and activated carbon as an adsorbent during CO_2 capture?

3. What is the effect of activation parameters on the quality of activated carbon?

4. What is the actual rate of carbon dioxide capture capacity of various kaolinite and kaolinite -activated carbon systems?

1.6 Research Aims and Objectives of the study

The main aim of this study was to successfully evaluate the performance of kaolinite and activated carbon (AC) for CO_2 capture. Other objectives are:

- To prepare activated carbon (AC) from sugarcane bagasse
- To characterize the produced AC and kaolinite using relevant analytical techniques
- To investigate the effect of activation parameters on the quality of AC
- To investigate the effect of temperature, flowrate, and height of bed on CO_2 adsorption capacity
- To evaluate the carbon dioxide capture capacity of various kaolinite and kaolinite - activated carbon systems.

1.7 Dissertation Structure

The outline of this dissertation is provided below:

- **Chapter 1: Introduction and background of study**

A general introduction to the purpose is given in this section, motivations, aims and objectives of the completed work.

- **Chapter 2: Literature review**

The details of CCS are discussed in chapter 2. The history of CCS is considered and its current application. The concepts of CO_2 capture, compression, transports, and storage are considered with the focus being on CO_2 capture. Within the concept of CO_2 capture, different capture technologies are considered with an emphasis on post-combustion CO_2 capture via adsorption. The chapter then proposes kaolinite and activated carbon as both an alternative CO_2 capture adsorbent and explores these interesting materials.

- **Chapter 3: Materials and experimental procedure**

The details of the materials, equipment and experimental method that were utilized are discussed in chapter 3.

- **Chapter 4: Characterization and analysis of kaolinite and activated carbon and the effect on the CO_2 adsorption capacity of the operating variables.**

The results pertaining to the analysis and characterization of the activated carbon and kaolinite samples are discussed in chapter 4. The effect of the operational parameters on CO_2 adsorption capacity of the selected materials is also discussed in this chapter.

- **Chapter 5: General conclusions and recommendations**

In chapter 5, the general conclusions and recommendations are discussed.

CHAPTER TWO

Literature review

2.1 Introduction

Information on carbon capture and sequestration (CCS) are discussed in this section. The background of CO_2 emissions is being considered; the application of the CCS proceeded. With the primary focus on CO_2 capture and sequestration, the main sources of CO_2 emission are explained. Within the concept of CO_2 capture, different capture technologies are considered with an emphasis on post-combustion CO_2 capture via adsorption. The chapter then considers the factors that influence post-combustion CO_2 capture and the various types of adsorbents used in the context of adsorption. Finally, this chapter proposes activated carbon and kaolinite as potential adsorbents for post-combustion CO_2 Capture and explores these interesting materials.

2.2 History of CO_2 emissions

The amount of greenhouse gasses raised by human activity by 70% within 1970 to 2004 were emitted into the atmosphere Liu *et al.* (2011). Figure 1.2 was produced by the National Oceanic and Atmospheric Administration (NOAA), a division of NASA (National Aeronautics and Space Administration) and shows the average atmospheric CO_2 concentration from 1958 to January 2017 (NASA, 2016). The atmospheric CO_2 concentration reached 406.13 ppm in January 2017. The trend shows that there is an increase in atmospheric CO_2 concentration. If business continues as usual a further increase will be seen.

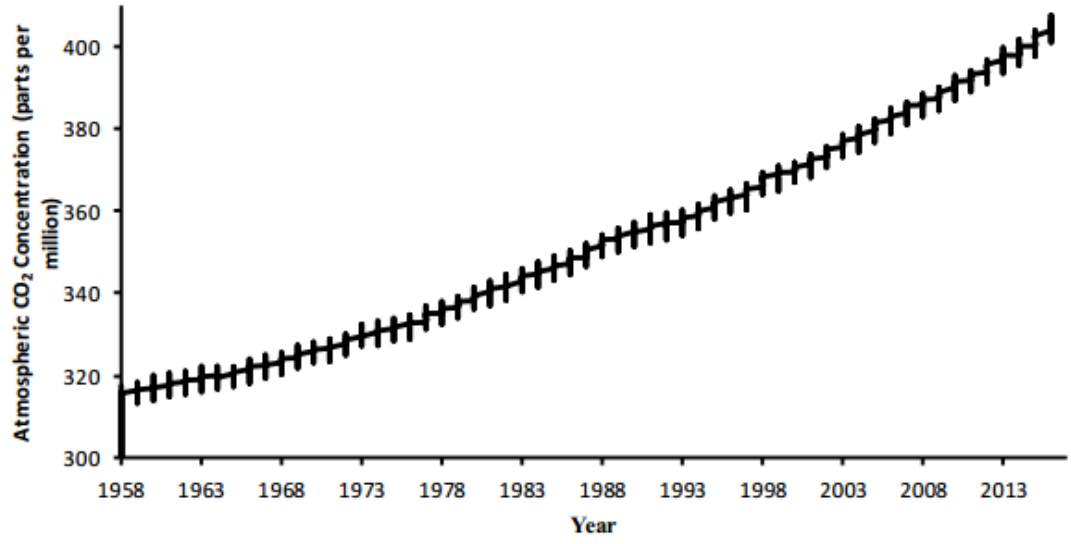

Figure 2.1: Atmospheric CO_2 concentration per year (Adapted from (NASA,2016))

The NASA Goddard Institute for Space Studies has systematically documented the Earth's surface temperature in the years after 1880 to measure the rise in average surface temperatures globally. Figure 2.2 shows the recorded mean global surface temperature from 1880 to present relevant to 1951 – 1980 average temperatures (NASA, 2016). The trend shows that the global average surface temperature is rising significantly. The most recent measurement shows that in 2016 the global mean surface temperature was 0.99 ºC warmer than the average temperature between 1951 – 1980. The Intergovernmental Panel on Climate Change (IPCC) predicts that if business proceeds as usual, anthropogenic GHG emissions will increase the mean global surface temperature by 6.4 ºC during the 21st century (Shao and Stangeland 2009).

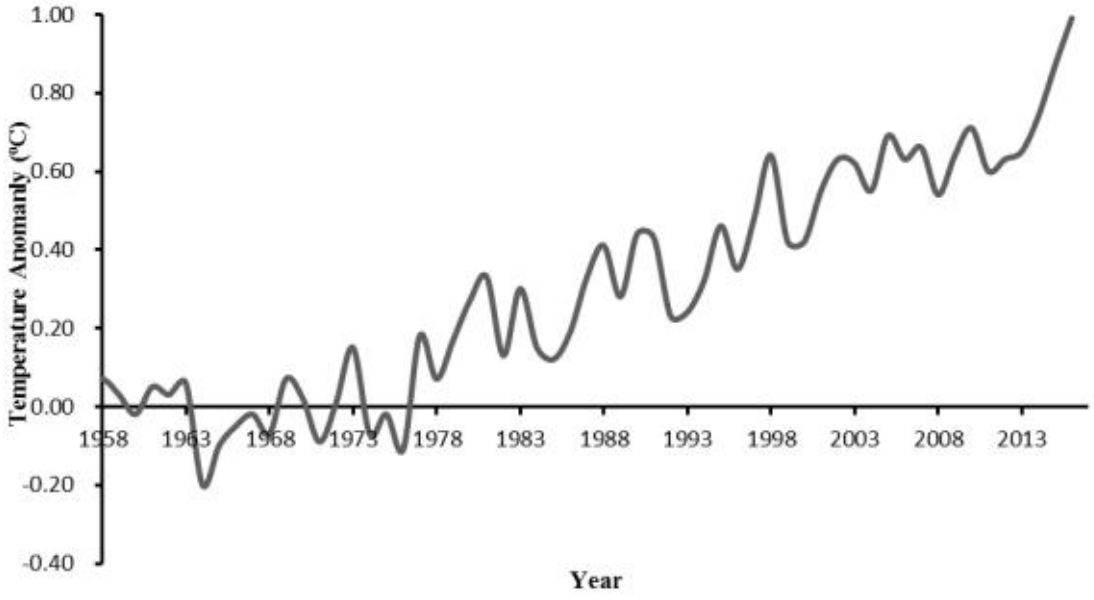

Figure 2.2: The change in global surface temperature relative to the 1951-1980 average temperature (Adapted from (NASA, 2016))

The global mean temperature increase will lead to changes in hydrological cycles, higher occurrences of harsh weather conditions (storms, heavy precipitation, heat waves etc.), ocean acidification, and a rise in sea levels (Zheng *et al.* 2019)

This information showed the concentration of CO_2 as it continues to rise in the atmosphere. To stop this trend, a dramatic strategy must be implemented so as not to affect the presence of life on earth for future generations. If CO_2 emissions can also be lowered in the atmosphere, the effect on global warming will also be extremely negligible.

The sources of primary energy today are fossil fuels, including natural gas, crude oil, and coal. (Pires *et al.* 2011). However, as mentioned in Chapter 1, fossil fuels result in CO_2 emissions

which have detrimental effects on the environment. This led to the need and development of solutions to mitigate CO_2 emissions, with the continued supply of energy from fossil fuels, resulting in the initiation of CCS.

CCS originated from the application of Enhanced Oil Recovery (EOR) which began in the United States of America (Aoki, Kusakabe and Morooka) in the early 1970s (Melzer 2012). Studies on CCS commenced in 1989 under the Carbon Capture and Sequestration Technologies (CCSTP) at MIT (Melzer 2012). Elsewhere in the world, the Norwegian government implemented a tax on CO_2 emissions in 1991, which was to be the major driver for the establishment of the world's first commercial CCS project (Melzer 2012; Goldthau 2013). Five years later, the world's first major CCS project commenced in Norway in the North Sea at Sleipner where 1 million tonnes per annum of CO_2 are being captured up to today and stored in the Utsira formation (Capture Ready, n.d.; Global CCS Institute, 2015). From this point in time, CCS has been proven to be a possible solution to the reduction of CO_2 emissions. Further research, as well as other large-scale CCS projects were initiated and today 15 large-scale CCS projects are in progress, with the further 7 under construction. (Global CCS Institute, 2015).

2.3 Main sources of CO_2 emission

A major cause of atmospheric CO_2 is the combustion of fossil fuels. In virtually every aspect of human daily activities, for power plants, fossil fuels, including oil, natural gas, and coal are utilized (Anderson, Hawkins and Jones 2016). Cement factories and energy plants are the primary promoters of CO_2 building that emits unlimited CO_2 in the atmosphere.

Between 1951 and today, nearly 321 billion tons of CO_2 were released into the atmosphere and more of these emissions occurred in the mid-1970s (Ming, Liu and Caillol 2014). Global CO_2 emissions rose by over 70% between 1970 and 2002 (Alhorr, Eliskandarani and Elsarrag 2014a). There have been major problems with the increase in CO_2 levels in the atmosphere and its harsh impact on the environment, which has led to numerous attempts to mitigate the elevated concentration of CO_2 from different sources (Singer *et al.* 2014). CO_2 emissions from energy plants including natural gas and coal are the most common sources of CO_2 in the atmosphere (Turnbull *et al.* 2016), therefore it is pertinent to recover and capture CO_2 to slow down the increased rate of CO_2 concentration from these sources being discharged into the atmosphere. Throughout the industrial era, electricity demand was on the increase and generation of power, in turn, accounted for almost a 50% increase from the beginning of the year 2000 (Luo *et al.* 2015; Shim and Hong 2016). Reports of global CO_2 fossil fuel emissions

also rose to about 25000 metric tons in 2002. By 2030, global energy demand is projected to rise by more than two thirds. The primary source of energy will remain as fossil fuels which will be on the increase by over 90% (Popp *et al.* 2014; He 2015). CO_2 emission sources are presented in Table 2.1, while the percentage of uncaptured and captured anthropogenic CO_2 is presented in figure 2.3.

Table 2.1: Sources of CO_2 emissions in South Africa

Sources of Likely Capturable CO_2	**Amount of CO_2 (Mt/a)**	**Sources of Unlikely to be Capturable**	**Amount of CO_2 (Mt/a)**
Electricity generation	137	Municipal wastes	9
Process industries	24	Agricultural wastes	41
Other energy production companies	26	Other wastes	36
Manufacturing companies	26	Thermal energy production	32
Total capturable CO_2	213	Total uncapturable CO_2	118
Total capturable and uncapturable CO_2	331		
Percentage capturable CO_2	64.40%		
Percentage uncapturable CO_2	35.60%		

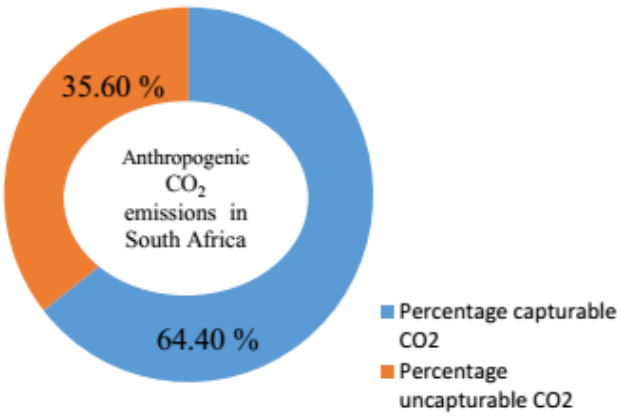

Figure 2.3: Captured and Uncaptured CO_2 percentage (Yoro and Sekoai 2016)

Table 2.1 above shows that the emissions from electricity generation (Varga 2013; Al-Salem 2015; Hermawan *et al.* 2015) are the biggest promoters of CO_2 discharged into the atmosphere. Therefore, the enormous possession of fossil fuels in human life needs a functional technique of slowing down the quantity of CO_2 released into the environment for energy needs. Zahra,

Fernandez and Goetheer (2011) "said this could be accomplished by constructing and incorporating high-efficiency power plants and production equipment for long-term storage with CO_2 capture."

2.4 Mitigating CO_2 emission

To reduce these, factors leading to high CO_2 emissions must be identified. A clear correlation between the anthropogenic CO_2 emissions denoted by C and the human population (P) is defined by the modified Kaya identity (Equation 2.1), the economic development represented by the gross domestic product (GDP), the production of energy (E), the carbon-based fuels used for the production of energy (C) and the sinks of CO_2 and SCO_2 (Bachu 2008; Pires *et al.* 2011).

$$CO_2 \text{ emission} = P \times \frac{GDP}{P} \times \frac{E}{GDP} \times \frac{C}{E} - SCO2 \qquad \text{Equation (2.1)}$$

In compliance with Equation 2.1, the increase in emissions of anthropogenic CO_2 is directly proportional to the increase in GDP per capita in the human population., the economy's energy intensity (E/GDP) and the energy system's carbon intensity (C/E) (Bachu 2008; Pires *et al.* 2011). There are five measures to reduce anthropogenic CO_2 emissions, depending on equation 2.1. (Bachu 2008; Pires *et al.* 2011). The first two approaches include decreasing population and economic outputs, which due to policy implementation are not a practical solution. (Bachu 2008). The third and fourth measures include increasing the energy recycling and transition to renewable energy sources like nuclear, wind, biomass, solar, coal replacement, in total or in partial, etc. (Bachu 2008; Pires *et al.* 2011). However, despite an abundance of available fossil fuels, high renewable energy cost are slowing down the adoption of green renewable energy sources. (Bachu 2008; Pires *et al.* 2011). In addition, the use of biomass can compete with other land and water uses, including production of food and forestation (Bachu 2008). SCO_2 includes CO_2 sinks in the fifth term, the constant utilisation of coal for the production of electricity and the application of CCS technology to mitigate emissions of CO_2 (Bachu 2008; Pires *et al.* 2011).

Pires *et al.* (2011) estimated that in this century, coal would become the principal energy source. The most appropriate technology for stabilizing atmospheric CO_2 emissions is maintaining CO_2 emissions from fossil fuels (Pires *et al.* 2011). By using a technique known as carbon capture and storage, this could be accomplished (CCS). CCS allows CO_2 from fixed sources to be captured, transported to storage locations and deposited in geological locations (Pires *et al.* 2011). Point sources, such as iron, power plants, refineries, cement, steel, and petrochemical sectors. The only technology to reduce emissions of CO_2 from the power generation industry

is known to be CCS (Cebrucean, Cebrucean and Ionel 2014). The IEA (2014) estimated that by 2050, CCS could reduce total emissions related to energy production by 14% (IEA, 2014).

2.5 Carbon dioxide capture and sequestration

Capture and sequestration of carbon dioxide is an obvious technique of capturing and storing CO_2. CCS technology is used in reducing atmospheric CO_2 emissions. CCS is the most accepted and widely used atmospheric CO_2 emission stabilization technology. The main advantage of CCS is that it can be implemented in many industries and makes it possible to continue using low-CO_2 fossil fuels to produce energy. The integrated CCS system performs the following process: CO_2 is obtained from point-of-generation sources like cement plants, steel manufacturing and coal power plants; it is compressed into a supercritical fluid and then transported and stored in geographic locations (Zhang and Huisingh 2017). CO_2 is injected or deposited in the ocean on the geological surface of the reservoir. Carbon capture and sequestration is a promising alternative throughout the medium to long term to reduce CO_2 emissions. This approach includes capturing CO_2 before it is emitted at energy plants and other sectors, carrying CO_2 to appropriate disposal sites, and either storing CO_2 underground or using CO_2 to obtain high-value products. A summary of the CCS method is displayed in figure 2.4. As illustrated in figure 2.4, CCS's three primary stages are: CO_2 capture, transport, and storage.

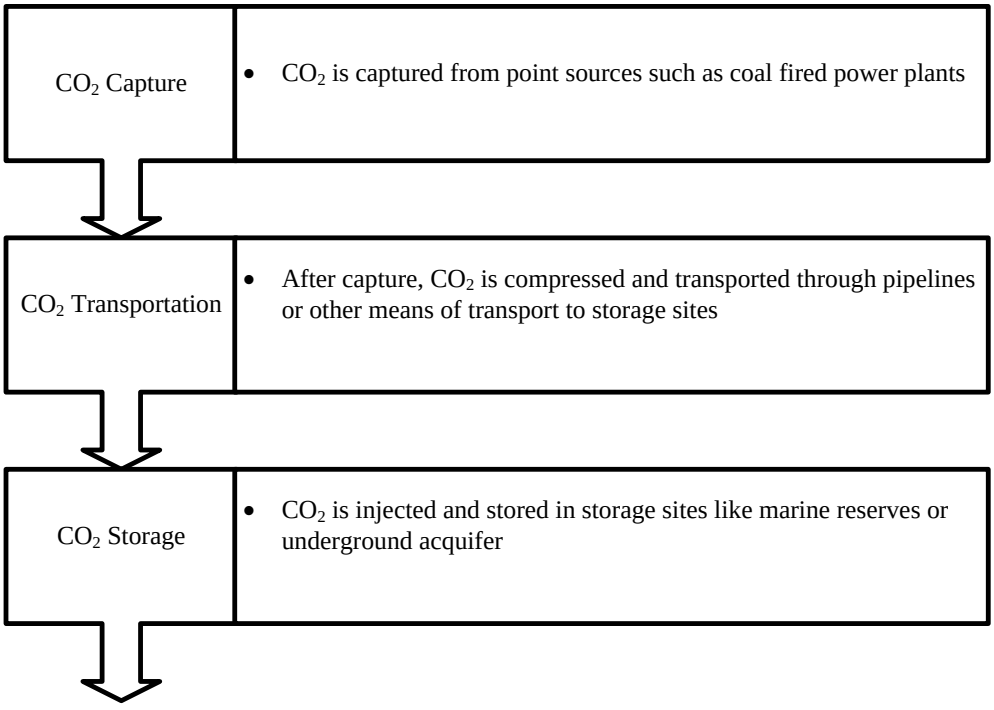

Figure 2.4: Diagram outlining the carbon capture and storage concept.

The CCS's conventional interpretation technique is to compress and transfer CO_2 to be stored in geological formations, drained into the sea, stored in biomass, or as carbonated minerals, or used in systems of industry. Industrial CO_2 application is presently thought to be restricted and the other storage methods are the most promising. Large point sources must be identified so that CCS is viable. Captured CO_2 adsorbents include zeolites, organic metal frameworks (activated carbons, nano-silicate clay minerals, MOFs, and functionalized polymers) (Cavalcanti *et al.* 2018). CCS technology's main purpose is decreasing CO_2 pollution in the atmosphere. CO_2 emitted from fossil fuels will be stored in secure locations at affordable rates for hundreds of years. Coping with global warming as an enabling alternative, CCS technology would be of great significance in reducing emissions of CO_2. In lowering CO_2 emissions, CCS technology will play a significant role. CCS is a relatively fresh idea aimed at protecting the environment from degradation while ensuring that the heavy reliance of the world on conventional energy resources is not impaired.

The aforementioned stages of CCS (Storage, Transport and Capture) will now be discussed. Capture is the first stage in CCS, but it will be discussed last as it is the main focus of this chapter.

2.5.1 CO_2 transport

CO_2 transport involves moving the captured CO_2 from the capture site to the geological storage site. In three phases, gas, liquid, or solid CO_2 can be transported. However, CO_2 in the gas phase occupies a large volume and will require very large transport and storage facilities. Gas occupies less volume when compressed to a liquid and can be transported via pipeline. It is possible to further compress CO_2 to the solid phase where it will occupy the least volume, however by doing this compression costs will increase substantially. Due to energy use and size constraints, CO_2 transport predominantly occurs in the liquid phase via pipelines. Transport of CO_2 and other gases via pipelines is an enhanced technology, with decades of practical experience, mostly in North America. Most of this experience is because of the EOR that is undertaken in North America, where there have been extensive CO_2 pipeline networks since the 1980s. The knowledge on pipeline transport of CO_2 is well regulated safe, mature and has been extensively documented. The transport of gas via pipeline is also applied in South Africa, since 2004 Sasol has piped natural gas from Mozambique to Secunda Mpumalanga.

However, because of the high energy costs of solidifying and transporting it as a solid one, and the large volume needed to transport it as a gas, CO_2 is primarily transported as a liquid

(Intergovernmental Panel on Climate Change, 2005). To achieve efficient CO_2 transport, the CO_2 being transported should be in the supercritical state (Almendra *et al.* 2011),. CO_2 exists in a supercritical state from a pressure of 73 atm and a temperature of 31 °C (Harvey *et al.* 2013). Almendra *et al.* (2011) states that CO_2 is usually transported between 12.8 °C and 43.3 °C in the temperature range and between 85 atm and 149.6 atm in the pressure range. Pipelines, ship, rail and road tankers are the means used to transport CO_2 (Almendra *et al.* 2011). The ship, rail and road tanker system requires storage at the site of CO_2 production in the event that the carrier is not available and the actual tanker to ferry the CO_2 to the storage site (Almendra *et al.* 2011). Compressors, valves, booster pumps, pig launchers and receivers, batching stations and instruments, metering stations and SCADA (Supervisory Control and Data Acquisition) systems constitute the pipeline system (Holloway *et al.* 2006; Almendra *et al.* 2011). To mitigate CO_2 emissions, large amounts of CO_2 will have to be transported from capture points to storage points hence pipelines are the most favourable means of transport (Intergovernmental Panel on Climate Change, 2005). According to (Almendra *et al.* 2011), the ship, rail and road tankers cost twice that which pipelines cost to transport CO_2 hence making pipeline transport the preferred means of transport for bulk CO_2 for CCS.

Currently, bulk CO_2 transport is done in the beverage and food industry, as well as the oil and petroleum industry (Intergovernmental Panel on Climate Change, 2005). In the beverage and food industry, CO_2 transport is done by means of road and ship tankers, because of the small quantities transported, whereas the oil and petroleum industry make use of pipeline transport (Holloway *et al.* 2006). In the world today, most CO_2 transport is done for EOR, mainly in the United States of America (Aoki, Kusakabe and Morooka) (Intergovernmental Panel on Climate Change, 2005). Examples of existing pipelines used for CO_2 transport include the Canyon Reef, which was the first CO_2 pipeline in the USA. Its stretches for 352km and has moved 12000 tonnes of man-made CO_2. An example of this is the Bravo Dome pipeline having a potential capacity of 7.3 Mt of CO_2 per year. Further examples include the Cortez pipeline and the Sheep Mountain pipeline (Intergovernmental Panel on Climate Change, 2005). These examples display the possibility and feasibility of pipeline networks that can transport CO_2 over long distances from source points to storage points.

Pipelines used for CO_2 transport extend to more than 2500 km in western USA where over 50 Mt of CO_2 are transported for EOR (Intergovernmental Panel on Climate Change, 2005). Pipelines have also been used and are extensively used in the oil and petroleum industry, hence knowledge in design and operation is readily available. This also adds to them being the

preferred means of CO_2 transport for CCS. Pipelines also have the added advantage that they are able to maintain a continuous supply of CO_2 whereas ship, road and rail tankers are batch transporters of CO_2 which means there is no need for intermediary storage of CO_2 in pipeline transport (Almendra *et al.* 2011). There is, however, a need for intermediary pumping stations to counteract the effect of pressure drop along the length of pipe (Almendra *et al.* 2011). The CO_2 transportation industry makes use of centrifugal, single-stage and radial split pumps for re-compression. Further discussion on CO_2 transport is beyond the scope of the project, but further information can be found in the Intergovernmental Panel on Climate Change (2005).

2.5.2 CO_2 storage

CO_2 storage involves the isolation of anthropogenic CO_2. The isolation of CO_2 is achieved by the injection of the CO_2 into the sub-surface of the earth. The period of isolation needs to be long-term, approximately 1000 years. The first step in CO_2 storage is to characterize geological formations to determine whether they are effective for large CO_2 storage. The characterization process includes studies on permeability, thickness, storage capacity, geological structures, and lithology of the storage site (EPA, 2013).

If CO_2 is captured mostly from coal-fired power plants successfully. In natural environments, like geological formations, it can be deposited in impermeable rocks and preserved in porous spaces until the underground water dissolves (Little and Jackson 2010). This method of CO_2 storage takes a long period of residence. This implies that unused geological systems, such as deep saline aquifers, can also accumulate CO_2. Geological storage of CO_2 is usually considered, according to existing literature, the most feasible solution to large amounts of CO_2 captured for storage (Michael *et al.* 2010; Czernichowski-Lauriol and Stead 2014). Over a long period of time, geological storage systems will accumulate nearly 10 million tons of CO_2 (Aydin, Karakurt and Aydiner 2010). Effective geological sites for storing CO_2 would however, require:

i. Suitable thickness and porosity.
ii. There must be a permeable rock reservoir and
iii. The cap rock should be highly sealable and have a sustainable geological formation.

The three major geological structures usually considered for CO_2 storage are exhausted or nearly degraded oil and gas reserves, unmineable coal beds and saline aquifers (Suekane *et al.* 2008; Streimikiene and Mikalauskiene 2010). An alternative CO_2 storage option is also to store CO_2 in the deep oceans; however, this raises environmental problems including eutrophication and acidification of the oceans. By releasing CO_2 at least 1000 m below sea level into deep

ocean waters, it will retain the CO_2 trapped in oceans. This CO_2 storage method is viable since cold deep-sea waters are unsaturated by CO_2 and possess considerable potential for subsequent dissolution. This is based on the hypothesis that CO_2 with a liquid-like density is super-critical below certain depths; and it is therefore less buoyant than water (Qanbari *et al.* 2011; Klapperich *et al.* 2014). However, the major drawbacks of this approach are the environmental problems that are related to it, as mentioned above.

2.5.3 CO_2 capture

The capture of CO_2 includes CO_2 separation from other gases at industrial process facilities that produce CO_2. Sreenivasulu *et al.* (2015) describes CO_2 capture as CO_2 removal from the combustion gases of the product or CO_2 removal from the fuel. When capturing CO_2, the CO_2 in the gas stream involved must be separated from other gases, which in conventional power plants is the flue gas stream produced from combusting fossil fuel. An example of an industrial process facility where CO_2 would be captured is power station. Flue gas is the CO_2 gas-containing mixture emitted at power stations throughout electricity generation. Flue/exhaust gas from power stations is commonly vented to the atmosphere. Flue gas consists of mainly N_2 and O_2 but also CO_2 at an approximate concentration of 10-15% (Saha *et al.* 2012). It is imperative to separate the CO_2 from the gases for storage as it would be impossible to store all the flue gas due to legislation and compression, transport, and storage costs.

The most costly stage, approximately two thirds of the CCS operation's overall cost, is CO_2 capture. (Li *et al.* 2011). Furthermore, CO_2 capture will decrease the plant's output by around 14 % and raise the quantity of energy utilized in the plant by 30-70 %, based on the mode of capture technology applied and the type of plant and fuel utilized (Cebrucean, Cebrucean and Ionel 2014). Numerous technologies have been developed and explored as such.

CCS has three primary techniques: pre, post and oxy- fuel combustion capture method. The fossil fuel reacts with air or oxygen during the pre-combustion process and is partly oxidized to form CO and H_2 (syngas). However, a CO_2 mixture and more H_2 are reacted with steam in a gasification reactor. CO_2 is then extracted, resulting in a gas rich in hydrogen which can also be used in multiple systems.

$(g)+H_2(g) \leftrightarrow CO_2(g) + H_2\,(g)$ Equation (2.2)

Figure 2.3 displays a diagram depicting pre-combustion CO_2 capture

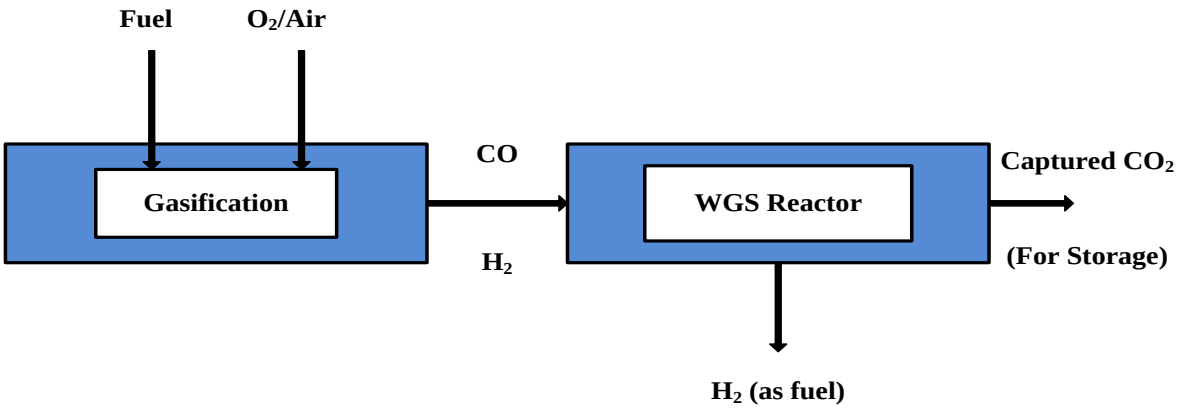

Figure 2.5: Pre-combustion CO_2 capture

When oxygen is applied for combustion rather than air, oxy-fuel combustion is generated in a flue gas composed primarily of pure CO_2 and appropriate for manufacturing technically. The key benefit of CO_2 capture by oxyfuel is that flue gas is obtainable at a low concentration of CO_2 which decreases the costs of separation (Yan *et al.* 2011a; Borgert and Rubin 2013). This is because, instead of air, the combustion of oxyfuel uses pure oxygen that removes N_2 from the flue gas stream. Figure 2.6 displays a diagram of CO_2 capture from oxyfuel combustion.

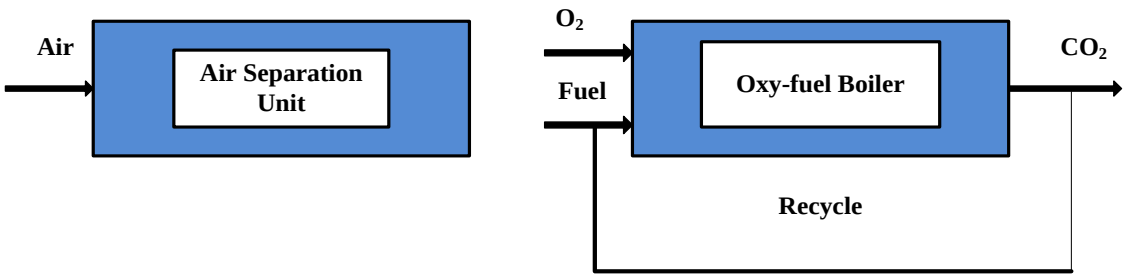

Figure 2.6: Oxy-fuel combustion CO_2 capture

Post-combustion CO_2 capture enables the capture of CO_2 after the generation of electricity from flue gas. Post-combustion CO_2 capture requires CO_2 capture from flue gas sources after generation of electricity (Favre 2007; Åkesson *et al.* 2012). Power plants consume CO_2, this technology is very necessary. It is also considered to be post-conversion capture; however it is known as post-combustion capture when used in power plants (Calvo-Muñoz *et al.* 2016). CO_2 capture following combustion is appropriate for membranes, powerful sorbent adsorption, solvent absorption and cryogenic separation (Schakel *et al.* 2014; Otto *et al.* 2015); Figure 2.7 displays CO_2 capture of post-combustion.

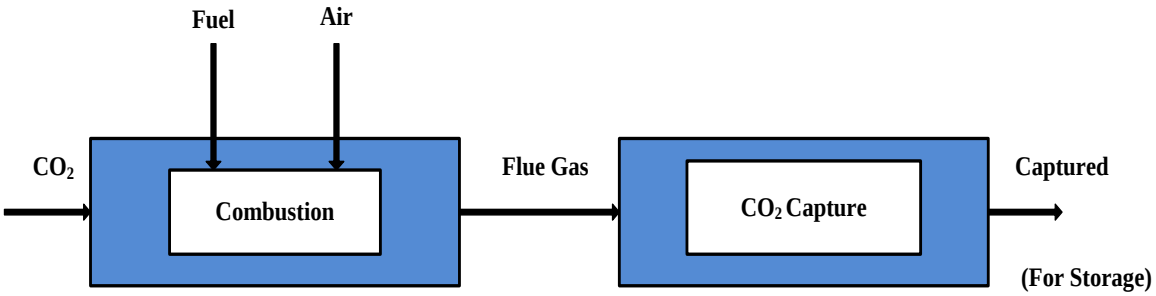

Figure 2.7: Post-combustion CO_2 capture

2.5.4 Factors influencing Post Combustion CO_2 Capture via Adsorption

The performance of the adsorption capture process is affected by many factors. Such variables are temperature, pressure, flue gas composition and the type of the adsorbent used. These variables affect the adsorption and assess the extent of the adsorption. These factors will be discussed in the following paragraphs.

An important factor for post-combustion CO_2 capture via adsorption is the temperature of the flue gas stream. The temperature will influence the type of adsorption that occurs, be it physisorption or chemisorption. Recall that chemisorption has a higher heat of adsorption and thus occurs at higher temperatures than physisorption (W John Thomas and Crittenden 1998). At equilibrium, a temperature increase can result to a decline in the adsorbed CO_2 magnitude. Conversely, a temperature drop will increase the magnitude of CO_2 adsorbed. This is because the adsorption is exothermic in nature. Le Chatelier's principle explains this; with a rise in temperature by an exothermic system will decrease the rate of exothermic reaction. Rojahn states that with chemisorption the magnitude of the adsorption will initially increase to a maximum with an increase in temperature and will decrease thereafter (Rojahn *et al.* 2018). Rojahn suggests that this is because with chemisorption the activation energy must be achieved first, the reaction then occurs and the resultant decrease is attributable to the exothermic existence of the reaction (Rojahn *et al.* 2018).

The pressure of the flue gas stream is another significant factor for post-combustion CO_2 capture by adsorption. The pressure affects the magnitude of the adsorbed CO_2. The magnitude of the adsorbed CO_2, and the flue gas pressure are directly proportional. The higher the CO_2-adsorbed partial pressure; the more CO_2 adsorbed. Conversely, the lower the partial of the CO_2, the less CO_2 adsorbed (Keller and Staudt 2005).

The flue gas composition is an important factor for post-combustion CO_2 capture via adsorption. The higher the concentration of CO_2, the easier the adsorption would be. The converse is true, the lower the CO_2 concentration, the more difficult the adsorption will be. Impurities may be found in the flue gas that will also influence the magnitude of the adsorbed CO_2.

The nature of the adsorbents is an important factor for post-combustion CO_2 capture via adsorption. The nature of the adsorbents applies to all adsorbent properties such as surface geometry, adsorbent chemistry, and the physical form of the adsorbent (W John Thomas and Crittenden 1998). The more favourable these properties are for adsorption, the greater the magnitude of adsorption. For example, the higher the surface area for physisorption, the greater the magnitude of adsorption (Ngoy 2016). For chemisorption, the chemistry of the adsorbent refers to the functional groups and affects the adsorption because different functional groups have affinity for different components of the flue gas.

2.6 Separation Technologies for Post-Combustion CO_2 Capture

A broad range of technologies are currently available that can be introduced to absorb and separate CO_2 from gas streams in coal-fired power plants (Yan *et al.* 2011b). These focus on chemical and physical processes, including technologies for cryogenic, adsorption, membrane, and absorption separation. In Figure 2.6 below, they are presented and discussed:

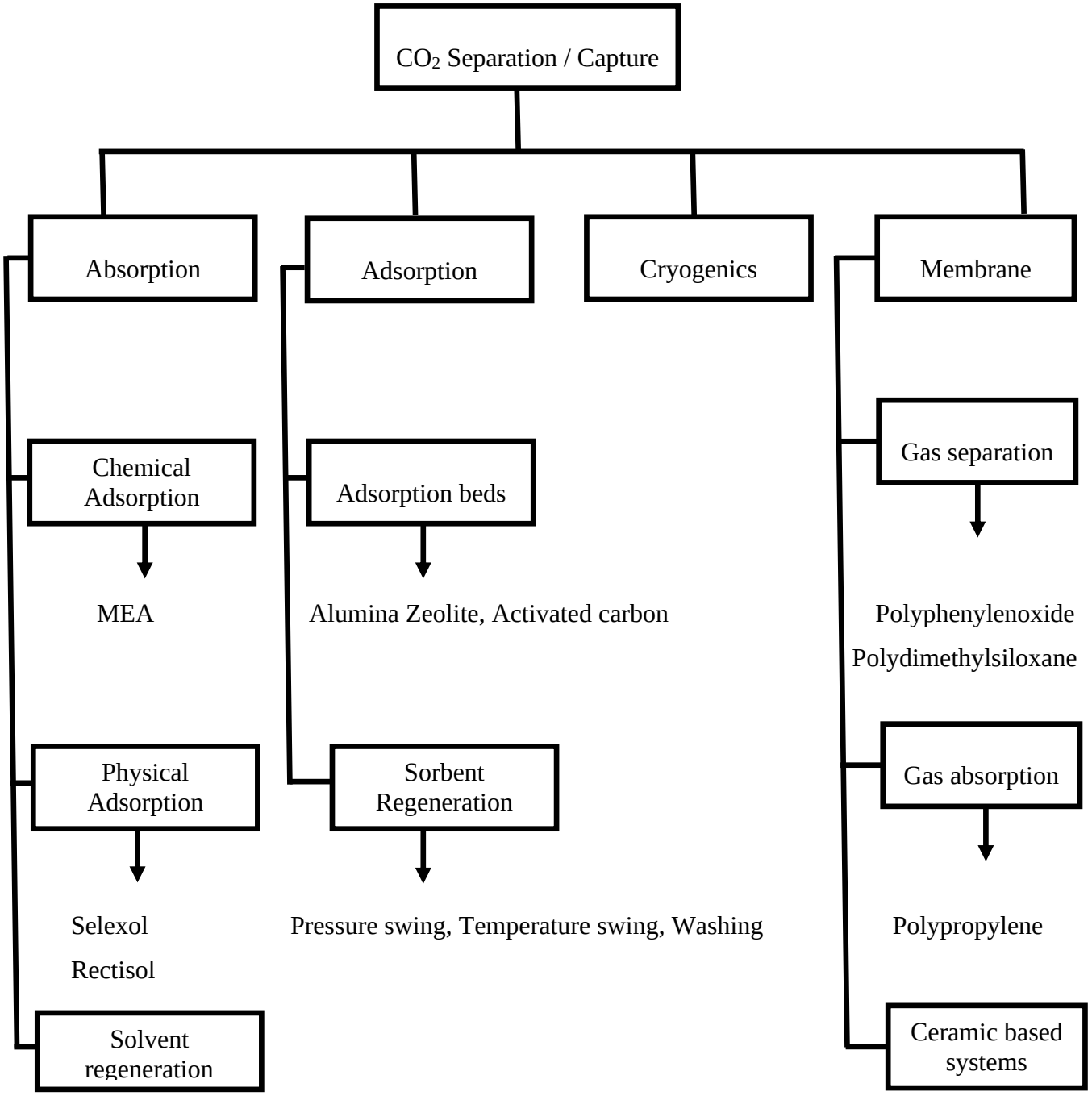

Figure 2.8: Different separations of CO_2 and capture technologies for post-combustion CO_2 capture (Siriwardane *et al.* 2001)

2.6.1 Cryogenic distillation process

The cryogenic separation of CO_2 is largely based on condensation and cooling principles. (Belaissaoui *et al.* 2012; Li, Jiang and He 2014). It is also used in CO_2 capture systems in which a high CO_2 concentration is present in the gas streams. The drawback with cryogenic separation is that most power plants have a diluted CO_2 stream (Fu *et al.* 2016; Scholes, Ho and Wiley

2016). Another drawback is that such technology is energy intensive, i.e., The separation of CO_2 needs high quantities of energy. Although the CO_2 concentration is quite low in most coal-fired power plants, depending on the combustion process used this method of CO_2 separation seems difficult to introduce. Moreover, cryogenic separation at very low temperatures is best achieved (Kansha *et al.* 2011). Although it is hard to achieve very low temperatures that are sufficient for CO_2 capture using such a technique for coal-fired power stations. Different components in gas mixtures are isolated by a sequence of cooling, compression, and separation phases in many other cryogenic separation processes (Fu *et al.* 2014). Impurities in processes of cryogenic separation lower CO_2 phase transition temperature to as low as -80 °C. Under this condition, the penalty for cooling energy rises dramatically, but there is a risk of developing CO_2 frost, which is a detriment to equipment safety (Khalel, Rabah and Barakat 2013).

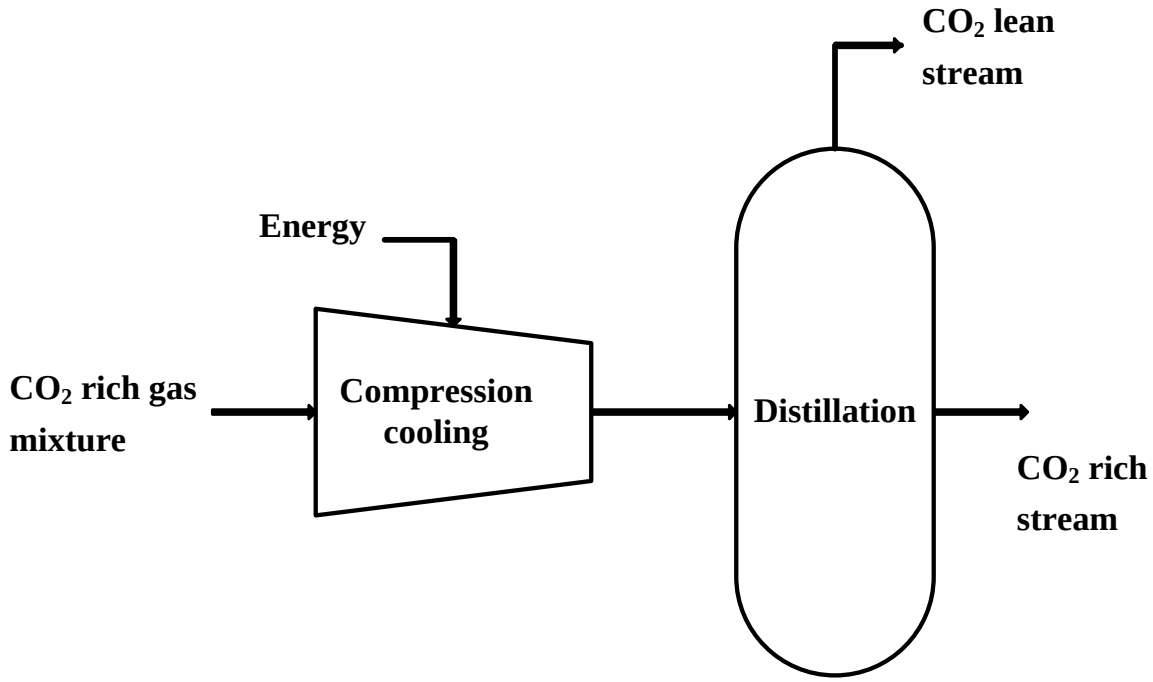

Figure 2.9: Separation by cryogenic distillation

2.6.2 Membrane Separation

Corti and Lombardi (2004) studied membrane CO_2 capture and confirmed that applying membrane-based CO_2 capture to trap flue gases will only be successful when the CO_2 concentration is greater than 10% in the flue gas. Based on modifications in the physical or chemical contact of the CO_2 gas with the membrane, the use of membranes to capture CO_2 functions. The membrane is constructed so that one gas can move through more easily than the other (Bandyopadhyay 2011). Compared with emerging technologies, like adsorption and absorption, there are some clear benefits to CO_2 capture using membranes over absorption and

adsorption processes, as they have basic modular systems, there is no need for waste streams and no energy during regeneration. In membrane separation, constraints on conventional gas absorption towers and processes of adsorption are eliminated, providing a basic modular approach with higher sensitivity and increased driving force (Aoki, Kusakabe and Morooka 2000; Li, Jiang and He 2014; Scholes *et al.* 2014). Despite the relatively new membrane technology, compared to other conventional approaches, it is commonly recognised for its high selectivity. (Yan *et al.* 2008; Brunetti *et al.* 2010). In addition, Inorganic ceramic membranes or organic polymeric membranes are applied in this technology (Stanislowski *et al.* 2013; Tomioka, Sakai and Mano 2013). Ceramic membranes are very inexpensive but achieving a significant degree of CO_2 separation is nearly impossible, and a high purity of CO_2 simultaneously with CO_2 in the flue gas via a single-stage ceramic or polymer membrane. This is a significant drawback of this technology for CO_2 capture. Polymeric membranes were thoroughly researched to capture CO_2. Under extreme conditions, these membranes are vulnerable to degradation, making them ineffective for the capture of CO_2 flue gas with contaminants such as water vapour and sulphur (IV) oxide (Kazemimoghadam and Mohammadi 2005; Chung *et al.* 2007; Olajire 2010; Daramola and Okosun 2015). Nevertheless, zeolite-based membrane technology offers great potential for CCS, like chemical inertness and high thermal stability.

The membrane technology is not adequate for post-combustion CO_2 capture. While polymer membranes have outstanding CO_2 capture selectivity and permeability, the thermal stability is very poor, and the effect of CO_2 on the membrane plasticizes these membranes. Therefore, the application of membrane technology in coal-fired thermal power plants for post-combustion CO_2 capture is minimal. Effective technologies for capturing CO_2 with reduced costs, high capacity and selectivity for CO_2 capture must be widely explored as a solution to the use of post-combustion CO_2 capture membranes (Wang *et al.* 2014).

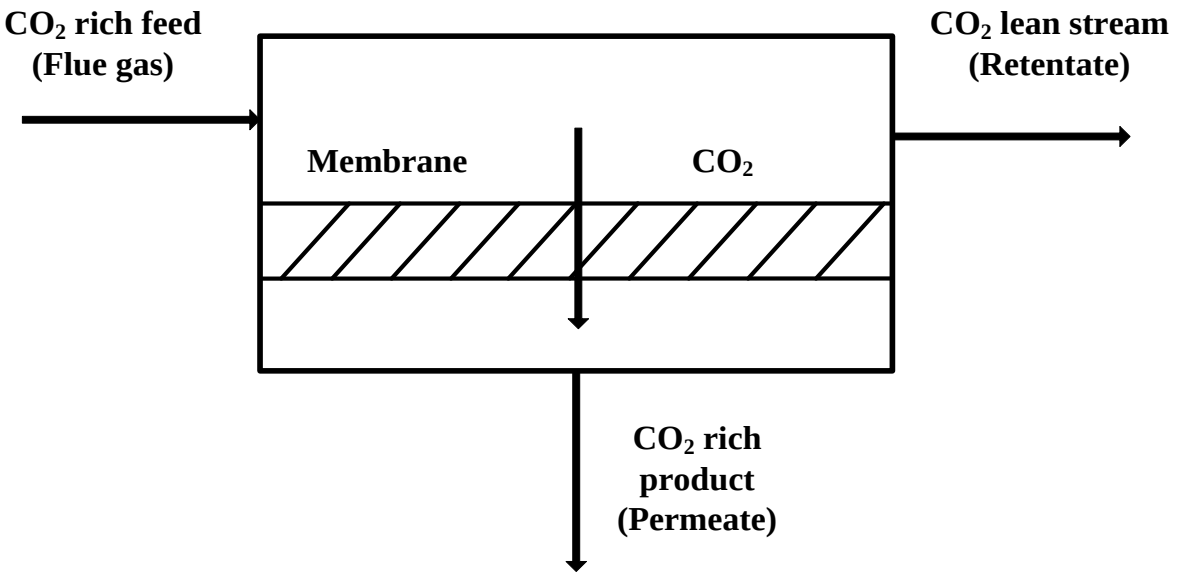

Figure 2.10: Separation of CO_2 using membrane

Membrane separation is preferred over all other forms of separation of gases. Their benefits include (Leung, Caramanna and Maroto-Valer 2014; Quan *et al.* 2017):

- With no moving parts, it is an easy and passive operation.
- It is an environmentally safe process without toxic chemical compounds being used.
- Less energy intensive since there is no phase shift in the separation of gases.
- Compared to equilibrium-based methods, it has greater separation efficiency.

Molecules migrate or penetrate via the membrane during membrane separation through a wide range of driving forces for transport. The transport method is determined primarily by the size of the pores or free volume elements of the membrane and the size of the separating molecules. The typical types of mechanisms for transporting membranes are described in Table 2.2.

Table 2. 2: Membrane transport mechanisms (Adapted from carbon capture: beyond 2020, 2010)

Pore size ($\boldsymbol{A}$)	**Transport mechanism**	**Application**
>200	Convective flow	No separation-typical gas filter
$\frac{\lambda}{D}$>1 (20-1000)	Knudsen flow	Very low separation
5-10	Surface flow	micro porous carbon with a pore size of 5-7$\dot{A}$ for separation of H_2 from hydrocarbon is an example of this
<5	Molecular sieving	Carbon membranes with pores of < 5$\dot{A}$. It is highly selective
Dense no permanent pores	Solution diffusion	Membranes for commercial polymeric gas separation. Used mostly for H_2 separation, air separation, natural gas CO_2 separation.
Dense	Ion transport ceramic	Under development for ultrapure H_2, O_2

The transportation mechanism for solution diffusion is of interest for gas separation applications, including CO_2 capture from flue gas. Polymeric membrane is an example of membranes with such mechanism. The relationship between selectivity and permeability is usually restricted to polymeric membranes. There are many advantages to polymeric membranes, including low production cost, high separation of performance, simple synthesis and mechanically stable (Pires *et al.* 2011). Polymeric membranes will not be added without cooling the flue gas for CO_2 capture by post-combustion. This is because the membrane is easily destroyed by high temperatures (Pires *et al.* 2011). In the steam reforming reaction in pre-combustion, polymeric membrane may also be applied to differentiate CO_2 from H_2. Polymeric membranes can be used in oxy-combustion to create oxygen-rich air streams (Pires *et al.* 2011). The use of polymeric membranes throughout the outlet stream is an effort to raise the amount of CO_2 captured by pre-combustion and oxy combustion (Pires *et al.* 2011).

The production of ceramic membranes led to significant disadvantages of polymeric membranes, such as thermal stability (Nwogu, Kajama and Gobina 2015). Ceramic membranes

can capture CO_2 at high temperatures, unlike polymeric membranes (Singo 2017). Mechanical stability and greater chemical stability are other benefits of ceramic membranes, resulting in a longer membrane lifetime (Hofs *et al.* 2011). Several studies were performed in which ceramic membranes were used to capture CO_2. Nwogu, Kajama and Gobina (2015) recorded performance evaluations of inorganic ceramic membranes for the separation of CO_2 gases. Daramola, Oloye and Yaya (2017) reported on the successful synthesis and characterization of the Nano composite Sodalite ceramic membrane by pore plugging hydrothermal synthesis for pre-combustion CO_2 capture.

There are many disadvantages that this technology offers, for CO_2 capture, considering the several benefits of membrane separation technology. The main problem is that a large membrane area is involved during this treatment of large flue gas flows produced by coal-fired power plants, leading to higher membrane capture technology costs (Pires *et al.* 2011). For this technology, another huge concern is that, it demands major energy compensation and costly post-combustion capture compression equipment, rendering the technology costly (Pires *et al.* 2011). Membrane technology is already being developed (Leung, Caramanna and Maroto-Valer 2014).

2.6.3 Absorption

CO_2 capture via gas absorption is the process in which CO_2 (the solute) from the flue gas mixture is dissolved into a liquid (the solvent) (Perry 2016). In the absorption process CO_2 will physically enter the bulk phase of the solvent and dissolves into it. In Figure 2.7, this approach is illustrated. It is evident from Figure 2.7 that the solute has penetrated the inside of the solvent bulk.

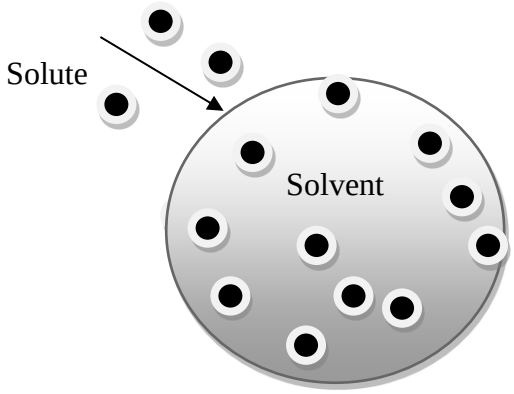

Figure 2.11: Schematic of absorption process

The absorption process, where there is a reaction between the solution and the solvent, may be physical or chemical. Physical absorption involves a physical process and follows Henry's Law. At a higher pressure and lower temperature, CO_2 is absorbed while desorption occurs at

lower pressures and higher temperatures. The absorbent molecules dissolve into the solvent throughout physical absorption and no chemical reaction takes place. The properties of the solvent and solute remain unchanged. Due to the physical nature of the process, there is a lower energy requirement to desorb the solute. This method is commonly used in industries where Selexol (polyethylene glycol dimethyl ethers) and Rectisol (methanol) are the standard solvents (Wang *et al.* 2011).

A reaction between the solvent and the solution is involved in chemical absorption. Chemical absorption contributes to the development of a new, solvent-soluble species, converting it into a chemical process, whereby the absorbent and the absorbate are separated using a larger energy input. Chemical absorbents have two main advantages over physical absorbents. The first advantage is the high selectivity to CO_2 while not co-absorbing hydrocarbons and other chemical species. Physical absorbents have been shown to absorb hydrocarbons and other chemical species which are often the desired product. The second advantage of using a chemical absorption process is its good absorption behaviour at low partial pressures. The most significant drawbacks to the use of chemical solvents are the high energy requirements for desorption, limitation of the absorption process due to stoichiometry, and degradation of the solvent. The use of a hybrid solvent which possess the advantages of both physical and chemical absorption properties have been developed to overcome the disadvantages of each solvent type described (Wang *et al.* 2011).

2.6.4 Adsorption

In processes involving chemical and environmental factors, this technology is commonly used. It utilizes various adsorbents, including activated carbon, kaolinite, polyaspartamide, porous silicates, zeolites, organic metal frameworks and metal oxides for CO_2 capture (Ben-Mansour *et al.* 2016). Interestingly, when it is used in power plants, CO_2 capture via adsorption with activated carbon fibres and a carbon fibre part is considered an effective method (Tseng, Wu and Juang 2015). Adsorption technology is gaining more recognition because of its features, that includes minimum energy requirements, simple maintenance, ease of use and versatility (Chen and Lu 2015).

CO_2 capture via gas adsorption is the process of capturing CO_2 (adsorbate) from the flue gas on the surface of a solid (the adsorbent) (Perry 2016). During the adsorption process molecules are drawn to another material and therefore adhere to the surface. Adsorption differs from

absorption because the molecules do not enter the bulk of that substance. Figure 2.8 shows this process, and it is clear that the adsorbate adheres to the outside of the adsorbent.

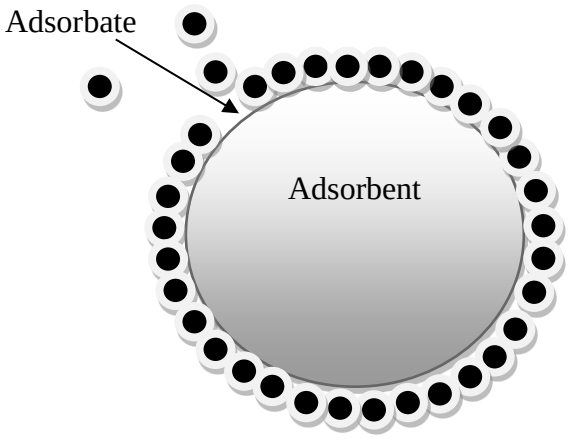

Figure 2.12: Schematic of adsorption process

The interactive forces between an adsorbate and the surfaces of the adsorbent affect the adsorption mechanism. A difference in surface energy causes the adsorbate to adhere to the surface of the adsorbent. This is an electrostatic force of attraction. Electrostatic forces are weak forces and as such the molecules are weakly held on the adsorbent surface and are thus quickly desorbed and the adsorbent can be easily regenerated.

This is distinct from absorption, where recovery of the solvent is more complicated and energy intensive (Osler 2017). The adsorption process can be a purely physical in nature, known as physisorption, or chemical in nature and involve a reaction between the adsorbate and adsorbent, known as chemisorption. The nature of the adsorption process is determined by the electrostatic forces present.

A physical process where the properties of the adsorbates and adsorbents remain unchanged is known as physisorption. During the physisorption process, the adsorbate approaches the adsorbent surface where repulsive and attractive forces become balanced and adsorption occurs. The types of forces present are called van der Waals forces. Before adsorption occurs, the adsorbate has three degrees of translational freedom. After adsorption occurs the adsorbate loses one degree of translational freedom. The decrease in the degree of translational freedom results in a decrease in both the entropy and Gibbs free energy (W John Thomas and Crittenden 1998). This causes an increase in the enthalpy, which means that the adsorption process is exothermic as shown in Equation 2.3 (W John Thomas and Crittenden 1998)

$\Delta G = \Delta H - T\Delta S$ Equation (2.3)

$\Delta G < 0, \Delta S < 0 \quad \therefore \Delta H > 0$

Therefore, the rate of adsorption that occurs during physisorption decreases with an increase in temperature because of the exothermic aspect of adsorption.

Chemisorption is a chemical process in which both the adsorbent and the adsorbate properties change due to the formation of covalent chemical bonds (IUPAC, 2002). An electron transfer occurs between the adsorbent and the adsorbate during chemisorption, leading to the formation of covalent bonds. Chemisorption does not follow the same thermodynamic structure as physisorption and is thus possible at a larger range of temperature, notwithstanding, chemisorption is still an exothermic process. Multilayer adsorption can be accomplished with physisorption under the optimum operating conditions (temperature and pressure). In contrast, chemisorption is limited by the number of sites where chemical bonding can occur. Another drawback of chemisorption is that due to chemical bonds, it is always difficult or impossible to recycle the adsorbent due to the high energy requirement to break the bonds (Fletcher 2008)

According to the nature of van der Waals forces, the adsorption potential in physisorption was therefore observed to reduce significantly with increased temperature and decreased partial pressures. Chemisorption has been shown to give better CO_2 adsorption at lower CO_2 concentrations.

Berger and Bhown (2011) and shows better CO_2 adsorption at higher temperatures than physisorption. Chemisorption has been adopted for CO_2 capture and optimized by manipulating and enhancing the surfaces of the adsorbents. To understand adsorbent behaviour and equipment design, it is important to carefully differentiate between chemisorption and physisorption. The heat of adsorption can be used as an indicator to determine whether physisorption or chemisorption occurs. The adsorption heat for CO_2 physisorption varies from -25 to -50 kJ/mol. The heat of adsorption for chemisorption of CO_2 ranges from -60 to -100kJ/mol depending on the adsorbent used (Berger and Bhown 2011). The nature of the adsorption depends on the heat of adsorption, temperature, pressure, and the nature of the adsorbate and adsorbent.

Table 2.3: Characteristics associated with physisorption and chemisorption (Adapted from (Fletcher 2008) and (Berger and Bhown 2011)

	Physisorption	**Chemisorption**
Heat of Adsorption (kJ/mol)	-25 to -50	60 to -100
Rate of Adsorption (273 K)	Fast	Slow
Effect of temperature increase on adsorption uptake	Decreases	Increases
Desorption	Easy- by reduced pressure or temperature	Difficult-high temperature needed for breaking bonds
Desorbed Species	Adsorbate unchanged	May be difficult to original adsorbate
Specificity to gases	Non-specific	Very Specific
Monolayer Coverage	Multilayer or mono condition dependent	Monolayer

a) Adsorption Isotherms and Adsorption Equilibria

The process of adsorption is commonly represented by adsorption isotherms. Adsorption isotherms are the function of gas at a constant temperature and equilibrium partial pressure adsorbed onto an adsorbent. The quantity of gas adsorbed is almost always given relative to the mass of the adsorbent used; this is intended to allow a comparison of various materials. The behaviour of adsorption systems can be predicted by adsorption isotherms since they are governed by the type of adsorption that occurs. Adsorption isotherms represent the equilibrium relationship between the adsorbent and adsorbate at any given temperature. Fletcher reported six types of adsorption isotherms according to Brunauer, Emmett and Teller (BET) theory. Fletcher states that all adsorption isotherms should fit one or a combination of the six recognised types classified (Fletcher 2008).

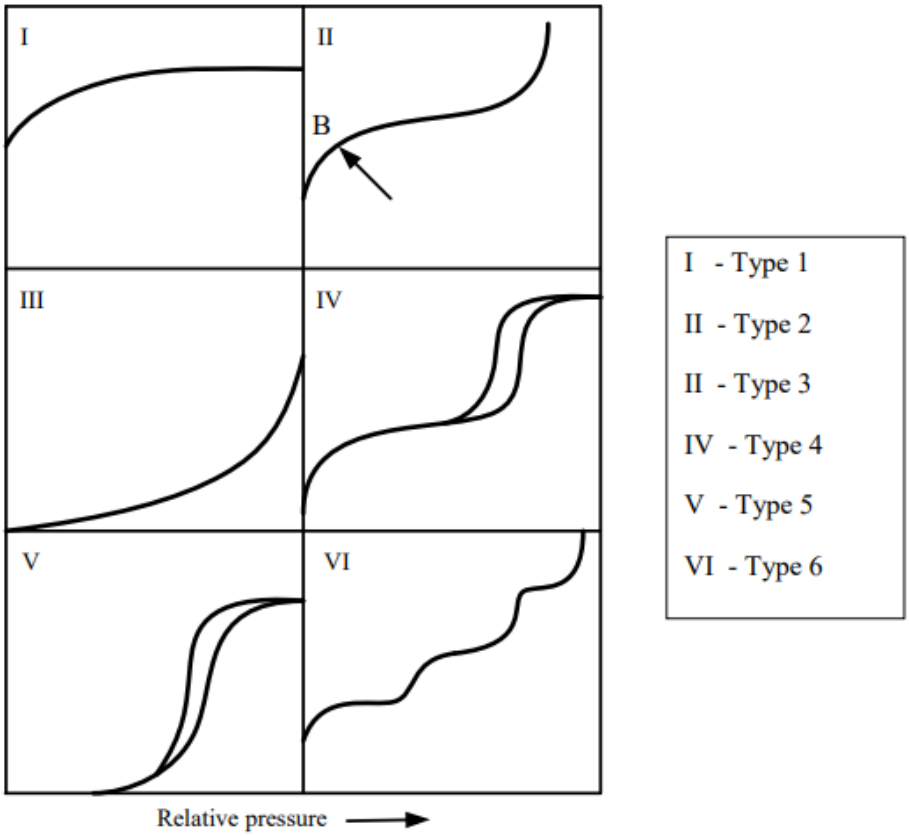

Figure 2.13: Possible adsorption isotherms according to the BET theory (Adapted from (Fletcher 2008))

Type I: This adsorption isotherm is typical to monolayer adsorption. Adsorbents that give Type I adsorption isotherms are microporous (having predominantly micropores). In this type of adsorption, a single layer of adsorbate forms on the surface of the adsorbent.

Type II: This adsorption isotherm is typical to multilayer adsorption. Adsorbents that give Type II adsorption isotherms can be both micro and macroporous (having both micropores and macropores). Single layer coverage is followed by multilayering of the adsorbate on the adsorbent surface. The inflection point (see point A on Figure 2.9) is a result of the implementation of the single layer and the initiation of multilayer adsorption.

Type III: This adsorption isotherm is typical to weak interactions between the adsorbent and adsorbate. Adsorbents that give Type III adsorption isotherms are non-porous or microporous. Type III adsorption isotherms are unfavourable as they are caused by weak interactions between the adsorbent and adsorbate which leads to slow adsorption.

Type IV: This adsorption isotherm is typical to adsorption where the adsorbate condenses inside the adsorbent pores. Adsorbents that give Type IV adsorption isotherms are mesoporous (having predominantly mesopores). As with Type II adsorption isotherms, the inflection point (see point B in Figure 2.9) confirms that monolayer adsorption is followed by multilayer adsorption. The difference is that type IV adsorption isotherms show a loop of hysteresis attributable to condensation that occurs inside the pores of the adsorbent.

Type V: This adsorption isotherm is typical to adsorption that is a combination of both Type III and Type IV. Adsorbents that give type V isotherms are microporous.

Type VI: This adsorption isotherm is typical to adsorption where a double phase transition occurs, for example, the adsorbate changes from a gas to liquid and liquid to solid during adsorption. This type of isotherm was introduced primarily as hypothetical with very few known examples. The shape of this isotherm is due to the formation of single layers of adsorption before progressing to subsequent layers. Each point of inflection indicates the completion of a single layer of adsorption (Fletcher 2008; Berger and Bhown 2011) and (W John Thomas and Crittenden 1998).

An equilibrium will be formed when the adsorbent and adsorbate are contacted for a long enough period and no more adsorbate will be adsorbed. Adsorption equilibrium is an important aspect to consider when designing adsorption systems and is represented by adsorption isotherms. There are several adsorption equilibria theories, and these include the Langmuir theory, the BET theory, the Freundlich theory, the Polanyi Potential theory and the Temkin theory amongst others. This study will focus on the Langmuir and BET theories as they are the most relevant to this study.

The Langmuir Theory**:** Type I adsorption isotherms are characteristic of the Langmuir theory, and in other literature are described as Langmuir isotherms. This isotherm can describe adsorption systems in which there is only a single layer of adsorbate covering at or before the relative pressure of unity is reached (Fletcher 2008). The single layer coverage means that this adsorption isotherm can used to describe chemisorption and can be expanded to define binary adsorbate systems (W John Thomas and Crittenden 1998). This theory suggests a dynamic equilibrium between the adsorbed stage and the gas phase. The rate at which the adsorbate hits the adsorbent surface is proportional to the product of the gas partial pressure (P) and the remaining exposed fraction $(1 - \theta)$ of the adsorbent surface and is therefore available as sites of adsorption. An important assumption of the Langmuir theory is that it assumes that all sites

are probable for adsorption to occur. The Langmuir theory also covers desorption. Langmuir theory predicts that the desorption rate of adsorbate from the adsorbent surface is directly proportional to the fractional surface coverage (θ) and that the adsorption and desorption rates are equal at equilibrium (W John Thomas and Crittenden 1998).

$$K_a P(1-\theta) = K_d \theta \qquad \text{Equation (3.1)}$$

Where k_a and k_d are the adsorption and desorption constants, respectively.

The more common form of equation 2.4 is:

$$\theta = \frac{q}{q_m} = \frac{bP}{(1+bP)} \qquad \text{Equation (3.2)}$$

Where, q is the adsorbate adsorbed, q_m is the total quantity (q) of adsorbate that could potentially be adsorbed in a single monolayer and $b = ka/kd$

The BET theory: Type II and Type IV isotherms are characteristics of BET theory. The BET theory is part of the Langmuir theory, since the presence of multilayer adsorption is accounted for. Accounting for the existence of multilayer coverage means that this adsorption isotherm can be applied to identify physisorption of gas molecules onto adsorbent surface. This theory is often widely used to describe the unique surface areas of various porous materials. This theory uses the same assumptions of the Langmuir theory as well as assumes that there can be infinite multilayers, each layer is independent of other layers, there is no contact between the layers and it is possible to apply the Langmuir principle to each layer. Based on these assumptions the equations used in Langmuir theory have been extended for BET theory as:

$$\frac{1}{v\left[\left(P/P_s\right)-1\right]} = \frac{c-1}{v_m c}\left(\frac{P}{P_s}\right) + \frac{1}{v_m c} \qquad \text{Equation 2.3}$$

In equation 2.9, the variables are defined as:

Ps is the saturation pressure at the adsorption temperature of the adsorbate molecules,

P is the equilibrium pressure at the adsorption temperature of the adsorbate molecules,

V is the adsorbed quantity of gas in volume units,

Vm is the monolayer adsorbed gas quantity,

C is the BET constant, which is expressed by:

$$c = exp\left(\frac{E_1 - E_L}{RT}\right)$$ Equation 2.4

Where E1 is the first layer adsorption heat and EL is that for the second and higher layers equal to the liquefaction heat, R is the gas constant and T is the temperature constant.

Large scale adsorption processes

Adsorption is an important industrial process and is applied in several different applications such as drying of air, sweetening of natural gas, as well as removal of solvents from air stream (W John Thomas and Crittenden 1998). In large industries, adsorption is mostly applied in packed beds where the solid adsorbent material is packed in a column with the bulk fluid from which a component is to be extracted is passed through the packed bed (Wauquier 1995; W John Thomas and Crittenden 1998; Yang 2003). Packed beds are arranged adjacent to each other in an adsorber stripper fashion to enable continuity of the adsorption process. As one bed adsorbs, another desorbs all in sequence such that the process is continuous.

b) Adsorption – Desorption Cycles

Desorption is the process whereby the adsorbent is regenerated by rendering it adsorbate free, and ready for the next adsorption cycle. In CO_2 capture both the adsorption and desorption processes should be studied as they are both important in the separation of CO_2. Regeneration of the adsorbent allows for the CO_2 capture process to be cyclic. Several desorption methods which can be used for CO2 adsorption exist. The various adsorption desorption cycles are pressure swing adsorption (PSA), temperature swing adsorption (TSA), electric swing adsorption (Alhorr, Eliskandarani and Elsarrag) and vacuum swing adsorption (VSA). PSA and TSA are the two main methods and will be discussed below.

Pressure Swing Adsorption: Pressure swing adsorption depends on the pressure variation within the adsorption column. Increasing pressure results in the adsorbate molecules interacting more with the adsorbent surface. At higher partial pressures, the kinetic energy of the adsorbate molecules is increased and facilitates the adsorbate's adsorption to the adsorbent. At higher pressures and lower temperatures, adsorption takes place. The adsorbent would then be regenerated by blocking the flow of gas and decreasing the pressure before equilibrium is reached (Mondal, Balsora and Varshney 2012). The decrease in pressure causes a decrease in the partial adsorbate pressure that promotes desorption. Adsorption desorption cycles can thus be controlled by controlling the pressure inside the packed column.

Temperature Swing Adsorption: Temperature swing adsorption depends on the temperature difference within the adsorption column. Decreasing temperature results in the adsorbate molecules adsorbing to the adsorbent surface attributed to the exothermic nature of adsorption. At low temperature and low/ambient pressure, adsorption takes place. Once equilibrium has been reached the adsorbent is then regenerate by stopping the gas flow and increasing the temperature (Mondal, Balsora and Varshney 2012). The increase in temperature leads to the endothermic process being favoured based on Le Chatlier's principle. The endothermic process is the desorption of the adsorbate. The adsorption desorption cycles can thus be controlled by controlling the temperature inside the packed column.

PSA is more commonly used than TSA because the PSA process gives shorter time periods of cycles and has a slightly lower operational cost. The shorter time periods of cycles associated with PSA is since TSA requires more time to heat up and cool down the adsorbent bed. This heating of the adsorbent bed increases the energy requirements and thus makes TSA more expensive than PSA (W John Thomas and Crittenden 1998). PSA may not always be more desirable, however, than TSA. When the adsorbate is firmly fixed to the adsorbent surface, TSA is favoured, or if there only need be slight temperature change between adsorption and desorption cycles as the energy requirements will not be as significant (W John Thomas and Crittenden 1998). Therefore, the selection between the application of the TSA and the PSA should be provided after the whole system has been completed and its specifications have been considered. At industrial scale, packed bed columns are used to remove CO_2. The solid adsorbent material is used to pack the column. At the bottom of the packed column, the CO_2 rich flue gas is fed and flows up to the adsorbent interface. The CO_2 moves from the gas phase to the solid phase. Numerous packed columns are used and are arranged adjacently to enable a continuous process. One packed column will adsorb CO_2 and when that adsorbent has reached equilibrium the flue gas will be rerouted to the next packed column and first packed bed will be desorbed and the adsorbent regenerated. Figure 2.14 depicts the description of how gas flows in the packed bed column.

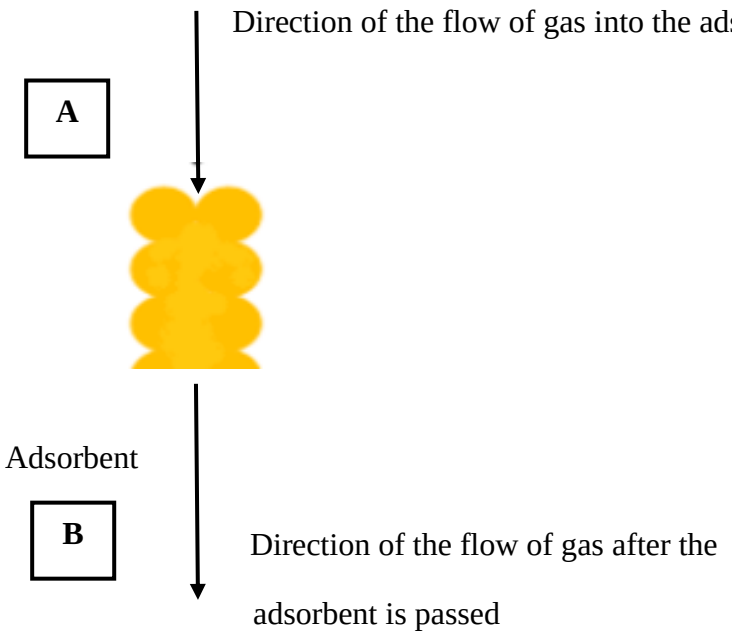

Figure 2.14: Description of how gas flows in the Packed-Bed column

2.7 Types of Adsorbents for CO_2 Capture

An adsorbent is the solid material that is used to target and remove adsorbate molecules from the bulk fluid in an adsorption process. It is important that the adsorbate be effectively removed from the bulk fluid as this is the target of any separation process. The efficiency and economic feasibility of the method of adsorption depends on the adsorbent used. Extensive research on the nature of adsorbents that would be ideal for CO_2 capture has recently been carried out. For an adsorbent to be effective it must be cost effective, can adsorb CO_2 efficiently at moderate operating conditions, and have no negative environmental effects. In addition, the following properties are expected of a good adsorbent.

High surface area: A large surface area is a desirable feature of an adsorbent since it ensures that there is more space for the adsorbate to adsorb.

High pore volume: Pore volume is the ratio of air volume to the total volume of a porous material and is an indication of the available free space within porous material. A high pore volume is a desirable property of an adsorbent because it implies that there is more space available for adsorption to occur.

Good pore size: Porosity is the collective term given to these pores, and their distribution in a solid structure. Pores are the minute spaces that are accessible to gases in solids. Pore size refers to porous diameter (Mosher, Liu and Wilcox 2011). Pore size is a major adsorption attribute for two reasons. Firstly, different gasses have various particle sizes dependent on intramolecular forces and bonding capacities. For adsorption to occur, particulate gas must be capable of penetrating adsorbent pores. When the pores are too wide for the gas molecule, so there is less possibility of adsorption. The second reason why pore sizes are critical to determine a good adsorbent is that different pore sizes have been seen to act differently throughout adsorption. Micropores (width not exceeding 2 nm), for example, can mainly undergo physisorption only at a pore-filing level. This differs from mesopores (width between 2 nm and 50 nm) and macropores (width greater than 50 nm) which display multilayer adsorption. Mesopores were known to be the best for CO_2 gas adsorption (Mosher, Liu and Wilcox 2011). Surface area, internal volume and pore size are referred to as the surface geometry of the adsorbent and are commonly measured using N_2 physisorption at 77 K. It is of importance to characterize an adsorbent in terms of its physical properties (pore size, pore volume and surface area), as these are the properties that influence the performance of the adsorbent (Yang 2003). Pore sizes vary within an adsorbent; Table 2.4 shows three different types of pores based on their sizes.

Table 2.4: Different types of pores and their properties (W John Thomas and Crittenden 1998)

Type of pore	**Diameter (nm)**	**Pore volume (cm^3/g)**	**Surface area (m^2/g)**
Micropores	< 2	0.15 – 0.5	100 – 1000
Mesopores (Transitional pores)	2 – 50	0.02 – 0.1	10 – 100
Macropores	> 50	0.2 – 0.5	0.5 - 2

High adsorption capacity***:*** Gray et al. suggests that for adsorbents to be competitive with conventional amine-based adsorbents they should achieve a CO_2 adsorption capacity of 3 – 6 mol CO_2/kg adsorbent (or 132 – 264 g CO_2/kg adsorbent) (Gray *et al.* 2008).

High selectivity for CO_2**:** Flue gas contains only 10 – 15 % CO_2 gas, with O_2, N_2, moisture and various other impurities making up the remainder (Saha *et al.* 2012). CO_2 should be adsorbed selectively over other flue gas components by a suitable adsorbent. The degree of selectivity

obtained has a major influence on the purity of CO_2 and, subsequently, the processes of pumping and storage.

Fast adsorption/desorption kinetics**:** The adsorption/desorption kinetics give a measure of the rate at which the adsorbent will adsorb and desorb CO_2. This offers an overview of the adsorbent's overall separation performance under the specific working conditions. For fixed-bed reactors, faster kinetics can reduce cyclic operation time as well as reduce the amount of adsorbent required for per volume of flue gas (Zhao 2012).

Sufficient recyclability and cyclic stability: It is important that the adsorbent can be regenerated and recycled. The recycled adsorbent should maintain its adsorption capacity. The adsorbent must be able to be used for many cyclic operations without noticeable deteriorations in performance.

Mechanical strength**:** The adsorbent must have suitable microstructure and morphology under several different operating conditions to overcome attrition, thermal degradation, and mechanical abrasion.

Thermally Suitable: The adsorbent must be thermally suitable at industrial adsorption/ desorption temperature.

Economical synthesis process: The synthesis process and raw materials required to produce the adsorbent should be simple, easy to scale up and inexpensive to compete with existing CO_2 capture technologies.

Finding an adsorbent that can satisfy all these characteristics is still a challenge for CO_2 capture. There are several proposed adsorbents that are being researched for CO_2 capture (Berger and Bhown 2011; Lee and Park 2015a) and (Riboldi *et al.* 2014). These adsorbents are classified as either non-carbonaceous or carbonaceous and have different properties.

2.7.1 Non-Carbonaceous Adsorbents

Non-carbonaceous adsorbents are characterized by the fact that they do not contain the element carbon in their chemical structures. Examples of non-carbonaceous adsorbents are zeolites and silica materials.

Zeolites

Zeolites are three-dimensional porous crystalline aluminosilicates, consisting of alkaline and alkaline earth elements such as sodium, potassium, and calcium (Hardie *et al.* 2005). Different types of zeolites can be synthesized by alteration of Si/Al ratio during the synthesis process to give different Zeolites that are suitable for different processes. Zeolites possess certain features that make them suitable for separation of gas. Zeolites are usually utilized in industry as selective catalysts, ion exchangers and adsorbents (Yang 1997). Zeolites are currently being extensively studied for CO_2 capture attributable to their desirable properties as adsorbents. These characteristics include uniform molecular pores (usually around 3 to 8 Å), high adsorption capacity, reversible and selective gas adsorption (Hardie *et al.* 2005). The crystalline lattice structure of zeolites makes them polar. This provides them with a high affinity to other polar molecules like H_2O (Hardie *et al.* 2005). Studies on zeolite adsorption of CO_2 have shown physisorption to be the primary mechanism of adsorption. Although chemisorption has been shown to occur which makes desorption difficult (Spigarelli 2013). Spigarelli (2013) reports that the adsorption capacity of zeolites ranges from 4 - 216 g CO_2/ kg zeolite, with moderate operating conditions (temperatures ranging 0-100 ºC and pressure ranging from 0.1 - 1 bar) (Spigarelli 2013). Due to their polar nature, zeolites have a higher H_2O affinity than CO_2. The CO_2 adsorption capacity of zeolites has been observed to decrease substantially in the presence of moisture (W John Thomas and Crittenden 1998). A summary of the advantages and disadvantages associated with zeolites is presented in Table 2.5.

Table 2.5: Advantages and disadvantages of zeolites (Adapted from (W John Thomas and Crittenden 1998), (Hardie et al. 2005) and (Spigarelli 2013))

Advantages	**Disadvantages**
i) Favourable adsorption kinetics	i) Impurities present (NOx, SOx, and H2O) have a significant impact on performance
ii) High adsorption capacity (0-100 0C, 0.1-1 bar) under mild operating conditions	ii) CO_2 has been seen to chemisorb to the surface of the zeolite
iii) Suitable for post-combustion CO_2 capture	iii) Desorption must take place using the energy and time intensive TSA for complete regeneration

Silica Materials

Silica materials are based on silica (SiO_2) and are a relatively new technology for CO_2 capture. Silica materials possess certain properties which have made them desirable for gas separation. These characteristics include high surface area, high internal pore volumes, desirable thermal stability, desirable mechanical strength, desirable chemical stability, and pore size that can be manipulated. Most applications of silica materials for CO_2 capture make use of silica material that has been impregnated or grafted with amines.

Amine functionalized silica materials are adsorbents which consist of a solid silica support onto which an amine has been immobilized or impregnated or grafted. The impregnation or grafting of amines onto a solid support addresses the major problems associated with amine adsorption, along with high regeneration costs (the large volume of liquid related to adsorption), corrosion equipment and the reduction of amine solvents due to evaporation. The most used amine has been poly (ethyleneimine) (PEI). Due to the high concentration of amine, approximately 33% NH_2 by weight, this amine was selected.

Silica materials show chemisorption, indicating that desorption will require a larger energy input. Also, the amines undergo irreversible reactions with SOx and NOx to produce unwanted products (Spigarelli 2013). The amine-loaded silica support studies MCM-41 and SBA-15 actually indicate a 4-9% loss of regenerated adsorbent CO_2 adsorption capacity (Spigarelli 2013). Adsorption potential of amine-functional silica materials under moderate operating conditions (0.05-1bar and 25-75ºC) ranges from 0.089 to 0.22g CO_2/kg adsorbent (Spigarelli 2013). Although their CO_2 adsorption capacity is low, adsorption capacity has also been found

to be not significantly affected by partial CO_2 pressure (Spigarelli 2013). This makes them extremely suitable for capturing CO_2 after combustion. Table 2.6 provides a description of the benefits and drawbacks associated with silica materials.

Table 2.6: Advantages and disadvantages of silica materials (Adapted from (Spigarelli 2013))

Advantages	**Disadvantages**
i) Adsorption capacity least impacted by partial CO_2 pressure	i) Degrade at temperatures around 100 ºC
ii) Humid environments improve performance of adsorption	ii) Unwanted-by products produce irreversible reactions with NOx and SOx
iii) Favourable adsorption kinetics	iii) Loss of adsorption capacity after desorption of 4.9%

Metal Organic Frameworks (MOFs)

MOFs have become well known for their high surface areas, variable pore structures and modifiable surface properties. These properties may be adjusted by varying the metallic clusters or the surrounding ligands (Millward and Yaghi 2005). Highly crystalline materials consisting of ordered, extended, one-dimensional, two-dimensional, and three-dimensional networks of metal ions or clusters linked to multifunctional organic ligands are said to be MOFs (Li *et al.* 1999; Millward and Yaghi 2005; MacGillivray and Lukehart 2014). MOFs find application in methane (CH_4) and H_2 adsorption, where they display good selectivity and high adsorption capacity (Eddaoudi *et al.* 2002). According to Lee and Park (2015b), MOFs have molecules that are reticulate leaving voids at the centers, resulting in a large body volume. MOFs have recently been studied for CO_2 capture where they display remarkably high adsorption capacities in pure CO_2 gas streams (Rowsell and Yaghi 2004). The drawbacks come with mixed gas streams, for example flue gas where the partial pressure of CO_2 is low, the adsorption capacity of MOFs decreases significantly (Rowsell and Yaghi 2004; Yu, Huang and Tan 2012; Lee and Park 2015b). Ultimately, increasing the partial CO_2 pressure would increase the operating cost of the adsorption operation. Research where MOFs have been treated with amines to enhance CO_2 capture is currently underway in an attempt to circumvent the low capacity challenge in low CO_2 partial pressures (Yu, Huang and Tan 2012). Furthermore, synthesis of MOFs is quite

a complex process and the raw materials (metal complexes and organic ligands) required are expensive (Millward and Yaghi 2005; Yu, Huang and Tan 2012).

Literature also states that MOFs have a high affinity for moisture which weakens their mechanical strength and makes them less durable (Eddaoudi *et al.* 2002; Yu, Huang and Tan 2012) Given that the target application is in post combustion capture, where CO_2 partial pressure is low and moisture may be present, more research to improve MOFs for post-combustion capture of CO_2 is necessary.

Alkali-based materials

Alkali-based materials are alkali-metal carbonates which are applied as dry adsorbents in CO_2 capture (Zhao *et al.* 2013). Alkali-based materials are able to operate at moderate temperatures of below 20. (Yu, Huang and Tan 2012). When capturing CO_2, alkali-based materials undergo the reaction shown:

$$M_2CO_3(s) + H_2O(g) + CO_2(g) \leftrightarrow 2MHCO_3(s) \qquad \text{Equation (2.5)}$$

$$\Delta H = -ve \ (Reaction\ is\ exothermic)$$

Where M can be sodium (Na) or potassium (K).

In the reverse reaction which occurs after heating, the alkali-based adsorbent is recovered, together with the CO_2 and H_2O in gaseous form. Passing this mixture through a condenser will ensure separation of the CO_2 from H_2O with a high purity CO_2 stream being produced. Adsorption of CO_2 using alkali-based materials occurs in the temperature range 60 - 110 °C, forming alkali-metal carbonates, and the reverse process occurs in the temperature range 100 – 200 °C, regenerating the alkali-metal carbonate (Wilcox 2012). For post-combustion CO_2 capture, alkali-metal carbonates are extremely desirable as they can withstand relatively high temperatures and do not require cooling of the flue gas before entering the CO_2 capture plant. Furthermore, the alkali-metal carbonates are moisture tolerant. Challenges, however, arise with recyclability, particularly stability of the adsorbent material over time while in continuous use (Wilcox 2012).

Metal Oxide Carbonate Materials

The use of metal oxides like calcium oxide (CaO) and magnesium oxide (MgO) as adsorbents is the basis of metal oxide carbonate materials. The CO_2 is captured in the form of an insoluble

carbonate. literature indicates that MgO has been identified to be an effective CO_2 capture adsorbent. (Yu, Lin and Cheng 2015). The advantages of using MgO as a CO_2 adsorbent include its low cost, abundance and low toxicity (Wilcox 2012). Drawbacks include the fact that these metal oxides have low CO_2 adsorption capacity. According to Bhatta *et al.* (2015), the adsorption by metal oxides is performed via:

$$MO\ (s) + CO_2(g) \leftrightarrow MCO_3\ (s)\ \Delta H = -175\ kJ/mol \qquad \text{Equation (2.6)}$$

The reverse process which regenerates the adsorbent occurs via:

$$MCO_3(s) \leftrightarrow MO(s) + CO_2\ (g)\ \Delta H = +179.2\ kJ/mol \qquad \text{Equation (2.7)}$$

Assuming perfect conditions and no heat losses, it is possible to design an adsorption-desorption cycle such that a small quantity of heat is added to recover the solid adsorbent as the enthalpies of reaction are approximately equal.

2.7.2 Carbonaceous Adsorbents

Carbonaceous adsorbents are materials that are carbon based. Carbon offers several advantages as an adsorbent. These include, light weight, good mechanical strength, desirable electrical and heat conductivities, high thermal stability. One of the most significant advantages that carbon adsorbents give is that they are not affected by the presence of moisture. Carbon is a moderately inexpensive raw material when compared with non-carbonaceous adsorbents because of its capacity to work at moderate pressures and temperatures, it will also consume less energy when compared to non-carbonaceous adsorbents. Examples of carbonaceous adsorbents are activated carbon, carbon molecular sieves (CMSs), carbonized polymers and resins, carbon nanotubes (CNTs), metal organic frameworks (MOFs), porous polymers, and amine impregnated CNTs.

Activated Carbons (AC)

According to Li *et al.* (2008) and Lee and Park (2015b), ACs are part of a group of carbons from carbon blacks to nuclear graphite. W John Thomas and Crittenden (1998) define ACs as a simple micro crystallite stacked in random orientation by thermal decomposition of different carbonaceous materials, which are then taken for activation. Activated carbons maybe prepared from several different materials that contain carbon, including coal, petroleum, and wood. ACs have pore structures that can be manipulated during preparation processes (Li *et al.* 2008; Yu,

Huang and Tan 2012), and display good thermal stability with a moderate cost of production (Li *et al.* 2008). To add to this, functional groups on the surfaces of ACs may be modified to enhance adsorption in CO_2 capture. Manipulating the pores entails altering pore size, to allow the ACs to act as molecular sieves. This can be very beneficial in CO_2 capture where the flue gas incorporates CO_2, O_2 and N_2 which are 3.6, 3.5 and 3.3 Â, respectively. Use of ACs in CO_2 also has the added benefit of thermal stability. ACs are stable at temperatures in excess of 500 °C compared to several other adsorbents, and in addition they are cheap to produce (Li *et al.* 2008; Lee and Park 2015b)

Ordered Porous Carbons (OPC)

OPCs have been mainly tested for gas storage and use in catalysis. OPCs display high specific surface areas, good chemical stabilities, large CO_2 adsorption capacities and may have their pore properties (volume and size) altered to enhance adsorption (W John Thomas and Crittenden 1998). For this reason, they are postulated to be good for CO_2 adsorption (W John Thomas and Crittenden 1998).

Carbon Molecular Sieves (CMS), Carbonized polymers and resins

Wahby *et al.* (2012) describes carbon molecular sieves as carbonaceous materials with small pore size distributions, which have a selective capacity for adsorption of unique components from a mixture. Depending on size, shape, adsorption rate or a difference in adsorption equilibrium, CMSs can separate molecules (Carruthers *et al.* 2012; Wahby *et al.* 2012). CMSs have a great potential in CO_2 capture. In the United States of America, CMSs produced from pyrolysis and activation of polyvinylidene have been commercialized and research is focusing on producing CMSs for CO_2 capture at a large scale (Carruthers *et al.* 2012). Research with CMSs in CO_2 capture has shown that for a high adsorption capacity to be achieved, well developed micro porosity is necessary. CMSs have the added advantage of being able to perform adsorption at temperatures between 0 and 50 °C, implying that energy costs with using this adsorbent are relatively low (Carruthers *et al.* 2012; Wahby *et al.* 2012). Carbonized polymers and resins are produced from resins which include phenol, formaldehyde and styrene amongst others (W John Thomas and Crittenden 1998). These materials are pyrolyzed with the products from the pyrolysis being carbonaceous adsorbents (W John Thomas and Crittenden 1998). These adsorbents are still under research and there is interest in their application for CO_2 capture.

Porous polymers

Porous polymers are porous solid materials that are synthesized from organic building blocks (Xu and Hedin 2014). According to Xu and Hedin (2014), there are no standardized names for them and they are similar in nature to conjugated porous polymers, porous aromatic frameworks and hyper-crosslinked polymers. Synthesis of porous polymers can be through simple and traditional reactions. Amongst adsorbents applied in CO_2 capture, use of porous polymers is advantageous in that they are organic in nature and because they are organic, they are biodegradable (Ngoy *et al.* 2014; Xu and Hedin 2014). Biodegradability is an important property in adsorbents as there is an environmental awareness drive to ensure that adsorbents used are environmentally friendly (Lu and Dai 2014; Ngoy *et al.* 2014). Given that porous adsorbents may also be synthesized from several different reactions, it is possible that the monomer units may be coupled and the polymer chain lengthened, allowing a larger surface area for CO_2 capture (Ngoy *et al.* 2014). Furthermore, the surface of the polymer may be grafted with amines to enhance the CO_2 capture of the adsorbent (Xu and Hedin 2014). Porous adsorbents, depending on the raw materials from which they are produced, could be less hydrophilic compared to other adsorbents. Porous adsorbents also possess good chemical and thermal stability (Xu and Hedin 2014). Drawbacks of porous adsorbents are that their adsorption capacities are low compared to other adsorbents such as MOFs and zeolites (Ngoy *et al.* 2014; Xu and Hedin 2014).

2.7.3 Activated carbon as an adsorbent for CO_2 Capture

Activated carbons are carbonaceous materials which were treated to form pores using oxygen. Pores increase the surface area and allows for more CO_2 adsorption to occur (JECFA, 1992). Activated carbon comes as black powder or granules and can be produced from several carbon-containing materials. It is advantageous that there is such a variety of raw materials. Activated carbons made from different sources do have differences in surface geometry. This has led to a broad variation in the performance of CO_2 adsorption of various activated carbon CO_2 adsorption with activated carbon through physisorption, the CO_2 adsorption capacity decreases with an increase in temperature. Activated carbons adsorb most efficiently at room temperature. Under moderate operating conditions (0.1 – 1 bar and 25 – 75 ºC), the adsorption capacity of activated carbon has been shown to be between 3-154 g CO_2 / kg activated carbon. At much higher pressures of 35 bar activated carbon was shown to have an adsorption capacity as high as 1130 g CO_2/kg activated carbon (Spigarelli 2013). It indicates that the activated carbon has excellent CO_2 capture capacity from high pressure gas streams, including pre-combustion, and

can be used for PSA. A disadvantage to activated carbons is that: the CO_2 adsorption capacity has been shown to be negatively affected by the presence of NO_2, SO_2 and moisture despite its hydrophobic nature. Table 2.5 provides a description of the benefits and drawbacks associated with activated carbon.

Table 2.7: Advantages and disadvantages of activated carbons (Adapted from (JECFA, 1992) and (Spigarelli 2013))

Advantages	**Disadvantages**
i) High thermal stability	i) Low CO_2 capacity at mild conditions
ii) Favourable adsorption kinetics	ii) Negatively impacted by NO_2, SO_2, and H_2O
iii) Broad selection of starting materials for activated carbon production contribute to lower costs for raw materials	iii) Wide range of starting materials implies that a broad variety of porous characteristics are often seen among adsorbents
iv) High capacity to adsorb at high pressures	
v) PSA can potentially create desorption	

2.7.4 Kaolinite as an adsorbent for CO_2 Capture

Mineral clay is one of the most available natural materials and is therefore available at a minimal cost. Kaolinite is chosen as the study material due to the possibility of a potential adsorbent, due to minimal cost, abundance of natural materials and good mechanical and chemical stability. Its crystal structure is composed of sheets of tetrahedral silicate and octahedral hydroxide. Kaolinite is an Al_2O_3 $2SiO_2.2H_2O$ chemical formula clay mineral with a 1.1 uncharged dioctahedral layer structure where each layer binds to a specific tetrahedral sheet of silica and a single octahedral sheet of alumina. The use of clays for adsorption and separation can be greatly expanded. To our best understanding, very few studies have explored kaolinite for CO_2 capture so far and studied extensively the parameters relating to its capacity for adsorption. Most research efforts have concentrated on clay minerals from an industrial perspective.

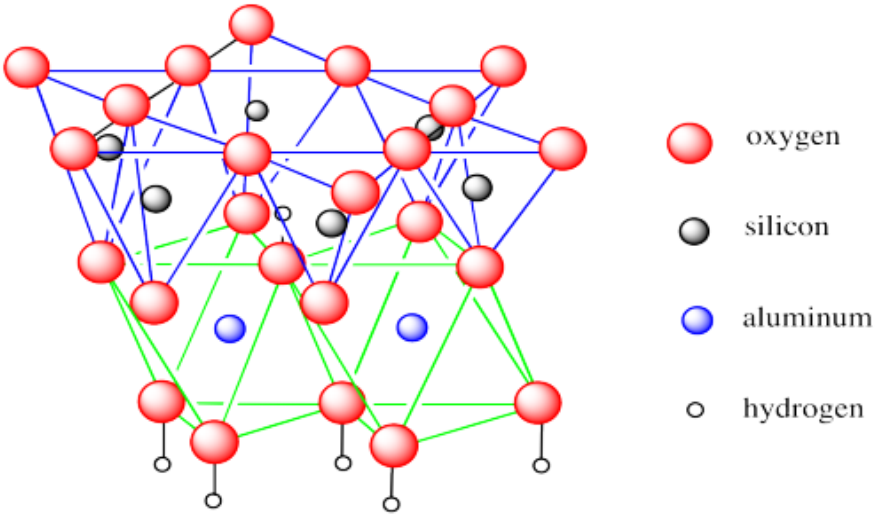

Figure 2.15: Structure of kaolinite

2.8 Coal, CO2 Emissions and CCS in South Africa

As mentioned in Chapter 1, South Africa is a significant emitter of CO_2 and is committed to reducing her CO_2 emissions. However, as was also mentioned in Chapter 1, South Africa is heavily dependent on the use of coal to meets its energy needs.

South Africa was estimated to be the world's 12th largest CO_2 emitter in 2014 and accounts for almost half of Africa's CO_2 emissions (Osler 2017). South Africa has made governmental commitments to decreasing its CO_2 emissions through CCS. The South African Center for Carbon Capture and Storage (SACCCS) was established to develop and implement the commercial application of CCS in South Africa. On 30 March 2009, the SACCCS was formed. The SACCCS has put into Africa. On 30 March 2009, the SACCCS was formed. The SACCCS has put in a place a five-stage plan, known as a CCS roadmap. The first stage was to verify whether the country has CO_2 rich streams where CO_2 can be captured. The second stage involved developing a geological storage atlas. Both stages have been successfully completed and have shown promising results for the possibility of implementing CCS (SACCCS, 2014. The third stage of the road map is a pilot CO_2 storage project experiment and is currently being undertaken (SACCCS, 2014.

The fourth and fifth phases of the CCS strategy are intended to promote the launch of a CCS demonstration plant capable of capturing 100 kt of CO2 per year by 2020) and manage the introduction of the commercial deployment of CCS (by 2025) respectively.

Figure 2.5 shows the companies in South Africa that are the highest direct emitters of CO_2. Eskom is the most significant of the CO_2 emitters out of the companies considered. This is due

to the use of coal for energy production. This study and much of the research currently being undertaken in South Africa is aimed at reducing the CO_2 emissions from these sources.

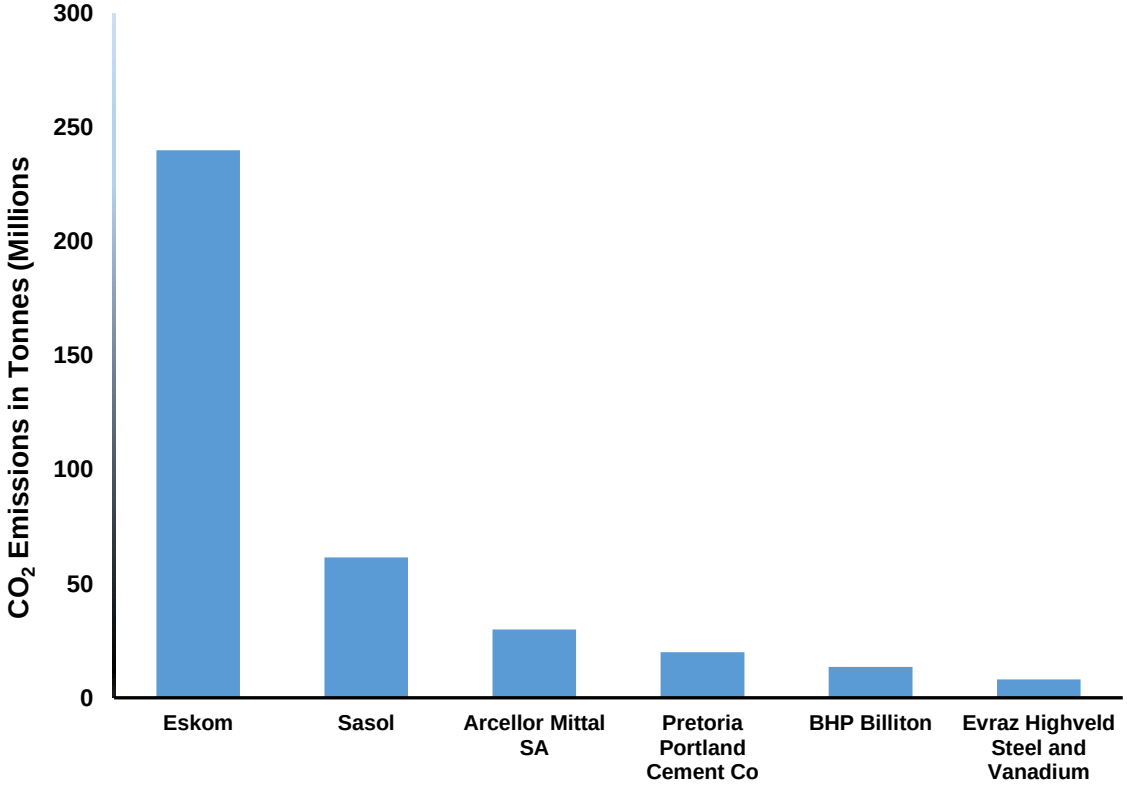

Figure 2.16: South Africa's highest CO_2 emitters (Adapted from (Beck *et al.* 2011)

2.9 Techniques for CO_2 capture in existing coal-fired power plants

To define techniques to capture CO_2 from coal fired power plants it is necessary to understand their means of operation. Figure 2.6 gives the schematic of a typical coal fired power plant. Fuel, in the form of coal, is fed to a combustor and combusted where heat and exhaust gas are produced. The produced heat heats up water to steam in a boiler. The steam is used to turn turbines which produce electrical energy. The produced flue/exhaust gas is made up of N_2, water vapour, CO_2, O_2, particulate matter (PM), nitrous oxides (NOx) and sulphur oxides (SOx). In a typical coal fired power plant the PM, NOx and SOx are removed and the gas that remains, known as flue gas, is emitted to the atmosphere. CCS proposes to add another stage onto the flow process to remove CO_2.

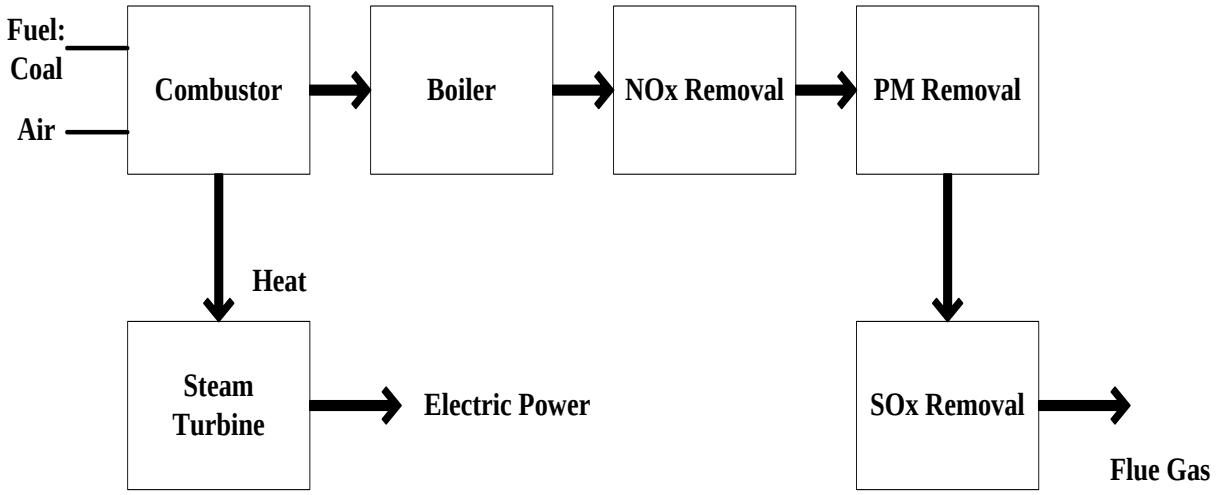

Figure 2.17: Flow diagram illustrating the structure of a coal-fired power plant

The most effective approach to CO_2 capture in a coal fired power plant will be the post-combustion capture approach, based on the schematic depicted in Figure 2.9. This is because the CO_2 is found in the gas that flows from the power plant. According to Li *et al.* (2015), post-combustion capture is appropriate for coal fired power plants due to the ease with which retrofitting can be carried out on existing power plants as compared to other approaches such as pre-combustion capture and oxy-fuel combustion capture. Post-combustion capture is therefore important in the South African context as South Africa has eighteen coal fired power plants, with two of the eighteen to fully come online soon, and comes thirteenth on the world CO_2 emissions list (International Energy Agency, 2004).

CHAPTER THREE

Materials and Experimental Procedure

This chapter contains the materials and equipment that were utilized. In this study, adsorption experiments were performed to test the CO_2 adsorption capacity of the selected adsorbents under different operating conditions. This chapter provides details of the materials, experimental equipment, and experimental procedures.

3.1 Introduction

In this study, kaolinite clay and activated carbon were utilized as adsorbents for CO_2 capture. Kaolinite clay is a layered silicate clay mineral, and its abundance is found in soils, it has potential to be used as an adsorbent for CO_2 capture owing to low cost, rich natural abundance, high mechanical and chemical stability and moreover the presence of clay minerals in soils acts as a pollutant collector to improve the environment while activated carbon is derived from carbon materials such as coconuts, nutshells, coal, rice husk, bagasse sugarcane, peat, and wood available for adsorption or chemical reactions. Activated carbon was produced from sugarcane bagasse and an activating chemical agent $ZnCl_2$ was impregnated onto the sugarcane bagasse to enhance the physical properties, CO_2 adsorption capacity and CO_2 affinity of the raw material. Chemical activation with zinc chloride ($ZnCl_2$) was considered to be more effective because it improved the pore development and surface characteristics of the activated carbon (AC) produced and required a lower temperature of activation (less energy costs), as well as a shorter activation time. It also yielded a higher surface area resulting in a higher adsorption capacity for activated carbon (AC) obtained in this study. The physicochemical properties of the synthesized activated carbon and kaolinite clay were evaluated using FTIR, BET and SEM techniques. The images of the adsorbents are shown in Figure 3.1. The adsorption capacity of the adsorbents was evaluated with custom-built CO_2 adsorption column equipment.

3.2 Materials and Equipment

Commercially available kaolinite clay was obtained from G & W mineral resources in Germiston, South Africa. Sugarcane bagasse was obtained from Umfolozi sugar mill (PTY) LTD, KwaZulu-Natal in South Africa while zinc chloride ($ZnCl_2$) was purchased from a local supplier, $ZnCl_2$ was used as the activating agent. The adsorption column used and coupling fittings were purchased from Swagelok, South Africa. The column has an inner diameter of 1cm with a length 20cm. The gaseous N_2 and CO_2, of analytical grade were obtained from

Afrox, South Africa. All distilled water, glassware, thermometers, timers, magnetic stirrers, oven, muffle furnace, crucibles, sieving pans, bubble flow meter; manual valves, attrition mill, mechanical sieve shaker, thermostatic water bath and desiccators were obtained from the university laboratory. The equipment used for analysis in this study include Scanning Electron Microscopy, Fourier Transform Infrared Spectroscopy (FTIR), Brunauer–Emmett–Teller instrument and custom-built adsorption column equipment. Figure 3.1 illustrates an overview of the experimental methodology used in this work.

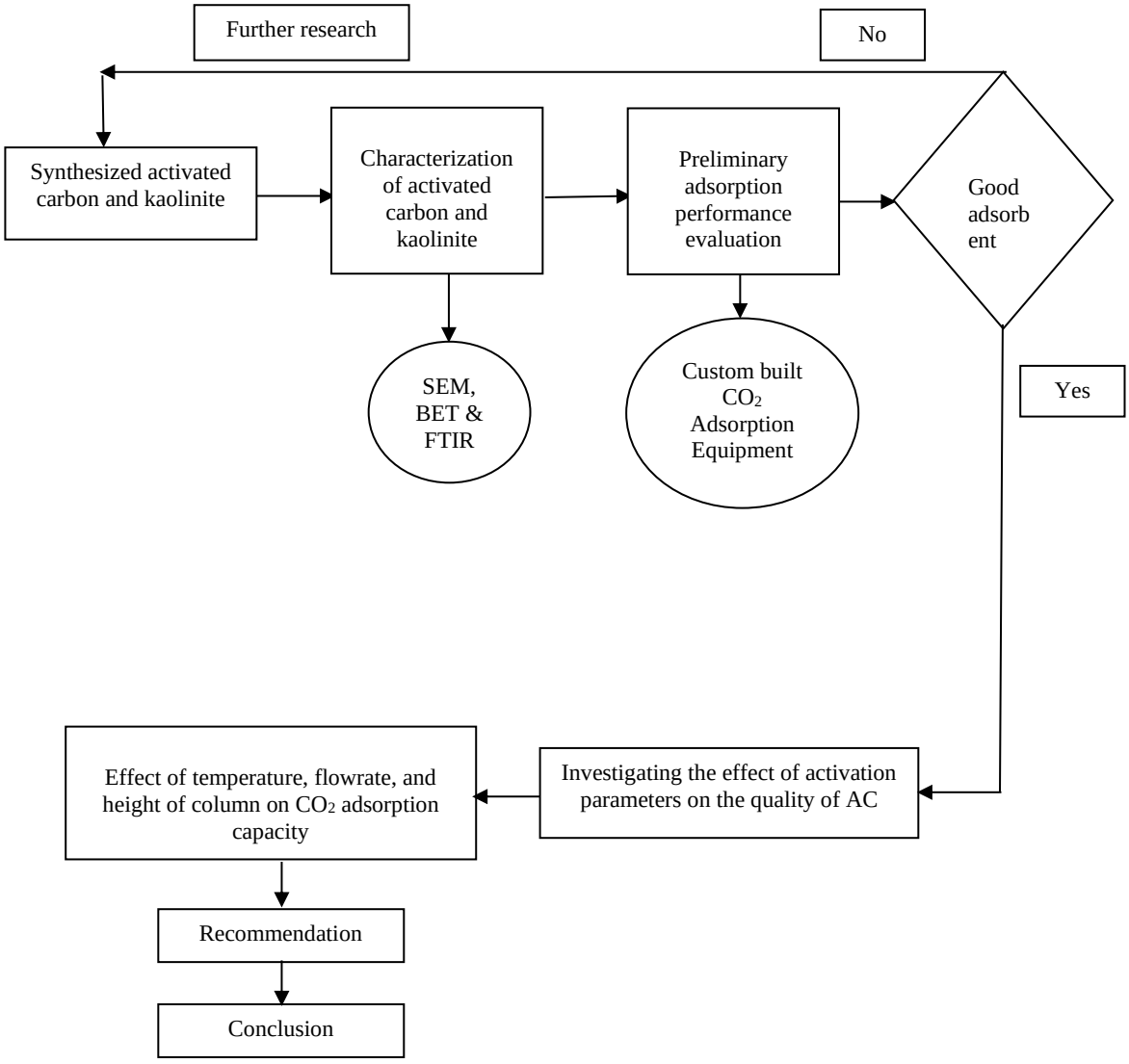

Figure 3.1: Summary of research methodology

3.3 Experimental Procedure

3.3.1 Production of AC: The sugar cane bagasse was washed with hot distilled water to eliminate dirt and other impurities, oven-dried at 110 °C for 2 hours prior activation. With the aid of an attrition mill as shown in Figure 3.2 (a), the material was then crushed for 15 minutes and separated into particles, sieved to a particle size of (<250 μm) using mechanical shaker displayed in Figure 3.2 (b), before activated carbon synthesis. The AC was produced using a chemical activating agent ($ZnCl_2$). During the chemical activation process, 10g of dried precursor was mixed well with 100 ml of solution containing 10g of $ZnCl_2$ for 2hours at room temperature. In this case, the target chemical ratio was 100% (activating agent / precursor). The resulting bagasse was then dried for 24 hrs at 110°C. After this, the obtained $ZnCl_2$–impregnated sugarcane bagasse was placed inside the tubular furnace as shown in Figure 3.3. During carbonization and activation, nitrogen gas flow of 200 mL/min was employed to create an inert atmosphere within the reactor. The temperature was raised to 500 °C (heating rate of 10 °C / min) during carbonization and held for 1 hour. The furnace and gas flow were subsequently shut off and the carbonized sugarcane bagasse AC was allowed to cool to room temperature naturally within the furnace after it was switched off. The char was washed continuously with deionized water to remove residual Zn. Finally, the product of ACs were ground to a fine powder (< 30 mesh size) and stored for the adsorption experiment.

Figure 3.2: Images of (a) Attrition mill and (b) Mechanical sieve shaker

Figure 3.3: Tubular furnace for carbonization

Figure 3.4: Images of adsorbents used in this study (a) Activated carbon (b) Kaolinite

3.3.2 Experimental apparatus: The adsorption apparatus consists of a packed bed adsorption column, bubble flow meter, thermostatic water bath, and gas cylinder supplying gas at a concentration of 99.99 volume % CO_2. CO_2 was used to mimic a flue gas source in this study. Bubble meter was installed to measure the feed flow rate set for the adsorption cell. The adsorption cell temperature was regulated by means of a temperature-controlled water bath. In Figure 3.5, a flow diagram of this setup is presented.

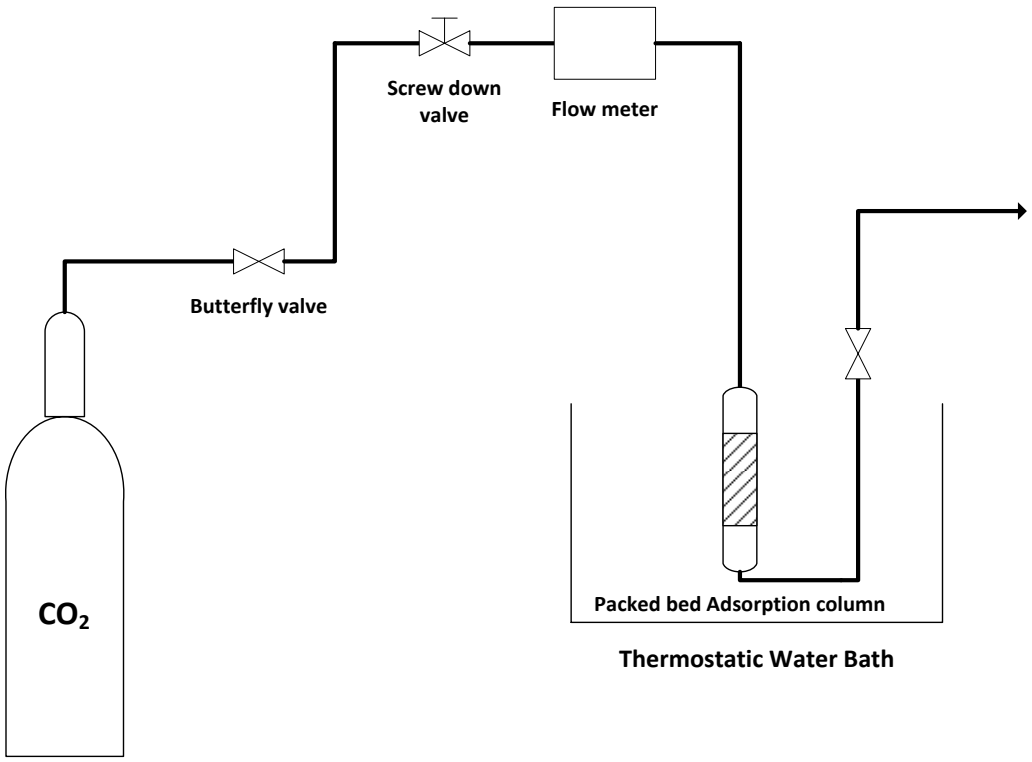

Figure 3.5: Process flow diagram of the adsorption set-up

3.3.3 Adsorption Experimental Procedures

The selected adsorbent was heated in a convection oven prior to the actual adsorption experiment in order to eliminate any unwanted gases and moisture. The adsorbent was heated overnight and cooled down in a desiccator at room temperature. Then the adsorbent was weighed and charged into the adsorption cell. The column was packed with 3.0 g of adsorbents (approximately 5.0 cm in packing height) and mounted in a temperature control bath to maintain a steady desired temperature. Throughout the experiment, the thermostatic water bath temperature was kept constant. The experiment was allowed to run for 1200 seconds (20 minutes) at each temperature (30, 50 and 70 °C). The height of the bed was varied from 3-5cm at each run to study the behaviour of the adsorbents. Experiments were performed at various flow rates and heights to see the effect of flow rate and height in the adsorption process at constant temperature. The feed gas flow rate was 30 mL/min. The column was opened after each run, and the adsorbent was changed. To continue the adsorption test, a new adsorbent material (3g) was fed into the column. To examine the impact of flow rates on the adsorption capacity of the adsorbents, the operating flow rate was varied from 30-70mL/min at constant temperature. Effect of bed height on the adsorption behaviour of the adsorbents was also investigated when the flow rate was varied (30, 40, 50, 60 and 70 mL/min). The experimental process is depicted by a process flow diagram in Figures 3.5; the sample's change in mass was

measured and used to determine the amount of adsorbed CO_2, by equation 3.1 below. Table 3.1 shows the range and values of the variables used in the experiment.

$$CO_2\ adsorption\ capacity = \frac{\text{weight of adsorbent after adsorption} - \text{weight of adsorbent before adsorption}}{weight\ of\ adsorbent\ before\ adsorption} \quad \text{Equation (3.1)}$$

Table 3.1: Experimental conditions for adsorption

Operating conditions	**Value (range)**
Adsorption temperatures (^oC)	30 – 70
Inlet gas flowrate (mL/min)	30 – 70
Height of column (cm)	3 - 5

3.4 Characterization of the Physiochemical Properties of Kaolinite clay and the synthesized Activated carbon (AC)

To characterize the synthesized activated carbon and kaolinite adsorbent, Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR), and N_2 physisorption (using BET) were performed.

3.4.1 FTIR Analysis

The functional groups present in the synthesized activated carbon and kaolinite were verified using FTIR. FTIR is widely used for the study of chemical bonds and functional groups. FTIR can be applied to analyse surface chemistry and to understand the interactions between surfaces during CO_2 adsorption. The chemical structure and functional groups of activated carbon fibres was determined by Fourier transform infrared (FTIR) spectroscopy.

3.4.2 SEM Analysis

The surface morphology of the synthesized activated carbon and kaolinite samples was observed using the scanning electron microscopes. SEM investigation was conducted at University of Cape Town's Electron Microscope Unit.

3.4.3 BET Analysis

BET clarifies the physical adsorption on a solid surface of gas molecules and forms the basis for an effective analytical method to measure the specific surface area of the material. Nitrogen physisorption at 77 K was performed on sugar cane based activated carbon (SBAC), kaolinite and kaolinite/activated carbon composite adsorbent to identify the BET surface area, pore size, and pore volume. A Micromeritics Tristar analyser was used to perform N_2 physisorption. The N_2 physisorption analysis was performed at Durban University of Technology's Department of Chemical Engineering.

CHAPTER FOUR

Results and Discussion

This chapter contains the results pertaining to the characterization of the synthesized activated carbon and kaolinite samples. The influence of the effect of the operating variables, including flow rate, operating temperature, and height of column bed on the adsorption capacity of activated carbon, kaolinite, and kaolinite – activated carbon composite adsorbent during CO_2 capture.

4.1 Introduction

This section discusses results of characterization obtained and the experimental results of CO_2 adsorption on the selected adsorbent materials: activated carbon, kaolinite, and kaolinite – activated carbon composite. The CO_2 adsorption experiments were carried out under test conditions previously provided in Chapter three. The findings reported here can be categorized into two major aspects: i) Characterization results indicating the physiochemical properties of the activated carbon and kaolinite adsorbent material and ii) CO_2 adsorption capacity of the selected adsorbent materials displaying the capacity of adsorption performance. This chapter also addresses the effects of process parameters (temperature, flowrate, and bed height) on adsorption behaviour of the adsorbents.

4.2 Characterization results of adsorbents

A summary of the characterization methods used in this analysis and what they were used for is shown in Figure 4.1.

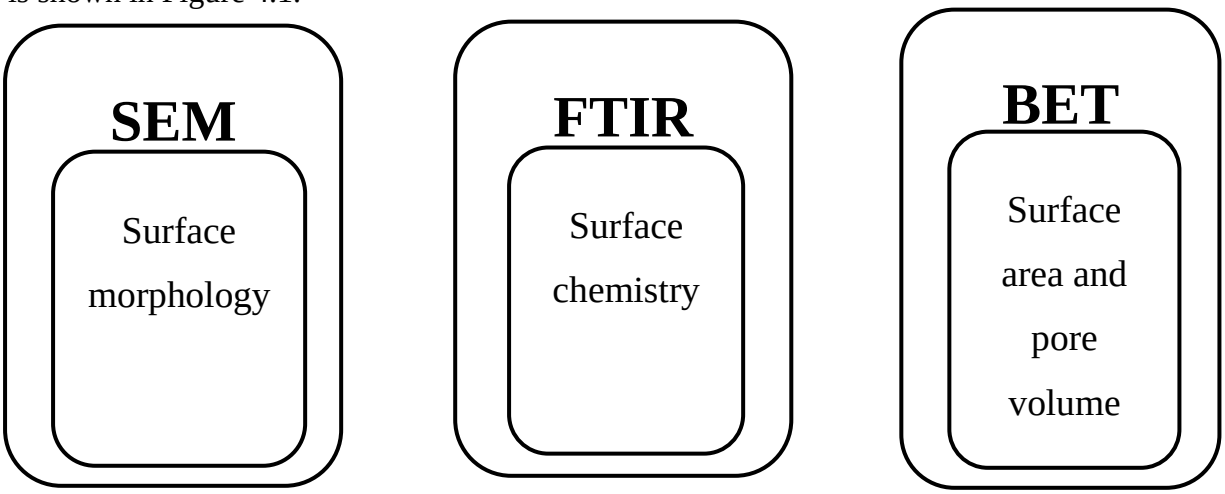

Figure 4.1: Methods of characterization used to analyse Activated carbon, kaolinite, and kaolinite – activated carbon.

4.2.1 Morphological Analysis

The surface morphology of all the samples (calcined kaolinite sample at 800°C for 2 hours and activated carbon at 500°C for 1 hour) were evaluated by the SEM at 50 000X magnification at a scale of 2µm, 5µm and 20µm and the obtained images are shown in Figure 4.2.

The SEM image of activated carbon in Figure 4.2 (a) displays a clear and pronounced variety of honey-comb structures, revealing a greater possibility of gas traps while kaolinite in figure 4.2 (b) sample revealed lesser developed array of honey-comb structures. It demonstrates that there are small cavities and attached fine particles on the kaolinite surface. The SEM images show that the outer surface of the activated carbon is composed of cavities. The cavities on the carbon surface tend to have resulted from $ZnCl_2$ evaporation throughout carbonization, leaving the area surrounded by $ZnCl_2$ (Demiral and Demiral 2008). Consequently, $ZnCl_2$ was an excellent activating agent for achieving higher surface area of activated carbon.

Activated carbon (a) showed that the $ZnCl_2$ used to activate sugarcane bagasse resulted to surface etching and the development of clear pores with a diameter of approximately 1 µm and a slight reduction in carbon particle size. The effective pores are narrow. Interestingly, it is observed that the carbon structure of the sample increases with the activation of the sugarcane bagasse with $ZnCl_2$, and it starts to cohere and form highly porous honey-comb structure of various sizes. These structures can help promote the movement of molecules of CO_2 gas by providing abundant adsorption sites. This shows that hydrocarbons are extracted by activation, which increases the AC's adsorption capacity.

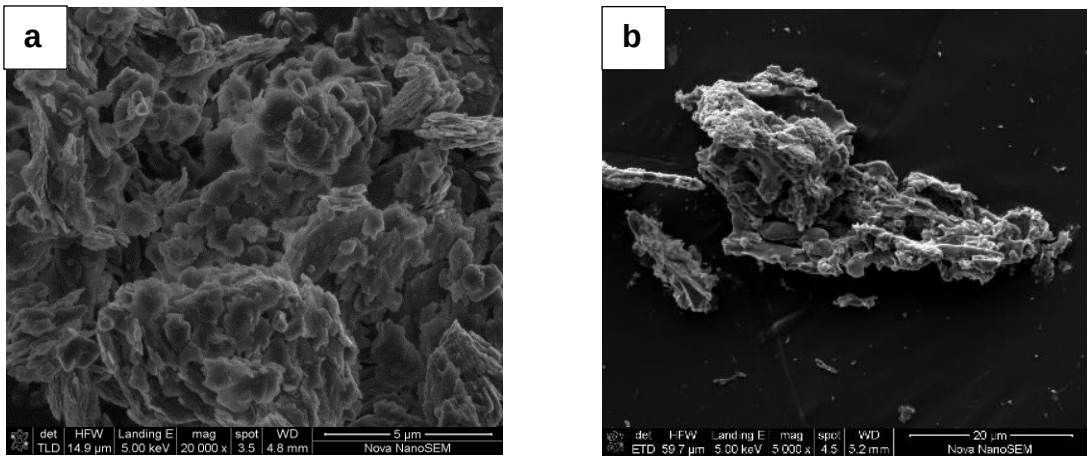

Figure 4.2: SEM images of (a) Activated carbon (b) Kaolinite

4.2.2 Fourier Transform InfraRed (FT-IR) Analysis

The FT-IR analysis was conducted to establish the availability of functional groups. Analysis of the functional groups was carried out on activated carbon (AC) and kaolinite (before and after CO_2 adsorption test). At a range of 500 - 4000 cm^{-1} wavelengths, the functional group analysis was performed. The variations in the FTIR spectrum of activated carbon can be shown in Figure 4.3 before and after CO_2 adsorption. While the FT-IR test results of kaolinite are shown in Figure 4.4 before and after CO_2 adsorption. Table 4.1 provides an overview of the characteristics of the shifted bands and the existing functional groups. As seen in Figure 4.3, the spectrum of the activated carbon displaced an absorption peak of 3671 cm^{-1}, clearly suggesting the existence of an O-H functional group belonging to the cellulose structure, which is the major component of lignocellulosic materials (Sharma, Kyotani and Tomita 2000)

First, due to the O-H stretch and H-bonding of the hydroxyl group in alcohols and phenols, the broad peak at 3671 cm^{-1} shifted and became weak at 3641 cm^{-1}. The asymmetry of this band indicates the presence of strong hydrogen bonds. The 537 cm^{-1} peak that moved to 542 cm^{-1} indicates the existence of the group C-H. At 1844 cm^{-1}, a strong band shifted to 1741 cm^{-1}, assigned to the anhydride compound groups of C=O.

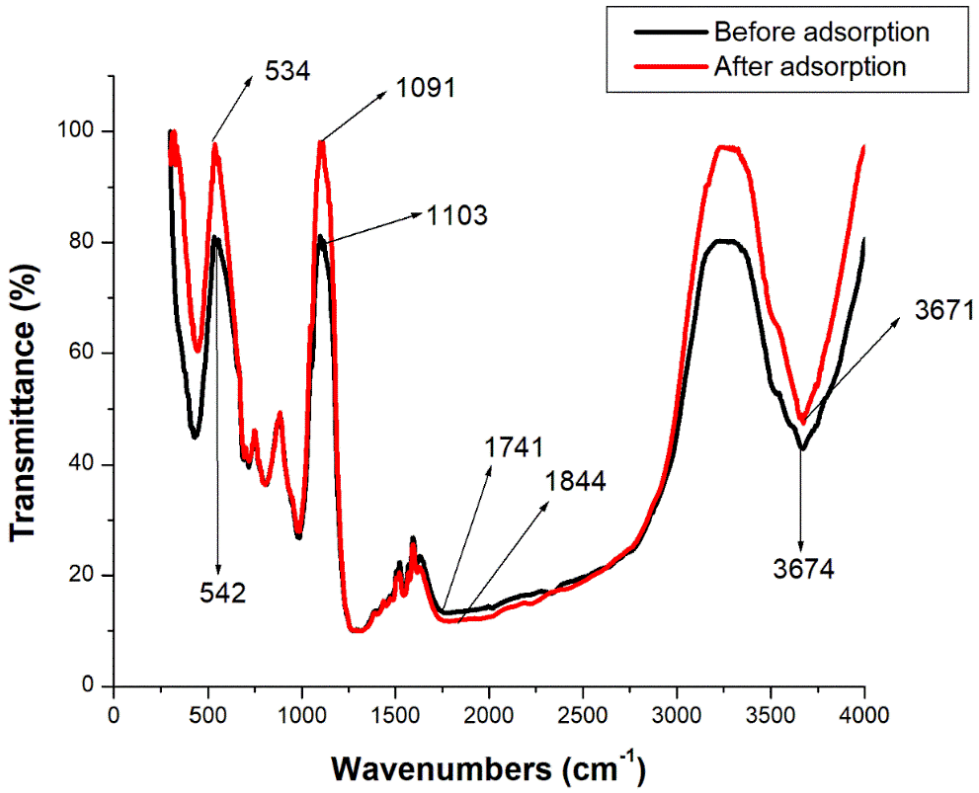

Figure 4.3: The FTIR spectrum of activated carbon before and after CO_2 adsorption

Table 4.1: FTIR spectral characteristics of activated carbon before and after adsorption

Absorption frequency (cm ^{1})		
Activated carbon before adsorption	**Activated carbon after adsorption**	**Assignments**
3674	3671	O–H stretch (in alcohol)
542	537	C–H bending
1103	1091	C–O stretch (in aliphatic ether)
1741	1844	C=O stretch (in anhydride)

Whereas for the kaolinite spectrum before and after adsorption of CO_2 in Figure 4.2, there is a 3305 cm^{-1} absorption peak shifted to 3482 cm^{-1} indicating the formation of the O-H group that may incorporate components of water, alcohol, and phenol. The comparison of the activated carbon FTIR spectra before and after CO_2 adsorption indicates the spectrum shift that emerged and it is shown that the functional groups of the adsorbent were actively involved in the adsorption process. (Chang *et al.* 2012). Overall, it can be concluded that the activated carbon (AC) has functional groups which could bind or trap contaminants like alcohols, phenols, alkanes, and alkyl halides. The hydroxyl group is strongly associated with pollutants and heavy metal ions (Lazim *et al.* 2015)

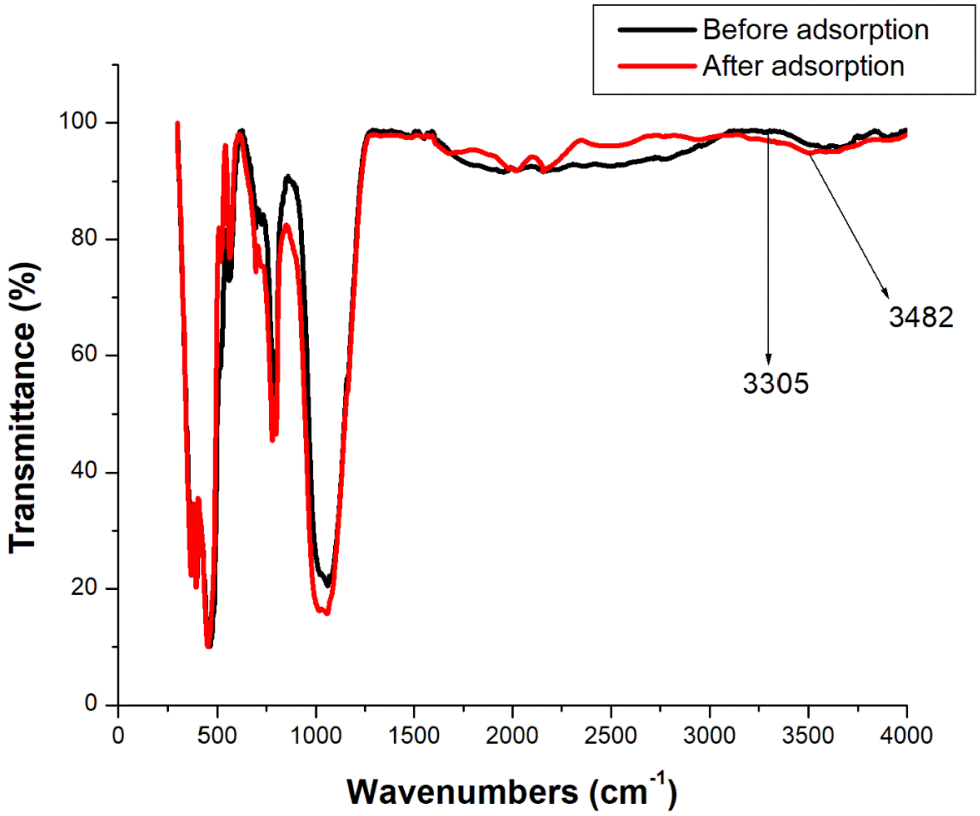

Figure 4.4: The FTIR spectrum of kaolinite before and after CO_2 adsorption.

Table 4.2: FTIR spectral characteristics of kaolinite before and after adsorption

Absorption frequency (cm^{-1})		
Kaolinite before adsorption	**Kaolinite after adsorption**	**Assignments**
3305	3482	O–H stretch (in alcohol)

4.2.3 Measurement of Pore Volume and BET Specific Surface Area

BET analysis was conducted to identify the physical properties of the adsorbent material which are pore size, pore volume and BET surface area. Specific surface area and pore structures are major factors that determine adsorption capacity of adsorbent materials, which are often used as an essential indicator for characterizing an adsorbent's adsorption performance. Values of these properties assist in accounting for the adsorption performance of the material. The parameters of specific surface area and pore structure of the activated carbon, kaolinite, and

kaolinite – activated carbon materials are displayed in Table 4.3. A description of the BET results obtained in this study is listed in Table 4.3.

Table 4.3: BET Surface area, pore volume and pore size

Sample	**BET surface area (m^2/g)**	**Total pore volume (cm^3/g)**	**Average pore diameter (Å)**
Activated carbon	713.4979	0.261030	30.277
Kaolinite	63.0691	0.023473	12.012
Kaolinite + Activated carbon	339.5635	0.120162	25.483

Activated carbon had a pore volume, pore size and BET surface area in this analysis that was much lower than that derived from the work of Yu *et al.* (2020) and Jiménez *et al.* (2012). In literature, AC is shown to have a pore size of 20.63nm, a pore volume of 0.228 cm^3/g, and a surface area of 1122.5 m^2/g (Yu *et al.* 2020). $ZnCl_2$ was used in this study to prepare the activated carbon adsorbent and the presumption was that it would significantly increase the pore size, pore volume and surface area. The correlation between the BET surface area and the pore volume has been shown by all three adsorbent samples, as the BET surface area was increased or decreased also did the pore volume. Furthermore, comparing the prepared activated carbon, to the one in literature, there is a decrease in pore size, pore volume and surface area. However, this indicates that higher pore size, surface area and pore volume results to higher adsorption capacity of CO_2. The activation process enhances pore development and produces new pores, leading to increased surface areas of BET as the activation temperature increases (Lua, Yang and Guo 2004).

The specific surface area, pore volume, and pore diameter of kaolinite in this study is 63.0691 m^2/g, 12.012cm^3/g, and 0.023 Å, respectively. From literature, kaolinite appears to have a pore surface area of 74.3 m^2/g, pore volume of 0.305 cm^3/g and pore diameter of 15.3 nm (Chen and Lu 2014). The kaolinite sample from this analysis can be found to have a lower surface area and pore volume. This is because amine molecules reached and blocked the kaolinite surface pores, thereby decreasing the textural properties of the sample of kaolinite.

4.3 Evaluation of the operating variables on the CO_2 adsorption performance of activated carbon and kaolinite samples.

The experimental results of CO_2 adsorption on the selected adsorbent materials: activated carbon, kaolinite and activated carbon/kaolinite composite is presented below. Table 4.4-4.6 presents the experimental results of CO_2 adsorption capacity among the adsorbents tested in this study. The obtained results were derived at 30 ºC to 70 ºC, 30mL/min to 70mL/min and 3cm to 5cm of varying temperatures, flowrates, and heights of column bed, respectively.

Table 4.4: CO_2 adsorption capacity of activated carbon at 30 ºC, 50 ºC, and 70 ºC

RUNS	Column Bed Height (cm)	Flow rate (mL)	Adsorbent Capacity ($mgCO_2/g$ AC)
Temperature at 30°C			
1		30	20.45
2		40	19.62
3	3	50	16.82
4		60	14.70
5		70	12.11
6		30	22.05
7		40	19.88
8	4	50	18.38
9		60	14.95
10		70	12.14
11		30	28.97
12		40	20.58
13	5	50	18.72
14		60	17.45
15		70	16.88
Temperature at 50°C			
16		30	6.81
17		40	5.68
18	3	50	3.73
19		60	2.62
20		70	1.93
21		30	8.08
22		40	7.35
23	4	50	4.90
24		60	3.25
25		70	2.25
26		30	9.34
27		40	8.41
28	5	50	6.61
29		60	3.67
30		70	2.94
Temperature at 70°C			
31		30	1.70
32		40	1.36
33	3	50	1.22
34		60	1.15
35		70	1.08
36		30	3.67
37		40	2.47
38	4	50	1.99
39		60	1.82
40		70	1.55
41		30	5.60
42		40	4.14
43	5	50	3.22
44		60	2.49
45		70	1.88

Table 4.5: CO_2 adsorption capacity of kaolinite - activated carbon at 30 ºC, 50 ºC, and 70 ºC

RUNS	Column Bed Height (cm)	Flow rate (mL)	Adsorbent Capacity ($mgCO_2/g$ AC + Kaolinite)
Temperature at 30°C			
1		30	15.21
2		40	14.22
3	3	50	13.82
4		60	12.70
5		70	12.11
6		30	17.00
7		40	16.88
8	4	50	15.78
9		60	13.34
10		70	12.98
11		30	18.54
12		40	17.01
13	5	50	16.90
14		60	15.40
15		70	13.25
Temperature at 50°C			
16		30	3.03
17		40	2.98
18	3	50	2.73
19		60	2.26
20		70	2.13
21		30	4.81
22		40	4.69
23	4	50	4.07
24		60	3.92
25		70	3.75
26		30	5.22
27		40	5.19
28	5	50	5.01
29		60	4.77
30		70	4.30
Temperature at 70°C			
31		30	1.75
32		40	1.66
33	3	50	1.22
34		60	1.20
35		70	1.08
36		30	1.81
37		40	1.79
38	4	50	1.65
39		60	1.56
40		70	1.31
41		30	1.89
42		40	1.80
43	5	50	1.72
44		60	1.64
45		70	1.48

Table 4.6: CO_2 adsorption capacity of kaolinite at 30 ºC, 50 ºC, and 70 ºC

RUNS	Column Bed Height (cm)	Flow rate (mL)	Adsorbent Capacity ($mgCO_2/g$ Kaolinite)
Temperature at 30°C			
1		30	10.55
2		40	10.21
3	3	50	10.09
4		60	09.90
5		70	08.15
6		30	11.99
7		40	11.01
8	4	50	10.88
9		60	10.21
10		70	10.00
11		30	12.98
12		40	12.61
13	5	50	12.33
14		60	12.29
15		70	11.11
Temperature at 50°C			
16		30	2.00
17		40	1.88
18	3	50	1.67
19		60	1.01
20		70	0.99
21		30	3.61
22		40	2.54
23	4	50	2.32
24		60	2.22
25		70	1.75
26		30	3.99
27		40	3.50
28	5	50	2.41
29		60	2.30
30		70	1.82
Temperature at 70°C			
31		30	1.11
32		40	1.01
33	3	50	0.95
34		60	0.70
35		70	0.59
36		30	1.20
37		40	1.09
38	4	50	0.99
39		60	0.86
40		70	0.65
41		30	1.29
42		40	1.22
43	5	50	1.18
44		60	1.10
45		70	1.01

4.3.1 Effect of Temperature

The effect of temperature from 30 to 70 ºC was examined. The effect of temperature on CO_2 adsorption capacity is an important factor for post-combustion CO_2 capture processes. It is expected that the temperature will influence the nature of the adsorption that occurs, i.e., physisorption or chemisorption. During the adsorption test, the effect of temperature on CO_2 adsorption was evaluated. The temperature was varied, and the CO_2 flowrate was kept constant for each run.

The behaviour that shows the effect of temperature on adsorbents' CO_2 adsorption capacity is also displayed in Figure 4.5. In other words, the adsorbents' CO_2 adsorption capability increased as the adsorption temperature decreased. As adsorption is an exothermic process, this is predicted (Yu, Huang and Tan 2012). The gas molecules are adsorbed by the adsorbent when active CO_2 gas molecules interacts with the adsorbent and heat is generated (that is heat of adsorption) (Mori and Yamada 1994). The kinetic energy of CO_2 gas molecules is improved by increasing adsorption temperature, so CO_2 molecules have high kinetic energy at high adsorption temperatures, so they travel faster and resulting in less adsorption time on the surface of the adsorbent, resulting in decreased capacity of adsorption at high adsorption temperatures. Increased temperatures give CO_2 molecules more internal energy in the gas phase. It should be observed that the increased energy allows the diffusion of gaseous molecules at a higher rate, At the same time, however, the probability of CO_2 being restricted or retained by fixed energy adsorption sites on the adsorbent surface is reduced. The highest adsorption capacity was obtained at 30 ºC for activated carbon, kaolinite, and kaolinite-activated carbon systems. The general trend observed is that CO_2 adsorption decreases with temperature increase. This result is consistent with literature since gas adsorption decreases when temperature increases. The kinetic energy of gases increases with temperature at a constant flow rate, leading in less surface CO_2 gas coverage. The pattern observed can be attributable to the exothermic existence of the method of adsorption.

It was expected that the nature of the adsorption would be chemisorption. Rojahn is in agreement and states that with chemisorption the magnitude of the adsorption will initially increase to a maximum with an increase in temperature and will decrease thereafter (Rojahn *et al.* 2018). Rojahn suggests that this is because with chemisorption the activation energy has to be achieved first, thereafter the reaction occurs and the subsequent decrease is attributed to exothermic nature of the reaction (Rojahn *et al.* 2018).

In this dissertation, the maximum amount of CO_2 adsorbed on activated carbon (AC) was 28.97 mg CO_2/g at 30 ºC, 18.54 mg CO_2/g of adsorbent was adsorbed by kaolinite – activated carbon at 30 ºC, constant flowrate of 70mL/min while 12.98 mg CO_2/g was adsorbed by kaolinite as displayed in Figure 4.5, Figure 4.6, and Figure 4.7 respectively.

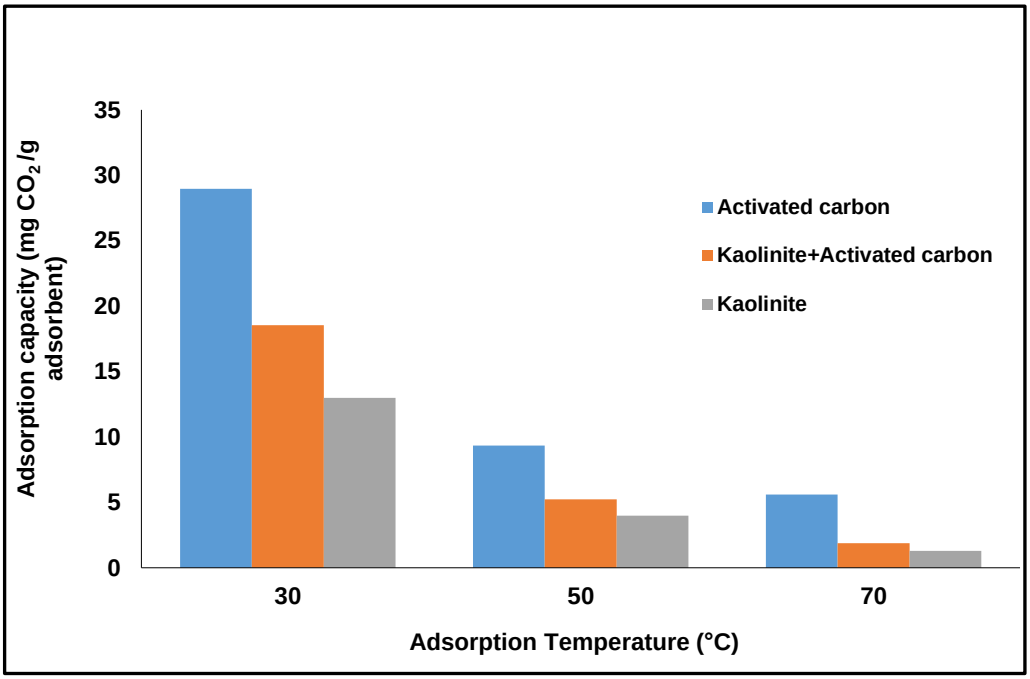

Figure 4.5: Effect of Temperature on the adsorbent systems at flowrate of 30mL/min and 5cm column height

4.3.2 Effect of Flowrate

Another important factor for post-combustion CO_2 capture processes is the effect of flow rate on CO_2 adsorption capacity. The flow rate is expected to influence the quantity of adsorbed CO_2. The effect of flowrate on CO_2 adsorption was evaluated during the adsorption experiment. The flowrate was varied while the temperature was kept constant at 30 ºC, 50 ºC and 70 ºC, respectively. Figure 4.6 shows the effect of flowrate on CO_2 adsorption capacity of activated carbon (AC), kaolinite, and kaolinite/activated carbon adsorbent systems, respectively. The highest CO_2 adsorbed was achieved using a flowrate of 30 mL/min. The CO_2 adsorbed with a flowrate of 40mL/min, 50mL/min, 60mL/min, and 70mL/min are lower than that achieved with a flowrate of 30 mL/min. Reducing the gas inlet flow rate has been found to increase contact time and improve mass transfer between CO_2 and the adsorbents. That is, the retention time of CO_2 molecules on the selected adsorbents inside the packed bed adsorption column is increased by lower flow rates, leading to high amount of CO_2 adsorbed. Adsorbate (CO_2) has more time

to reach the adsorbent at a lower flow rate, resulting in greater CO_2 adsorption power (Ahmad and Hameed 2010). For a higher amount of CO_2 to be adsorbed and trapped in the pores of the adsorbents, longer residence times are needed. As a result of the aforementioned reasons, at different flow rates of 30, 40, 50, 60 and 70 mL/min CO_2, the maximum amount of CO_2 adsorbed by sugarcane bagasse-based activated carbon was 28.97, 20.58, 18.72, 17.45 and 16.88 mg CO_2/g of adsorbent. However, it should be emphasized that for repeatability and accuracy, the experiments were severely replicated.

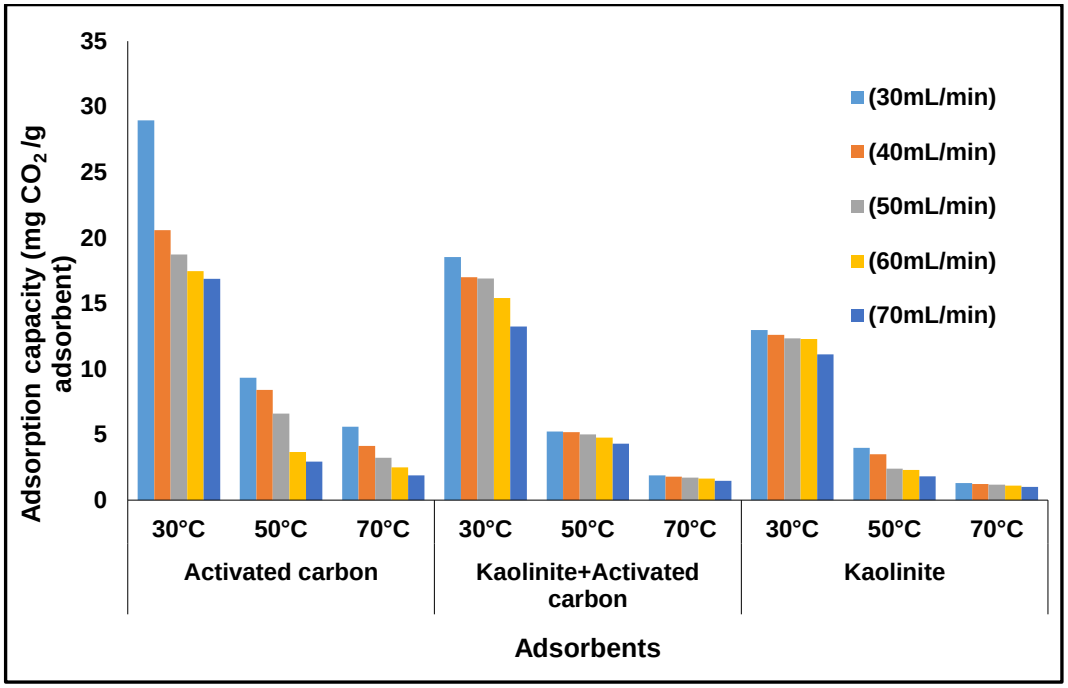

Figure 4.6: Effect of Flowrate on the adsorbent systems at fixed 5cm column height of different temperatures

4.3.3 Effect of bed height of column

As the height of the bed increased, the CO_2 adsorption capacity of the packed bed also increased; the determined heights of bed (3cm =10.7g, 4cm = 13.6g and 5cm = 17.6g) were applied to examine the effect on the CO_2 adsorption performance of various activated carbon, kaolinite, and kaolinite -activated carbon systems. At about 30 mL/min to 70mL/min, the flow rate was kept constant. The effect of bed height for CO_2 adsorption onto activated carbon and kaolinite samples at heights of 3, 4, and 5 cm is shown in Figure 4.7, which indicated that as bed height increases, CO_2 adsorption capacity also increases. The highest adsorption capacity of CO_2 for activated carbon, kaolinite, and kaolinite -activated carbon systems was achieved at height of 5cm. The good performance of CO_2 adsorption on activated carbon (AC) at bed height of 5.0 cm may also be due to greater possibilities of interaction between CO_2 gas and activated

adsorbent particles. Interestingly, since an increase in bed height induces higher mass transfer resistance and slower adsorption kinetics, the mass transfer zone also broadened (Nouri *et al*. 2013). This was due to an increase in surface area and the amount of available adsorption binding sites. As the amount of adsorbent has increased, the time for adsorbate and adsorbent interaction also increased (Fat'hi *et al.* 2014; Teutscherova *et al.* 2018).

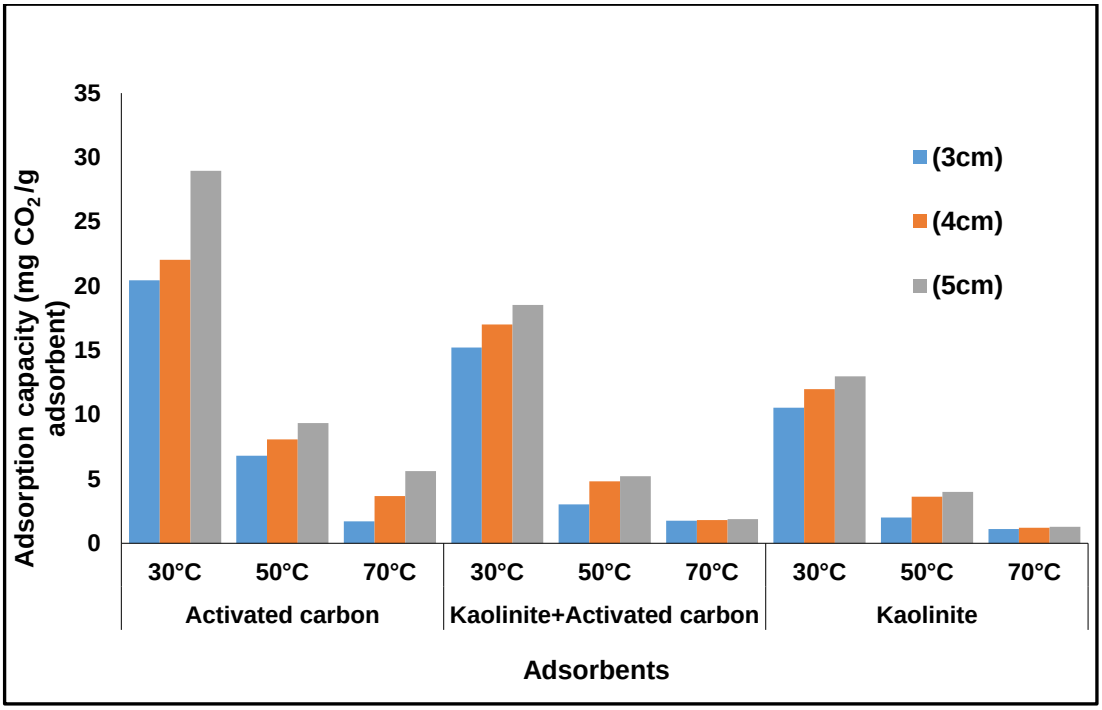

Figure 4.7: Effect of column height on the adsorbent systems at flowrate of 30mL/min, and different temperatures

4.3.4 Effect of activating parameters on the quality of Activated carbon

Based on the findings of the control experiment, each of the process parameters of activation time, activation agent ($ZnCl_2$), and impregnation ratio of $ZnCl_2$/Char had significant impacts on the adsorption capacity of the prepared AC. Whereas the carbonization of the sugarcane bagasse at 500 °C (heating rate of 10 °C / min) for 1 hour is one of the decisive factors to produce high-quality AC from chemical activation using $ZnCl_2$. Impregnation operates on the precursor, fixes the carbon, and increases its composition in the final product. Resultantly, the temperature chosen for the carbonization phase of the samples for activated carbon preparation, 500 °C, is in conjunction with the thermal conversion pattern of the material. Therefore, the optimum activation parameters for the preparation of mainly microporous activated carbons

with a high surface area (SBET = 713.4979 m^2/g) and total volume of the pore (V = 0.261030 cm^3/g) are 1.1 impregnation ratio and at 500 °C temperature.

CHAPTER FIVE

Conclusions and Recommendations for Future work

This chapter summarizes the major findings of the study and provides some recommendations for future studies.

5.1 Conclusions

A big issue affecting the world is climate change, because of the increase in GHG concentrations in the atmosphere, particularly CO_2. Increasing population and economic growth have resulted in higher energy demand. Fossil fuels make up the major source of this energy, which when combusted produce CO_2, a GHG which traps heat in the earth's atmosphere. This heating has several adverse effects on societies and the environment which brings about the need to reduce CO_2 emissions. South Africa is not spared, a nation largely dependent on coal as a fossil fuel for energy production. There are many methods for reducing CO_2 emissions and Carbon capture and storage (CCS) with a potential of reducing global emissions by 20 % is an option worth considering. Power stations in South Africa make use of pulverized coal combustion boilers and thus a post combustion capture approach best suits the scenario. The most widely applied capture method is absorption which has several shortcomings including high heats of regeneration and high corrosion rates. For this purpose, this research focused on the synthesis and performance assessment of activated carbon and kaolinite for CO_2 capture by adsorption. In the commencement of this study, to achieve the aforementioned aims, the questions below were expected to be answered in the course of the study.

1. How effectively can an adsorption experiment be used to describe the behaviour and performance of kaolinite and activated carbon as an adsorbent for CO_2 capture?

2. What is the effect of the operating variables, such as flow rate, operating temperature, and height of column bed on the adsorption capacity of kaolinite and activated carbon as an adsorbent during CO_2 capture?

3. What is the effect of activation parameters on the quality of activated carbon?

4. What is the rate of carbon dioxide capture capacity of various kaolinite and kaolinite - activated carbon systems?

The main aim of this study was to successfully evaluate the performance of kaolinite and activated carbon (AC) for CO_2 capture. Other objectives are:

- To prepare activated carbon (AC) from sugarcane bagasse
- To characterize the produced AC and kaolinite using relevant analytical techniques
- To investigate the effect of temperature, flowrate, and height of column on CO_2 adsorption capacity
- To evaluate the carbon dioxide capture capacity of various kaolinite and kaolinite - activated carbon systems.

The following outcomes resulted from this research effort:

i. Information on the effect of operating conditions (temperature, flowrate, and height of column) on CO_2 adsorption capacity
ii. Information on the carbon dioxide capture capacity of various kaolinite and kaolinite - activated carbon systems.
iii. Peer reviewed paper publication and conference presentations
iv. A well written report in the form of a dissertation and an award.

$ZnCl_2$ was successfully impregnated onto sugarcane bagasse This was confirmed by FTIR technique. The synthesised kaolinite adsorbent was not suitable for CO_2 capture. This was confirmed using BET, SEM, and custom-built CO_2 adsorption equipment. The CO_2 adsorption capacity of the synthesised kaolinite was low. However, kaolinite/activated carbon composite adsorbent did have more suitable characteristics for CO_2 adsorption and showed an increase in CO_2 adsorption capacity when compared to the base material (kaolinite).

The study presented in this research reveals that sugar cane bagasse can be used as a starting material to prepare activated carbon for CO_2 adsorption and to minimize greenhouse gas emissions. The AC was prepared from sugarcane bagasse under the following operating conditions: Impregnation ratio (1:1), time of treatment (1 hour), activating temperature (500 °C), heating rate (10 °C/min). The impregnation ratio ($ZnCl_2$ / bagasse) was employed when producing the AC because a large activating agent: precursor often results in a limited specific surface due to collapse of the pore structure. The choice of choosing temperature of 500 °C during carbonization for treatment time of 1 hour (heating rate of 10 °C / min) was because the carbon matter was fully pyrolyzed at this temperature. The moderate temperature (500 °C) promotes the formation of large surface areas and micro-pore volumes, with $713 m^2/g$,

0.26cm^2/g, and 30 Å, respectively in this study. The adsorption of CO_2 in the ACs prepared from literature presented BET surface areas between 473 and 1361m^2/g. and micropore volume between 0.18 and 0.51cm^2/g. Consequently, our results are within the context of the literature. At higher temperature (above 500 °C) and with prolonged activation time, the pore walls tend to collapse due to suitering and realignment of the carbon structure, thus decreasing the pore characteristics and specific surface area needed for efficient adsorbent – adsorbate interaction. These operating parameters were selected based on literature studies and it showed that the optimal conditions for producing AC were with the activation temperature of 500 °C and soaking time of 0.5 - 1.0 h under a constant heating rate of 10 °C /min. However, the main objective of this work was to compare the performance of AC and kaolinite while following a proven and appropriate AC production method.

The adsorption performance of the prepared activated carbons, kaolinite, and kaolinite - activated carbon systems were then tested under (30–70) °C temperature range and (30–70) mL/min inlet CO_2 flow rate range. Decrease in temperature, increase in bed height, and decrease in initial flowrate of CO_2 content resulted in higher CO_2 adsorption. Activated carbon with larger surface area had a better performance for CO_2 adsorption. However, at 30 ºC, the activated carbon (AC) offered an adsorption capacity of 28.97 mg CO_2/g, the highest capacity among all the adsorbents tested. Kaolinite-activated carbon offered CO_2 adsorption capacities of 18.54 mg CO_2/g. kaolinite (KAO) provided the lowest capacity of 12.98 mg CO_2/g. The more favourable adsorption capacity of CO_2 on activated carbon- kaolinite at low flowrate implies that the affinity of CO_2 is higher for activated carbon- kaolinite than for kaolinite because of the presence of the activated carbon in KAC. The CO_2 adsorption capacity ranking can then be written as Activated carbon > Kaolinite- activated carbon > Kaolinite. As the temperature increased to 70 ºC, this ranking remained unchanged. At the higher temperature, the CO_2 adsorption capacity for each adsorbent was reduced. The capacities at 70 ºC for 5cm are 5.60 mg CO_2/g for SBAC, 1.89 mg CO_2/g for KAC, and 1.29 mg CO_2/g for KAO. It appears that the sugar cane based activated carbon (SBAC) had stronger adsorption sites compared to the kaolinite and activated carbon-kaolinite. It can be concluded, according to these findings, that the use of activated carbon derived from sugar cane bagasse and kaolinite is a promising route for CO_2 capture.

5.2 Recommendations for future work

Based on the results of this study, the following recommendations are proposed for future research:

- The adsorption behaviour of different activated carbon and kaolinite activated carbon systems was investigated in this study during CO_2 capture and effect of important operating parameters for adsorption capacity were obtained. It is however recommended that further work be done on studying the kinetics of the material synthesized in this report. Kinetics are an important aspect of industrial processes and should be studied extensively, particularly where CO_2 capture is involved as determining process economic feasibility is important.
- The development of a more robust method of synthesis is also recommended, scaling up to further to bigger batch or continuous production of the adsorbent material. The first stage of the CO_2 capture process is adsorption, the second stage is desorption which recovers the captured CO_2 and more importantly the adsorbent material. It is recommended that studies on desorption with this material be performed, temperature swing adsorption (TSA) or pressure swing adsorption (PSA) or desorption by dissolving in water as the adsorbent is soluble in water. Further investigations of a combination of adsorption and absorption when moisture is introduced in the gas stream should be carried out.
- Studies on the desorption using kaolinite and activated carbon are recommended. Desorption is an essential mechanism by which the adsorbate (CO_2) is released from or through a surface. Since it applies to post-combustion capture, moisture is a barrier, therefore, it is proposed to investigate the effect of the presence of moisture in flue gas. Using actual flow from power plants, the performance of the CO_2 capture adsorbent should also be investigated.
- Finally, this study serves as a precursor to studies with flue gas samples from actual power plants which should be conducted in future work. Optimization studies should be carried out to determine the exact conditions at which adsorption will be maximized. An economic evaluation would also be necessary alongside further performance tests to determine the feasibility of deploying the adsorbent at a larger scale.

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APPENDICES

Appendix A: Adsorption runs and calculations results

In Appendix A, additional information used to calculate the adsorption capacity results is presented here.

$$CO_2\ adsorption\ capacity = \frac{\text{weight of adsorbent after adsorption} - \text{weight of adsorbent before adsorption}}{weight\ of\ adsorbent\ before\ adsorption}$$

The sample's change in mass was measured and used to determine the amount of adsorbed CO_2.

Appendix B Table B.1: CO_2 adsorption capacity of activated carbon at 30 ºC, 50 ºC, and 70 ºC

RUNS	Column Bed Height (cm)	Flow rate (mL/min)	Adsorbent Capacity ($mgCO_2/g$ AC)
Temperature at 30°C			
1		30	20.45
2		40	19.62
3	3	50	16.82
4		60	14.70
5		70	12.11
6		30	22.05
7		40	19.88
8	4	50	18.38
9		60	14.95
10		70	12.14
11		30	28.97
12		40	20.58
13	5	50	18.72
14		60	17.45
15		70	16.88
Temperature at 50°C			
16		30	6.81
17		40	5.68
18	3	50	3.73
19		60	2.62
20		70	1.93
21		30	8.08
22		40	7.35
23	4	50	4.90
24		60	3.25
25		70	2.25
26		30	9.34
27		40	8.41
28	5	50	6.61
29		60	3.67
30		70	2.94
Temperature at 70°C			
31		30	1.70
32		40	1.36
33	3	50	1.22
34		60	1.15
35		70	1.08
36		30	3.67
37		40	2.47
38	4	50	1.99
39		60	1.82
40		70	1.55
41		30	5.60
42		40	4.14
43	5	50	3.22
44		60	2.49
45		70	1.88

Table B.2: CO_2 adsorption capacity of kaolinite - activated carbon at 30 ºC, 50 ºC, and 70 ºC

RUNS	Column Bed Height(cm)	Flow rate (mL/min)	Adsorbent Capacity ($mgCO_2$/g AC + kaolinite)
Temperature at 30°C			
1		30	15.21
2		40	14.22
3	3	50	13.82
4		60	12.70
5		70	12.11
6		30	17.00
7		40	16.88
8	4	50	15.78
9		60	13.34
10		70	12.98
11		30	18.54
12		40	17.01
13	5	50	16.90
14		60	15.40
15		70	13.25
Temperature at 50°C			
16		30	3.03
17		40	2.98
18	3	50	2.73
19		60	2.26
20		70	2.13
21		30	4.81
22		40	4.69
23	4	50	4.07
24		60	3.92
25		70	3.75
26		30	5.22
27		40	5.19
28	5	50	5.01
29		60	4.77
30		70	4.30
Temperature at 70°C			
31		30	1.75
32		40	1.66
33	3	50	1.22
34		60	1.20
35		70	1.08
36		30	1.81
37		40	1.79
38	4	50	1.65
39		60	1.56
40		70	1.31
41		30	1.89
42		40	1.80
43	5	50	1.72
44		60	1.64
45		70	1.48

Table B.3: CO_2 adsorption capacity of kaolinite at 30 °C, 50 °C, and 70 °C

RUNS	Column Bed Height(cm)	Flow rate (mL/min)	Adsorbent Capacity ($mgCO_2/g$ Kaolinite)
Temperature at 30°C			
1		30	10.55
2		40	10.21
3	3	50	10.09
4		60	09.90
5		70	08.15
6		30	11.99
7		40	11.01
8	4	50	10.88
9		60	10.21
10		70	10.00
11		30	12.98
12		40	12.61
13	5	50	12.33
14		60	12.29
15		70	11.11
Temperature at 50°C			
16		30	2.00
17		40	1.88
18	3	50	1.67
19		60	1.01
20		70	0.99
21		30	3.61
22		40	2.54
23	4	50	2.32
24		60	2.22
25		70	1.75
26		30	3.99
27		40	3.50
28	5	50	2.41
29		60	2.30
30		70	1.82
Temperature at 70°C			
31		30	1.11
32		40	1.01
33	3	50	0.95
34		60	0.70
35		70	0.59
36		30	1.20
37		40	1.09
38	4	50	0.99
39		60	0.86
40		70	0.65
41		30	1.29
42		40	1.22
43	5	50	1.18
44		60	1.10
45		70	1.01

Appendix C: Adsorption Equipment

C1. Packed-bed column

Figure C1 indicates the specific adsorption set-up of the packed-bed column included in this work for the investigation of adsorption of CO_2. The set-up is coupled to a gas cylinder with carbon dioxide (99.9%). A bubble flowmeter that measures the CO_2 flow rate in mL/min as it enters the system is also connected to the set-up, a thermostatic water bath was used to control the temperature of the system desired values. Figure C1 gives a description of this equipment.

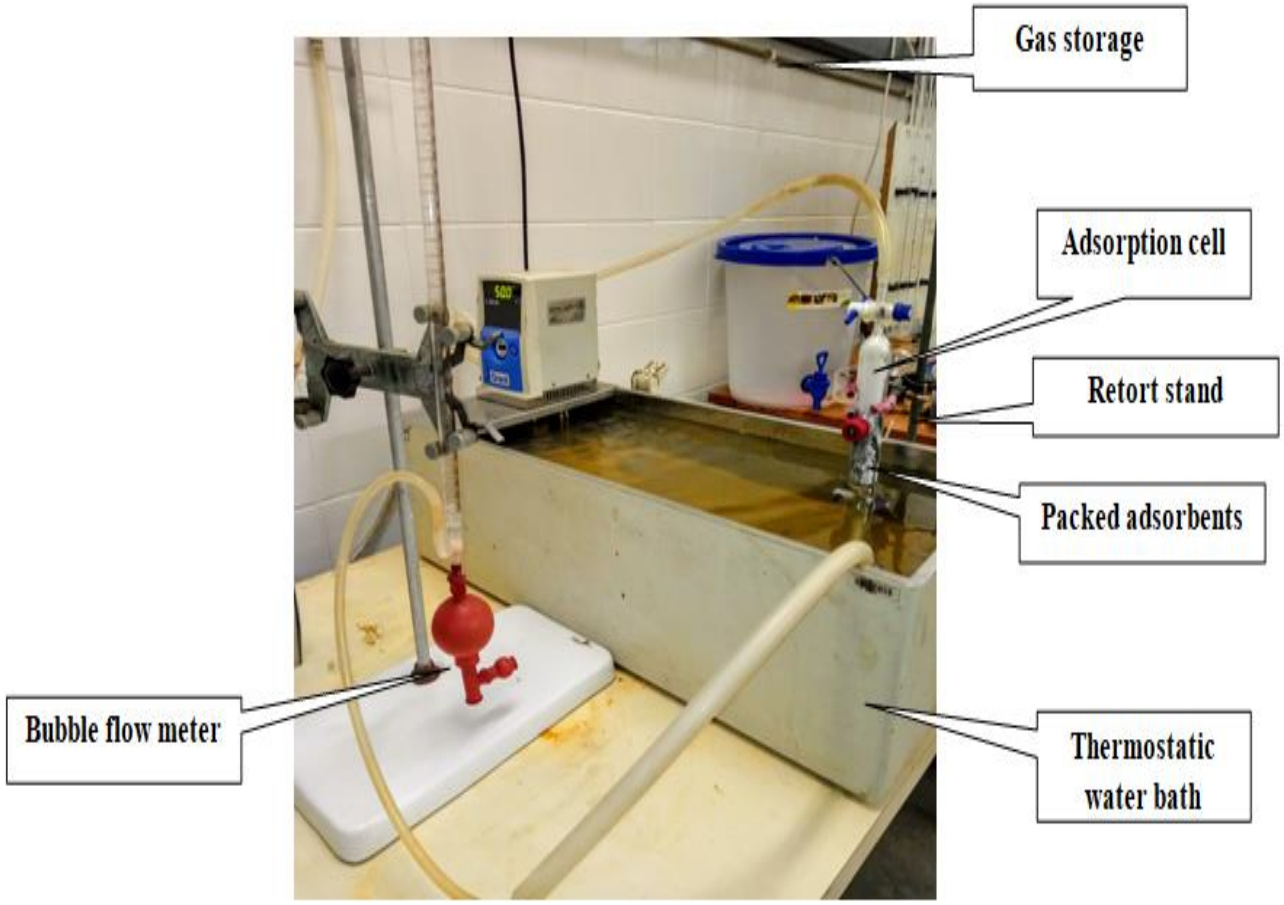

Figure C1: Photograph of the experimental setup (original in colour)